

Contents

NEET Solved Paper 2018

2018-1-2018-8

1.	Some Basic Concepts of Chemistry	1-22
2.	Structure of Atom	23-47
3.	Classification of Elements and Periodicity in Properties	48-63
4.	Chemical Bonding and Molecular Structure	64-100
5.	States of Matter	101-123
6.	Thermodynamics	124-149
7.	Equilibrium	150-186
8.	Redox Reactions	187-203
9.	Hydrogen	204-218
10.	The s-Block Elements	219-239
11.	The p-Block Elements (Group 13 and 14)	240-260
12.	Organic Chemistry : Some Basic Principles and Techniques	261-300
13.	Hydrocarbons	301-337
14.	Environmental Chemistry	338-352
15.	The Solid State	353-373
16.	Solutions	374-401
17.	Electrochemistry	402-430
18.	Chemical Kinetics	431-463

19. Surface Chemistry	464-482
20. General Principles and Processes of Isolation of Elements	483-495
21. The p-Block Elements (Group 15, 16, 17 and 18)	496-525
22. The d and f-Block Elements	526-547
23. Coordination Compounds	548-576
24. Haloalkanes and Haloarenes	577-603
25. Alcohols, Phenols and Ethers	604-634
26. Aldehydes, Ketones and Carboxylic Acids	635-672
27. Amines	673-707
28. Biomolecules	708-729
29. Polymers	730-748
30. Chemistry in Everyday Life	749-760

Chapter

1

Some Basic Concepts of Chemistry

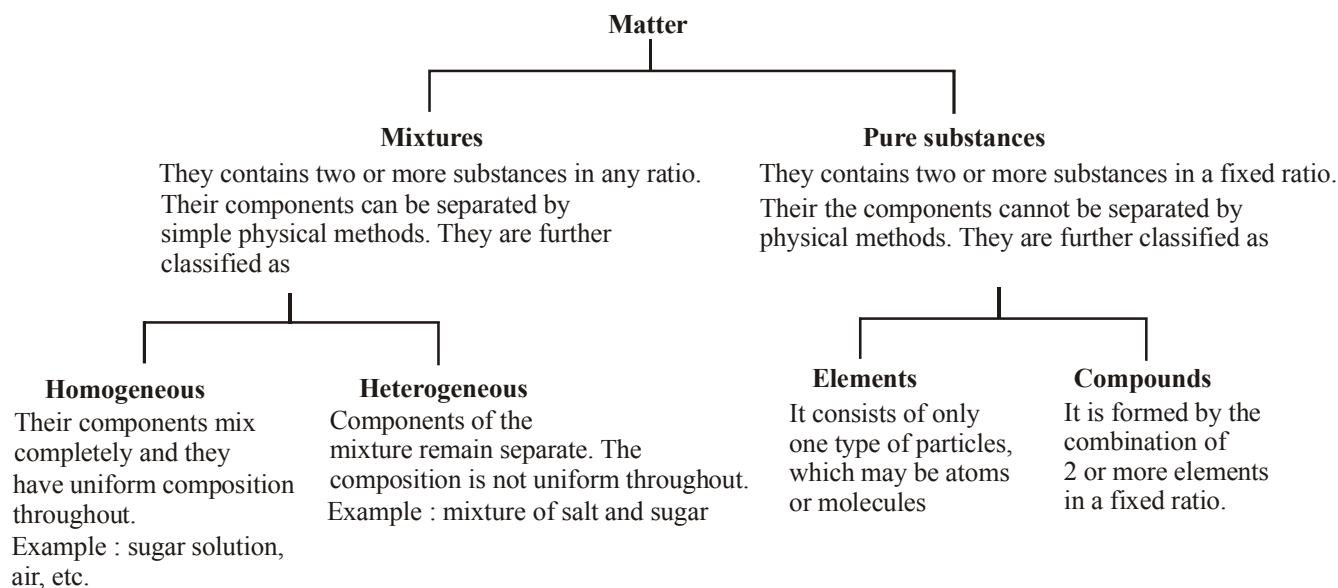
NATURE OF MATTER

Anything which has mass and occupies space is called matter.

Matter can exist in three physical states: solid, liquid and gas. These three states are interconvertible by changing the conditions of temperature and pressure.



At macroscopic level, matter is classified as



PROPERTIES OF MATTER AND THEIR MEASUREMENT

Every substance has characteristic properties which can be classified as physical properties and chemical properties.

Physical properties are those which can be measured or observed without changing the identity or composition of the substance. Ex: colour, odour, m.pt, b.pt, etc.

Chemical properties are those which require a chemical change for their measurement.

Many properties of matter are quantitative in nature which can be measured under the following system of units.

The International System of Units (SI)

The SI system has seven base units which pertain to seven fundamental scientific quantities. The other physical quantities

such as speed, volume, density, etc. can be derived from these units. These base units are listed as follows:

Physical Quantity	Symbol	SI unit	Symbol
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I _v	candela	cd

UNCERTAINTY IN MEASUREMENT AND SIGNIFICANT FIGURES

Precision and Accuracy

Very large or very small numbers, having many zeros can be expressed by using scientific notation for such numbers i.e., exponential notation in which any number can be represented in the form $N \times 10^n$ where n is an exponent having +ve or -ve value and N can vary between 1 to 10.

Every experimental measurement has some amount of uncertainty associated with it. However, one would always like the results to be precise and accurate. Precision refers to the closeness of various measurements for the same quantity while accuracy is the agreement of particular value to the true value of the result.

Significant Figures

The uncertainty in experimental or calculated values is indicated by mentioning the number of significant figures. Significant figures are meaningful digits which are known with certainty. The uncertainty is indicated by writing the certain digits and the last uncertain digit.

The rules for determining the number of significant figures are:

- All non-zero digits are significant. For ex: in 285 cm, there are 3 significant figures.
- Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. For ex: 0.03 has one significant figure.
- Zeros between two non-zero digits are significant. For ex: 2.005 has four significant figures.
- Zeros at the end or right are significant provided they are on the right side of the decimal point. For ex: 0.200 g has 3 significant figures.
- If a number ends in zeros that are not to right of a decimal the zeros may or may not be significant. For e.g., 3500 may have two, three or five significant figures.
- Counting no. of objects have infinite significant figures.
- In numbers written in scientific notation, all digits are significant.

LAWS OF CHEMICAL COMBINATION

The combination of elements to form compounds is governed by following five basic laws :

(i) Laws of Conservation of Mass

It states that matter can neither be created nor destroyed,

(ii) Law of Definite Proportion/Composition

It states that a given compound always contains exactly the same proportion of elements by weight.

(iii) Law of Multiple Proportions

It states that if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

For ex :



Here, masses of oxygen (i.e., 16 g and 32 g) which combine with a fixed mass of H (2g) bear a simple ratio, 16 : 32 i.e. 1:2.

(iv) Gay Lussac's law of Gaseous Volumes

According to this law, when gases combine or are produced in a chemical reaction, they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

(v) Avogadro Law

It states that equal volumes of gases at same temperature and pressure should contain equal number of molecules.

DALTON'S ATOMIC THEORY

In 1808, Dalton published '*A new system of chemical philosophy*' in which he proposed the following :

- Matter consists of indivisible atoms.
- All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
- Compounds are formed when atoms of different elements combine in a fixed ratio.
- Atoms are neither created nor destroyed in a chemical reaction. Dalton's theory could explain the laws of chemical combination.

ATOMIC AND MOLECULAR WEIGHT

Atomic Mass :

Atomic mass is the number of times an atom of an element is heavier than 1/12 th of an atom of C-12.

$$\text{Atomic weight of an element} = \frac{\text{Weight of 1 atom of element}}{1/12 \times \text{weight of 1 atom of C-12}}$$

Determination of atomic weight :

Atomic weight $\times$ specific heat = 6.4 (app.)

Molecular weight : It is the number of times a molecule of any compound is heavier than 1/12 th of an atom of C-12

$$\text{Molecular weight} = \frac{\text{Weight of one molecule}}{1/12 \times \text{weight of one C-12 atom}}$$

Determination of molecular weight :

(i) Vapour density method :

$$\text{Vapour density} = \frac{\text{Wt. of a certain vol. of a gas or vapour under certain temperature and pressure}}{\text{Wt. of the same volume of H}_2 \text{ under same temperature and pressure}}$$

$$\text{Molecular weight} = 2 \times \text{vapour density}$$

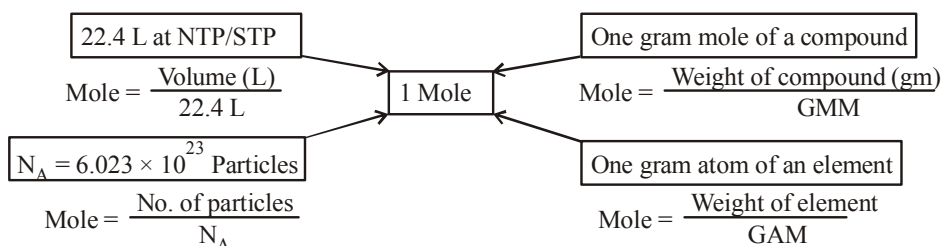
(ii) Diffusion method :

- It is based on **Graham's law** of diffusion.
- Graham's law** states that : *The rate of diffusion of different gases, under similar conditions of temperature and pressure are inversely proportional to the square roots of their density (or molecular weights).*

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

MOLE CONCEPT

Mole : Mole is a unit which represents 6.023×10^{23} particles of same nature.



1 Mole = 6.023×10^{23} particles.

1 Mole of atoms = 6.023×10^{23} Atoms.

1 Mole of molecules = 6.023×10^{23} molecules

1 Mole of electrons = 6.023×10^{23} electrons.

The number 6.023×10^{23} is called *Avogadro number* (N_A)

EQUIVALENT WEIGHT

Equivalent weight of a substance (element or compound) is defined as "The number of parts by weight of it, that will combine with or displace directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen, 35.5 parts by weight of chlorine or the equivalent parts by weight of another element".

$$\text{Eq. wt of elements} = \frac{\text{Molecular mass}}{\text{Basicity of acid}}$$

$$\text{Eq. wt of an acid} = \frac{\text{Molecular mass}}{\text{Basicity of acid}}$$

$$\text{Eq. wt of a base} = \frac{\text{Molecular mass}}{\text{Acidity of base}}$$

Equivalent mass for salts

$$= \frac{\text{Formula mass}}{(\text{Valency of cation}) (\text{No. of cations})}$$

Equivalent mass for oxidising agents

$$= \frac{\text{Formula mass}}{\text{No. of electrons gained per molecule}}$$

Equivalent mass for reducing agents

$$= \frac{\text{Formula mass}}{\text{No. of electrons lost per molecule}}$$

PERCENTAGE COMPOSITION AND CHEMICAL FORMULAE

Percentage Composition

The percentage composition of an element in a compound is given by:

Mass % of an element

$$= \frac{\text{mass of the element in compound}}{\text{molar mass of compound}} \times 100$$

For ex: Percentage composition of water is:

Molar mass of water = 18.02 g

$$\text{Mass \% of H} = \frac{2 \times 1.008}{18.02} \times 100 = 11.18\%$$

$$\text{Mass \% of O} = \frac{16.00}{18.02} \times 100 = 88.79\%$$

Chemical Formulae

It is of two types :

(i) **Molecular formulae :** Chemical formulae that indicate the actual number and type of atoms in a molecule are called *molecular formulae*.

Example : Molecular formula of benzene is C_6H_6 .

(ii) **Empirical formulae :** Chemical formulae that indicate only the relative number of atoms of each type in a molecule are called *empirical formulae*.

Example : Empirical formula of benzene is "CH".

Determination of Chemical Formulae :

(a) **Determination of empirical formulae :**

Step (I) : Determination of percentage of each element

Step (II) : Determination of mole ratio

Step (III) : Making it whole number ratio

Step (IV) : Simplest whole ratio

(b) **Determination of molecular formulae**

Step (I) : First of all find empirical formulae

Step (II) : Calculate the empirical weight

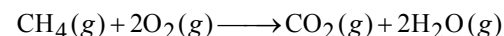
Step (III) : Molecular formulae = n (Empirical formulae)

$$n = \frac{\text{Molecular weight}}{\text{Empirical weight}}$$

STOICHIOMETRY

It deals with the calculation of masses of reactant and products involved in a chemical reaction.

For ex: the balanced equation for combustion of CH_4 is:

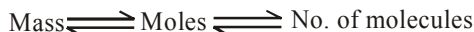


The coefficients of 2 for O_2 and H_2O are called stoichiometric coefficients. The coefficient for CH_4 and CO_2 is one in each case. According to the above chemical reaction,

(i) One mole of $\text{CH}_4(g)$ reacts with 2 moles of $\text{O}_2(g)$ to give 1 mole of $\text{CO}_2(g)$ and 2 moles of $\text{H}_2\text{O}(g)$.

- (ii) One molecule of CH_4 (g) reacts with 2 molecules of O_2 (g) to give 1 molecule of CO_2 (g) and 2 molecules of H_2O (g).
 (iii) 22.4 L of CH_4 (g) reacts with 44.8 L of O_2 (g) to give 22.4 L of CO_2 (g) and 44.8 L of H_2O (g).
 (iv) 16 g of CH_4 (g) reacts with 2×32 g of O_2 (g) to give 44 g of CO_2 (g) and 2×18 g of H_2O (g).

The given data can be interconverted as:



The calculations based on the knowledge of chemical equations are also called **stoichiometry calculations**. The following steps are generally followed for carrying out such calculations :

- Write the balanced chemical equation.
- Write the molar relationship from the equation between the given and the required species.
- Convert these moles into the desired parameters such as mass, volume, etc.
- Apply unitary method to calculate the result.

Limiting Reagent

The reactant which gets consumed and limits the amount of product formed is called limiting reagent. The moles of product are always determined by the starting moles of limiting reactant.

EXPRESSION OF STRENGTH/CONCENTRATION OF SOLUTION

The concentration of the solution or the amount of substance present in its given volume can be expressed in any of the following ways:

1. Mass Percent or Weight Percent (w/W%)

$$\text{Mass percent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

(i) Weight-weight percent (w/W) :

$$\text{Weight percent} = \frac{\text{Weight of solute (gm)}}{\text{Weight of solution (gm)}} \times 100$$

(ii) Volume-volume percent (v/V) :

Volume – volume percentage

$$= \frac{\text{Volume of solute (ml.)}}{\text{Volume of solution (ml.)}} \times 100$$

(iii) Weight – volume percentage (w/V) :

Weight – volume percentage

$$= \frac{\text{Weight of solute (gm)}}{\text{Volume of solution (ml)}} \times 100$$

2. Normality :

The number of gram equivalents of the solute dissolved per litre of the solution. It is denoted by 'N' :

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (lit.)}}$$

$\therefore$ Gram equivalents of solute

$$= \frac{\text{Weight of solute (gm)}}{\text{Equivalent weight of solute}}$$

3. Mole Fraction :

If a substance A dissolves in substance B and their number of moles are n_A and n_B , then their mole fractions (x) are given by

$$x_A = \frac{n_A}{n_A + n_B} \text{ and } x_B = \frac{n_B}{n_A + n_B}$$

Also, $x_A + x_B = 1$

4. Molarity :

It is defined as the number of moles of solute in 1 litre of solution. Thus,

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

5. Molality :

It is defined as the number of moles of solute present in 1 kg of solvent. Thus,

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

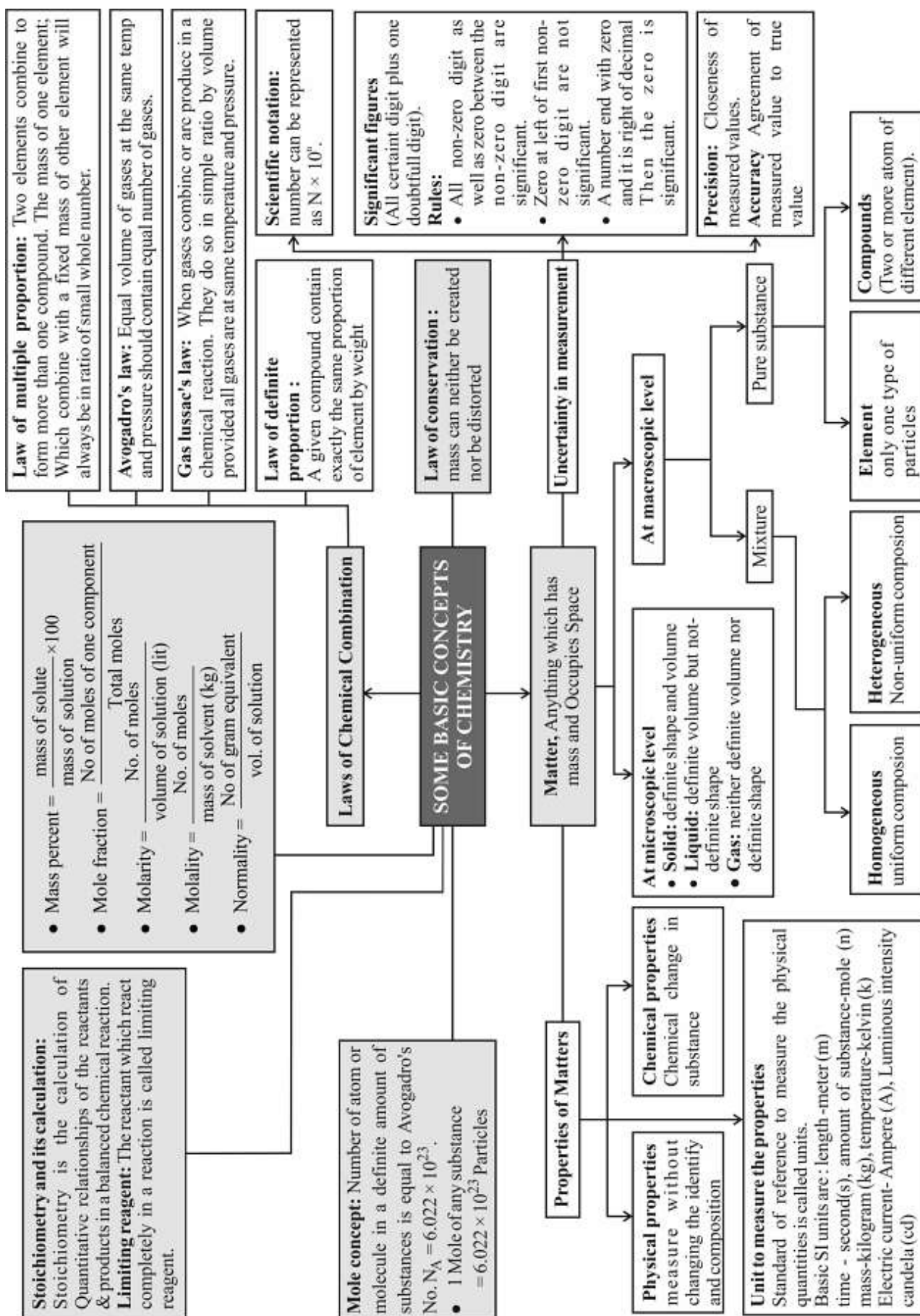
6. ppm. (Parts per million) :

The parts of the component per million parts (10^6) of the solution.

$$\text{ppm} = \frac{w}{w + W} \times 10^6$$

where, w = weight of solute, W = weight of solvent

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- The oxide of an element contains 67.67% oxygen and the vapour density of its volatile chloride is 79. Equivalent weight of the element is:
(a) 2.46 (b) 3.82 (c) 4.36 (d) 4.96
- The empirical formula of a compound is CH_2O . Its molecular weight is 180. The molecular formula of compound is :
(a) $\text{C}_4\text{H}_8\text{O}_4$ (b) $\text{C}_3\text{H}_6\text{O}_3$
(c) $\text{C}_6\text{H}_{12}\text{O}_6$ (d) $\text{C}_5\text{H}_{10}\text{O}_5$
- 0.4 moles of HCl and 0.2 moles of CaCl_2 were dissolved in water to have 500 mL of solution, the molarity of Cl^- ion is:
(a) 0.8 M (b) 1.6 M (c) 1.2 M (d) 10.0 M
- 10^{21} molecules are removed from 200 mg of CO_2 . The moles of CO_2 left are :
(a) 2.88×10^{-3} (b) 28.8×10^{-3}
(c) 288×10^{-3} (d) 28.8×10^3
- The weight of NaCl decomposed by 4.9g of H_2SO_4 , if 6 g of sodium hydrogen sulphate and 1.825 g of HCl , were produced in the reaction is:
(a) 6.921 g (b) 4.65 g (c) 2.925 g (d) 1.4 g
- Which one of the following pairs of compounds illustrate the law of multiple proportions ?
(a) H_2O and Na_2O (b) MgO and Na_2O
(c) Na_2O and BaO (d) SnCl_2 and SnCl_4
- The molecular weight of O_2 and SO_2 are 32 and 64 respectively. At 15°C and 150 mm Hg pressure, one litre of O_2 contains 'N' molecules. The number of molecules in two litres of SO_2 under the same conditions of temperature and pressure will be :
(a) $\text{N}/2$ (b) N (c) 2N (d) 4N
- In the final answer of the expression
$$\frac{(29.2 - 20.2)(1.79 \times 10^5)}{1.37}$$
the number of significant figures is :
(a) 1 (b) 2 (c) 3 (d) 4
- The number of significant figures for the three numbers 161 cm, 0.161 cm, 0.0161 cm are
(a) 3, 4 and 5 respectively (b) 3, 4 and 4 respectively
(c) 3, 3 and 4 respectively (d) 3, 3 and 3 respectively
- A gas occupies a volume of 300 cc at 27°C and 620 mm pressure. The volume of gas at 47°C and 640 mm pressure is:
(a) 260 cc (b) 310 cc (c) 390 cc (d) 450 cc
- The prefix 10^{18} is
(a) giga (b) kilo (c) exa (d) nano
- A sample was weighted using two different balances. The results were
(i) 3.929 g (ii) 4.0 g
How would the weight of the sample be reported?
(a) 3.93 g (b) 3g (c) 3.9 g (d) 3.929 g
- The weight of one molecule of a compound of molecular formula $\text{C}_{60}\text{H}_{122}$ is
(a) 1.2×10^{-20} g (b) 5.025×10^{23} g
(c) 1.4×10^{-21} g (d) 6.023×10^{-20} g
- Among the following pairs of compounds, the one that illustrates the law of multiple proportions is
(a) NH_3 and NCl_3 (b) H_2S and SO_2
(c) CS_2 and FeSO_4 (d) CuO and Cu_2O
- Irrespective of the source, pure sample, of water always yields 88.89% mass of oxygen and 11.11% mass of hydrogen. This is explained by the law of
(a) conservation of mass (b) multiple proportions
(c) constant composition (d) constant volume
- The volume of 20 volume H_2O_2 required to get 5 litres of O_2 at STP is
(a) 250ml (b) 125ml (c) 100ml (d) 50ml.
- Given $P = 0.0030\text{m}$, $Q = 2.40\text{m}$, $R = 3000\text{m}$, Significant figures in P, Q and R are respectively
(a) 2, 2, 1 (b) 2, 3, 4 (c) 4, 2, 1 (d) 4, 2, 3
- The prefix zepto stands for (in m)
(a) 10^9 (b) 10^{-12}
(c) 10^{-15} (d) 10^{-21}
- Two samples of lead oxide were separately reduced to metallic lead by heating in a current of hydrogen. The weight of lead from one oxide was half the weight of lead obtained from the other oxide. The data illustrates
(a) law of reciprocal proportions
(b) law of constant proportions
(c) law of multiple proportions
(d) law of equivalent proportions
- Number of valency electrons in 4.2 gram of N_3^- ion is
(a) $4.2N_A$ (b) $0.1N_A$ (c) $1.6N_A$ (d) $3.2N_A$
- 100 ml of solution of H_2O_2 on decomposition gives 1500 ml of O_2 at N.T.P. The H_2O_2 has the volume strength
(a) 8.6 volume (b) 10 volume
(c) 15 volume (d) 25 volume
- Which of the following is the best example of law of conservation of mass?
(a) 12 g of carbon combines with 32 g of oxygen to form 44 g of CO_2
(b) When 12 g of carbon is heated in a vacuum there is no change in mass
(c) A sample of air increases in volume when heated at constant pressure but its mass remains unaltered
(d) The weight of a piece of platinum is the same before and after heating in air
- With increase of temperature, which of these changes?
(a) Molality (b) Weight fraction of solute
(c) Molarity (d) Mole fraction
- A gas is found to have formula $(\text{CO})_n$. If its vapour density is 56, the value of n will be:
(a) 7 (b) 5 (c) 4 (d) 3
- The least count of an instrument is 0.01 cm. Taking all precautions, the most possible error in the measurement can be :
(a) 0.005 cm (b) 0.01 cm (c) 0.0001 cm (d) 0.1 cm

26. A metallic chloride contains 47.22% metal. Calculate the equivalent weight of metal.
(a) 39.68 (b) 31.76 (c) 36.35 (d) 33.46
27. One litre hard water contains 12.00 mg Mg^{2+} . Milli-equivalents of washing soda required to remove its hardness is :
(a) 1 (b) 12.16
(c) 1×10^{-3} (d) 12.16×10^{-3}
28. The percentage weight of Zn in white vitriol [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] is approximately equal to (Zn = 65, S = 32, O = 16 and H = 1)
(a) 33.65 % (b) 32.56 % (c) 23.65 % (d) 22.65 %
29. 25 ml of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a titre value of 35 ml. The molarity of barium hydroxide solution was
(a) 0.14 (b) 0.28 (c) 0.35 (d) 0.07
30. 6.02×10^{20} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is
(a) 0.02 M (b) 0.01 M (c) 0.001 M (d) 0.1 M
(Avogadro constant, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)
31. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 ml of 1.2 M second solution. What is the molarity of the final mixture?
(a) 2.70 M (b) 1.344 M (c) 1.50 M (d) 1.20 M
32. What volume of hydrogen will be liberated at NTP by the reaction of Zn on 50 ml dilute H_2SO_4 of specific gravity 1.3 and having purity 40%?
(a) 3.5 litre (b) 8.25 litre (c) 6.74 litre (d) 5.94 litre
33. Following is the composition of a washing soda sample :
- | Substance | Molecular Wt. | Mass percent |
|--------------------------|---------------|--------------|
| Na_2CO_3 | 106.0 | 84.8 |
| NaHCO_3 | 84.0 | 8.4 |
| NaCl | 58.5 | 6.8 |
- On complete reaction with excess HCl, one kilogram of the washing soda will evolve:
(a) 9 mol of CO_2 (b) 16 mol of CO_2
(c) 17 mol of CO_2 (d) 18 mol of CO_2
34. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the value of 0.1 M aqueous KOH solution required is
(a) 40 mL (b) 20 mL (c) 10 mL (d) 60 mL
35. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is
(a) 2.28 mol kg^{-1} (b) 0.44 mol kg^{-1}
(c) 1.14 mol kg^{-1} (d) 3.28 mol kg^{-1}
36. The equivalent weight of MnSO_4 is half of its molecular weight when it is converted to :
(a) Mn_2O_3 (b) MnO_2 (c) MnO_4^- (d) MnO_4^{2-}
37. What is the molarity of 0.2N Na_2CO_3 solution?
(a) 0.1 M (b) 0 M (c) 0.4 M (d) 0.2 M
38. The molar solution of H_2SO_4 is equal to :
(a) N/2 solution (b) N solution
(c) 2N solution (d) 3N solution
39. The equivalent weight of a solid element is found to be 9. If the specific heat of this element is $1.05 \text{ Jg}^{-1} \text{ K}^{-1}$, then its atomic weight is :
(a) 17 (b) 21 (c) 25 (d) 27
40. The maximum number of molecules are present in
(a) 15 L of H_2 gas at STP
(b) 5 L of N_2 gas at STP
(c) 0.5 g of H_2 gas
(d) 10 g of O_2 gas
41. The vapour density of a gas is 11.2, then 11.2 g of this gas at N.T.P. will occupy a volume-
(a) 11.2 L (b) 22.4 L (c) 11.2 mL (d) 22.4 mL
42. What is the mass of 1 molecule of CO.
(a) 2.325×10^{-23} (b) 4.65×10^{-23}
(c) 3.732×10^{-23} (d) 2.895×10^{-23}
43. Calculate the volume at STP occupied by 240 gm of SO_2 .
(a) 64 (b) 84 (c) 59 (d) 73
44. The number of gram molecules of oxygen in 6.02×10^{24} CO molecules is
(a) 10 gm molecules (b) 5 gm molecules
(c) 1 gm molecules (d) 0.5 gm molecules
45. Which has maximum number of molecules?
(a) 7 gm N_2 (b) 2 gm H_2
(c) 16 gm NO_2 (d) 16 gm O_2
46. Number of atoms in 558.5 gram Fe (at. wt. of Fe = 55.85 g mol^{-1}) is
(a) twice that in 60 g carbon (b) 6.023×10^{22}
(c) half that in 8 g He (d) $558.5 \times 6.023 \times 10^{23}$
47. How many moles of magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$ will contain 0.25 mole of oxygen atoms?
(a) 1.25×10^{-2} (b) 2.5×10^{-2}
(c) 0.02 (d) 3.125×10^{-2}
48. 7.5 grams of a gas occupy 5.6 litres of volume at STP. The gas is
(a) N_2O (b) NO (c) CO (d) CO_2
49. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. The equivalent weight of the metal is
(a) 3.325 (b) 33.25 (c) 12 (d) 20
50. The number of molecules in 16 g of methane is
(a) 3.0×10^{23} (b) $\frac{16}{6.02} \times 10^{23}$
(c) 6.023×10^{23} (d) $\frac{16}{3.0} \times 10^{23}$

51. Number of g of oxygen in 32.2 g $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ is
 (a) 20.8 (b) 2.24
 (c) 22.4 (d) 2.08
52. The number of water molecules present in a drop of water (volume 0.0018 ml) at room temperature is
 (a) 1.084×10^{18} (b) 6.023×10^{19}
 (c) 4.84×10^{17} (d) 6.023×10^{23}
53. The number of moles of oxygen in one litre of air containing 21% oxygen by volume, under standard conditions are
 (a) 0.0093 mole (b) 0.21 mole
 (c) 2.10 mole (d) 0.186 mole
54. The number of molecules in 8.96 litre of a gas at 0°C and 1 atm. pressure is approximately
 (a) 6.023×10^{23} (b) 12.04×10^{23}
 (c) 18.06×10^{23} (d) 24.08×10^{23}
55. The mass of a molecule of water is
 (a) 3×10^{-25} kg (b) 3×10^{-26} kg
 (c) 1.5×10^{-26} kg (d) 2.5×10^{-26} kg
56. How many atoms are contained in one mole of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)?
 (a) $20 \times 6.02 \times 10^{23}$ atoms/mol
 (b) $45 \times 6.02 \times 10^{23}$ atoms/mol
 (c) $5 \times 6.02 \times 10^{23}$ atoms/mol
 (d) None of these
57. How many moles of helium gas occupy 22.4 litre at 0°C and 1 atm pressure?
 (a) 0.11 (b) 1.11 (c) 0.90 (d) 1.0
58. Number of moles of NaOH present in 2 litre of 0.5 M NaOH is :
 (a) 1.5 (b) 2.0 (c) 1.0 (d) 2.5
59. O_2 , N_2 are present in the ratio of 1 : 4 by weight. The ratio of number of molecules is :
 (a) 7 : 32 (b) 1 : 4 (c) 2 : 1 (d) 4 : 1
60. The hydrogen phosphate of certain metal has formula MHPO_4 . The formula of metal chloride would be
 (a) MCl (b) M_2Cl_2 (c) MCl_2 (d) MCl_3
61. Number of moles of KMnO_4 required to oxidize one mole of $\text{Fe}(\text{C}_2\text{O}_4)$ in acidic medium is
 (a) 0.167 (b) 0.6 (c) 0.2 (d) 0.4
62. 10 g CaCO_3 gives on strong heating CO_2 . It gives quicklime (in grams)
 (a) 5g (b) 4.4 g (c) 5.6 g (d) 4 g
63. What is the weight of oxygen required for the complete combustion of 2.8 kg of ethylene?
 (a) 2.8 kg (b) 6.4 kg (c) 9.6 kg (d) 96 kg
64. In the reaction

$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$
 When 1 mole of ammonia and 1 mole of O_2 are made to react to completion,
 (a) 1.0 mole of H_2O is produced
 (b) 1.0 mole of NO will be produced
 (c) all the oxygen will be consumed
 (d) all the ammonia will be consumed
65. Assuming fully decomposed, the volume of CO_2 released at STP on heating 9.85 g of BaCO_3 (Atomic mass, Ba = 137) will be
 (a) 2.24L (b) 4.96L (c) 1.12L (d) 0.84L
66. In a compound C, H and N atoms are present in 9 : 1 : 3.5 by weight. Molecular weight of compound is 108. Molecular formula of compound is
 (a) $\text{C}_2\text{H}_6\text{N}_2$ (b) $\text{C}_3\text{H}_4\text{N}$
 (c) $\text{C}_6\text{H}_8\text{N}_2$ (d) $\text{C}_9\text{H}_{12}\text{N}_3$
67. The simplest formula of a compound containing 50% of element X (atomic mass 10) and 50% of element Y (atomic mass 20) is
 (a) XY (b) XY_3 (c) X_2Y (d) X_2Y_3
68. The empirical formula of an acid is CH_2O_2 , the probable molecular formula of acid may be :
 (a) $\text{C}_3\text{H}_6\text{O}_4$ (b) CH_2O (c) CH_2O_2 (d) $\text{C}_2\text{H}_4\text{O}_2$
69. An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of the compound is :
 (a) $\text{C}_3\text{H}_5\text{O}_2$ (b) $\text{C}_4\text{H}_{10}\text{O}_2$
 (c) $\text{C}_6\text{H}_{10}\text{O}_4$ (d) $\text{C}_3\text{H}_{10}\text{O}_2$
70. The number of atoms in 4.25 g of NH_3 is approximately
 (a) 6×10^{23} (b) 2×10^{23} (c) 4×10^{23} (d) 1×10^{23}
71. 30 g of magnesium and 30 g of oxygen are reacted, then the residual mixture contains
 (a) 50 g of Magnesium oxide and 10 g of oxygen
 (b) 40 g of Magnesium oxide and 20 g of oxygen
 (c) 45 g of Magnesium oxide and 15 g of oxygen
 (d) 60 g of Magnesium oxide only
72. The mass of BaCO_3 produced when excess CO_2 is bubbled through a solution of 0.205 mol $\text{Ba}(\text{OH})_2$ is :
 (a) 81 g (b) 40.5 g (c) 20.25 g (d) 162 g
73. A compound contains 54.55 % carbon, 9.09% hydrogen, 36.36% oxygen. The empirical formula of this compound is :
 (a) $\text{C}_3\text{H}_5\text{O}$ (b) $\text{C}_4\text{H}_8\text{O}_2$
 (c) $\text{C}_2\text{H}_4\text{O}_2$ (d) $\text{C}_2\text{H}_4\text{O}$
74. In the reaction

$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$
 , when 1 mole of ammonia and 1 mole of O_2 are made to react to completion
 (a) 1.0 mole of H_2O is produced
 (b) 1.0 mole of NO will be produced
 (c) all the ammonia will be consumed
 (d) all the oxygen will be consumed
75. A gas is found to have a formula $[\text{CO}]_x$. If its vapour density is 70, the value of x is :
 (a) 2.5 (b) 3.0 (c) 5.0 (d) 6.0

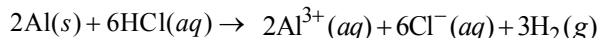
EXERCISE - 2

Applied Questions

- 0.5400 g of a metal X yields 1.020 g of its oxide X_2O_3 . The number of moles of X is :
(a) 0.01 (b) 0.02 (c) 0.04 (d) 0.05
- 12 L of H_2 and 11.2 L of Cl_2 are mixed and exploded. Find the composition by volume of mixture.
(a) 11.2, 11.2, 22.4 (b) 0.8, 0, 22.4
(c) 0.8, 0.8, 22.4 (d) 0.8, 11.2, 22.4
- The hydrated salt $Na_2CO_3 \cdot xH_2O$ undergoes 63% loss in mass on heating and becomes anhydrous. The value of x is
(a) 3 (b) 5 (c) 7 (d) 10
- On adding excess of $CaCl_2$ to a solution containing Na_2CO_3 and $NaHCO_3$, x g of precipitate was obtained. On adding in drops to the filtrate, a further y g of precipitate was obtained. In another experiment to the same amount of solution excess of $CaCl_2$ was added, boiled and filtered. The amount of the precipitate in the second experiment would be
(a) $x + y$ (b) $x + \frac{y}{2}$
(c) $\frac{x+y}{2}$ (d) none of these
- 10 moles SO_2 and 15 moles O_2 were allowed to react over a suitable catalyst. 8 moles of SO_3 were formed. The remaining moles of SO_2 and O_2 respectively are -
(a) 2 moles, 11 moles (b) 2 moles, 8 moles
(c) 4 moles, 5 moles (d) 8 moles, 2 moles
- If 0.5 mol of $BaCl_2$ is mixed with 0.2 mole of Na_3PO_4 , find the maximum amount of $Ba_3(PO_4)_2$ that can be formed.
(a) 1 mole (b) 0.5 mole
(c) 0.1 mole (d) 0.01 mole
- On reduction 1.644 gm of hot iron oxide give 1.15 gm of iron. Evaluate the equivalent weight of iron.
(a) 18.62 (b) 19.13
(c) 18.95 (d) 12.95
- The volume of chlorine at STP required to liberate all the bromine and iodine in 100 ml of 0.1 M each of KI and MBr_2 will be:
(a) 0.224 L (b) 0.336 L (c) 0.448 L (d) 0.560 L
- 6.8 gm H_2O_2 present in 100 ml of its solution. What is the molarity of solution?
(a) 1 M (b) 2 M (c) 3 M (d) 0.5 M
- 1 c.c. N_2O at NTP contains :
(a) $\frac{1.8}{224} \times 10^{22}$ atoms (b) $\frac{6.02}{22400} \times 10^{23}$ molecules
(c) $\frac{1.32}{224} \times 10^{23}$ electrons (d) All of these
- The specific heat of a metal is 0.16 cal g^{-1} . The equivalent mass of the metal is 20.04, the correct atomic mass of the metal is :
(a) 40 (b) 20.04 (c) 40.08 g (d) 80.16 g
- A metal oxide has the formula Z_2O_3 . It can be reduced by hydrogen to give free metal and water. 0.1596 g of the metal oxide requires 6 mg of hydrogen for complete reduction. The atomic weight of the metal is
(a) 27.9 (b) 159.6 (c) 79.8 (d) 55.8
- Ratio of C_p and C_v of a gas 'X' is 1.4. The number of atoms of the gas 'X' present in 11.2 litres of it at NTP will be
(a) 6.02×10^{23} (b) 1.2×10^{23}
(c) 3.01×10^{23} (d) 2.01×10^{23}
- Percent by mass of a solute (molar mass = 28 g) in its aqueous solution is 28. Calculate the mole fraction (X) and molality (m) of the solute in the solution.
(a) $X=0.2, m=10$ (b) $X=0.2, m=125/9$
(c) $X=0.8, m=125/9$ (d) $X=0.8, m=10$
- The density of 0.5 M glucose solution is 1.0900 g ml^{-1} . The molality of the solution is
(a) 0.1000 (b) 0.2000 (c) 0.2500 (d) 0.5000
- Haemoglobin contains 0.334% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (at. wt. of Fe is 56) present in one molecule of haemoglobin are
(a) 1 (b) 6
(c) 4 (d) 2
- Specific volume of cylindrical virus particle is $6.02 \times 10^{-2} \text{ cc/gm}$. whose radius and length 7 Å & 10 Å respectively. If $N_A = 6.02 \times 10^{23}$, find molecular weight of virus
(a) $3.08 \times 10^3 \text{ kg/mol}$ (b) $3.08 \times 10^4 \text{ kg/mol}$
(c) $1.54 \times 10^4 \text{ kg/mol}$ (d) 15.4 kg/mol
- Percentage of Se in peroxidase anhydrase enzyme is 0.5% by weight (at. wt. of Se = 78.4) then minimum molecular weight of peroxidase anhydrase enzyme is
(a) 1.568×10^3 (b) 15.68
(c) 2.136×10^4 (d) 1.568×10^4
- In Haber process 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end?
(a) 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
(b) 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen
(c) 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
(d) 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen
- Malachite has the formula $Cu_2CO_3(OH)_2$. What percentage by mass of malachite is copper?
(a) 25% (b) 50.9% (c) 57.5% (d) 63.5%
- What volume of hydrogen gas, at 273 K and 1 atm. pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen ?
(a) 67.2 L (b) 44.8 L (c) 22.4 L (d) 89.6 L

22. The number of atoms of Cr and O are 4.8×10^{10} and 9.6×10^{10} respectively. Its empirical formula is
 (a) Cr_2O_3 (b) CrO_2
 (c) Cr_2O_4 (d) None of these
23. The unit J Pa^{-1} is equivalent to
 (a) m^3 (b) cm^3
 (c) dm^3 (d) None of these
24. Sulphur forms the chlorides S_2Cl_2 and SCl_2 . The equivalent mass of sulphur in SCl_2 is
 (a) 8 g/mol (b) 16 g/mol
 (c) 64.8 g/mol (d) 32 g/mol
25. How many moles of KI are required to produce 0.4 moles of K_2HgI_4 ?
 (a) 0.4 (b) 0.8
 (c) 3.2 (d) 1.6
26. 100 ml O_2 and H_2 kept at same temperature and pressure. What is true about their number of molecules
 (a) $N_{\text{O}_2} > N_{\text{H}_2}$ (b) $N_{\text{O}_2} < N_{\text{H}_2}$
 (c) $N_{\text{O}_2} = N_{\text{H}_2}$ (d) $N_{\text{O}_2} + N_{\text{H}_2} = 1 \text{ mole}$
27. The percentage of P_2O_5 in diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ is
 (a) 23.48 (b) 46.96 (c) 53.78 (d) 71.00
28. Under similar conditions of pressure and temperature, 40 ml of slightly moist hydrogen chloride gas is mixed with 20 ml of ammonia gas, the final volume of gas at the same temperature and pressure will be
 (a) 100 ml (b) 20 ml
 (c) 40 ml (d) 60 ml
29. How many gram of sulphur can be obtained by the reaction of 1 mol of SO_2 with 22.4 L of H_2S at STP?
 (a) 96 g (b) 48 g
 (c) 32 g (d) None of these
30. 3 g of Mg is burnt in a closed vessel containing 3 g of oxygen. The weight of excess reactant left is
 (a) 0.5 g of oxygen (b) 1.0 g of oxygen
 (c) 1.0 g of Mg (d) 0.5 g of Mg
31. The mass of carbon anode consumed (giving only carbondioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall process is (Atomic mass: $\text{Al} = 27$)
 (a) 270 kg (b) 540 kg (c) 90 kg (d) 180 kg
32. Volume occupied by one molecule of water (density = 1 g cm^{-3}) is :
 (a) $9.0 \times 10^{-23} \text{ cm}^3$ (b) $6.023 \times 10^{-23} \text{ cm}^3$
 (c) $3.0 \times 10^{-23} \text{ cm}^3$ (d) $5.5 \times 10^{-23} \text{ cm}^3$
33. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl ?
 (a) 0.044 (b) 0.333 (c) 0.011 (d) 0.029
34. Which has the maximum number of molecules among the following?
 (a) 44 g CO_2 (b) 48 g O_3
 (c) 8 g H_2 (d) 64 g SO_2
35. If we consider that $1/6$, in place of $1/12$, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of a substance will
 (a) decrease twice
 (b) increase two fold
 (c) remain unchanged
 (d) be a function of the molecular mass of the substance
36. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be
 (a) 1.45 (b) 1.64 (c) 1.88 (d) 1.22
37. The molality of a urea solution in which 0.0100 g of urea, $[(\text{NH}_2)_2\text{CO}]$ is added to 0.3000 dm^3 of water at STP is :
 (a) $5.55 \times 10^{-4} \text{ m}$ (b) 33.3 m
 (c) $3.33 \times 10^{-2} \text{ m}$ (d) 0.555 m
38. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is
 (a) 3 (b) 4 (c) 5 (d) 6
39. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g. of CO_2 . The empirical formula of the hydrocarbon is :
 (a) C_2H_4 (b) C_3H_4 (c) C_6H_5 (d) C_7H_8
40. Experimentally it was found that a metal oxide has formula $\text{M}_{0.98}\text{O}$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be :
 (a) 7.01% (b) 4.08% (c) 6.05% (d) 5.08%
41. Liquid benzene (C_6H_6) burns in oxygen according to the equation $2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \longrightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$
 How many litres of O_2 at STP are needed to complete the combustion of 39 g of liquid benzene? (Mol. wt. of $\text{O}_2 = 32$, $\text{C}_6\text{H}_6 = 78$)
 (a) 74 L (b) 11.2 L (c) 22.4 L (d) 84 L
42. An organic compound whose empirical and molecular formula are same, contains 20% carbon, 6.7% hydrogen, 46.7% nitrogen and the rest oxygen. On heating it yields ammonia, leaving a solid residue. The solid residue gives a violet colour with dilute solution of alkaline copper sulphate. The organic compound is
 (a) $\text{NH}_2\text{COONH}_4$ (b) HCOONH_4
 (c) NH_2NHCHO (d) NH_2CONH_2
43. In order to prepare one litre normal solution of KMnO_4 , how many grams of KMnO_4 are required if the solution is to be used in acid medium for oxidation?
 (a) 158 g (b) 62.0 g (c) 31.6 g (d) 790 g
44. If $1\frac{1}{2}$ moles of oxygen combine with Al to form Al_2O_3 the weight of Al used in the reaction is ($\text{Al} = 27$)
 (a) 27 g (b) 54 g (c) 49.5 g (d) 31 g
45. Number of moles of MnO_4^- required to oxidize one mole of ferrous oxalate completely in acidic medium will be :
 (a) 0.6 moles (b) 0.4 moles
 (c) 7.5 moles (d) 0.2 moles
46. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be:
 (a) 3 mol (b) 4 mol (c) 1 mol (d) 2 mol

47. In the reaction,



- (a) 11.2 L $\text{H}_2(g)$ at STP is produced for every mole $\text{HCl}(aq)$ consumed
 (b) 6 L $\text{HCl}(aq)$ is consumed for every 3 L $\text{H}_2(g)$ produced
 (c) 33.6 L $\text{H}_2(g)$ is produced regardless of temperature and pressure for every mole Al that reacts
 (d) 67.2 $\text{H}_2(g)$ at STP is produced for every mole Al that reacts.

DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
 (b) Statement -1 is True, Statement -2 is True ; Statement-2 is NOT a correct explanation for Statement -1
 (c) Statement -1 is True, Statement -2 is False
 (d) Statement -1 is False, Statement -2 is True
48. **Statement-1** : Volume of a gas is inversely proportional to the number of moles of gas.
Statement-2 : The ratio by volume of gaseous reactants and products is in agreement with their mole ratio.
49. **Statement-1** : One mole of SO_2 contains double the number of molecules present in one mole of O_2 .
Statement-2 : Molecular weight of SO_2 is double to that of O_2 .
50. **Statement-1** : 1.231 has three significant figures.
Statement-2 : All numbers right to the decimal point are significant.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

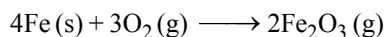
Exemplar Questions

1. Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is 3.0 g. On the basis of given data, mark the correct option out of the following statements.

Students	Readings	
	(i)	(ii)
A	3.01	2.99
B	3.05	2.95

- (a) Results of both the students are neither accurate nor precise.
 (b) Results of student A are both precise and accurate.
 (c) Results of student B are neither precise nor accurate.
 (d) Results of student B are both precise and accurate.
2. A measured temperature on Fahrenheit scale is 200°F . What will this reading be on Celsius scale?
 (a) 40°C (b) 94°C
 (d) 93.3°C (d) 30°C
3. What will be the molarity of a solution, which contains 5.85 g of $\text{NaCl}(s)$ per 500 mL?
 (a) 4 mol L^{-1} (b) 20 mol L^{-1}
 (c) 0.2 mol L^{-1} (d) 2 mol L^{-1}
4. If 500 mL of a 5 M solution is diluted to 1500 mL, what will be the molarity of the solution obtained?
 (a) 1.5 M (b) 1.66 M
 (c) 0.017 M (d) 1.59 M
5. The number of atoms present in one mole of an element is equal to Avogadro number. Which of the following element contains the greatest number of atoms?
 (a) 4 g He (b) 46 g Na
 (c) 0.40 g Ca (d) 12 g He
6. If the concentration of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in blood is 0.9 g L^{-1} , what will be the molarity of glucose in blood?
 (a) 5 M (b) 50 M
 (c) 0.005 M (d) 0.5 M
7. What will be the molality of the solution containing 18.25 g of HCl gas in 500 g of water?
 (a) 0.1 m (b) 1 M
 (c) 0.5 m (d) 1 m
8. One mole of any substance contains 6.022×10^{23} atoms/molecules. Number of molecules of H_2SO_4 present in 100 mL of 0.02 M H_2SO_4 solution is.....
 (a) 12.044×10^{20} molecules (b) 6.022×10^{23} molecules
 (c) 1×10^{23} molecules (d) 12.044×10^{23} molecules
9. What is the mass percent of carbon in carbon dioxide?
 (a) 0.034% (b) 27.27%
 (c) 3.4% (d) 28.7%
10. The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound?
 (a) $\text{C}_9\text{H}_{18}\text{O}_9$ (b) CH_2O
 (c) $\text{C}_6\text{H}_{12}\text{O}_6$ (d) $\text{C}_2\text{H}_4\text{O}_2$
11. If the density of a solution is 3.12 g mL^{-1} , the mass of 1.5 mL solution in significant figures is.....
 (a) 4.7 g (b) $4680 \times 10^{-3}\text{ g}$
 (c) 4.680 g (d) 46.80 g
12. Which of the following statements about a compound is incorrect?
 (a) A molecule of a compound has atoms of different elements.
 (b) A compound cannot be separated into its constituent elements by physical methods of separation.
 (c) A compound retains the physical properties of its constituent elements.
 (d) The ratio of atoms of different elements in a compound is fixed.

13. Which of the following statements is correct about the reaction given below?



- (a) Total mass of iron and oxygen in reactants = total mass of iron and oxygen in product therefore it follows law of conservation of mass.
 (b) Total mass of reactants = total mass of product, therefore, law of multiple proportions is followed.
 (c) Amount of Fe_2O_3 can be increased by taking any one of the reactants (iron or oxygen) in excess.
 (d) Amount of Fe_2O_3 produced will decrease if the amount of any one of the reactants (iron or oxygen) is taken in excess.
14. Which of the following reactions is not correct according to the law of conservation of mass?
- (a) $2\text{Mg(s)} + \text{O}_2\text{(g)} \longrightarrow 2\text{MgO(s)}$
 (b) $\text{C}_3\text{H}_8\text{(g)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{O(g)}$
 (c) $\text{P}_4\text{(s)} + 5\text{O}_2\text{(g)} \longrightarrow \text{P}_4\text{O}_{10}\text{(s)}$
 (d) $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(g)}$
15. Which of the following statements indicates that law of multiple proportion is being followed?
- (a) Sample of carbon dioxide taken from any source will always have carbon and oxygen in the ratio 1 : 2.
 (b) Carbon forms two oxides namely CO_2 and CO , where masses of oxygen which combine with fixed mass of carbon are in the simple ratio 2 : 1.
 (c) When magnesium burns in oxygen, the amount of magnesium taken for the reaction is equal to the amount of magnesium in magnesium oxide formed.
 (d) At constant temperature and pressure 200 mL of hydrogen will combine with 100 mL oxygen to produce 200 mL of water vapour.

NEET/AIPMT (2013-2017) Questions

16. In an experiment it showed that 10 mL of 0.05 M solution of chloride required 10 mL of 0.1 M solution of AgNO_3 , which of the following will be the formula of the chloride (X stands for the symbol of the element other than chlorine):

[NEET Kar. 2013]

- (a) X_2Cl (b) X_2Cl_2
 (c) XCl_2 (d) XCl_4

17. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of solution is : [2013]
 (a) 0.01 M (b) 0.001 M
 (c) 0.1 M (d) 0.02 M
18. When 22.4 litres of $\text{H}_2\text{(g)}$ is mixed with 11.2 litres of $\text{Cl}_2\text{(g)}$, each at S.T.P., the moles of HCl(g) formed is equal to : [2014]
 (a) 1 mole of HCl(g) (b) 2 moles of HCl(g)
 (c) 0.5 moles of HCl(g) (d) 1.5 moles of HCl(g)
19. 1.0 g of magnesium is burnt with 0.56 g O_2 in a closed vessel. Which reactant is left in excess and how much ? [2014]
 (At. wt. Mg = 24 ; O = 16)
 (a) Mg, 0.16 g (b) O_2 , 0.16 g
 (c) Mg, 0.44 g (d) O_2 , 0.28 g
20. If Avogadro number N_A is changed from $6.022 \times 10^{23} \text{ mol}^{-1}$ to $6.022 \times 10^{20} \text{ mol}^{-1}$ this would change : [2015 RS]
 (a) the definition of mass in units of grams
 (b) the mass of one mole of carbon
 (c) the ratio of chemical species to each other in a balanced equation.
 (d) the ratio of elements to each other in a compound
21. What is the mass of precipitate formed when 50 mL of 16.9% solution of AgNO_3 is mixed with 50 mL of 5.8% NaCl solution ? [2015 RS]
 (Ag = 107.8, N = 14, O = 16, Na = 23, Cl = 35.5)
 (a) 28 g (b) 3.5 g
 (c) 7 g (d) 14 g
22. A mixture of gases contains H_2 and O_2 gases in the ratio of 1 : 4 (w/w). What is the molar ratio of the two gases in the mixture? [2015]
 (a) 4 : 1 (b) 16 : 1
 (c) 2 : 1 (d) 1 : 4
23. 20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample ? [2015 RS]
 (a) 75 (b) 96
 (c) 60 (d) 84
24. The number of water molecules is maximum in : [2015 RS]
 (a) 18 molecules of water
 (b) 1.8 gram of water
 (c) 18 gram of water
 (d) 18 moles of water

Hints & Solutions

EXERCISE - 1

- (b) Equivalent weight of an element is its weight which reacts with 8 gm of oxygen to form oxide.
Thus eq. weight of the given element

$$= \frac{32.33}{67.67} \times 8 = 3.82$$
- (c) Empirical formula weight = 12 + 2 + 16 = 30

$$n = \frac{180}{30} = 6$$

 Molecular formula = $(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$.
- (b) $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$

$$\begin{array}{ccc} 0.4 \text{ moles} & & 0.4 \text{ moles} \end{array}$$

$$\text{CaCl}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{Cl}^-$$

$$\begin{array}{ccc} 0.2 \text{ moles} & & 2 \times 0.2 = 0.4 \text{ moles} \end{array}$$

 Total Cl^- moles = 0.4 + 0.4 = 0.8 moles

$$\text{Molarity} = \frac{\text{Moles}}{\text{Vol. in L}}$$

$$\therefore \text{Molarity of } \text{Cl}^- = \frac{0.8}{0.5} = 1.6 \text{ M.}$$
- (a) No. of moles = $\frac{\text{Wt. in g}}{\text{Mol. wt}}$

$$\text{No. of moles in 200 mg} = \frac{200}{1000 \times 44}$$

$$= 4.5 \times 10^{-3} \text{ moles}$$

$$\text{No. of moles in } 10^{21} \text{ molecules}$$

$$= \frac{10^{21}}{6.02 \times 10^{23}} = 1.67 \times 10^{-3} \text{ moles}$$

$$\text{No. of moles left} = (4.5 - 1.67) \times 10^{-3} = 2.88 \times 10^{-3}$$
- (c) $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$

$$\begin{array}{cccc} x \text{ g} & 4.9 \text{ g} & 6 \text{ g} & 1.825 \text{ g} \end{array}$$

 According to law of conservation of mass "mass is neither created nor destroyed during a chemical change"

$$\therefore \text{Mass of the reactants} = \text{Mass of products}$$

$$x + 4.9 = 6 + 1.825$$

 or $x = 2.925 \text{ g}$
- (d) SnCl_2 SnCl_4

$$119 : 2 \times 35.5 \quad \quad \quad 119 : 4 \times 35.5$$

 Chlorine ratio in both compounds is

$$= 2 \times 35.5 : 4 \times 35.5 = 1 : 2$$
- (c) According to Avogadro's law "equal volumes of all gases contain equal number of molecules under similar conditions of temperature and pressure". Thus if 1 L of one gas contains N molecules, 2 L of any other gas under the same conditions of temperature and pressure will contain 2N molecules.
- (c) On calculation we find

$$\frac{(29.2 - 20.2)(1.79 \times 10^5)}{1.37} = 1.17 \times 10^6$$

 As the least precise number contains 3 significant figures therefore, answers should also contain 3 significant figures.
- (d) We know that all non-zero digits are significant and the zeros at the beginning of a number are not significant. Therefore number 161 cm, 0.161 cm and 0.0161 cm have 3, 3 and 3 significant figures respectively.
- (b) From $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{V_1 \times 640}{(273 + 47)} = \frac{620 \times 300}{(273 + 27)}$$

$$V_1 = \frac{620 \times 300 \times 320}{640 \times 300} = 310 \text{ cc}$$
- (c) Exa = 10^{18}
- (a) Out of two 3.929 g is more accurate and will be reported as 3.93 after rounding off.
- (c) M.W. = $60 \times 12 + 122 = 842$

$$\text{Weight of one molecule} = \frac{842}{6.02 \times 10^{23}} \text{ gm}$$

$$= 140 \times 10^{-23} \text{ gm} = 1.4 \times 10^{-21} \text{ gm}$$
- (d) In CuO and Cu_2O the O : Cu is 1 : 1 and 1 : 2 respectively. This is law of multiple proportion.
- (c) The H : O ratio in water is fixed, irrespective of its source. Hence it is law of constant composition.
- (a) 20 volume H_2O_2 means that 1 mL of this H_2O_2 solution produces 20 mL of O_2 at N.T.P. on decomposition by heat.

$$\therefore \text{For 20 mL of } \text{O}_2, \text{ the volume of 20 volume } \text{H}_2\text{O}_2 \text{ required} = 1 \text{ mL}$$

 For 1 mL of O_2 , the volume of 20 volume

$$\text{H}_2\text{O}_2 \text{ required} = \frac{1}{20} \text{ mL}$$

 For 5000 mL or 5L of O_2 , the volume of 20

$$\text{volume } \text{H}_2\text{O}_2 \text{ required} = \frac{1}{20} \times 5000 \text{ mL} = 250 \text{ mL}$$
- (b) Given P = 0.0030m, Q = 2.40m & R = 3000m. In P(0.0030) initial zeros after the decimal point are not significant. Therefore, significant figures in P(0.0030) are 2. Similarly in Q (2.40) significant figures are 3 as in this case final zero is significant. In R = (3000) all the zeros are significant hence, in R significant figures are 4 because they come from a measurement.
- (d) 1 zepto = 10^{-21}
- (c)

20. (b) Number of valence electrons in a N_3^- ion = 1

Now, 1 mol or 42 g of N_3^- has $= 6.023 \times 10^{23}$ ions

So, 42 g of N_3^- has $6.023 \times 4 \times 10^{23}$ valency e^-

1 g of N_3^- has $\frac{6.023 \times 1 \times 10^{23}}{42}$ valency e^-

4.2 g of N_3^- has $\frac{4.2 \times 6.023 \times 1 \times 10^{23}}{42}$ valency e^- i.e., 0.1

N_A valency e^- .

21. (c) Given 100 mL of H_2O_2 gives 1500 mL of O_2 at NTP.

$\Rightarrow$ 1 mL of H_2O_2 gives 15 mL of O_2 at NTP.

As we know that when 1 mL of H_2O_2 gives 10 mL of O_2 at N.T.P., the solution is called 10 volume H_2O_2 i.e., the volume strength of H_2O_2 is 10 volume.

So, when 1 mL of H_2O_2 gives 15 mL of O_2 at N.T.P., the volume strength of H_2O_2 is 15 volume.

22. (a)

23. (c) Among all the given options molarity is correct because the term molarity involve volume which increases on increasing temperature.

24. (c) As we know that,

Molecular mass = $2 \times$ Vapour density

$$\Rightarrow (12 + 16)n = 2 \times 56 \Rightarrow n = \frac{112}{28} = 4$$

25. (a) In case of instrumental error, most possible error is equal to the least count of the instrument. So, most possible instrumental error can be 0.01 cm for the instrument which has a least count 0.01 cm.

26. (b) Suppose weight of metallic chloride = 100 gm

Then weight of metal = 47.22 gm

Weight of chlorine = $100 - 47.22 = 52.78$ gm

$$\therefore \text{Equivalent weight of metal} = \frac{47.22}{52.78} \times 35.5 = 31.76$$

27. (a) $Mg^{++} + Na_2CO_3 \longrightarrow MgCO_3 + 2Na^+$

1 g eq. 1 g eq.

1 g eq. of $Mg^{2+} = 12$ g of $Mg^{2+} = 12000$ mg

= 1000 milli eq. of Na_2CO_3

$\therefore 12$ mg $Mg^{++} = 1$ milli eq. Na_2CO_3

28. (d) Molecular weight of $ZnSO_4 \cdot 7H_2O$

$$= 65 + 32 + (4 \times 16) + 7(2 \times 1 + 16) = 287.$$

$$\therefore \text{percentage mass of zinc (Zn)} = \frac{65}{287} \times 100 = 22.65\%$$

29. (d) $25 \times N = 0.1 \times 35$; $N = 0.14$

$Ba(OH)_2$ is diacid base

$$\text{hence } N = M \times 2 \text{ or } M = \frac{N}{2}$$

$$M = 0.07 \text{ M}$$

30. (b) Moles of urea present in 100 ml of sol. = $\frac{6.02 \times 10^{20}}{6.02 \times 10^{23}}$

$$\therefore M = \frac{6.02 \times 10^{20} \times 1000}{6.02 \times 10^{23} \times 100} = 0.01 \text{ M}$$

[$\therefore$ M = Moles of solute present in 1L of solution]

31. (b) From the molarity equation.

$$M_1 V_1 + M_2 V_2 = MV$$

Let M be the molarity of final mixture,

$$M = \frac{M_1 V_1 + M_2 V_2}{V} \text{ where } V = V_1 + V_2$$

$$M = \frac{480 \times 1.5 + 520 \times 1.2}{480 + 520} = 1.344 \text{ M}$$

32. (d) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
(50 mL)

Normality of H_2SO_4 ,

$$N = \frac{\text{purity \%} \times \text{sp. gravity} \times 10}{\text{equ wt of } H_2SO_4}$$

$$= \frac{40 \times 1.3 \times 10}{98} = 10.61 \text{ N}$$

i.e. 1 L of H_2SO_4 contains = 10.61 gm H_2SO_4

$$50 \text{ mL of } H_2SO_4 \text{ contains} = \frac{10.61}{1000} \times 50 \text{ g } H_2SO_4 \\ = 0.5305 \text{ g } H_2SO_4$$

According to the reaction,

1 gm equivalent of H_2SO_4 will liberate

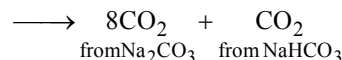
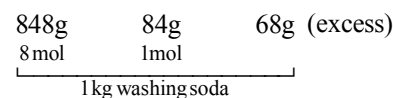
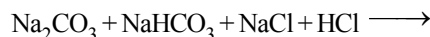
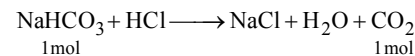
= 1 gm equivalent of H_2

So, 0.5305 of H_2SO_4 will liberate

= 0.5305 gm equivalent of H_2

$$= \frac{0.5305}{2} \times 22.4 \text{ L at NTP} = 5.9416 \text{ L of } H_2 \text{ at NTP}$$

33. (a) $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$
1 mol 1 mol



from Na_2CO_3 from $NaHCO_3$

Thus, on complete reaction with HCl, 1kg of washing soda will evolve 9 mol of CO_2 .

34. (a) $N_1 V_1 = N_2 V_2$ (Note : H_3PO_3 is dibasic $\therefore M = 2N$)

$$20 \times 0.2 = 0.1 \times V \quad (\text{Thus } 0.1 \text{ M} = 0.2 \text{ N})$$

$$\therefore V = 40 \text{ ml}$$

35. (a) Apply the formula $d = M \left(\frac{1}{m} + \frac{M_2}{1000} \right)$

where M = molarity, M_2 = molecular weight of CH_3COOH
 d = density, m = molality.

$$\therefore 1.02 = 2.05 \left(\frac{1}{m} + \frac{60}{1000} \right)$$

On solving we get, $m = 2.28 \text{ mol/kg}$

36. (b) For equivalent weight of $MnSO_4$ to be half of its molecular weight, change in oxidation state must be equal to 2. It is possible only when oxidation state of Mn in product is +4. Since oxidation state of Mn in $MnSO_4$ is +2. So, MnO_2 is correct answer.

In MnO_2 , O.S. of Mn = +4

$$\therefore \text{Change in O.S. of Mn} = +4 - (+2) = +2$$

37. (a) $\text{Molarity} = \text{Normality} \times \frac{\text{Equivalent mass}}{\text{Molecular mass}}$

$$= 0.2 \times \frac{M}{2 \times M} = 0.1 \text{ M}$$
38. (a) $\text{Molarity} = \frac{\text{Normality}}{\text{Replaceable hydrogen atom}}$
 $\therefore \text{H}_2\text{SO}_4$ is dibasic acid.
 $\therefore$ Molar solution of $\text{H}_2\text{SO}_4 = \text{N}/2 \text{ H}_2\text{SO}_4$
39. (d) Using Dulong and Petit's law,
 At. weight $\times$ Specific heat = 6.4 approx

$$\text{Approx. Atomic weight} = \frac{6.4}{\text{Specific heat}}$$

$$= \frac{6.4}{(1/4.18) \times 1.05 \text{ Jg}^{-1}} = 25.4780$$

$$\text{Valency} = \frac{\text{App. weight}}{\text{Equ. weight}} = \frac{25.4780}{9} = 2.83 \approx 3$$

 $\therefore \text{Atomic weight} = \text{valency} \times \text{Equ. wt.}$

$$= 3 \times 9 = 27$$
40. (a) No. of molecules in different cases
 (a) $\therefore$ 22.4 litre at STP contains

$$= 6.023 \times 10^{23} \text{ molecules of H}_2$$

 $\therefore$ 15 litre at STP contains $= \frac{15}{22.4} \times 6.023 \times 10^{23}$

$$= 4.03 \times 10^{23} \text{ molecules of H}_2$$

 (b) $\therefore$ 22.4 litre at STP contains

$$= 6.023 \times 10^{23} \text{ molecules of N}_2$$

 $\therefore$ 5 litre at STP contains $= \frac{5}{22.4} \times 6.023 \times 10^{23}$

$$= 1.344 \times 10^{23} \text{ molecules of N}_2$$

 (c) $\therefore$ 2 gm of $\text{H}_2 = 6.023 \times 10^{23} \text{ molecules of H}_2$
 $\therefore$ 0.5 gm of $\text{H}_2 = \frac{0.5}{2} \times 6.023 \times 10^{23}$

$$= 1.505 \times 10^{23} \text{ molecules of H}_2$$

 (d) Similarly 10 g of O_2 gas

$$= \frac{10}{32} \times 6.023 \times 10^{23} \text{ molecules of O}_2$$

$$= 1.88 \times 10^{23} \text{ molecules of O}_2$$

 Thus (a) will have maximum number of molecules
41. (a) Molecular mass of any gas occupies 22.4 L at N.T.P.

$$\text{Vapour density} = \frac{\text{Molecular mass}}{2}$$

 Vapour density of any gas occupies a volume of 11.2 litres at N.T.P.
42. (b) Gram molecular weight of CO = 12 + 16 = 28 g
 6.023×10^{23} molecules of CO weight 28 g
 1 molecule of CO weighs $= \frac{28}{6.02 \times 10^{23}} = 4.65 \times 10^{-23} \text{ g}$
43. (b) Molecular weight of $\text{SO}_2 = 32 + 2 \times 16 = 64$
 64 g of SO_2 occupies 22.4 litre at STP

$$240 \text{ g of SO}_2 \text{ occupies} = \frac{22.4}{64} \times 240 = 84 \text{ litre at STP}$$
44. (b) 6.02×10^{23} molecules of CO = 1 mole of CO
 6.02×10^{24} CO molecules = 10 moles CO
 $= 10 \text{ g atoms of O} = 5 \text{ g molecules of O}_2$
45. (b) 2g of H_2 means one mole of H_2 , hence contains
 6.023×10^{23} molecules. Others have less than one mole,
 so have less no. of molecules.
46. (a) $\text{Fe (no. of moles)} = \frac{558.5}{55.85} = 10 \text{ moles} = 10 N_A \text{ atoms.}$
 No. of moles in 60 g of C = $60/12 = 5 \text{ moles} = 5 N_A \text{ atoms.}$
47. (d) 1 Mole of $\text{Mg}_3(\text{PO}_4)_2$ contains 8 mole of oxygen atoms
 $\therefore$ 8 mole of oxygen atoms $\equiv$ 1 mole of $\text{Mg}_3(\text{PO}_4)_2$
 $0.25 \text{ mole of oxygen atom} \equiv \frac{1}{8} \times 0.25 \text{ mole of Mg}_3(\text{PO}_4)_2$

$$= 3.125 \times 10^{-2} \text{ mole of Mg}_3(\text{PO}_4)_2$$
48. (b) $PV = nRT \quad \therefore 5.6 \times 1 = \frac{7.5}{\text{M. Wt.}} \times 0.0821 \times 273$
 M. Wt = 30.12 Hence gas NO.
49. (b)
$$\frac{\text{Wt. of metal oxide}}{\text{Wt. of metal chloride}}$$

$$= \frac{\text{Eq. wt of metal} + \text{Eq. wt of oxygen}}{\text{Eq. wt of metal} + \text{Eq. wt of chlorine}}$$

$$\frac{3}{5} = \frac{E + 8}{E + 35.5} \quad \therefore E = 33.25$$
50. (c) 16 g CH_4 is 1 mol. Hence number of molecules
 $= \text{Avogadro number} = 6.023 \times 10^{23}$.
51. (c) M. Wt of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is 322 g which contains 224 g oxygen.
 $\therefore$ 32.2 g will contain 22.4 g oxygen.
52. (b) $0.0018 \text{ ml} = 0.0018 \text{ g} = 0.0001 \text{ mole of water} = 10^{-4} \text{ mole}$
 $\therefore$ number of water molecules $= 6.023 \times 10^{23} \times 10^{-4}$

$$= 6.023 \times 10^{19}$$
53. (a) 21% of 1 litre is 0.21 litre.
 $22.4 \text{ litres} = 1 \text{ mole at STP}$
 $\therefore 0.21 \text{ litre} = \frac{0.21}{22.4} = 0.0093 \text{ mol}$
54. (d) At S.T.P. 22.4 litre of gas contains 6.023×10^{23} molecules
 $\therefore$ molecules in 8.96 litre of gas

$$= \frac{6.023 \times 10^{23} \times 8.96}{22.4} = 24.08 \times 10^{22}$$
55. (b) Mass of one molecule of Water

$$= \frac{18}{6.023 \times 10^{23}} = 3 \times 10^{-23} \text{ g} = 3 \times 10^{-26} \text{ Kg}$$
56. (b) Total atoms in 1 molecule of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 $= 12 + 22 + 11 = 45$
 $\therefore$ Total atoms in 1 mole of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 $= 45 \times 6.02 \times 10^{23} \text{ atoms/mol.}$
57. (d) 22.4 L of He at STP = 1 mole.
58. (c) Given $V = 2 \text{ L}$, Molarity = 0.5M, Moles = ?

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{V \text{ of solution in L}} \text{ or } 0.5 = \frac{\text{Moles}}{2}$$

 $\therefore \text{Moles} = 2 \times 0.5 = 1.0$
59. (a) Let mass of $\text{O}_2 = 1 \text{ g}$

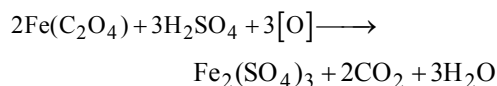
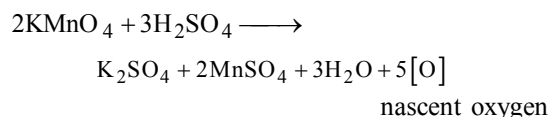
∴ Mass of $N_2 = 4\text{g}$

$$\text{No. of molecules of } O_2 = \frac{1}{32}$$

$$\text{No. of molecules of } N_2 = \frac{4}{28}$$

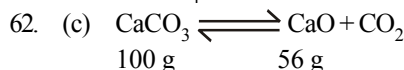
$$\text{Ratio of no. of molecules} = \frac{1}{32} : \frac{4}{28} = \frac{1}{32} : \frac{1}{7} = 7 : 32$$

60. (c) Formula of metal phosphate is $M^{++}H^+PO_4^{---}$.
Valency of metal + 2. Hence metal chloride is MCl_2 .
61. (b) The required equation is

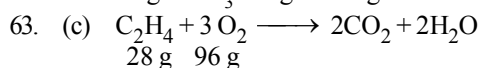


O required for 1 mol. of $Fe(C_2O_4)$ is 1.5, 5O are obtained from 2 moles of $KMnO_4$

∴ 1.5 [O] will be obtained from $= \frac{2}{5} \times 1.5 = 0.6$ moles of $KMnO_4$.



10 g $CaCO_3$ will give 5.6 g CaO



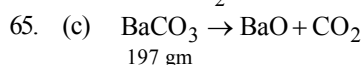
∴ 28 g of C_2H_4 undergo complete combustion by = 96 g of O_2

∴ 2.8 kg of C_2H_4 undergo complete combustion by = 9.6 kg of O_2 .

64. (c) According to Stoichiometry they should react as follow
 $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
4 mole of NH_3 requires 5 mole of O_2 .

1 mole of NH_3 requires $= \frac{5}{4} = 1.25$ mole of O_2 .

Hence O_2 is consumed completely.



∴ 197 gm of $BaCO_3$ released carbon dioxide = 22.4 litre at STP

∴ 1 gm of $BaCO_3$ released carbon dioxide $= \frac{22.4}{197}$ litre

∴ 9.85 gm of $BaCO_3$ released carbon dioxide

$$= \frac{22.4}{197} \times 9.85 = 1.12 \text{ litre}$$

	Percentage	R.N.A	Simplest ratio
C	9	$\frac{9}{12} = \frac{3}{4}$	3
H	1	$\frac{1}{1} = 1$	4

$$N \quad 3.5 \quad \frac{3.5}{14} = \frac{1}{4} \quad 1$$

Empirical formula $= C_3H_4N$

$$(C_3H_4N)_n = 108$$

$$(12 \times 3 + 4 \times 1 + 14)_n = 108$$

$$(54)_n = 108$$

$$n = \frac{108}{54} = 2$$

∴ molecular formula $= C_6H_8N_2$

67. (c) 50% of X (Atomic mass 10), 50% of Y (Atomic mass 20).

Relative number of atoms of X $= \frac{50}{10} = 5$ and than

$$Y = \frac{50}{20} = 2.5$$

Simple Ratio 2 : 1. Formula X_2Y

68. (c) The acid with empirical formula CH_2O_2 is formic acid, $H-COOH$.

69. (c)

Element	%	Relative no. of atoms	Simplest ratio of atoms

C	49.3	$49.3/12 = 4.1$	$4.1/2.74 = 1.5$

		$1.5 \times 2 = 3$	

H	6.84	$6.84/1 = 6.84$	$6.84/2.74 = 2.5$

		$= 2.5 \times 2 = 5$	

O	43.86	$43.86/16 = 2.74$	$2.74/2.74 = 1$

		$1 \times 2 = 2$	

∴ Empirical formula $= C_3H_5O_2$

Empirical formula mass

$$= (3 \times 12) + (5 \times 1) + (2 \times 16) = 36 + 5 + 32 = 73$$

Molecular mass $= 2 \times \text{Vapour density}$

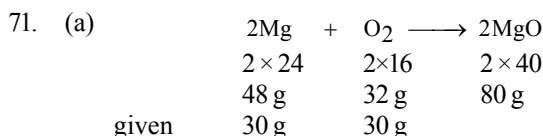
$$= 2 \times 73 = 146$$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = 146/73 = 2$$

$$\text{Molecular formula} = \text{Empirical formula} \times 2 \\ = (C_3H_5O_2) \times 2 = C_6H_{10}O_4$$

70. (a) Number of atoms $= \frac{4.25 \times 6.023 \times 10^{23} \times 4}{17} = 6 \times 10^{23}$

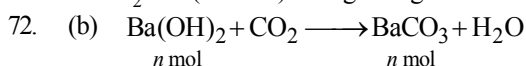
(One molecule of NH_3 contains 4 atoms 1 N and 3H)



Actually

Reacting 30 g 20 g 50g (formed)

O_2 left $(30 - 20) = 10\text{ g}$ MgO formed 50 g.



$$n \text{ mol } Ba(OH)_2 = n \text{ mol } BaCO_3$$

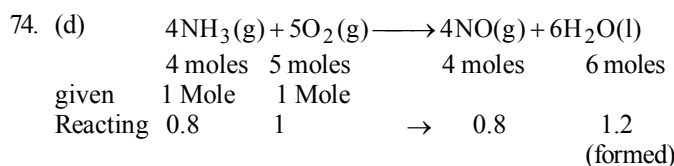
$$\therefore 0.205 \text{ mol } Ba(OH)_2 \equiv 0.205 \text{ mol } BaCO_3$$

$$\text{Wt. of substance} = \text{No. of moles} \times \text{Molecular mass} \\ = 0.205 \times 197.3 = 40.5 \text{ g}$$

73. (d)

C	54.55	$54.55/12 = 4.5$	$4.5/2.27 = 2$
H	9.09	$9.09/1 = 9.09$	$9.09/2.27 = 4$
O	36.36	$36.36/16 = 2.27$	$2.27/2.27 = 1$

Hence empirical formula of the compound $= C_2H_4O$



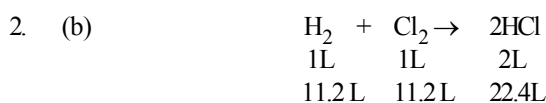
All, O_2 consumed being limiting.

75. (c) As we know that,
Molecular mass of $[\text{CO}]_x = 2 \times \text{V.D.}$
 $\Rightarrow (12 + 16)x = 2 \times 70 \Rightarrow 28x = 140 \Rightarrow x = 5$

EXERCISE - 2

1. (b) Mass of oxygen combined with 0.5400 g of $X = 1.0200 - 0.5400 = 0.4800$ g

$$\text{Mol of } X = \frac{2 \times 0.48}{48} = 0.02$$



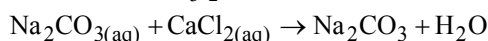
Volume of $\text{H}_2 = [12 - 11.2] = 0.8$ L,

Volume of $\text{Cl}_2 = \text{Zero}$, Volume of $\text{HCl} = 22.4$ L

3. (d) The loss in mass is due to elimination of water of crystallisation of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$.

$$\text{Hence, } \frac{18x \times 100}{106 + 18x} = 63 \Rightarrow x = 10$$

4. (b) On adding CaCl_2 , only CaCO_3 will be precipitated whereas $\text{Ca}(\text{HCO}_3)_2$ is soluble.



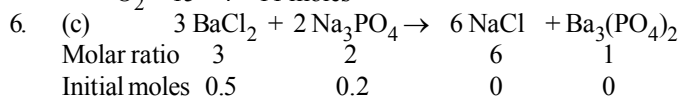
On boiling, $\text{Ca}(\text{HCO}_3)_2$ changes into sparingly soluble CaCO_3 as :



Hence, total mass of precipitate in second case

$$= x + \frac{y}{2}$$

5. (a) $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$
- | | | |
|---------------------|----------|------|
| 10 | 15 | 0 |
| $10 - 2x$ | $15 - x$ | $2x$ |
| $\therefore 2x = 8$ | $x = 4$ | |
- Hence, remaining, $\text{SO}_2 = 10 - 8 = 2$ moles,
 $\text{O}_2 = 15 - 4 = 11$ moles



Limiting reagent is Na_3PO_4 hence it would be consumed, and the yield would be decided by its initial moles.

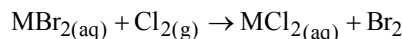
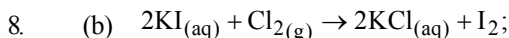
2 moles of Na_3PO_4 give 1 mole of $\text{Ba}_3(\text{PO}_4)_2$,

$\therefore$ 0.2 moles of Na_3PO_4 would give 0.1 mole of $\text{Ba}_3(\text{PO}_4)_2$

7. (a) Weight of iron oxide = 1.644 gm
Weight of iron after reduction = 1.15 gm
weight of displaced oxygen = $1.644 - 1.15 = 0.494$ gm

$$\therefore \text{Equivalent weight of iron} = \frac{1.15}{0.494} \times 8 = 18.62$$

Thus equivalent weight of metal is = 18.62.



Mol of Cl_2 required for liberating iodine from KI

$$= \frac{1}{2} \times \text{mol of KI} = \frac{1}{2} \times 100 \times 10^{-3} \times 0.1 = 0.005$$

Mol of Cl_2 required for liberating bromine from MBr_2
= mol of $\text{MBr}_2 = 0.1 \times 100 \times 10^{-3} = 0.01$

Hence, volume of Cl_2 (STP) required = $(0.005 + 0.01) \times 22.4 = 0.336$ L

9. (b) $\therefore$ Weight of H_2O_2 in 100 ml of H_2O_2 solution = 6.8 gm
 $\therefore$ Weight of H_2O_2 in 1000 ml of its solution = $6.8 \times 10 = 68$ gm
Molecular weight of $\text{H}_2\text{O}_2 = 34$

$$\text{Then, Molarity} = \frac{68}{34} = 2\text{M}$$

10. (d) At NTP 22400 cc of $\text{N}_2\text{O} = 6.02 \times 10^{23}$ molecules

$$\therefore 1 \text{ cc } \text{N}_2\text{O} = \frac{6.02 \times 10^{23}}{22400} \text{ molecules}$$

$$= \frac{3 \times 6.02 \times 10^{23}}{22400} \text{ atoms} = \frac{1.8}{224} \times 10^{22} \text{ atoms}$$

No. of electrons in a molecule of $\text{N}_2\text{O} = 7 + 7 + 8 = 22$

Hence no. of electrons

$$= \frac{6.02 \times 10^{23}}{22400} \times 22 \text{ electrons} = \frac{1.32 \times 10^{23}}{224}$$

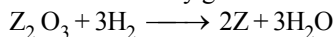
11. (c) Following Dulong-Pettit law, approx. atomic mass

$$= \frac{6.4}{\text{Specific heat}} = \frac{6.4}{0.16} = 40$$

$$\text{Valency of the metal} = \frac{40}{\text{Equiv. mass}} = \frac{40}{20.04} = 2$$

Correct atomic mass = valency $\times$ eq. mass = $2 \times 20.04 = 40.08$

12. (d) The reaction may be given as



0.1596 g of Z_2O_3 react with $\text{H}_2 = 6 \text{ mg} = 0.006 \text{ g}$

$$\therefore 1 \text{ g of } \text{H}_2 \text{ react with } = \frac{0.1596}{0.006} = 26.6 \text{ g of } \text{Z}_2\text{O}_3$$

$\therefore$ Eq. wt. of $\text{Z}_2\text{O}_3 = 26.6$ (from the definition of eq. wt.)

Eq. wt. of $\text{Z} + \text{Eq. wt. of O} = 26.6$

$\Rightarrow$ Eq. wt. of $\text{Z} = 26.6 - 8 = 18.6$

Valency of metal in $\text{Z}_2\text{O}_3 = 3$

$$\text{Eq. wt. of metal} = \frac{\text{Atomic wt.}}{\text{valency}}$$

$\therefore$ At. wt. of $\text{Z} = 18.6 \times 3 = 55.8$

13. (a) $C_p / C_v = 1.4$ shows that the gas is diatomic.

22.4 litre at NTP = 6.02×10^{23} molecules

11.2 L at NTP = 3.01×10^{23} molecules

$$= 3.01 \times 10^{23} \times 2 \text{ atoms} = 6.02 \times 10^{23} \text{ atoms}$$

14. (b) Mol. of solute in 100 g solution = $\frac{28}{28} = 1$

$$\text{Mol. of water in 100 g solution} = \frac{100 - 28}{18} = 4$$

$$\text{Mol. fraction of solute} = \frac{1}{1 + 4} = 0.2 ;$$

$$\text{Molality} = \frac{1 \times 1000}{72} = \frac{125}{9}$$

15. (d) Mass of 1 L (= 1000 ml) solution = $1000 \times 1.090 = 1090 \text{ g}$
 Mass of glucose in 1 L = $0.5 \times 180 = 90 \text{ g}$
 Mass of water = $1090.0 \text{ g} - 90.0 \text{ g} = 1000 \text{ g}$

$$\text{Hence, molality} = \frac{0.5 \times 1000}{1000} = 0.5$$

16. (c) Mass of iron in 100 g haemoglobin = 0.334 g
 $\therefore$ In 67200 g haemoglobin, mass of iron

$$= \frac{67200 \times 0.334}{100} = 672 \times 0.33 \text{ g}$$

$\therefore$ The number of Fe atoms in one molecule of haemoglobin

$$= \frac{672 \times 0.334}{56} = 4$$

17. (d) Specific volume (volume of 1 gm) of cylindrical virus particle = $6.02 \times 10^{-2} \text{ cc/gm}$
 Radius of virus (r) = $7 \text{ \AA} = 7 \times 10^{-8} \text{ cm}$
 Length of virus = $10 \times 10^{-8} \text{ cm}$
 Volume of virus

$$\pi r^2 l = \frac{22}{7} \times (7 \times 10^{-8})^2 \times 10 \times 10^{-8} = 154 \times 10^{-23} \text{ cc}$$

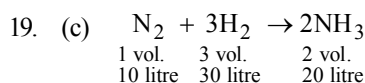
$$\text{Wt. of one virus particle} = \frac{\text{volume}}{\text{specific volume}}$$

$$\therefore \text{Mol. wt. of virus} = \text{Wt. of } N_A \text{ particle}$$

$$= \frac{154 \times 10^{-23}}{6.02 \times 10^{-2}} \times 6.02 \times 10^{23} = 15400 \text{ g/mol} = 15.4 \text{ kg/mole}$$

18. (d) 0.5 g of Se = 100 g enzyme

$$78.4 \text{ g of Se} = \frac{100}{0.5} \times 78.4 = 1.568 \times 10^4 \text{ g enzyme}$$



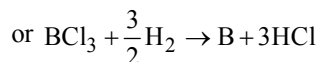
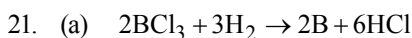
It is given that only 50% of the expected product is formed hence only 10 litre of NH_3 is formed

$$\text{N}_2 \text{ used} = 5 \text{ litres, left} = 30 - 5 = 25 \text{ litres}$$

$$\text{H}_2 \text{ used} = 15 \text{ litres, left} = 30 - 15 = 15 \text{ litres}$$

20. (c) Percentage by mass of copper in malachite

$$= \frac{2 \times 63.5}{221} = 57.5\%$$



Now, since 10.8 gm boron requires hydrogen

$$= \frac{3}{2} \times 22.4 \text{ L at N.T.P}$$

hence 21.6 gm boron requires hydrogen

$$\frac{3}{2} \times \frac{22.4}{10.8} \times 21.6 = 67.2 \text{ L at N.T.P.}$$

22. (b) Ratio of atoms of Cr and O = $4.8 \times 10^{10} : 9.6 \times 10^{10} = 1 : 2$
 Hence, empirical formula = CrO_2

23. (a) Joule is the unit of work and Pascal is unit of pressure.

$$\text{J Pa}^{-1} = \frac{\text{J}}{\text{Pa}} = \frac{\text{Work}}{\text{Pressure}} = \frac{\text{Nm}}{\text{Nm}^{-2}} = \text{m}^3$$

24. (b) The atomic weight of sulphur = 32

In SCl_2 valency of sulphur = 2

$$\text{So equivalent mass of sulphur} = \frac{32}{2} = 16$$

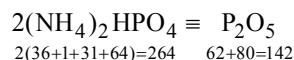


Moles of KI required to produce 0.4 moles of K_2HgI_4
 $= 2 \times 0.4 = 0.8$

26. (c) This is Avogadro's hypothesis.

According to this, equal volume of all gases contain equal no. of molecules under similar condition of temperature and pressure.

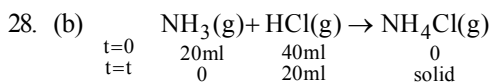
27. (c) 1 mole of $(\text{NH}_4)_2\text{HPO}_4$ would give $\frac{1}{2}$ mole of P_2O_5



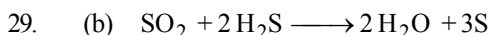
$$2(36+1+31+64)=264 \quad 62+80=142$$

$$\% \text{ of } \text{P}_2\text{O}_5 = \frac{\text{wt. of } \text{P}_2\text{O}_5}{\text{wt. of salt}} \times 100$$

$$= \frac{142}{264} \times 100 = 53.78\%$$

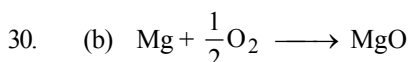


Final volume = 20 ml



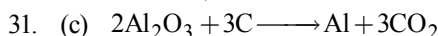
22.4 L (STP) of $\text{H}_2\text{S} = 1 \text{ mol}$

$$\text{Mass of S produced} = \frac{3 \times 32}{2} \text{ g} = 48 \text{ g}$$



$$\text{Mass of oxygen required for 3 g of Mg} = \frac{16 \times 3}{24} = 2 \text{ g}$$

Hence, excess reactant = $3 - 2 = 1 \text{ g oxygen}$



Gram equivalent of $\text{Al}_2\text{O}_3 \equiv$ gm equivalent of C

$$\text{Now equivalent weight of Al} = \frac{27}{3} = 9$$

$$\text{Equivalent weight of C} = \frac{12}{4} = 3 \quad (\text{C} \xrightarrow{0} \text{CO}_2^{+4})$$

$$\begin{aligned} \text{No. of gram equivalent of Al} &= \frac{270 \times 10^3}{9} \\ &= 30 \times 10^3 \end{aligned}$$

Hence,

$$\text{No. of gram equivalent of C} = 30 \times 10^3$$

Again,

$$\text{No. of gram equivalent of C}$$

$$= \frac{\text{mass in gram}}{\text{gram equivalent weight}}$$

$$\Rightarrow 30 \times 10^3 = \frac{\text{mass}}{3}$$

$$\Rightarrow \text{mass} = 90 \times 10^3 \text{ g} = 90 \text{ kg}$$

$$32. \quad (c) \quad \text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$1 \text{ gram cm}^{-3} = \frac{1 \text{ gram}}{\text{cm}^3}$$

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{1 \text{ gram}}{1 \text{ gram cm}^{-3}} = 1 \text{ cm}^3$$

$\therefore$ Volume occupied by 1 gram water = 1 cm³

or Volume occupied by

$$\frac{6.023 \times 10^{23}}{18} \text{ molecules of water} = 1 \text{ cm}^3$$

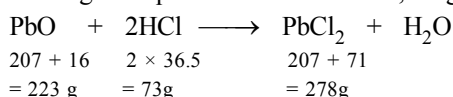
$$[\therefore 1 \text{ g water} = \frac{1}{18} \text{ moles of water}]$$

Thus volume occupied by 1 molecule of water

$$= \frac{1 \times 18}{6.023 \times 10^{23}} \text{ cm}^3 = 3.0 \times 10^{-23} \text{ cm}^3.$$

i.e. the correct answer is option (c).

33. (d) Writing the equation for the reaction, we get



$$\text{No. of moles of PbO} = \frac{6.5}{223} = 0.029$$

$$\text{No. of moles of HCl} = \frac{3.2}{36.5} = 0.0877$$

Thus PbO is the limiting reactant 1 mole of PbO produce 1 mole PbCl₂.

0.029 mole PbO produces 0.029 mole PbCl₂.

34. (c) No. of molecules

$$\text{Moles of CO}_2 = \frac{44}{44} = 1 \quad N_A$$

$$\text{Moles of O}_3 = \frac{48}{48} = 1 \quad N_A$$

$$\text{Moles of H}_2 = \frac{8}{2} = 4 \quad 4N_A$$

$$\text{Moles of SO}_2 = \frac{64}{64} = 1 \quad N_A$$

35. (a) Relative atomic mass

$$= \frac{\text{Mass of one atom of the element}}{1/12^{\text{th}} \text{ part of the mass of one atom of Carbon} - 12}$$

$$\text{or } \frac{\text{Mass of one atom of the element}}{\text{mass of one atom of the C} - 12} \times 12$$

Now if we use $1/6$ in place of $1/12$ the formula becomes

$$\text{Relative atomic mass} = \frac{\text{Mass of one atom of element}}{\text{Mass of one atom of carbon}} \times 6$$

$\therefore$ Relative atomic mass decrease twice

36. (d) Since molarity of solution is 3.60 M. It means 3.6 moles of H₂SO₄ is present in its 1 litre solution.

$$\text{Mass of 3.6 moles of H}_2\text{SO}_4$$

$$= \text{Moles} \times \text{Molecular mass}$$

$$= 3.6 \times 98 \text{ g} = 352.8 \text{ g}$$

$$\therefore 1000 \text{ ml solution has } 352.8 \text{ g of H}_2\text{SO}_4$$

29% H₂SO₄ by mass means 29 g of H₂SO₄ is present in 100 g of solution

$$\therefore 352.8 \text{ g of H}_2\text{SO}_4 \text{ is present in}$$

$$= \frac{100}{29} \times 352.8 \text{ g of solution} = 1216 \text{ g of solution}$$

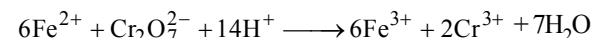
$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{1216}{1000} = 1.216 \text{ g/ml} = 1.22 \text{ g/ml}$$

37. (a) Molality = Moles of solute / Mass of solvent in kg

$$\text{Molality} = \frac{0.01/60}{0.3} = \frac{0.01}{60 \times 0.3};$$

$$d = 1 \text{ g/ml} = 5.55 \times 10^{-4} \text{ m}$$

38. (d) The following reaction occurs:



From the above equation, we find that Mohr's salt (FeSO₄(NH₄)₂SO₄·6H₂O) and dichromate reacts in 6 : 1 molar ratio.

39. (d) $\therefore$ 18 gm, H₂O contains = 2 gm H

$$\therefore 0.72 \text{ gm H}_2\text{O contains} = \frac{2}{18} \times 0.72 \text{ gm} = 0.08 \text{ gm H}$$

$$\therefore 44 \text{ gm CO}_2 \text{ contains} = 12 \text{ gm C}$$

$$\therefore 3.08 \text{ gm CO}_2 \text{ contains} = \frac{12}{44} \times 3.08 = 0.84 \text{ gm C}$$

$$\therefore \text{C} : \text{H} = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 = 7 : 8$$

$$\therefore \text{Empirical formula} = \text{C}_7\text{H}_8$$

40. (b) For one mole of the oxide

$$\text{Moles of M} = 0.98$$

$$\text{Moles of O}^{2-} = 1$$

$$\text{Let moles of M}^{3+} = x$$

$$\therefore \text{Moles of M}^{2+} = 0.98 - x$$

On balancing charge

$$(0.98 - x) \times 2 + 3x - 2 = 0$$

$$x = 0.04$$

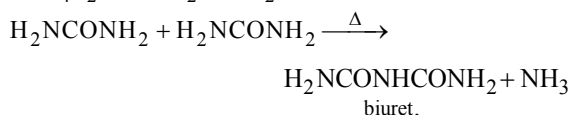
$$\therefore \% \text{ of M}^{3+} = \frac{0.04}{0.98} \times 100 = 4.08\%$$

41. (d) $2\text{C}_6\text{H}_6 + 15\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
 $\frac{2(78)}{15(32)}$
 $\therefore 156 \text{ gm of benzene required oxygen} = 15 \times 22.4 \text{ litre}$
 $\therefore 1 \text{ gm of benzene required oxygen} = \frac{15 \times 22.4}{156} \text{ litre}$
 $\therefore 39 \text{ gm of Benzene required oxygen}$
 $= \frac{15 \times 22.4 \times 39}{156} = 84.0 \text{ litre}$

42. (d)

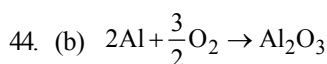
Element	Percentage	Atomic mass	Relative no. of atoms	Simplest ratio
C	20%	12	1.66	1
H	6.7%	1	6.7	4
N	46.7%	14	3.33	2
O	26.6%	16	1.66	1

Empirical formula = Molecular formula
 $= \text{CH}_4\text{N}_2\text{O}$ or NH_2CONH_2



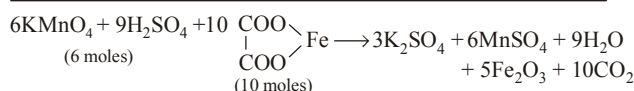
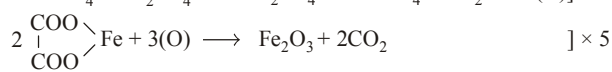
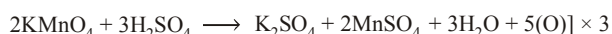
When an aqueous solution of biuret is treated with dilute sodium hydroxide and a drop of copper sulphate, a violet colour is produced. This test is known as biuret test, is characteristic of compounds having the group $-\text{CONH}$.

43. (c) Eq. wt of KMnO_4 in acid medium is 31.6 g. Hence this much amount must be dissolved in 1 litre to prepare normal solution.



According to equation $\frac{3}{2}$ mole of O_2 combines with 2 mole Al.
 2 mole Al = 54 gm

45. (a)



From above equation 6 moles MnO_4^- required to oxidise 10 moles of oxalate.

Thus number of moles of MnO_4^- required to oxidise one

$$\text{mole of oxalate} = \frac{6}{10} = 0.6 \text{ moles}$$



In this reaction oxygen is the limiting agent. Hence amount of H_2O produced depends on the amount of O_2 taken

$\therefore 0.5 \text{ mole of } \text{O}_2 \text{ gives } \text{H}_2\text{O} = 1 \text{ mol}$

$\therefore 2 \text{ mole of } \text{O}_2 \text{ gives } \text{H}_2\text{O} = 4 \text{ mol}$

47. (a) $2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 6\text{Cl}^{-}(\text{aq}) + 3\text{H}_2(\text{g})$
 $\therefore 6 \text{ moles of HCl produces} = 3 \text{ moles of } \text{H}_2$
 $= 3 \times 22.4 \text{ L of } \text{H}_2 \text{ at S.T.P}$

$$\therefore 1 \text{ mole of HCl produces} = \frac{3 \times 22.4}{6} \text{ L of } \text{H}_2 \text{ at S.T.P}$$

$$= 11.2 \text{ L of } \text{H}_2 \text{ at STP}$$

48. (d) We know that from the reaction $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ that the ratio of the volume of gaseous reactants and products is in agreement with their molar ratio. The ratio of $\text{H}_2 : \text{Cl}_2 : \text{HCl}$ volume is 1 : 1 : 2 which is the same as their molar ratio. Thus volume of gas is directly related to the number of moles. Therefore, the assertion is false but reason is true.

49. (d) One mole of any substance corresponding to 6.023×10^{23} entities in respective of its weight.

Molecular weight of $\text{SO}_2 = 32 + 2 \times 16 = 64 \text{ gm}$.

Molecular weight of $\text{O}_2 = 16 \times 2 = 32 \text{ gm}$.

$\therefore$ Molecular weight of SO_2 is double to that of O_2

50. (d) 1.231 has four significant figures all no. from left to right are counted, starting with the first digit that is not zero for calculating the no. of significant figure.

EXERCISE - 3

Exemplar Questions

1. (b) Average of readings of student A

$$= \frac{3.01 + 2.99}{2} = 3.00$$

Average of readings of student B

$$= \frac{3.05 + 2.95}{2} = 3.00$$

Correct reading = 3.00

Since, average value in both the cases is close to the correct value. Hence, readings of both are accurate.

Readings of student A differ only by 0.02 and also close to the correct reading hence, readings are precise too. But readings of student B differ by 0.1 and hence are not precise.

2. (c) The relation between the temperatures on two scales is given by the following relationship :

$$^{\circ}\text{F} = \frac{9}{5} T^{\circ}\text{C} + 32$$

$$\therefore T^{\circ}\text{C} = (^{\circ}\text{F} - 32) \times \frac{5}{9} = \frac{200 - 32}{9} \times 5$$

$$\Rightarrow T^{\circ}\text{C} = \frac{168 \times 5}{9} = 93.3^{\circ}\text{C}$$

3. (c) Molarity = $\frac{\text{weight} \times 1000}{\text{molecular weight} \times \text{volume (mL)}}$

$$= \frac{5.85 \times 1000}{58.5 \times 500} = 0.2 \text{ mol L}^{-1}$$

4. (b) For dilution, a general formula is
- $$\begin{array}{ccc} M_1 V_1 & = & M_2 V_2 \\ \text{(Before dilution)} & & \text{(After dilution)} \\ 500 \times 5M & = & 1500 \times M_2 \\ M_2 = \frac{5}{3} = 1.66 M \end{array}$$
5. (d) number of atoms = No. of moles $\times N_A$
- Moles of 4 g He = $\frac{4}{4} = 1 \text{ mol} \Rightarrow N_A \text{ atoms}$
- 46 g Na = $\frac{46}{23} = 2 \text{ mol} \Rightarrow 2 N_A \text{ atoms}$
- 0.40 g Ca = $\frac{0.40}{40} = 0.1 \text{ mol} \Rightarrow 0.1 N_A \text{ atoms}$
- 12 g He = $\frac{12}{4} = 3 \text{ mol} \Rightarrow 3 N_A \text{ atoms}$
- i.e. 12 g He contains greatest number of atoms.
6. (c) In the given question, 0.9 g L⁻¹ means that 1000 mL (or 1L) solution contains 0.9 g of glucose.
Molecular mass of glucose (C₆H₁₂O₆) = 180 u
- $$\therefore \text{Number of moles of glucose} = \frac{0.9}{180} = 0.005 \text{ M}$$
- $$= 5 \times 10^{-3} \text{ mol glucose}$$
- Hence, 1000 mL or 1L solution contains 0.005 mole glucose or the molarity of glucose is 0.005 M.
7. (d) Molality (m) = $\frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$
- $\therefore$ Molecular weight of HCl = 36.5 g
- $$\therefore \text{Moles of HCl} = \frac{18.25}{36.5} = 0.5$$
- $$m = \frac{0.5 \times 1000}{500} = 1 \text{ m}$$
8. (a) Number of millimoles of H₂SO₄.
- $$\begin{aligned} &= \text{molarity} \times \text{volume in mL} \\ &= 0.02 \times 100 = 2 \text{ millimoles} \\ &= 2 \times 10^{-3} \text{ mol} \end{aligned}$$
- Number of molecules = Number of moles $\times N_A$.
- $$\begin{aligned} &= 2 \times 10^{-3} \times 6.022 \times 10^{23} \\ &= 12.044 \times 10^{20} \text{ molecules} \end{aligned}$$
9. (b) Molecular mass of CO₂ = 44 g
- $\therefore$ 44 g of CO₂ contain C = 12 g atoms of carbon
- $$\therefore \% \text{ of C in CO}_2 = \frac{12}{44} \times 100 = 27.27\%$$
- i.e. mass percent of carbon in CO₂ is 27.27%.
10. (c) Empirical formula mass of CH₂O = 30
- Molecular mass = 180 (Given)
- $$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{180}{30} = 6$$
- $\therefore$ Molecular formula = $n \times$ empirical formula
- $$\begin{aligned} &= 6 \times \text{CH}_2\text{O} \\ &= \text{C}_6\text{H}_{12}\text{O}_6 \end{aligned}$$
11. (a) For a solution, Mass = volume $\times$ density
- $$= 1.5 \text{ mL} \times 3.12 \text{ g mL}^{-1} = 4.68 \text{ g}$$
- The digit 1.5 has only two significant figures, so the answer must also be limited to two significant figure. So it is rounded off to 4.7 g.
12. (c) The properties of a compound are quite different from the properties of constituent elements. e.g., ammonia is a compound containing hydrogen and nitrogen combined together in a fixed proportion. But the properties of ammonia are completely different from its constituents, hydrogen and nitrogen.
13. (a) According to the law of conservation of mass, Total mass of reactants = Total mass of products
14. (b) In this equation
- $$\begin{array}{ccccccc} \text{C}_3\text{H}_8(\text{g}) & + & \text{O}_2(\text{g}) & \longrightarrow & \text{CO}_2(\text{g}) & + & \text{H}_2\text{O}(\text{g}) \\ 44\text{g} & & 32\text{g} & & 44\text{g} & & 18\text{g} \end{array}$$
- i.e. mass of reactants $\neq$ mass of products
- Hence, law of conservation of mass is not obeyed.
15. (b) In CO₂, 12 parts by mass of carbon combine with 32 parts by mass of oxygen while in CO, 12 parts by mass of carbon combine with 16 parts by mass of oxygen. Therefore, the masses of oxygen combine with a fixed mass of carbon (12 parts) in CO₂ and CO are 32 and 16 respectively. These masses of oxygen bear a simple ratio of 32 : 16 or 2 : 1 to each other.
- This is an example of law of multiple proportion.

NEET/AIPMT (2013-2017) Questions

16. (c) Millimoles of solution of chloride
- $$= 0.05 \times 10 = 0.5$$
- Millimoles of AgNO₃ solution = $10 \times 0.1 = 1$
- So, the millimoles of AgNO₃ are double than the chloride solution.
- $$\therefore \text{XCl}_2 + 2\text{AgNO}_3 \longrightarrow 2\text{AgCl} + \text{X}(\text{NO}_3)_2$$
17. (a) $M = \frac{6.02 \times 10^{20} \times 1000}{100 \times 6.02 \times 10^{23}} = \frac{6.02 \times 10^{21}}{6.02 \times 10^{23}} = 0.01 \text{ M}$
18. (a)
- | | | | | |
|-------------------------------|---|-----------------|-------------------|------|
| H ₂ | + | Cl ₂ | $\longrightarrow$ | 2HCl |
| t = 0 22.4 lit | | 11.2 lit | | 0 |
| t = 0 or 1 mole | | 0.5 mole | | 0 |
| at time t | | (1 - 0.5) | | |
| 0.5 $\times$ 2 = 0.5 = 1 mole | | | | |
19. (a) Initially
- | | | | | |
|------------------------------|---|--------------------------|-------------------|-----|
| Mg | + | $\frac{1}{2}\text{O}_2$ | $\longrightarrow$ | MgO |
| 1g | | 0.56 | | |
| or $\frac{1}{24}$ mole | | $\frac{0.56}{32}$ mole | | |
| 0.0416 mole | | 0.0175 mole | | |
| (0.0416 - 2 $\times$ 0.0175) | | (2 $\times$ 0.0175) mole | | |
| = 0.0066 mole | | | | |

$$\therefore \text{Mass of Mg} = 0.0066 \times 24$$

$$= 0.158 \approx 0.16 \text{ g}$$

20. (b) If 6.022×10^{23} changes to $6.022 \times 10^{20}/\text{mol}$ than this would change mass of one mole of carbon.

21. (c) 50 ml of 16.9% solution of AgNO_3

$$\left(\frac{16.9}{100} \times 50 \right) = 8.45 \text{ g of AgNO}_3$$

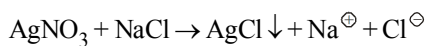
$$n_{\text{mole}} = \frac{8.45 \text{ g}}{(107.8 + 14 + 16 \times 3) \text{ g/mol}}$$

$$= \left(\frac{8.45 \text{ g}}{169.8 \text{ g/mol}} \right) = 0.0497 \text{ moles}$$

50 ml of 5.8% solution of NaCl contain

$$\text{NaCl} = \left(\frac{5.8}{100} \times 50 \right) = 2.9 \text{ g}$$

$$n_{\text{NaCl}} = \frac{2.9 \text{ g}}{(23 + 35.5) \text{ g/mol}} = 0.0495 \text{ moles}$$



$$\therefore \begin{array}{ccc} 1 \text{ mole} & 1 \text{ mole} & 1 \text{ mole} \\ 0.049 \text{ mole} & 0.049 \text{ mole} & 0.049 \text{ mole of AgCl} \end{array}$$

$$n = \frac{w}{M} \rightarrow w = (n_{\text{AgCl}}) \times \text{Molecular Mass}$$

$$= (0.049) \times (107.8 + 35.5)$$

$$= 7.02 \text{ g}$$

22. (a) Ratio of weight of gases = $w_{\text{H}_2} : w_{\text{O}_2} = 1 : 4$

$$\text{Ratio of moles of gases} = n_{\text{H}_2} : n_{\text{O}_2} = \frac{1}{2} : \frac{4}{32}$$

$$\therefore \text{Molar Ratio} = \frac{1}{2} \times \frac{32}{4} = 4 : 1$$

23. (d) $\text{MgCO}_3 \longrightarrow \text{MgO} + \text{CO}_2$

84 g of MgCO_3 form 40 g of MgO

$$\therefore 20 \text{ g of MgCO}_3 \text{ form } \frac{40 \times 20}{84} \text{ g of MgO}$$

$$= 9.52 \text{ g of MgO}$$

Since 8.0 g of MgO is formed

$$\text{Purity of sample} = \frac{8}{9.52} \times 100 = 84.0\%$$

24. (d) No. of moles of water

In 1.8 g of $\text{H}_2\text{O} = 0.1$ moles

In 18 g of $\text{H}_2\text{O} = 1$ moles

1 mole contain 6.022×10^{23} molecules of water

therefore maximum number of molecules is in 18 moles of water.

Chapter

2

Structure of Atom

SUB-ATOMIC PARTICLES

Many different kinds of sub-atomic particles were discovered in the twentieth century. Three of these are electron, proton and neutron.

Electron

Electrons are the basic constituent of all atoms. They were discovered by cathode ray discharge tube experiment. Cathode rays consist of negatively charged particles called electrons.

The charge to mass ratio of electron is given by

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1}$$

where $m_e \rightarrow$ mass of e^-

$e \rightarrow$ magnitude of charge on electron.

Charge on electron is $-1.6 \times 10^{-19} \text{ C}$ and the mass of electron is $9.1 \times 10^{-31} \text{ kg}$.

Charge and Mass of Fundamental Subatomic Particles

Name	Symbol	Absolute charge/c	Relative charge	Mass(kg)	Mass(u)	Approx. mass(u)
Electron	e	-1.6×10^{-19}	-1	9.1×10^{-31}	0.00054	0
Proton	p	$+1.6 \times 10^{-19}$	+1	1.67×10^{-27}	1.00727	1
Neutron	n	0	0	1.67×10^{-27}	1.00867	1

ATOMIC MODELS

Thomson Model of Atom

It is also called plum pudding, raisin pudding or water melon model. It can be visualised as a pudding or watermelon of positive charge with plums or seeds (e^- s) embedded into it. An important feature of this model is that the mass of atom is assumed to be uniformly distributed over the atom. The model was able to explain the overall neutrality of atom but was not consistent with results of later experiments.

Rutherford's Model of Atom

Rutherford performed the α -particle scattering experiment. A stream of high energy α -particles from a radioactive source was directed at a thin foil of gold metal. It was observed that:

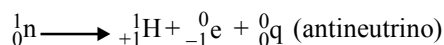
- Most of α -particles passed through gold foil undeflected
- A small fraction of α -particles was deflected by small angles.

Proton

The smallest and lightest positive ion is proton. These positively charged particles are called canal rays. The credit for the discovery of proton goes to **Goldstein**. **Thomson** and **Wein** estimated the value of e/m as 9.578×10^4 coulomb per gram for the positively charged particle proton. Proton is obtained when the only one electron present in hydrogen atom is removed. Hydrogen atom consists of one electron, one proton and no neutron.

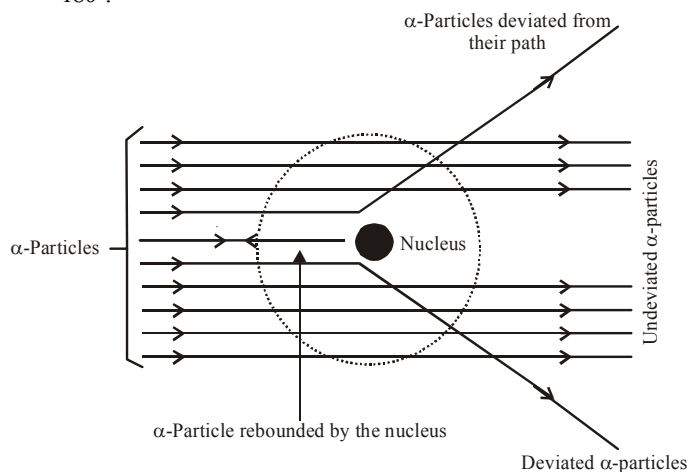
Neutron

The electrically neutral particles present in the atom are neutrons. It was discovered by **James Chadwick** in 1932. Neutron is relatively heavier out of the three fundamental particles of atom. It is assumed that a neutron is a result of joining together of an electron and a proton. A neutron, being unstable, decays as follows :



Its half-life is 20 minutes.

- A few α -particles bounced back, i.e., were deflected by nearly 180° .



On the basis of the observations, following conclusions were drawn.

- Most of the space in the atom is empty.
- The deflection of particles was due to the positive charge which is concentrated in a very small volume
- The volume occupied by the nucleus is small as compared to the total volume of the atom.

Thus, according to this model,

- The positive charge and most of the mass of the atom was densely concentrated in a small region called the nucleus of atom.
- The nucleus is surrounded by e^{-1} s that move around the nucleus with a very high speed in circular paths called orbits.
- e^{-1} s and nucleus are held together by electrostatic forces of attraction.

Drawback of Rutherford model: (i) It cannot explain the stability of atom. (ii) It does not explain the electronic structure of atom.

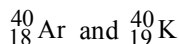
Atomic Number and Mass Number

- Atomic number (Z) = number of protons in nucleus of atom
= number of e^{-1} s in a neutral atom
- Mass number (A) = number of protons (Z) + number of neutrons (n)

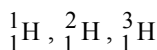
For example,	$^{16}_8\text{O}$	$^{14}_7\text{N}$	$^{23}_{11}\text{Na}$
Protons	8	7	11
Neutrons	8	7	12
Mass number	16	14	23

Isobars and Isotopes

- Isobars are the atoms with same mass number but different atomic number. For ex:



- Isotopes are atoms of the same element with same atomic number but different mass number. For ex: Hydrogen has 3 isotopes



Isosters

They are the molecules which have the same number of atoms and electrons.

Ex.	CO_2	N_2O
Atoms =	$1 + 2$	$2 + 1$
=	3	3
Electrons =	$6 + 8 \times 2$	$7 \times 2 + 8$
=	22	22

DEVELOPMENTS LEADING TO BOHR'S MODEL OF ATOM

Two developments played a major role in the formulation of Bohr's model of atom. These are:

- Dual character of electromagnetic radiation
- Atomic spectra which is explained by assuming quantized electronic energy levels in atoms.

Dual Nature of Electromagnetic Radiation

It means that the radiations possess both wave-like and particle-like properties, i.e.,

- Wave nature** : Electromagnetic radiations are waves which are transmitted when electrically charged particle moves under acceleration, producing alternate electric and magnetic fields. Electromagnetic radiations are of many types, differing from one another in wavelength (or frequency). They constitute the electromagnetic spectrum.

These radiations are characterised by frequency (ν) and wavelength (λ). SI unit of ν is Hertz (Hz) or s^{-1}

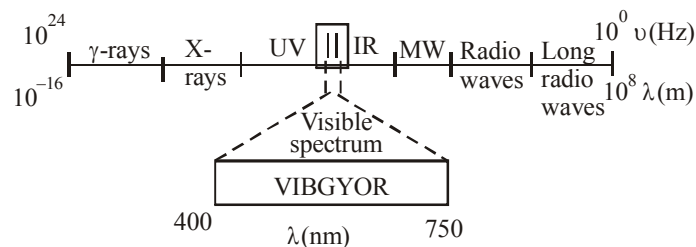
SI unit of λ is m.

ν , λ and c (speed of light) are related as $c = \nu\lambda$

$$\bar{\nu} = \text{wave number} = \frac{1}{\lambda}$$

Electromagnetic spectrum: It is defined as the arrangement of various types of electromagnetic radiation in terms of increasing (or decreasing) wave lengths (or frequency). The complete range of electromagnetic waves is called electromagnetic spectrum. The wavelength of various waves increases in the following order

Cosmic rays < γ -rays < X-rays < UV rays < Visible < IR rays
< Micro waves < Radio waves



- Particle nature**

According to Planck, atoms and molecules emit energy only in discrete quantities and gave the name quantum to the smallest quantity of energy that can be emitted or absorbed. The energy of quantum of radiation is given by:

$$E = h\nu$$

where $\nu \rightarrow$ frequency

$h \rightarrow$ Planck's constant ($6.6 \times 10^{-34} \text{ Js}$)

Photoelectric effect: when a beam of light strikes the surface of a metal, e^{-1} s are ejected from it and the phenomenon is called photoelectric effect. For each metal, there is a minimum frequency (ν_0) called threshold frequency below which photoelectric effect is not observed.

Work function : A part of the photons energy that is absorbed by the metal surface to release the e^{-1} s known as work function of the surface. The remaining part of energy goes into K.E.

At $\nu > \nu_0$, ejected e^{-1} s come out with some K.E.

$$\therefore h\nu = h\nu_0 + \frac{1}{2}m\nu^2 \text{ i.e. } E = E_0 + KE$$

Where, E : energy of radiation

E_0 : minimum energy

Electromagnetic wave theory could explain phenomenon like interference, diffraction, etc., but it could not explain some other phenomenon like black body radiation, photoelectric effect, etc. These phenomenon could be explained only if em waves are supposed to have particle nature. It was explained by **Max Planck** and is called the **Planck's Quantum Theory**.

ATOMIC SPECTRA

Spectrum is a series of coloured bands which are formed when white light passes through a prism. A spectrum is of mainly three types :

- (i) Emission spectrum
- (ii) Absorption spectrum
- (iii) Molecular spectrum

Emission Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called emission spectrum. Emission spectra are of the following two types

- (i) Continuous spectrum and
- (ii) line spectrum or atomic spectrum
- (i) **Continuous Spectrum** : When sunlight or a glowing heat fluorescent substance like tungsten wire present in an electric bulb is analysed with the help of a spectroscope, the spectrum obtained on a screen is observed as divided into bands of seven colours, which are in a continuous sequence. Such a spectrum is called a continuous spectrum.
- (ii) **Line Spectrum** : In the gas phase, the emission spectra of atoms is not continuous, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra.

Absorption Spectra

It is observed when a continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength leaves dark spaces in the bright continuum spectrum.

Molecular Spectrum

Molecular spectrum is given by molecules and it is also known as band spectrum.

LINE SPECTRUM OF HYDROGEN

The spectrum of hydrogen consists of several lines named after their discover.

The visible lines of the H-spectrum obey the following formula:

$$\bar{\nu} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where $\bar{\nu}$ = wave number,

$109,677 \text{ cm}^{-1}$ = Rydberg's const (R_H)

Series	n_1	n_2	Spectral region
Lyman	1	2, 3, ...	UV
Balmer	2	3, 4, ...	Visible
Paschen	3	4, 5, ...	IR
Brackett	4	5, 6, ...	IR
Pfund	5	6, 7, ...	IR

BOHR'S MODEL FOR H-ATOM

This model is based on following postulates :

- (i) The electron in H-atom moves around the nucleus in circular paths called orbits, stationary states or energy states.

- (ii) The energy of e^- in the orbit does not change. The energy change takes place only when an e^- jump from lower energy orbit to higher energy orbit or vice versa.
- (iii) The frequency of radiation absorbed or emitted is given by:

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

Where, E_1 = energy of lower state

E_2 = energy of higher state

- (iv) The angular momentum of an electron in a given stationary state is $mvr = \frac{nh}{2\pi}$
- (v) Frequency (ν) associated with the absorption and emission of photon is given as :

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$= 1.09677 \times 10^7 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ m}^{-1}$$

Features of Bohr's Model

According to Bohr's theory of H-atom:

- (i) The stationary states for e^- are numbered as 1, 2, 3, ... and are known as principal quantum numbers.
- (ii) The radii of the stationary states are given by:
 $r_n = n^2 a_0$ where $a_0 = 52.9 \text{ pm}$
- (iii) The energy of the stationary state is given by:

$$E_n = -R_H \left(\frac{1}{n^2} \right) \text{ where, } R_H \rightarrow \text{Rydberg constant}$$

- (iv) Bohr's theory can be applied to ions containing only one e^- like He^+ , Li^{2+} , Be^{3+} and so on. The energy of stationary states of these ions is given by:

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J}$$

and, radii by the expression

$$r_n = \frac{52.9 (n^2)}{Z} \text{ pm}$$

Limitations of the Bohr's Model

Bohr's model ,

- (i) was unable to explain the spectrum of atoms other than hydrogen.
- (ii) could not explain the ability of atoms to form molecules by chemical bonds.
- (iii) was unable to explain splitting of spectral lines in magnetic field (Zeeman effect).
- (iv) was unable to explain the splitting of lines in electrical field (Stark effect)

DUAL BEHAVIOUR OF MATTER

DeBroglie's concept was experimentally verified by **Davisson and Germer** by observing diffraction effect (a property shown by waves) with an electron beam.

On the basis of dual nature of matter, de Broglie gave the following relation between wavelength (λ) and momentum (p) of material particle, i.e.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad \text{where, } h = \text{Planck's constant}$$

HEISENBERG'S UNCERTAINTY PRINCIPLE

According to the principle, it is impossible to determine simultaneously, the exact position and exact momentum of an electron. Mathematically,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta (mv_x) \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta v_x \geq \frac{h}{4\pi m}$$

Here

Δx is uncertainty of position,

Δp is uncertainty of momentum and

h is Planck's constant

QUANTUM MECHANICAL MODEL OF ATOM

The branch of science that takes into account dual behaviour of matter is called quantum mechanics.

Schrodinger Wave Equation

Schrodinger (1927) gave a mathematical expression known as a **Schrodinger wave equation**. His theory is based on quantum mechanical model of atom in which the concept of probability of finding the electron at any position around the nucleus at any instant of time is considered.

Significance of wave function : An atomic orbital is the wave function ψ for an e^- in an atom. ψ^2 is known as probability density. ψ^2 gives the probability of finding the e^- around the nucleus.

QUANTUM NUMBERS

The position of an electron in any atom can be ascertained with the help of quantum numbers. In an atom, a shell consists of subshells and the sub-shell consists of orbitals. Each orbital can accommodate only two electrons, which have opposite spins.

Quantum numbers are designated as **principal quantum number** (n), **azimuthal quantum number** (l), **magnetic quantum number** (m) and **spin quantum number** (s). The four quantum numbers provide the following information

- n defines the shell, determines the size of the orbital and the energy of the orbital. An atom has K, L, M, N, O, P, Q, etc. shell.
- l identifies the subshell and determines the shape of the

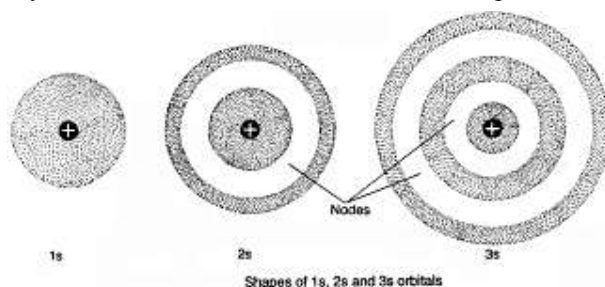
orbital. There are $(2l + 1)$ orbitals of each type in a subshell, i.e., one s-orbital ($l = 0$); three p-orbitals ($l = 1$) and five d-orbitals ($l = 2$) per sub-shell.

- m_l designates the orientation of the orbital. For a given value of l , m_l has $(2l + 1)$ values.
- m_s refers to orientation of the spin of the e^- . m_s can have two values $+\frac{1}{2}$ or $-\frac{1}{2}$.

SHAPES OF ATOMIC ORBITALS

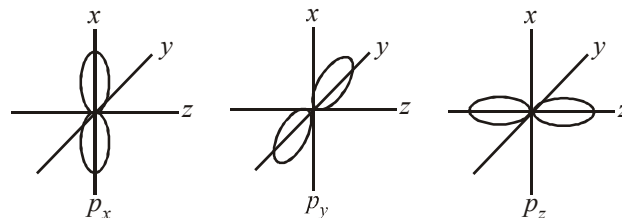
(i) s-orbital:

For s-orbitals $l = 0$, so there is only one value of m i.e. $m = 0$. Thus, s-orbital can have only one orientation i.e. the probability of finding electron is same in all directions at a given distance from the nucleus. Hence s-orbital is symmetrical around the nucleus and thus has spherical shape.



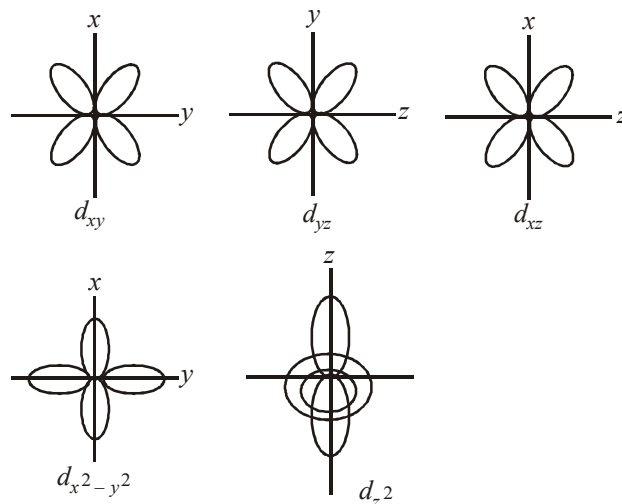
(ii) p-orbital:

For p-orbitals $l = 1$, the permissible values of m are $+1, 0$ and -1 . Thus, there are three p-orbitals, designated as p_x, p_y and p_z , in each p-subshell.



(iii) d-orbital

For d-orbitals $l = 2$ i.e. the permissible values of m are $-2, -1, 0, +1, +2$. This indicates for the five d-orbitals designated as $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ and d_{z^2} .



NODES OF ORBITALS

The region where probability density function reduces to zero is called nodes.

Generally ns – orbital has $(n - 1)$ nodes

Number of spherical/radial nodes in any orbital $= n - \ell - 1$

Number of planar nodes in any orbital $= \ell$

$\therefore$ Total number of nodes in any orbital $= n - 1$

ENERGIES OF ORBITALS

The energy of orbitals for H-atom depends only on n and increases as follows:

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$$

The orbitals having same energy are called degenerate. For multi e^- atoms, energy of an e^- depends on n and ℓ . The lower the value of $(n + \ell)$ for an orbital, the lower is its energy. If two orbitals have same value of $(n + \ell)$, the orbital with lower value of n will have lower energy.

Filling of Orbitals in Atom

- (i) **Aufbau principle:** It states that in the ground state of atoms, orbitals are filled in order of their increasing energies.

The order in which energies of orbitals increase is:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 4f < 5d < 6p < 7s.$$

- (ii) **Pauli Exclusion principle:** It states that no two e^- s in an atom can have same set of four quantum numbers.

- (iii) **Hund's rule of maximum multiplicity:** It states that pairing of e^- s in orbitals belonging to same subshell (p , d or f) does not take place until each orbital belonging to that subshell has got one e^- each, i.e., it is singly occupied.

Writing The Configuration of Atoms/ Ions

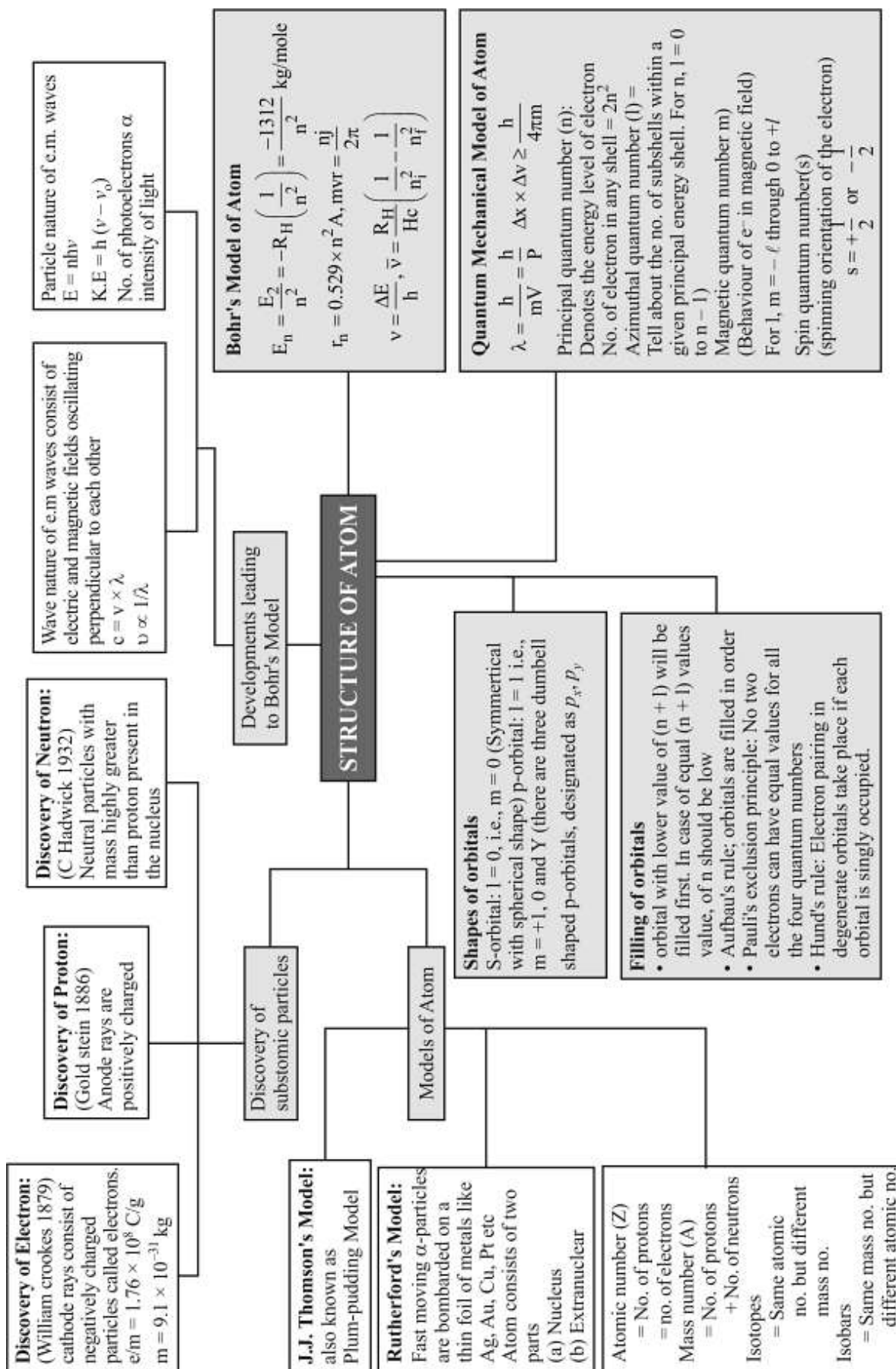
First of all, the configuration of the atom is written. Then, appropriate number of electrons are deducted from the outermost shell for the configuration of the cation. Similarly, appropriate number of electrons are added to the outermost shell for the configuration of the anion.

Stability of Completely Filled or Half-filled Sub-shells

The completely filled or exactly half-filled sub-shells are stable due to following reasons.

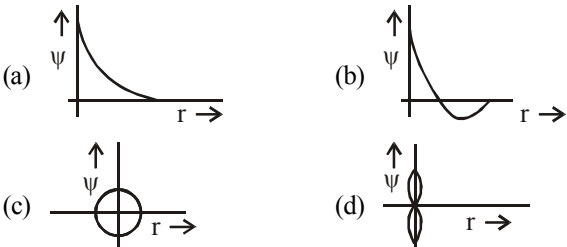
- (i) Orbitals which are either half filled or fully filled are more symmetrical and therefore possess lower energy i.e. extra stability.
- (ii) When orbitals are half filled or fully filled, the exchange of electrons between the orbitals is maximum. Such exchanges leads to greater stability of electrons in the orbitals, because low exchange energy results in to higher stabilization.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- The ion that is isoelectronic with CO is
(a) CN^- (b) O_2^+ (c) O_2^- (d) N_2^+
- Set of isoelectronic species is
(a) $\text{N}_2, \text{CO}_2, \text{CN}^-, \text{O}_2$ (b) $\text{N}_2, \text{H}_2\text{S}, \text{CO}$
(c) $\text{N}_2, \text{CO}, \text{CN}^-, \text{O}_2^{2+}$ (d) $\text{Ca}, \text{Mg}, \text{Cl}$
- The wave-function (ψ) for a 2s-electron as a function of its distance from the nucleus (r) can be sketched as:

- The combination of three 2p orbitals of one atom and three 2p orbitals of another atom can give rise to :
(a) three molecular orbitals
(b) six (π 2p) molecular orbitals
(c) four (π 2p) and two (σ 2p) molecular orbitals
(d) two molecular orbital which are symmetrical around the bond axis
- The species isoelectronic with C_2H_4 is
(a) O_2^+ (b) CN^-
(c) N_2^+ (d) O_2
- Cathode rays are deflected by
(a) an electric field only (b) magnetic field only
(c) by both (d) by none
- The number of neutrons in dipositive zinc ion with mass number 70 is
(a) 34 (b) 36 (c) 38 (d) 40
- Which has the highest e/m ratio ?
(a) He^{2+} (b) H^+ (c) He^+ (d) D^+
- One would expect proton to have very large :
(a) ionization potential (b) radius
(c) charge (d) hydration energy
- Which is correct statement about proton ?
(a) Proton is nucleus of deuterium
(b) Proton is α -particle
(c) Proton is ionized hydrogen molecule
(d) Proton is ionized hydrogen atom
- Which one of the following is expected to have largest size?
(a) F^- (b) O^{2-} (c) Al^{3+} (d) N^{3-}
- The maximum number of electrons in p-orbital with $n = 6$; $m = 0$ is
(a) 6 (b) 2 (c) 14 (d) 10
- The compound in which cation is isoelectronic with anion is :
(a) NaCl (b) CsF (c) NaI (d) K_2S
- What is the ratio of mass of an electron to the mass of a proton?
(a) 1 : 2 (b) 1 : 1 (c) 1 : 1837 (d) 1 : 3
- The increasing order for the values of e/m (charge/mass) is
(a) e, p, n, α (b) n, p, e, α (c) n, p, α, e (d) n, α, p, e
- If the mass number of an element is W and its atomic number is N , then
(a) Number of $e^- = W - N$ (b) Number of ${}_1\text{H}^1 = W - N$
(c) Number of ${}_0n^1 = W - N$ (d) Number of ${}_0n^1 = N$
- According to Bohr's theory the energy required for an electron in the Li^{2+} ion to be emitted from $n = 2$ state is (given that the ground state ionization energy of hydrogen atom is 13.6 eV)
(a) 61.2 eV (b) 13.6 eV (c) 30.6 eV (d) 10.2 eV
- Which one is correct for the de-Broglie equation?
(a) $E = \lambda/p$ (b) $p = h/\lambda$
(c) $E = h/p$ (d) none of these
- Which of the following pairs is correctly matched ?
(a) Isoelectronic $\text{N}^{3-}, \text{O}^{2-}, \text{Cr}^{3-}$
(b) Isotones ${}_{14}\text{Si}^{30}, {}_{15}\text{P}^{31}, {}_{16}\text{S}^{32}$
(c) Isotopes ${}_{20}\text{Ca}^{40}, {}_{19}\text{K}^{40}$
(d) Isobars ${}_8\text{O}^{16}, {}_8\text{O}^{17}, {}_8\text{O}^{18}$
- The spectrum of He is expected to be similar to that of
(a) H (b) Li^+ (c) Na (d) He^+
- Which of the following statements do not form a part of Bohr's model of hydrogen atom ?
(a) Energy of the electrons in the orbits are quantized
(b) The electron(s) in the orbit nearest to the nucleus has the lowest energy
(c) Electrons revolve in different orbits around the nucleus
(d) The position and velocity of the electrons in the orbit cannot be determined simultaneously.
- The radius of hydrogen atom in the ground state is 0.53 Å. The radius of Li^{2+} ion (atomic number = 3) in a similar state is
(a) 0.17 Å (b) 0.265 Å (c) 0.53 Å (d) 1.06 Å
- The Bohr orbit radius for the hydrogen atom ($n = 1$) is approximately 0.530 Å. The radius for the first excited state ($n = 2$) orbit is (in Å)
(a) 0.13 (b) 1.06 (c) 4.77 (d) 2.12
- MO configuration of He_2^- is
(a) $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^1$ (b) $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma^* 2s)^1$
(c) $(\sigma 1s)^2, (\sigma^* 1s)^1, (\sigma 2s)^2$ (d) $(\sigma 1s)^2, (\sigma^* 1s)^1, (\sigma^* 2s)^2$
- The quantum number which is responsible for the size of electron cloud is
(a) spin (b) azimuthal
(c) principal (d) magnetic

26. "Electrons are filled in energy orbitals, in increasing order of energy." This statement is related to
 (a) Planck's rule (b) Hund's rule
 (c) Pauli's rule (d) Aufbau principle
27. The energy of second Bohr orbit of the hydrogen atom is -328 kJ mol^{-1} ; hence the energy of fourth Bohr orbit would be:
 (a) -41 kJ mol^{-1} (b) -82 kJ mol^{-1}
 (c) -164 kJ mol^{-1} (d) $-1312 \text{ kJ mol}^{-1}$
28. The orbital angular momentum for an electron revolving in an orbit is given by $\sqrt{l(l+1)} \cdot \frac{h}{2\pi}$. This momentum for an s-electron will be given by
 (a) zero (b) $\frac{h}{2\pi}$ (c) $\sqrt{2} \cdot \frac{h}{2\pi}$ (d) $+\frac{1}{2} \cdot \frac{h}{2\pi}$
29. The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be (Rydberg constant = $1.097 \times 10^7 \text{ m}^{-1}$)
 (a) 406 nm (b) 192 nm
 (c) 91 nm (d) $9.1 \times 10^{-8} \text{ nm}$
30. The frequency of radiation emitted when the electron falls from $n=4$ to $n=1$ in a hydrogen atom will be (Given : ionization energy of H = $2.18 \times 10^{-18} \text{ J atom}^{-1}$ and $h = 6.625 \times 10^{-34} \text{ J s}$)
 (a) $1.54 \times 10^{15} \text{ s}^{-1}$ (b) $1.03 \times 10^{15} \text{ s}^{-1}$
 (c) $3.08 \times 10^{15} \text{ s}^{-1}$ (d) $2.00 \times 10^{15} \text{ s}^{-1}$
31. According to Bohr's theory, the angular momentum of an electron in 5th orbit is
 (a) $10 h/\pi$ (b) $2.5 h/\pi$ (c) $25 h/\pi$ (d) $1.0 h/\pi$
32. Which of the following transitions of electrons in the hydrogen atom will emit maximum energy?
 (a) $n_5 \rightarrow n_4$ (b) $n_4 \rightarrow n_3$
 (c) $n_3 \rightarrow n_2$ (d) all will emit same energy
33. The allowed values of m for $l = 2$ is
 (a) $0, \pm 1$ (b) $\pm 1, \pm 2$
 (c) $0, \pm 1, \pm 2$ (d) $0, \pm 2$
34. Pick out the isoelectronic structure from the following:
 (i) $\text{C}^+ \text{H}_3$ (ii) $\text{H}_3 \text{O}^+$
 (iii) NH_3 (iv) CH_3^-
 (a) i and ii (b) iii and iv
 (c) ii, iii and iv (d) iii, iv and i
35. The first emission line of hydrogen atomic spectrum in the Balmer series appears is (R = Rydberg constant)
 (a) $\frac{5}{36} R \text{ cm}^{-1}$ (b) $\frac{3}{4} R \text{ cm}^{-1}$
 (c) $\frac{7}{144} R \text{ cm}^{-1}$ (d) $\frac{9}{400} R \text{ cm}^{-1}$
36. Identify the correct statement:
 (a) s and p orbitals are degenerate
 (b) sp and sp^2 orbitals are degenerate
 (c) p and sp^3 orbitals are degenerate
 (d) All sp^3 orbitals are degenerate
37. Correct set of four quantum numbers for valence electron of rubidium ($Z = 37$) is
 (a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
 (c) $5, 1, 1, +\frac{1}{2}$ (d) $6, 0, 0, +\frac{1}{2}$
38. Zeeman effect refers to the :
 (a) splitting up of the lines in an emission spectrum in the presence of an external electrostatic field
 (b) random scattering of light by colloidal particles
 (c) splitting up of the lines in an emission spectrum in a magnetic field
 (d) emission of electrons from metals when light falls upon them
39. The energy of electron in first energy level is $-21.79 \times 10^{-12} \text{ erg per atom}$. The energy of electron in second energy level is :
 (a) $-54.47 \times 10^{-12} \text{ erg atom}^{-1}$
 (b) $-5.447 \times 10^{-12} \text{ erg atom}^{-1}$
 (c) $-0.5447 \times 10^{-12} \text{ erg atom}^{-1}$
 (d) $-0.05447 \times 10^{-12} \text{ erg atom}^{-1}$
40. Which of the following statements about the electron is incorrect?
 (a) It is negatively charged particle
 (b) The mass of electron is equal to the mass of neutron.
 (c) It is a basic constituent of all atoms.
 (d) It is a constituent of cathode rays.
41. In a Bohr model of an atom, when an electron jumps from $n = 3$ to $n = 1$, how much energy will be emitted?
 (a) $2.15 \times 10^{-11} \text{ ergs}$ (b) $2.389 \times 10^{-12} \text{ ergs}$
 (c) $0.239 \times 10^{-10} \text{ ergs}$ (d) $0.1936 \times 10^{-10} \text{ ergs}$
42. When atoms are bombarded with alpha particles, only a few in million suffer deflection, others pass out undeflected. This is because
 (a) the force of repulsion on the moving alpha particle is small
 (b) the force of attraction between alpha particle and oppositely charged electrons is very small
 (c) there is only one nucleus and large number of electrons
 (d) the nucleus occupies much smaller volume compared to the volume of the atom
43. The ionisation potential of a hydrogen atom is -13.6 eV . What will be the energy of the atom corresponding to $n = 2$.
 (a) -3.4 eV (b) -6.8 eV (c) -1.7 eV (d) -2.7 eV
44. If the energy of a photon is given as : $= 3.03 \times 10^{-19} \text{ J}$ then, the wavelength (λ) of the photon is :
 (a) 656 nm (b) 65.6 nm (c) 656 nm (d) 0.656 nm

45. In the photo-electron emission, the energy of the emitted electron is
 (a) greater than the incident photon
 (b) same as than of the incident photon
 (c) smaller than the incident photon
 (d) proportional to the intensity of incident photon
46. Uncertainty in position of a n electron (mass = 9.1×10^{-28} g) moving with a velocity of 3×10^4 cm/s accurate upto 0.001% will be (use $h/4\pi$) in uncertainty expression where $h = 6.626 \times 10^{-27}$ erg-second).
 (a) 1.93 cm (b) 3.84 cm (c) 5.76 cm (d) 7.68 cm
47. The configuration $1s^2, 2s^2, 2p^5, 3s^1$ shows :
 (a) excited state of O_2^-
 (b) excited state of neon atom
 (c) excited state of fluorine atom
 (d) ground state of fluorine atom
48. Positron is :
 (a) electron with positive charge
 (b) a nucleus with one neutron and one proton
 (c) a nucleus with two protons
 (d) a helium nucleus
49. The position of both, an electron and a helium atom is known within 1.0 nm. Further the momentum of the electron is known within 5.0×10^{-26} kg ms $^{-1}$. The minimum uncertainty in the measurement of the momentum of the helium atom is
 (a) 50 kg ms $^{-1}$ (b) 80 kg ms $^{-1}$
 (c) 8.0×10^{-26} kg ms $^{-1}$ (d) 5.0×10^{-26} kg ms $^{-1}$
50. If electron, hydrogen, helium and neon nuclei are all moving with the velocity of light, then the wavelength associated with these particles are in the order
 (a) Electron > hydrogen > helium > neon
 (b) Electron > helium > hydrogen > neon
 (c) Electron < hydrogen < helium < neon
 (d) Neon < hydrogen < helium < electron
51. The de Broglie wavelength of a tennis ball of mass 60 g moving with a velocity of 10 metres per second is approximately
 (a) 10^{-31} metres (b) 10^{-16} metres
 (c) 10^{-25} metres (d) 10^{-33} metres
 Planck's constant, $h = 6.63 \times 10^{-34}$ Js
52. Which of the following is related with both wave nature and particle nature ?
 (a) Interference (b) $E = mc^2$
 (c) Diffraction (d) $E = h\nu$
53. If the radius of first Bohr orbit be a_0 , then the radius of the third orbit would be
 (a) $3 \times a_0$ (b) $6 \times a_0$
 (c) $9 \times a_0$ (d) $1/9 \times a_0$
54. The ratio of the radius of the first Bohr orbit for the electron orbiting the hydrogen nucleus to that of the electron orbiting the deuterium nucleus (mass nearly twice that of the hydrogen nucleus) is approximately
 (a) 2 : 1 (b) 1 : 1
 (c) 1 : 2 (d) 4 : 1
55. The de-Broglie wavelength of an electron in the ground state of hydrogen atom is : [K.E. = 13.6 eV; 1eV = 1.602×10^{-19} J]
 (a) 33.28 nm (b) 3.328 nm (c) 0.3328 nm (d) 0.0332 nm
56. The mass of a photon with a wavelength equal to 1.54×10^{-8} cm is
 (a) 0.8268×10^{-34} kg (b) 1.2876×10^{-33} kg
 (c) 1.4285×10^{-32} kg (d) 1.8884×10^{-32} kg
57. When a metal surface is exposed to solar radiations
 (a) The emitted electrons have energy less than a maximum value of energy depending upon frequency of incident radiations
 (b) The emitted electrons have energy less than maximum value of energy depending upon intensity of incident radiation
 (c) The emitted electrons have zero energy
 (d) The emitted electrons have energy equal to energy of photons of incident light
58. The wavelength of a moving electron having 4.55×10^{-25} J of kinetic energy is :
 (a) 7.27×10^{-7} metre (b) 72.7×10^{-7} metre
 (c) 7.27×10^{-9} metre (d) 72.7×10^{-9} metre
59. Which one of the following represents noble gas configuration :
 (a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 5d^6, 6s^2$
 (b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 5d^1, 6s^2$
 (c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6$
 (d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4f^{14}, 5s^2, 5p^6, 5d^1$
60. Number of unpaired electrons in N^{2+} is
 (a) 2 (b) 0 (c) 1 (d) 3
61. The total number of electrons that can be accommodated in all orbitals having principal quantum number 2 and azimuthal quantum number 1 is
 (a) 2 (b) 4 (c) 6 (d) 8
62. An ion has 18 electrons in the outermost shell, it is
 (a) Cu^+ (b) Th^{4+} (c) Cs^+ (d) K^+
63. For azimuthal quantum number $\ell = 3$, the maximum number of electrons will be
 (a) 2 (b) 6 (c) 0 (d) 14
64. If magnetic quantum number of a given atom represented by-3, then what will be its principal quantum number?
 (a) 2 (b) 3 (c) 4 (d) 5
65. For which one of the following sets of four quantum numbers, an electron will have the highest energy?
- | n | l | m | s |
|-------|-----|-----|------|
| (a) 3 | 2 | 1 | 1/2 |
| (b) 4 | 2 | -1 | 1/2 |
| (c) 4 | 1 | 0 | -1/2 |
| (d) 5 | 0 | 0 | -1/2 |
66. Which of the following should be the possible sub-shells, for $n + \ell = 7$?
 (a) $7s, 6p, 5d, 4f$ (b) $4f, 5p, 6s, 4d$
 (c) $7s, 6p, 5d, 6d$ (d) $4s, 5d, 6p, 7s$
67. Wavelength associated with electron motion
 (a) increases with increase in speed of electron
 (b) remains same irrespective of speed of electron
 (c) decreases with increase of speed of e^- (electron)
 (d) is zero.

93. The velocity of particle A is 0.1 ms^{-1} and that of particle B is 0.05 ms^{-1} . If the mass of particle B is five times that of particle A, then the ratio of de-Broglie wavelengths associated with the particles A and B is
 (a) 2 : 5 (b) 3 : 4
 (c) 6 : 4 (d) 5 : 2
94. In hydrogen atomic spectrum, a series limit is found at 12186.3 cm^{-1} . Then it belong to
 (a) Lyman series (b) Balmer series
 (c) Paschen series (d) Brackett series
95. The atom/ion that has the highest number of unpaired electrons is
 (a) Mg^{2+} (b) F
 (c) N (d) S^{2-}
96. For Balmer series in the spectrum of atomic hydrogen, the wave number of each line is given by $\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ where R_H is a constant and n_1 and n_2 are integers. Which of the following statement(s) is (are) correct?
 I. As wavelength decreases, the lines in the series converge.
 II. The integer n_1 is equal to 2.
 III. The ionization energy of hydrogen can be calculated from the wave number of these lines.
 IV. The line of longest wavelength corresponds to $n_2 = 3$.
 (a) I, II and III (b) II, III and IV only
 (c) I, II and IV (d) II and IV only
97. In which one of the following pairs the two species are both isoelectronic and isotopic?
 (Atomic numbers : Ca = 20, Ar = 18, K = 19, Mg = 12, Fe = 26, Na = 11)
 (a) $^{40}\text{Ca}^{2+}$ and ^{40}Ar (b) $^{39}\text{K}^+$ and $^{40}\text{K}^+$
 (c) $^{24}\text{Mg}^{2+}$ and ^{25}Mg (d) ^{23}Na and $^{24}\text{Na}^+$
98. Which set of quantum numbers are not possible?

	n	l	m	s
(a)	3	2	0	+1/2
(b)	2	2	1	+1/2
(c)	1	0	0	-1/2
(d)	3	2	-2	+1/2
99. Two fast moving particles X and Y are associated with de Broglie wavelengths 1 nm and 4 nm respectively. If mass of X is nine times the mass of Y, the ratio of kinetic energies of X and Y would be
 (a) 3 : 1 (b) 9 : 1
 (c) 5 : 12 (d) 16 : 9
100. The wavelength (in cm) of second line in the Lyman series of hydrogen atomic spectrum is (Rydberg constant = $R \text{ cm}^{-1}$)
 (a) $\left(\frac{8R}{9} \right)$ (b) $\left(\frac{9}{8R} \right)$
 (c) $\left(\frac{4}{3R} \right)$ (d) $\left(\frac{3R}{4} \right)$

EXERCISE - 2

Applied Questions

1. If the shortest wavelength of the spectral line of H-atom in the Lyman series is X, then the longest wavelength of the line in Balmer series of Li^{2+} is
 (a) $9x$ (b) $\frac{x}{9}$
 (c) $\frac{5x}{4}$ (d) $\frac{4x}{5}$
2. Given : The mass of electron is $9.11 \times 10^{-31} \text{ kg}$
 Plank constant is $6.626 \times 10^{-34} \text{ Js}$,
 the uncertainty involved in the measurement of velocity within a distance of $0.1 \text{ \AA}$ is
 (a) $5.79 \times 10^7 \text{ ms}^{-1}$ (b) $5.79 \times 10^8 \text{ ms}^{-1}$
 (c) $5.79 \times 10^5 \text{ ms}^{-1}$ (d) $5.79 \times 10^6 \text{ ms}^{-1}$
3. The number of nodal planes in a p_x orbital is
 (a) one (b) two
 (c) three (d) zero
4. The size of isoelectronic species C^{4-} , N^{3-} and Mg^{2+} is affected by
 (a) nuclear charge (Z)
 (b) principle quantum number
 (c) interelectronic repulsion
 (d) None of these
5. The ratio of magnetic moments of Fe(III) and Co(II) is
 (a) 7 : 3 (b) 3 : 7
 (c) $\sqrt{7} : \sqrt{3}$ (d) $\sqrt{3} : \sqrt{7}$
6. If the nitrogen atom has electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates.
 (a) Heisenberg uncertainty principle
 (b) Hund's rule
 (c) Pauli exclusion principle
 (d) Bohr postulate of stationary orbits

7. The orbital diagram in which the Aufbau principle is violated is :

	2s	2p
(a)	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow \uparrow$
(b)	$\uparrow$	$\uparrow\downarrow \uparrow \uparrow$
(c)	$\uparrow\downarrow$	$\uparrow \uparrow \uparrow$
(d)	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow \uparrow$

8. If a proton and α -particle are accelerated through the same potential difference, the ratio of de-Broglie wavelengths λ_p and λ_α is

- (a) 3 (b) $2\sqrt{2}$
(c) 1 (d) 2

9. In hydrogen atom, energy of first excited state is -3.4 eV. Find out KE of the same orbit of Hydrogen atom

- (a) $+3.4$ eV (b) $+6.8$ eV (c) -13.6 eV (d) $+13.6$ eV

10. The ions O^{2-} , F^- , Na^+ , Mg^{2+} and Al^{3+} are isoelectronic. Their ionic radii show

- (a) a decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+}
(b) a significant increase from O^{2-} to Al^{3+}
(c) a significant decrease from O^{2-} to Al^{3+}
(d) an increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}

11. Kinetic energy of an electron in hydrogen atom increases after transition from an orbit n_1 to another orbit n_2 . Then

- (a) $n_1 < n_2$
(b) $n_1 > n_2$
(c) it is not possible to predict
(d) none of these

12. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen

- (a) $5 \rightarrow 2$ (b) $4 \rightarrow 1$ (c) $2 \rightarrow 5$ (d) $3 \rightarrow 2$

13. Consider the ground state of Cr atom ($Z=24$). The number of electrons with the azimuthal quantum numbers, $\ell = 1$ and 2 are, respectively

- (a) 16 and 4 (b) 12 and 5 (c) 12 and 4 (d) 16 and 5

14. In a multi-electron atom, which of the following orbitals described by the three quantum members will have the same energy in the absence of magnetic and electric fields?

- (A) $n=1, \ell=0, m=0$ (B) $n=2, \ell=0, m=0$
(C) $n=2, \ell=1, m=1$ (D) $n=3, \ell=2, m=1$
(E) $n=3, \ell=2, m=0$
(a) (D) and (E) (b) (C) and (D)
(c) (B) and (C) (d) (A) and (B)

15. Li and a proton are accelerated by the same potential, their de Broglie wavelengths λ_{Li} and λ_p have the ratio (assume $m_{Li} = 9m_p$)

- (a) 1 : 2 (b) 1 : 4
(c) 1 : 1 (d) $1 : 3\sqrt{3}$

16. Which two orbitals are both located between the axes of coordinate system, and not along the axes?

- (a) d_{xy}, d_{z^2} (b) d_{yz}, p_x
(c) $d_{x^2-y^2}, p_z$ (d) none of these

17. Uncertainty in the position of an electron (mass = 9.1×10^{-31} kg) moving with a velocity 300 ms^{-1} , accurate upto 0.001% will be ($h = 6.63 \times 10^{-34}$ Js)

- (a) $1.92 \times 10^{-2} \text{ m}$ (b) $3.84 \times 10^{-2} \text{ m}$
(c) $19.2 \times 10^{-2} \text{ m}$ (d) $5.76 \times 10^{-2} \text{ m}$

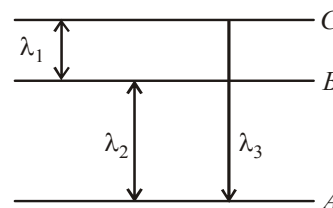
18. The number of radial nodes of 3s and 2p orbitals are respectively

- (a) 2, 0 (b) 0, 2 (c) 1, 2 (d) 2, 1

19. The energy of an electron in the first Bohr orbit of H atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are)

- (a) -3.4 eV (b) -4.2 eV
(c) -6.8 eV (d) Both (a) and (c)

20. Energy levels, A, B, C, of a certain atom correspond to increasing values of energy i.e., $E_A < E_B < E_C$. If $\lambda_1, \lambda_2, \lambda_3$ are the wave lengths of radiations corresponding to the transition from C to B, B to A and C to A respectively, which of the following statements is correct ?



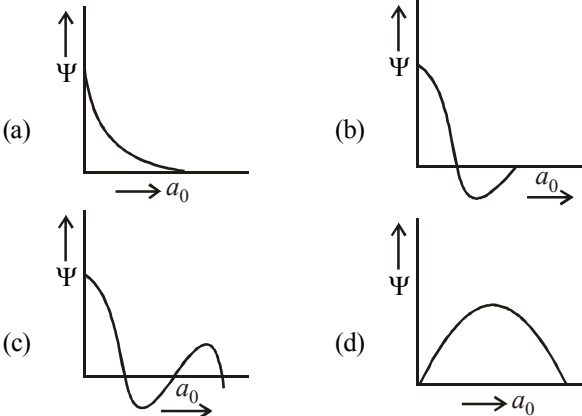
- (a) $\lambda_3 = \lambda_1 + \lambda_2$ (b) $\lambda_3 = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$
(c) $\lambda_1 + \lambda_2 + \lambda_3 = 0$ (d) $\lambda_3^2 = \lambda_1^2 + \lambda_2^2$

21. Number of protons, neutrons and electrons in the element $^{231}_{89}\text{Y}$ is

- (a) 89, 231, 89 (b) 89, 89, 242
(c) 89, 142, 89 (d) 89, 71, 89

22. Which one of the following is not the characteristic of Planck's quantum theory of radiation ?

- (a) The energy is not absorbed or emitted in whole number or multiple of quantum
(b) Radiation is associated with energy
(c) Radiation energy is not emitted or absorbed continuously but in the form of small packets called quanta
(d) This magnitude of energy associated with a quantum is proportional to the frequency.

23. The magnetic moment of a particular ion is $2\sqrt{6}$ B.M. The ion is
 (a) Mn^{2+} (b) Fe^{3+}
 (c) Co^{2+} (d) Co^{3+}
24. If the de-Broglie wavelength of a particle of mass m is 100 times its velocity, then its value in terms of its mass (m) and Planck's constant (h) is
 (a) $\frac{1}{10}\sqrt{\frac{m}{h}}$ (b) $10\sqrt{\frac{h}{m}}$ (c) $\frac{1}{10}\sqrt{\frac{h}{m}}$ (d) $10\sqrt{\frac{m}{h}}$
25. Which of the following graph correspond to one node

26. The five d -orbitals are designated as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} . Choose the correct statement.
 (a) The shapes of the first three orbitals are similar but that of the fourth and fifth orbitals are different
 (b) The shapes of all five d -orbitals are similar
 (c) The shapes of the first four orbitals are similar but that of the fifth orbital is different
 (d) The shapes of all five d -orbitals are different
27. The magnetic moment of M^{x+} (atomic number of $\text{M} = 25$) is $\sqrt{15}$ B.M. The number of unpaired electrons and the value of x respectively are
 (a) 4, 3 (b) 3, 4
 (c) 3, 2 (d) 5, 2
28. The magnetic moments of Cu ($Z = 29$), Ti ($Z = 22$), and Cr ($Z = 24$) are in the ratio of
 (a) $1:\sqrt{5}:4$ (b) $4:\sqrt{5}:1$
 (c) $1:2:6$ (d) $1:\sqrt{3}:\sqrt{21}$
29. If uncertainty in position and momentum are equal, then uncertainty in velocity is :
 (a) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (b) $\sqrt{\frac{h}{2\pi}}$ (c) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$ (d) $\sqrt{\frac{h}{\pi}}$
30. The energy absorbed by each molecule (A_2) of a substance is 4.4×10^{-19} J and bond energy per molecule is 4.0×10^{-19} J. The kinetic energy of the molecule per atom will be:
 (a) 2.2×10^{-19} J (b) 2.0×10^{-19} J
 (c) 4.0×10^{-20} J (d) 2.0×10^{-20} J
31. A 0.66 kg ball is moving with a speed of 100 m/s. The associated wavelength will be ($h = 6.6 \times 10^{-34}$ Js):
 (a) 1.0×10^{-32} m (b) 6.6×10^{-32} m
 (c) 6.6×10^{-34} m (d) 1.0×10^{-35} m
32. The energies E_1 and E_2 of two radiations are 25 eV and 50 eV, respectively. The relation between their wavelengths i.e., λ_1 and λ_2 will be :
 (a) $\lambda_1 = \lambda_2$ (b) $\lambda_1 = 2\lambda_2$
 (c) $\lambda_1 = 4\lambda_2$ (d) $\lambda_1 = \frac{1}{2}\lambda_2$
33. If $n = 6$, the correct sequence for filling of electrons will be :
 (a) $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$
 (b) $ns \rightarrow (n-1)d \rightarrow (n-2)f \rightarrow np$
 (c) $ns \rightarrow (n-2)f \rightarrow np \rightarrow (n-1)d$
 (d) $ns \rightarrow np \rightarrow (n-1)d \rightarrow (n-2)f$
34. According to the Bohr Theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon ?
 (a) $n = 6$ to $n = 1$ (b) $n = 5$ to $n = 4$
 (c) $n = 6$ to $n = 5$ (d) $n = 5$ to $n = 3$
35. Which of the following sets of quantum numbers represents the highest energy of an atom?
 (a) $n = 3, l = 0, m = 0, s = +1/2$ (b) $n = 3, l = 1, m = 1, s = +1/2$
 (c) $n = 3, l = 2, m = 1, s = +1/2$ (d) $n = 4, l = 0, m = 0, s = +1/2$
36. Which one of the following constitutes a group of the isoelectronic species?
 (a) $\text{C}_2^{2-}, \text{O}_2^-, \text{CO}, \text{NO}$ (b) $\text{NO}^+, \text{C}_2^{2-}, \text{CN}^-, \text{N}_2$
 (c) $\text{CN}^-, \text{N}_2, \text{O}_2^{2-}, \text{C}_2^{2-}$ (d) $\text{N}_2, \text{O}_2^-, \text{NO}^+, \text{CO}$
37. The ionization enthalpy of hydrogen atom is $1.312 \times 10^6 \text{ J mol}^{-1}$. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ is
 (a) $8.51 \times 10^5 \text{ J mol}^{-1}$ (b) $6.56 \times 10^5 \text{ J mol}^{-1}$
 (c) $7.56 \times 10^5 \text{ J mol}^{-1}$ (d) $9.84 \times 10^5 \text{ J mol}^{-1}$
38. In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainty with which the position of the electron can be located is ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$, mass of electron, $m_e = 9.1 \times 10^{-31} \text{ kg}$)
 (a) $5.10 \times 10^{-3} \text{ m}$ (b) $1.92 \times 10^{-3} \text{ m}$
 (c) $3.84 \times 10^{-3} \text{ m}$ (d) $1.52 \times 10^{-4} \text{ m}$
39. The energy required to break one mole of $\text{Cl}-\text{Cl}$ bonds in Cl_2 is 242 kJ mol^{-1} . The longest wavelength of light capable of breaking a single $\text{Cl}-\text{Cl}$ bond is ($c = 3 \times 10^8 \text{ ms}^{-1}$ and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$).
 (a) 594 nm (b) 640 nm (c) 700 nm (d) 494 nm
40. Ionisation energy of He^+ is $19.6 \times 10^{-18} \text{ J atom}^{-1}$. The energy of the first stationary state ($n = 1$) of Li^{2+} is
 (a) $4.41 \times 10^{-16} \text{ J atom}^{-1}$ (b) $-4.41 \times 10^{-17} \text{ J atom}^{-1}$
 (c) $-2.2 \times 10^{-15} \text{ J atom}^{-1}$ (d) $8.82 \times 10^{-17} \text{ J atom}^{-1}$
41. The electrons identified by quantum numbers n and ℓ :
 (A) $n = 4, \ell = 1$ (B) $n = 4, \ell = 0$
 (C) $n = 3, \ell = 2$ (D) $n = 3, \ell = 1$

can be placed in order of increasing energy as :

- (a) $(C) < (D) < (B) < (A)$ (b) $(D) < (B) < (C) < (A)$
 (c) $(B) < (D) < (A) < (C)$ (d) $(A) < (C) < (B) < (D)$
42. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] :
- (a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$ (c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$
43. Given that the abundances of isotopes ^{54}Fe , ^{56}Fe and ^{57}Fe are 5%, 90% and 5%, respectively, the atomic mass of Fe is
 (a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05
44. Energy of an electron is given by $E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right)$.
 Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be :
 ($h = 6.62 \times 10^{-34} \text{ Js}$ and $c = 3.0 \times 10^8 \text{ ms}^{-1}$)
 (a) $1.214 \times 10^{-7} \text{ m}$ (b) $2.816 \times 10^{-7} \text{ m}$
 (c) $6.500 \times 10^{-7} \text{ m}$ (d) $8.500 \times 10^{-7} \text{ m}$
45. A 600 W mercury lamp emits monochromatic radiation of wavelength 331.3 nm. How many photons are emitted from the lamp per second?
 $h = 6.62 \times 10^{-34} \text{ Js}$ velocity of light $= 3 \times 10^8 \text{ ms}^{-1}$
 (a) 1.0×10^{19} (b) 1.0×10^{23}
 (c) 1.0×10^{21} (d) 2.0×10^{23}
46. The de-Broglie wavelength of a particle with mass 1 kg and velocity 100 m/s is
 (a) $6.6 \times 10^{-33} \text{ m}$ (b) $6.6 \times 10^{-36} \text{ m}$
 (c) $3.3 \times 10^{-33} \text{ m}$ (d) $3.3 \times 10^{-36} \text{ m}$

DIRECTIONS for Qs. 47 to 49 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

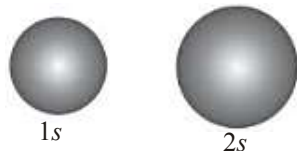
- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
 (b) Statement -1 is True, Statement -2 is True ; Statement-2 is NOT a correct explanation for Statement -1
 (c) Statement -1 is True, Statement -2 is False
 (d) Statement -1 is False, Statement -2 is True
47. **Statement-1** : The position of an electron can be determined exactly with the help of an electron microscope.
Statement-2 : The product of uncertainty in the measurement of its momentum and the uncertainty in the measurement of the position cannot be less than a finite limit.
48. **Statement-1** : The radius of the first orbit of hydrogen atom is 0.529 Å.
Statement-2 : Radius of each circular orbit (r_n) - $0.529 \text{ Å} (n^2/Z)$, where $n = 1, 2, 3$ and Z = atomic number.
49. **Statement-1** : Nuclide $^{30}\text{Al}_{13}$ is less stable than $^{40}\text{Ca}_{20}$
Statement-2 : Nuclide having odd number of protons and neutrons are generally unstable.
50. **Statement-1** : Angular momentum of an electron in any orbit is given by angular momentum $= \frac{n \cdot h}{2\pi}$, where n is the principal quantum number.
Statement-2 : The principal quantum number, n , can have any integral value.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Which of the following conclusions could not be derived from Rutherford's α -particle scattering experiment?
 (a) Most of the space in the atom is empty.
 (b) The radius of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m .
 (c) Electrons move in a circular path of fixed energy called orbits.
 (d) Electrons and the nucleus are held together by electrostatic forces of attraction.
2. Which of the following options does not represent ground state electronic configuration of an atom?
 (a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
 (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^1$
 (d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
3. The probability density plots of 1s and 2s orbitals are given in figure.



The density of dots in a region represents the probability density of finding electrons in the region.

On the basis of above diagram which of the following statements is incorrect?

- (a) 1s and 2s orbitals are spherical in shape.
 (b) The probability of finding the electron is maximum near the nucleus.
 (c) The probability of finding the electron at a given distance is equal in all directions.
 (d) The probability density of electrons for 2s orbital decreases uniformly as distance from the nucleus increases.
4. Which of the following statement is not correct about the characteristics of cathode rays?
 (a) They start from the cathode and move towards the anode.
 (b) They travel in straight line in the absence of an external electrical or magnetic field.
 (c) Characteristics of cathode rays do not depend upon the material of electrodes in cathode ray tube.
 (d) Characteristics of cathode rays depend upon the nature of gas present in the cathode ray tube.

5. Which of the following statements about the electron is incorrect?
- It is a negatively charged particle.
 - The mass of electron is equal to the mass of neutron.
 - It is a basic constituent of all the atoms.
 - It is a constituent of cathode rays.
6. Which of the following properties of atom could be explained correctly by Thomson model of atom?
- Overall neutrality of atom
 - Spectra of hydrogen atom
 - Position of electrons, protons and neutrons in atom
 - Stability of atom
7. Two atoms are said to be isobars if
- they have same atomic number but different mass number
 - they have same number of electrons but different number of neutrons
 - they have same number of neutrons but different number of electrons
 - sum of the number of protons and neutrons is same but the number of protons is different
8. The number of radial nodes for $3p$ orbital is
- 3
 - 4
 - 2
 - 1
9. Number of angular nodes for $4d$ orbital is
- 4
 - 3
 - 2
 - 1
10. Which of the following is responsible to rule out the existence of definite paths or trajectories of electrons?
- Pauli's exclusion principle
 - Heisenberg's uncertainty principle
 - Hund's rule of maximum multiplicity
 - Aufbau principle
11. Total number of orbitals associated with third shell will be
- 2
 - 4
 - 9
 - 3
12. Orbital angular momentum depends on
- l
 - n and l
 - n and m
 - m and s
13. Chlorine exists in two isotopic forms Cl-37 and Cl-35 , but its atomic mass is 35.5. This indicates the ratio of Cl-37 and Cl-35 is approximately
- 1 : 2
 - 1 : 1
 - 1 : 3
 - 3 : 1
14. The pair of ions having same electronic configuration is
- Cr^{3+} , Fe^{3+}
 - Fe^{3+} , Mn^{2+}
 - Fe^{3+} , Co^{3+}
 - Sc^{3+} , Cr^{3+}
15. For the electrons of oxygen atom, which of the following statements is correct?
- Z_{eff} for an electron in a $2s$ orbital is the same as Z_{eff} for an electron in a $2p$ orbital.
 - An electron in the $2s$ orbital has the same energy as an electron in the $2p$ orbital.
 - Z_{eff} for an electron in $1s$ orbital is the same as Z_{eff} for an electron in a $2s$ orbital.
 - The two electrons present in the $2s$ orbital have spin quantum numbers m_s but of opposite sign.
16. If travelling at same speeds, which of the following matter waves have the shortest wavelength?
- Electron
 - Alpha particle (He^{2+})
 - Neutron
 - Proton

NEET/AIPMT (2013-2017) Questions

17. According to law of photochemical equivalence the energy absorbed (in ergs/mole) is given as ($h = 6.62 \times 10^{-27}$ ergs, $c = 3 \times 10^{10}$ cm s^{-1} , $N_A = 6.02 \times 10^{23}$ mol $^{-1}$) [NEET Kar. 2013]
- $\frac{1.196 \times 10^{16}}{\lambda}$
 - $\frac{1.196 \times 10^8}{\lambda}$
 - $\frac{2.859 \times 10^5}{\lambda}$
 - $\frac{2.859 \times 10^{16}}{\lambda}$
18. Based on equation $E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right)$, certain conclusions are written. Which of them is not correct ? [2013]
- Larger the value of n , the larger is the orbit radius.
 - Equation can be used to calculate the change in energy when the electron changes orbit.
 - For $n = 1$, the electron has a more negative energy than it does for $n = 6$ which mean that the electron is more loosely bound in the smallest allowed orbit.
 - The negative sign in equation simply means that the energy or electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.
19. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers? $n = 3, l = 1$ and $m = -1$ [2013]
- 6
 - 4
 - 2
 - 10
20. The value of Planck's constant is 6.63×10^{-34} Js. The speed of light is 3×10^{17} nm s^{-1} . Which value is closest to the wavelength in nanometer of a quantum of light with frequency of 6×10^{15} s^{-1} ? [2013]
- 25
 - 50
 - 75
 - 10
21. What is the maximum number of orbitals that can be identified with the following quantum numbers? $n = 3, l = 1, m_l = 0$ [2014]
- 1
 - 2
 - 3
 - 4
22. Calculate the energy in joule corresponding to light of wavelength 45 nm : (Planck's constant $h = 6.63 \times 10^{-34}$ Js; speed of light $c = 3 \times 10^8$ ms^{-1}) [2014]
- 6.67×10^{15}
 - 6.67×10^{11}
 - 4.42×10^{-15}
 - 4.42×10^{-18}
23. Two electrons occupying the same orbital are distinguished by [2016]
- Principal quantum number
 - Magnetic quantum number
 - Azimuthal quantum number
 - Spin quantum number
24. Which one is the wrong statement ? [2017]
- The uncertainty principle is $\Delta E \times \Delta t \geq h/4\pi$
 - Half filled and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement.
 - The energy of $2s$ orbital is less than the energy of $2p$ orbital in case of Hydrogen like atoms
 - de-Broglies's wavelength is given by $\lambda = \frac{h}{mv}$, where m = mass of the particle, v = group velocity of the particle

Hints & Solutions

EXERCISE - 1

- (a) We know that ions which have the same number of electrons are called isoelectronic. We also know that both CO and CN^- have 14 electrons, therefore these are isoelectronic.
- (c) The molecule which contains same number of electrons are called isoelectronic. eg. $\text{N}_2 = \text{CO} = \text{CN}^- = \text{O}_2^{2-} = 14e^-$
- (b) The plot given in option (b) is the correct sketch of wave function (ψ) for a 2s-electron as a function of its distance from the nucleus (r). As ψ has no significance, so the plot of ψ versus r also has no significance.
- (c) Three 2p orbitals of one atom and three 2p orbitals of another atom give rise to four (π 2p) and two (σ 2p) molecular orbitals.
Among $2p_x$, $2p_y$ and $2p_z$ orbitals of two atoms $2p_z$ combines with $2p_z$ along z-axis give rise to two σ 2p molecular orbitals, while $2p_x$ combines with $2p_x$ and $2p_y$ combines with $2p_y$ give rise to two π $2p_x$ and two π $2p_y$ molecular orbitals.
- (d) Those species which contain same no. of electrons are called isoelectronic species. C_2H_4 has 16 electrons. The no. of electrons in other given species are
 $\text{O}_2^+ = 15e^-$; $\text{CN}^- = 14e^-$; $\text{N}_2^+ = 13e^-$;
 $\text{O}_2 = 16e^-$
 So, O_2 is isoelectronic with C_2H_4 .
- (c) Cathode rays are made up of negatively charged particles (electrons) which are deflected by both the electric and magnetic fields.
- (d) Number of neutrons = Mass number – Atomic number
 $= 70 - 30 = 40$.
- (b) e/m for $\text{He}^+ = 1/4$ e/m for $\text{He}^{2+} = 2/4$
 e/m for $\text{D}^+ = 1/2$ e/m for $\text{H}^+ = 1/1$
 $\therefore$ Value of e/m is highest for H^+ .
- (d) Size of H^+ (proton) is very small, so its hydration energy is very large.

$$\text{Hydration energy} \propto \frac{1}{\text{Size}}$$
- (d) Proton is the nucleus of H-atom (H-atom devoid of its electron)
- (d)

	F^-	O^{2-}	Al^{3+}	N^{3-}
No. of e^- s	10	10	10	10
Nuclear charge	9	8	13	7

 (Number of protons)
 All the four given species are isoelectronic and size of isoelectronic species decreases with increase in nuclear charge. Among the four concerned atoms, N has lowest atomic number (nuclear charge), hence N^{3-} ion will be largest in size.
- (b) For p orbital with $n = 6$ and $m = 0$ indicates $6p_z$ orbital. It contains maximum of 2 electrons with spins opposite to each other.
- (d)
$$\begin{aligned} \text{NaCl:} \quad \text{No. of } e^- \text{ in } \text{Na}^+ &= \text{At. No. of Na} - 1 \\ &= 11 - 1 = 10 \\ \text{No. of } e^- \text{ in } \text{Cl}^- &= \text{At. No. of Cl} + 1 \\ &= 17 + 1 = 18 \\ \text{CsF:} \quad \text{No. of } e^- \text{ in } \text{Cs}^+ &= 55 - 1 = 54 \\ \text{No. of } e^- \text{ in } \text{F}^- &= 9 + 1 = 10 \\ \text{NaI:} \quad \text{No. of } e^- \text{ in } \text{Na}^+ &= 11 - 1 = 10 \\ \text{No. of } e^- \text{ in } \text{I}^- &= 53 + 1 = 54 \\ \text{K}_2\text{S:} \quad \text{No. of } e^- \text{ in } \text{K}^+ &= 19 - 1 = 18 \\ \text{No. of } e^- \text{ in } \text{S}^{2-} &= 16 + 2 = 18 \end{aligned}$$
- (c)
- (d) $\frac{e}{m}$ for (i) neutron $= \frac{0}{1} = 0$
 (ii) α -particle $= \frac{2}{4} = 0.5$
 (iii) proton $= \frac{1}{1} = 1$
 (iv) electron $= \frac{1}{1/1837} = 1837$
- (c) No. of neutrons = Mass number – Atomic number
 $= W - N$.
- (c) Energy of electron in 2nd orbit of $\text{Li}^{+2} = -13.6 \frac{z^2}{n^2}$

$$= \frac{-13.6 \times (3)^2}{(2)^2} = -30.6 \text{ eV}$$
 Energy required $= 0 - (-30.6) = 30.6 \text{ eV}$
- (b) $E = mc^2$ (Einstein relation) (1)
 $E = h\nu$ (2)
 From (1) and (2),
 $mc^2 = h\nu$

$$\Rightarrow mc^2 = \frac{hc}{\lambda} \quad \left(\because \nu = \frac{c}{\lambda} \right)$$

$$\Rightarrow mc\lambda = h$$

$$\Rightarrow \lambda = \frac{h}{mc}$$

$$\Rightarrow \lambda = \frac{h}{p} \quad (\because mc = p)$$

$$\Rightarrow p = \frac{h}{\lambda}$$
- (b)
 - No. of electrons in N^{3-} , O^{2-} and Cr^{3-} are respectively 10, 10 and 27 so these species are not isoelectronic with each other.
 - No. of neutrons in ${}_{14}\text{Si}^{30}$, ${}_{15}\text{P}^{31}$ and ${}_{16}\text{S}^{32}$ are respectively 16, 16 and 16. So, ${}_{14}\text{Si}^{30}$, ${}_{15}\text{P}^{31}$ and ${}_{16}\text{S}^{32}$ are isotones.

- Atoms of the same element having same atomic no. and different mass no. are called isotopes. So $^{40}_{20}\text{Ca}$ and $^{40}_{19}\text{K}$ are not isotopes.
 - Isobars are the atoms of different elements having same mass no. and different atomic no. So, $^{16}_8\text{O}$, $^{17}_8\text{O}$ and $^{18}_8\text{O}$ are isobars.
20. (b) Both He and Li^+ contain 2 electrons each therefore their spectrum will be similar.
21. (d) This statement is known as uncertainty principle which was given by Heisenberg it is not a Bohr's postulate.
22. (a) For hydrogen atom (n) = 1 (due to ground state)
Radius of hydrogen atom (r) = 0.53 Å.
Atomic number of Li (Z) = 3.
Radius of Li^{2+} ion = $r_1 \times \frac{n^2}{Z} = 0.53 \times \frac{(1)^2}{3} = 0.17$
23. (d) Given : Radius of hydrogen atom = 0.530 Å, Number of excited state (n) = 2 and atomic number of hydrogen atom (Z) = 1. We know that the Bohr radius.
$$(r) = \frac{n^2}{Z} \times \text{Radius of atom} = \frac{(2)^2}{1} \times 0.530$$
$$= 4 \times 0.530 = 2.12 \text{ Å}$$
24. (a) He_2^- contains 5 electrons. So, the molecular orbital electronic configuration is $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$
25. (c) Principal quantum number (n) gives the information about the size of electron cloud i.e., the approximate distance of electron cloud from the nucleus.
26. (d) The given statement is related to Aufbau principle. According to this principle the electrons first occupy the orbital with lowest energy available to them and then enter into higher energy orbitals only when the lower energy orbitals are filled.
27. (b) We know that $E_n = \frac{-1312}{n^2} \text{ kJ mol}^{-1}$
 $n = 4$ (Fourth Bohr orbit)
Given $E_4 = \frac{-1312}{4^2} = -82 \text{ kJ mol}^{-1}$
28. (a) For s -electron, $\ell = 0$
 $\therefore$ Orbital angular momentum = $\sqrt{0(0+1)} \frac{h}{2\pi} = 0$
29. (c) $\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$
$$\frac{1}{\lambda} = 1.097 \times 10^7 \left(\frac{1}{1} - \frac{1}{\infty} \right) = 1.097 \times 10^7 \text{ m}^{-1}$$
$$\lambda = 91.15 \times 10^{-9} \text{ m} \approx 91 \text{ nm}$$
30. (c)
$$v = \frac{1}{h} \times \text{IE} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$
$$= \frac{2.18 \times 10^{-18}}{6.625 \times 10^{-34}} \times \left[\frac{1}{1} - \frac{1}{16} \right] = 3.08 \times 10^{15} \text{ s}^{-1}$$
31. (b) Angular momentum of an electron in n^{th} orbit is given by

$$mvr = \frac{nh}{2\pi}$$

For $n = 5$, we have

$$\text{Angular momentum of electron} = \frac{5h}{2\pi} = \frac{2.5h}{\pi}$$

32. (c) ΔE for two energy levels = $21.79 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ J/atom}$
33. (c) For every ℓ , quantum number ' m ' can take values from $-\ell$ to $+\ell$. So for $\ell = 2$, $m = -2, -1, 0, +1, +2$
34. (c) (i) CH_3^+ 8 electrons
(ii) H_3O^+ 10 electrons
(iii) NH_3 10 electrons
(iv) CH_3^- 10 electrons
So, (ii), (iii) and (iv) are isoelectronic species with 10 electrons each.
35. (a) $\Delta E = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right];$
First line in Balmer series results in the transition : $n_2 = 3$ to $n_1 = 2$.
36. (d) Those orbitals which are equal in energies are called degenerate orbitals. All sp^3 orbitals are degenerate as these are equal in energies.
37. (a) Rubidium is an alkali metal. It has one valence electron in $5s$ orbital. So, principal quantum number, $n = 5$
azimuthal quantum number $\ell = 0$
Note :

orbital :	s	p	q	f
value of ℓ :	0	1	2	3

magnetic quantum number,
 $m = -\ell$ to $\ell = 0$
spin quantum number, $s = +\frac{1}{2}$
So, correct set of quantum number is 5, 0, 0, $+\frac{1}{2}$
38. (c) Zeeman effect refers to splitting of lines of an emission spectrum in magnetic field.
39. (b) If we assume the atom to be hydrogen like, energy of n^{th} energy level
$$E_n = \frac{E_1}{n^2} \text{ where } E_1 \text{ is energy of first energy level}$$
$$E_2 = -\frac{E_1}{2^2} = -\frac{E_1}{4} = \frac{-21.79 \times 10^{-12}}{4}$$
$$= -5.447 \times 10^{-12} \text{ erg per atom.}$$

40. (b) 41. (d)
42. (d) The nucleus occupies much smaller volume compared to the volume of the atom.
43. (a) Energy of an electron $E = \frac{-E_0}{n^2}$
For energy level ($n = 2$)
 $E = -\frac{13.6}{(2)^2} = -\frac{13.6}{4} = -3.4 \text{ eV}.$
44. (c) The energy of photon,
 $E = \frac{hc}{\lambda} = 3.03 \times 10^{-19}$
or $\lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3.03 \times 10^{-19}}$
or $\lambda = \frac{19.878}{3.03} \times 10^{-7} = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}$
45. (c) K.E. of emitted electron
 $= h\nu - h\nu_0$ (i.e. smaller than $h\nu$).
46. (a) Given mass of an electron (m) = $9.1 \times 10^{-28} \text{ g}$;
Velocity of electron (v) = $3 \times 10^4 \text{ cm/s}$;
Accuracy in velocity = $0.001\% = \frac{0.001}{100}$;
Actual velocity of the electron
 $(\Delta v) = 3 \times 10^4 \times \frac{0.001}{100} = 0.3 \text{ cm/s}.$
Planck's constant (h) = $6.626 \times 10^{-27} \text{ erg-sec}.$
 $\therefore$ Uncertainty in the position of the electron
 $(\Delta x) = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-27} \times 7}{4 \times 22 \times (9.1 \times 10^{-28}) \times 0.3}$
 $= 1.93 \text{ cm}$
47. (b) Atomic number of the given element = 10
Electronic configuration = $1s^2, 2s^2 p^6$
 $1s^2 2s^2 2p^6$ is electronic configuration of Ne.
 $1s^2 2s^2 2p^5 3s^1$ is excited oxidation state.
48. (a) Positron is electron with positive charge, ${}_{+1}e^0$
49. (d) By Heisenberg uncertainty Principle $\Delta x \times \Delta p = \frac{h}{4\pi}$ (which is constant)
As Δx for electron and helium atom is same thus momentum of electron and helium will also be same therefore the momentum of helium atom is equal to $5 \times 10^{-26} \text{ kg.m.s}^{-1}.$
50. (a) $\lambda = h/mv$; for the same velocity, λ varies inversely with the mass of the particle.
51. (d) $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{60 \times 10^{-3} \times 10} = 10^{-33} \text{ m}$
52. (d) (i) Interference and diffraction support the wave nature of electron.
(ii) $E = mc^2$ supports the particle nature of electron.
- (iii) $E = h\nu = \frac{hc}{\lambda}$ is de-Broglie equation and it supports both wave nature and particle nature of electron.
53. (c) Radius of n th orbit $r_n = \frac{a_0}{Z} \times n^2$; $\therefore r_3 = 9a_0$
54. (b) $r_n = \frac{a_0 n^2}{Z}, r_1 = \frac{a_0 (1)^2}{1}$ for hydrogen
 $r_2 = \frac{a_0 (1)^2}{1}$ for deuterium $\therefore \frac{r_1}{r_2} = \frac{1}{1} = 1:1$
55. (b) For electron in the ground state,
 $mvr = \frac{h}{2\pi} \Rightarrow mv = \frac{h}{2\pi r}$
Now, $mv = \frac{h}{\lambda}$
So, $\frac{h}{\lambda} = \frac{h}{2\pi r} \Rightarrow \lambda = 2\pi r$
 $\lambda = 2 \times 3.14 \times 0.53 \text{ \AA} = 3.328 \text{ \AA}$
 $= 3.328 \times 10^{-10} \text{ m}$
 $= 0.3328 \times 10^{-9} \text{ m} = 0.3328 \text{ nm}$
56. (c) We know that $\lambda = \frac{h}{mu}$; $\therefore m = \frac{h}{u\lambda}$
The velocity of photon (u) = $3 \times 10^8 \text{ m sec}^{-1}$
 $\lambda = 1.54 \times 10^{-8} \text{ cm} = 1.54 \times 10^{-10} \text{ meter}$
 $\therefore m = \frac{6.626 \times 10^{-34} \text{ Js}}{1.54 \times 10^{-10} \text{ m} \times 3 \times 10^8 \text{ m sec}^{-1}}$
 $= 1.4285 \times 10^{-32} \text{ kg}$
57. (a)
58. (a) $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}}$
 $\lambda = \frac{6.6 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 4.55 \times 10^{-25}}}$
 $= \frac{6.6 \times 10^{-34}}{9 \times 10^{-28}} = 0.727 \times 10^{-6}$
 $= 7.27 \times 10^{-7} \text{ metres}$
59. (c) Noble gas must have 8 electrons in its outer most shell. Among the given configuration only option (c) has 8 electron in its outermost orbital.
i.e. the configuration is 2, 8, 18, 18, 8. So option (c) is the right answer.
60. (c) $N(7) = 1s^2 2s^2 2p^3$
 $N^{2+} = 1s^2, 2s^2 2p^1$
Unpaired electrons = 1.
61. (c) $n = 2, l = 1$ means $2p$ -orbital. Electrons that can be accommodated = 6 as p sub-shell has 3 orbital and each orbital contains 2 electrons.
62. (a) $\text{Cu}^+ = 29 - 1 = 28 e^-$
thus the electronic configuration of Cu^+ is
 $\text{Cu}^+(28) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
 $18e^-$

63. (d) $\ell = 3$ means f -subshell. Maximum no. of electrons $= 4\ell + 2$
 $= 4 \times 3 + 2 = 14$
64. (c) If $m = -3$; $\ell = 3$,
 $[m \text{ ranges from } -\ell \text{ to } +\ell]$
 So $n = 4$ as nature of ℓ ranges from 0 to $(n-1)$.
 So option (c) is the answer.
65. (b) The sub-shell are $3d, 4d, 4p$ and $4s$, $4d$ has highest energy as $n + \ell$ value is maximum for this.
66. (a) $n + \ell = 7$
 $7 + 0 = 7s$; $6 + 1 = 6p$; $5 + 2 = 5d$; $4 + 3 = 4f$
67. (c) $\lambda = \frac{h}{mv}$; $\therefore \lambda \propto \frac{1}{v}$ hence answer (c).
68. (d) According to Hund's rule electron pairing in p, d and f orbitals cannot occur until each orbital of a given subshell contains one electron each or is singly occupied.
69. (d) We know that atomic number of gadolinium is 64. Therefore the electronic configuration of gadolinium is $[\text{Xe}] 4f^7 5d^1 6s^2$. Because the half filled and fully filled orbitals are more stable.
70. (a) Quantum number $n = 3, l = 2, m = +2$ represent an orbital with
 $s = \pm \frac{1}{2} \quad \left(3d_{xy} \text{ or } 3d_{x^2-y^2} \right)$
 which is possible only for one electron.
71. (a) No. of radial nodes in $3p$ -orbital $= (n - \ell - 1)$
 $[\text{for } p \text{ orbital } \ell = 1]$
 $= 3 - 1 - 1 = 1$
72. (b) The sub-shell with lowest value of $(n + \ell)$ is filled up first. When two or more sub-shells have same $(n + \ell)$ value the subshell with lowest value of ' n ' is filled up first therefore the correct order is
- | orbital | $4s$ | $3d$ | $4p$ | $5s$ | $4d$ |
|------------|---------|---------|---------|---------|---------|
| $n + \ell$ | $4 + 0$ | $3 + 2$ | $4 + 1$ | $5 + 0$ | $4 + 2$ |
| value | $= 4$ | $= 5$ | $= 5$ | $= 5$ | $= 6$ |
73. (d) The orbitals which have same energy are called degenerate orbitals eg. p_x, p_y and p_z .
74. (a) Using the relation,
 $\Delta x \cdot \Delta v = \frac{h}{4\pi m}$ [Heisenberg's uncertainty principle]
 or $\Delta x = \frac{h}{4\pi m \cdot \Delta v}$
 Thus, $\Delta x_A = \frac{h}{4\pi \times 0.05 \times m} \dots (i)$
 $\Delta x_B = \frac{h}{4\pi \times 0.02 \times 5m} \dots (ii)$
 Dividing (i) by (ii), we get
 $\frac{\Delta x_A}{\Delta x_B} = \frac{0.02 \times 5}{0.05} = \frac{10}{5} \text{ or } 2$
75. (b) Magnetic quantum no. represents the orientation of atomic orbitals in an atom. For example p_x, p_y & p_z have orientation along X-axis, Y-axis & Z-axis
76. (c) $\text{Fe}^{++} (26 - 2 = 24) = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6$ hence no. of d electrons retained is 6. [Two $4s$ electron are removed]
77. (d) Angular speed is $\frac{V}{r}$. $V_n \propto \frac{1}{n}$ and $r_n \propto n^2$.
 $\therefore$ Angular speed is inversely proportional to n
78. (b) $E = h\nu = h \frac{c}{\lambda}$
 So, $E \propto \frac{1}{\lambda}$
 $\lambda_1 : \lambda_2 = 3000 \text{ \AA} : 6000 \text{ \AA} = 1 : 2$
 Hence, $E_1 : E_2 = 2 : 1$
79. (b) $n = 4$ represents 4^{th} orbit
 $\ell = 3$ represents f subshell
 $m = -2$ represents orientation of f -orbital
 $s = 1/2$ represents direction of spin of electron.
 $\therefore$ The orbital is $4f$.
80. (d) Electronic configuration of element with atomic no 24 is
 $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$
 Exactly half filled d -orbital has extra stability.
81. (b) For $4d$ orbitals, $n = 4, l = 2$
 $\left[\begin{array}{l} \text{For } s \text{ orbital } l = 0 \\ \text{For } p \text{ orbital } l = 1 \\ \text{For } d \text{ orbital } l = 2 \end{array} \right]$
 $m = -2, -1, 0, +1 \text{ or } +2$
 $s = +\frac{1}{2} \text{ and } -\frac{1}{2}$
 Thus choice b having $n = 4, l = 2, d = 1$ and $s = \frac{1}{2}$ is correct.
82. (c) $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{0.200 \times \frac{5}{3600}} = 2.4 \times 10^{-30} \text{ m}$
83. (c)
84. (b) Number of nodal planes in d orbitals is 2.
85. (c) Atomic number 9 is for F and ion is F^- .
86. (a) $\Delta p = m\Delta v$
 Substituting the given values of Δx and m , we get
 $1 \times 10^{-18} \text{ g cm s}^{-1} = 9 \times 10^{-28} \text{ g} \times \Delta v$
 or $\Delta v = \frac{1 \times 10^{-18}}{9 \times 10^{-28}}$
 $= 1.1 \times 10^9 \text{ cm s}^{-1} \approx 1 \times 10^9 \text{ cm s}^{-1}$
 i.e. option (a) is correct.
87. (d) The number of sub shell is $(2l + 1)$. The maximum number of electrons in the sub shell is $2(2l + 1) = (4l + 2)$
88. (b) $m = -l$ to $+l$, through zero thus for $l = 2$, values of m will be $-2, -1, 0, +1, +2$.
 Therefore for $l = 2$, m cannot have the value -3 .
89. (b) Total no. of atomic orbitals in a shell $= n^2$.
 Given $n = 4$; Hence number of atomic orbitals in 4^{th} shell will be 16.

90. (a) $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 1 \times 10^3}$
 $= 3.97 \times 10^{-10} \text{ meter} = 0.397 \text{ nanometer} \approx 0.40 \text{ nm}$

91. (a) For He^+
 $\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$
 $= R_H (2)^2 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = R_H \left(\frac{1}{(1)^2} - \frac{1}{(2)^2} \right)$

For H

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For same frequency,

$$R_H \left(\frac{1}{(1)^2} - \frac{1}{(2)^2} \right) = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\therefore \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{1}{1^2} - \frac{1}{2^2}$$

$$\therefore n_1 = 1 \text{ \& } n_2 = 2$$

92. (c) Among isoelectronic species ionic radii increases as the charge increases.

Order of ionic radii $\text{Ca}^{2+} < \text{K}^+ < \text{Cl}^- < \text{S}^{2-}$

The number of electrons remains the same but nuclear charge increases with increase in the atomic number causing decrease in size.

93. (d) Given, $v_A = 0.1 \text{ ms}^{-1}$ and $v_B = 0.05 \text{ ms}^{-1}$ also, $m_B = 5m_A$

de-Broglie wavelength, $\lambda = \frac{h}{mv}$

$$\therefore \frac{\lambda_A}{\lambda_B} = \frac{h/m_A v_A}{h/m_B v_B} = \frac{m_B v_B}{m_A v_A}$$

$$= \frac{5m_A \times 0.05}{m_A \times 0.1} = 5 \times 0.5 = 2.5 = 5/2$$

$$\therefore \lambda_A : \lambda_B = 5 : 2$$

94. (c) Series limit is the last line of the series, i.e. $n_2 = \infty$.

$$\therefore \bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = R \left[\frac{1}{n_1^2} - \frac{1}{\infty^2} \right] = \frac{R}{n_1^2}$$

$$\therefore \bar{\nu} = 12186.3 = \frac{109677.76}{n_1^2}$$

$$\Rightarrow n_1^2 = \frac{109677.76}{12186.3} = 9 \Rightarrow n_1 = 3$$

$\therefore$ The line belongs to Paschen series.

95. (c) The electronic configuration of the given species is

Mg^{2+}	: $1s^2 2s^2 2p^6$
F	: $1s^2 2s^2 2p^5$
N	: $1s^2 2s^2 2p^3$
S^{2-}	: $1s^2 2s^2 2p^6 3s^2 3p^6$
Ti^{3+}	: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

Therefore, N has the highest number of unpaired electrons.

96. (c) (1) Beyond a certain wavelength the line spectrum becomes band spectrum.

(2) For Balmer series $n_1 = 2$

(3) For calculation of longest wavelength use nearest value of n_2 . Hence for longest wavelength in Balmer series of hydrogen spectrum,
 $n_1 = 2$ & $n_2 = 3$.

97. (b) $^{39}\text{K}^+$ and $^{40}\text{K}^+$ contains same number of electrons so they are isoelectronic. They have same atomic numbers but different mass numbers so they are also isotopes.

98. (b) Value of $l = 0 \dots \dots \dots (n-1)$
 l cannot be equal to n .

99. (d) de Broglie wavelength $\lambda = \frac{h}{mv}$

$$\frac{\lambda_1}{\lambda_2} = \frac{m_2 v_2}{m_1 v_1}; \frac{1}{4} = \frac{1}{9} \times \frac{v_2}{v_1}$$

$$\frac{v_2}{v_1} = \frac{9}{4}$$

$$\frac{v_1}{v_2} = \frac{4}{9}$$

$$\text{KE} = \frac{1}{2} mv^2$$

$$\frac{\text{KE}_1}{\text{KE}_2} = \frac{m_1}{m_2} \times \frac{v_1^2}{v_2^2} = \frac{9}{1} \times \left(\frac{4}{9} \right)^2 = \frac{16}{9}$$

100. (a) $\bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

For second line in Lyman series
 $n_2 = 3$

$$\therefore \frac{1}{\lambda} = R \left[\frac{1}{1^2} - \frac{1}{3^2} \right] = R \left[\frac{1}{1} - \frac{1}{9} \right] = \frac{8R}{9}$$

EXERCISE - 2

1. (d) $\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

To calculate shortest wavelength take $n_2 = \infty$ and longest wavelength take nearest value of n_2 .

For H-atom,

$$\frac{1}{\lambda_{\text{shortest}}} \quad n_2 = \infty, Z = 1, n_1 = 1$$

$$\therefore \frac{1}{x} = R_H \text{ (Lyman series)}$$

For $\frac{1}{\lambda_{\text{longest}}}$ for Li^{2+} , $Z = 3$, $n_1 = 2$, $n_2 = 3$ (Balmer series)

$$\frac{1}{\lambda_{\text{longest}}} = \frac{1}{x} \times 3^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{4x}$$

$$\therefore \lambda_{\text{longest}} = \frac{4x}{5}$$

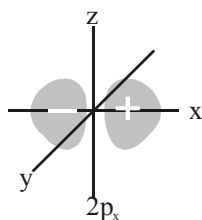
2. (d) We know that $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

$$\Delta x \cdot m \Delta v > \frac{h}{4\pi} \quad \Delta v > \frac{h}{4\pi \Delta x m}$$

$$\Delta v = \frac{6.626 \times 10^{-34}}{4\pi \times 0.1 \times 10^{-10} \times 9.11 \times 10^{-31}}$$

$$= \frac{66}{4\pi \times 9} \times 10^7 = 5.79 \times 10^6 \text{ m/sec}$$

3. (a) p_x orbital being dumbbell shaped, have number of nodal planes = 1



4. (a) Because number of protons (nuclear charge) is different while number of electrons is same in isoelectronic species.

5. (c) Fe(III) = [Ar] $3d^5$ unpaired electrons = 5;

$$\text{Magnetic moment} = \sqrt{5(5+2)};$$

$$\text{Ratio} = \sqrt{7} : \sqrt{3}$$

$$\text{Co(II)} = [\text{Ar}] 3d^7 \text{ unpaired electrons} = 3;$$

$$\text{Magnetic moment} = \sqrt{3(3+2)}$$

$$\text{Ratio} = \sqrt{7} : \sqrt{3}$$

6. (c) As per Pauli exclusion principle "no two electrons in the same atom can have all the four quantum numbers equal or an orbital cannot contain more than two electrons and it can accommodate two electrons only when their directions of spin are opposite".
7. (b) According to Aufbau principle, the orbital of lower energy ($2s$) should be fully filled before the filling of orbital of higher energy starts.

8. (b) $\lambda_p = \frac{h}{\sqrt{2eVm_p}};$

$$\lambda_{\text{He}^{2+}} = \frac{h}{\sqrt{2 \times 2eVm_{\text{He}^{2+}}}} = \frac{h}{\sqrt{2 \times 2eV \times 4m_p}}$$

$$\therefore \frac{\lambda_p}{\lambda_{\text{He}^{2+}}} = 2\sqrt{2}$$

9. (a) Total energy (E_n) = K.E + P.E
in first excited state

$$E = \frac{1}{2}mv^2 + \left[-\frac{ze^2}{r} \right] = +\frac{1}{2}\frac{ze^2}{r} - \frac{ze^2}{r}$$

$$-3.4 \text{ eV} = -\frac{1}{2}\frac{ze^2}{r}$$

$$\therefore \text{K.E} = \frac{1}{2}\frac{ze^2}{r} = +3.4 \text{ eV}$$

10. (c) Amongst isoelectronic species, ionic radii of anion is more than that of cations. Further size of anion increase with increase in -ve charge and size of cation decrease with increase in +ve charge. Hence ionic radii decreases from O^{2-} to Al^{+++} .

11. (b) K.E. of an electron in a Bohr orbit is equal to the magnitude of the total energy but of opposite sign. So it varies inversely to the square of principal quantum number.

12. (a) The lines falling in the visible region comprise Balmer series. Hence the third line from red would be $n_1 = 2$, $n_2 = 5$ i.e., $5 \rightarrow 2$.

13. (b) Electronic configuration of Cr atom ($Z = 24$)

$$= 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$$

when $\ell = 1$, p -subshell,

Numbers of electrons = 12

when $\ell = 2$, d -subshell,

Numbers of electrons = 5

14. (a) The energy of an orbital is given by $(n + \ell)$ in (D) and (E). $(n + \ell)$ value is $(3 + 2) = 5$ hence they will have same energy, since there are n values are also same.

$$(h = 6.63 \times 10^{-34} \text{ Js})$$

15. (d) $\lambda_p = \frac{h}{\sqrt{2eVm_p}}; \lambda_{Li} = \frac{h}{\sqrt{2 \times 3eVm_{Li}}}$

$$= \frac{h}{\sqrt{2 \times 3eV \times 9m_p}}$$

$$\text{Hence, } \frac{\lambda_{Li^{3+}}}{\lambda_p} = \sqrt{\frac{2eVm_p}{2 \times 3eV \times 9m_p}} = \frac{1}{3\sqrt{3}}$$

16. (d)

17. (a) Given $m = 9.1 \times 10^{-31} \text{ kg}$

$$h = 6.6 \times 10^{-34} \text{ Js}$$

$$\Delta v = \frac{300 \times .001}{100} = 0.003 \text{ ms}^{-1}$$

From Heisenberg's uncertainty principle

$$\Delta x = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 0.003 \times 9.1 \times 10^{-31}} = 1.92 \times 10^{-2} \text{ m}$$

18. (a) Number of radial nodes $= (n - l - 1)$
 For $3s$: $n = 3, l = 0$ (Number of radial node $= 2$)
 For $2p$: $n = 2, l = 1$ (Number of radial node $= 0$)
19. (a) The energy of an electron on Bohr orbits of hydrogen atoms is given by the expression

$$E_n = -\frac{\text{Constant}}{n^2}$$

Where n takes only integral values. For the first Bohr orbit, $n = 1$ and it is given that $E_1 = -13.6 \text{ eV}$

$$\text{Hence } E_n = -\frac{13.6 \text{ eV}}{n^2}$$

Now out of given values of energy, only -3.4 eV can be obtained by substituting $n = 2$ in the above expression.

20. (b) From the given data, we have
 $(E_C - E_B) + (E_B - E_A) = (E_C - E_A)$
 or $\left(\frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}\right) = \frac{hc}{\lambda_3}$ [or $\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{\lambda_3}$]
 or $\boxed{\lambda_3 = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}}$ [$\therefore \frac{\lambda_1 + \lambda_2}{\lambda_1 \cdot \lambda_2} = \frac{1}{\lambda_3}$]
21. (c) In Y_{89}^{231} number of protons and electrons is 89 and number of neutrons $= A - Z = 231 - 89 = 142$
22. (a) Energy is always absorbed or emitted in whole number or multiples of quantum.
23. (d) Magnetic moment

$$= 2\sqrt{6} = \sqrt{24} \text{ B.M.} = \sqrt{n(n+2)} \text{ B.M.}$$

Hence, $n = 4$ (unpaired electrons)

$\text{Co}^{3+} - [\text{Ar}] 3d^6$, 4 unpaired electrons.

24. (b) Let wavelength of particle be x

$$\text{So, velocity} = \frac{x}{100}$$

$$\lambda = \frac{h}{mv}; \quad x = \frac{h \times 100}{m \times x}$$

$$x^2 = 100 \frac{h}{m} \quad \text{or} \quad x = 10 \sqrt{\frac{h}{m}}$$

25. (b)
26. (c) First four orbitals contain four lobes, while fifth orbital consists of only two lobes. The lobes of d_{xy} orbital lie between x and y axis. Similarly in the case of d_{yz} and d_{zx} , their lobes lie between yz and zx axis respectively. Four lobes of $d_{x^2-y^2}$ orbital are lying along x and y axis while two lobes of d_{z^2} orbital are lying along z -axis.

27. (b) $\sqrt{n(n+2)} = \sqrt{15}$, $n = 3$ (n = number of unpaired electrons)

$$\text{Therefore, } x = 4 \quad \therefore \text{M}^{4+} = [\text{Ar}] 3d^3$$

28. (a)

29. (a) We know $\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$
 since $\Delta p = \Delta x$ (given)

$$\therefore \Delta p \cdot \Delta p = \frac{h}{4\pi}$$

$$\text{or } m \Delta v \cdot m \Delta v = \frac{h}{4\pi} \quad [\therefore \Delta p = m \Delta v]$$

$$\text{or } (\Delta v)^2 = \frac{h}{4\pi m^2}$$

$$\text{or } \Delta v = \sqrt{\frac{h}{4\pi m^2}} = \frac{1}{2m} \sqrt{\frac{h}{\pi}}$$

Thus option (a) is the correct option.

30. (d) K.E per atom

$$= \frac{(4.4 \times 10^{-19}) - (4.0 \times 10^{-19})}{2}$$

$$= \frac{0.4 \times 10^{-19}}{2} = 2.0 \times 10^{-20}$$

31. (d) $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.66 \times 100} = 1 \times 10^{-35} \text{ m}$

32. (b) Given $E_1 = 25 \text{ eV}$ $E_2 = 50 \text{ eV}$

$$E_1 = \frac{hc}{\lambda_1} \quad E_2 = \frac{hc}{\lambda_2} \quad \therefore \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1}$$

$$\therefore \frac{\lambda_2}{\lambda_1} = \frac{25}{50} = \frac{1}{2} \quad \therefore \lambda_1 = 2\lambda_2$$

33. (a) $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$ [$n = 6$]

34. (c) Energy of photon obtained from the transition $n = 6$ to $n = 5$ will have least energy.

$$\Delta E = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

35. (c) (a) $n = 3, \ell = 0$ means $3s$ -orbital and $n + \ell = 3$
 (b) $n = 3, \ell = 1$ means $3p$ -orbital $n + \ell = 4$
 (c) $n = 3, \ell = 2$ means $3d$ -orbital $n + \ell = 5$
 (d) $n = 4, \ell = 0$ means $4s$ -orbital $n + \ell = 4$

Increasing order of energy among these orbitals is $3s < 3p < 4s < 3d$

$\therefore 3d$ has highest energy.

36. (b) Species having same number of electrons are **isoelectronic**. On calculating the number of electrons in each given species, we get.

$$\text{CN}^- (6 + 7 + 1 = 14); \text{N}_2 (7 + 7 = 14);$$

$$\text{O}_2^{2-} (8 + 8 + 2 = 18); \text{C}_2^{2-} (6 + 6 + 2 = 14);$$

$$\text{O}_2^- (8 + 8 + 1 = 17); \text{NO}^+ (7 + 8 - 1 = 14)$$

$$\text{CO} (6 + 8 = 14); \text{NO} (7 + 8 = 15)$$

From the above calculation we find that all the species listed in choice (b) have 14 electrons each so it is the correct answer.

37. (d) (ΔE), The energy required to excite an electron in atom of hydrogen from $n = 1$ to $n = 2$ is ΔE (difference in energy E_2 and E_1)
Values of E_2 and E_1 are,

$$E_2 = \frac{-1.312 \times 10^6 \times (1)^2}{(2)^2} = -3.28 \times 10^5 \text{ J mol}^{-1}$$

$$E_1 = -1.312 \times 10^6 \text{ J mol}^{-1}$$

$$\begin{aligned} \therefore \Delta E = E_2 - E_1 &= [-3.28 \times 10^5] - [-1.312 \times 10^6] \text{ J mol}^{-1} \\ &= (-3.28 \times 10^5 + 1.312 \times 10^6) \text{ J mol}^{-1} \\ &= 9.84 \times 10^5 \text{ J mol}^{-1} \end{aligned}$$

Thus the correct answer is (d)

38. (b) According to Heisenberg uncertainty principle.

$$\Delta x \cdot m \Delta v = \frac{h}{4\pi} \quad \Delta x = \frac{h}{4\pi m \Delta v}$$

$$\text{Here } \Delta v = \frac{600 \times 0.005}{100} = 0.03$$

$$\begin{aligned} \text{So, } \Delta x &= \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.03} \\ &= 1.92 \times 10^{-3} \text{ meter} \end{aligned}$$

39. (d) Energy required to break one mole of Cl – Cl bonds in Cl_2

$$\begin{aligned} &= \frac{242 \times 10^3}{6.023 \times 10^{23}} = \frac{hc}{\lambda} \\ &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda} \\ \therefore \lambda &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{242 \times 10^3} \\ &= 0.4947 \times 10^{-6} \text{ m} = 494.7 \text{ nm} \end{aligned}$$

40. (b) I. $E = \frac{Z^2}{n^2} \times 13.6 \text{ eV}$... (i)

$$\text{or } \frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2} \quad \dots \text{(ii)}$$

Given $I_1 = -19.6 \times 10^{-18}$, $Z_1 = 2$,
 $n_1 = 1$, $Z_2 = 3$ and $n_2 = 1$

Substituting these values in equation (ii).

$$-\frac{19.6 \times 10^{-18}}{I_2} = \frac{4}{1} \times \frac{1}{9}$$

$$\begin{aligned} \text{or } I_2 &= -19.6 \times 10^{-18} \times \frac{9}{4} \\ &= -4.41 \times 10^{-17} \text{ J/atom} \end{aligned}$$

41. (b) (A) 4p (B) 4s
(C) 3d (D) 3p

According to Bohr Bury's ($n + \ell$) rule, increasing order of energy will be (D) < (B) < (C) < (A).

Note : If the two orbitals have same value of ($n + \ell$) then the orbital with lower value of n will be filled first.

42. (c) As per Bohr's postulate,

$$mvr = \frac{nh}{2\pi}$$

$$\text{So, } v = \frac{nh}{2\pi mr}$$

$$\text{KE} = \frac{1}{2}mv^2$$

$$\text{So, KE} = \frac{1}{2}m \left(\frac{nh}{2\pi mr} \right)^2$$

$$\text{Since, } r = \frac{a_0 \times n^2}{z}$$

So, for 2nd Bohr orbit

$$r = \frac{a_0 \times 2^2}{1} = 4a_0$$

$$\text{KE} = \frac{1}{2}m \left(\frac{2^2 h^2}{4\pi^2 m^2 \times (4a_0)^2} \right)$$

$$\text{KE} = \frac{h^2}{32\pi^2 m a_0^2}$$

43. (b) Average atomic mass of Fe

$$= \frac{(54 \times 5) + (56 \times 90) + (57 \times 5)}{100} = 55.95$$

44. (a) $\Delta E = 2.178 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{hc}{\lambda}$

$$\Rightarrow 2.178 \times 10^{-18} \times \frac{3}{4} = \frac{hc}{\lambda}$$

$$= \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$\lambda = \frac{6.62 \times 10^{-34} \times 3 \times 10^8 \times 4}{2.178 \times 10^{-18} \times 3}$$

$$= 1.214 \times 10^{-7} \text{ m}$$

45. (c) Energy emitted by the bulb = 600 W = 600 Js⁻¹
(1W = 1 Js⁻¹)

$$\lambda = 331.3 \times 10^{-9} \text{ m}$$

$$\text{Energy of one photon} = h\nu = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{331.3 \times 10^{-9}}$$

$$= 0.059 \times 10^{-17} \approx 0.06 \times 10^{-17} \text{ J}$$

No. of photon emitted from the lamp per second

$$= \frac{600}{0.06 \times 10^{-17}} = 1.0 \times 10^{21}$$

46. (b) de Broglie wavelength $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{1 \times 100}$

$$= 6.6 \times 10^{-36} \text{ m}$$

47. (d) The statement-1 is false but the statement-2 is true exact position and exact momentum of an electron can never be determined according to Heisenberg's uncertainty principle. Even not with the help of electron microscope because when electron beam of electron microscope strikes the target electron of atom, the impact causes the change in velocity and position of electron.

Thus the product of uncertainty in position and momentum is

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \approx 0.57 \text{ ergs sec/gram}$$

48. (a) Both statement-1 and statement-2 are true and Statement-2 is the correct explanation of Statement-1.

$$\text{Radius, } r_n = \frac{n^2 h^2}{4\pi e^2 m Z} = \frac{n^2}{Z} \times 0.529 \text{ \AA} \cdot r_n$$

For first orbit of H-atom

$$n = 1$$

$$r_1 = \frac{(1)^2}{1} \times 0.529 \text{ \AA} = 0.529 \text{ \AA}$$

49. (a) It is observed that a nucleus which is made up of even number of nucleons (No. of n & p) is more stable than nuclei which consist of odd number of nucleons. If number of neutron or proton is equal to some numbers i.e., 2, 8, 20, 50, 82, or 126 (which are called magic numbers), then these possess extra stability.
50. (b) Both Statement-1 and Statement-2 are correct. Statement-2 is **not** the correct explanation of Statement-1.

EXERCISE - 3

Exemplar Questions

- (c) The concept of electrons move in a circular path of fixed energy called orbits was given by Bohr and not derived from Rutherford's scattering experiment.
- (b) The correct configuration for copper ($z = 29$) should be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. Due to extra stability of fully filled orbital of d -subshell, the last electron enters into d -orbital instead of s -orbital.
- (d) The probability density of electrons in $2s$ orbital first increases then decreases and after that it increases again as distance increases from nucleus.
- (d) The characteristics of cathode rays do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.
- (b) The mass of electron is very small as compared to the mass of the neutron.
Mass of electron = $9.1 \times 10^{-31} \text{ kg}$
Mass of neutron = $1.67 \times 10^{-27} \text{ kg}$
- (a) J. J. Thomson, in 1898, proposed plum pudding model of atom. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. This model was able to explain the overall neutrality of the atom.
- (d) Isobars have the same mass number (i.e., sum of protons and neutrons) but different atomic number (i.e., number of protons) e.g., ${}_{26}\text{Fe}^{58}$ and ${}_{27}\text{Ni}^{58}$ are isobars.
- (d) For hydrogen atom ($1s$) = number of radial nodes = $n - l - 1$
Number of radial nodes for $3p$ orbital = $3 - 1 - 1 = 1$
- (c) Number of angular nodes = l
 $l = 2$ for d -orbital
 $\therefore$ Number of angular nodes = 2
- (b) The important implications of Heisenberg uncertainty principle is that it rules out existence of definite paths or trajectories of electrons and other similar particles.
- (c) Total number of orbitals associated with n^{th} shell = n^2
 $\therefore$ Total number of orbitals associated with third shell = $(3)^2 = 9$
- (a) Orbital angular momentum, $mvr = \frac{h}{2\pi} \sqrt{l(l+1)}$
Hence, it depends only on ' l ', l can have values ranging from 0 to $(n-1)$.
- (c) The fractional atomic mass (35.5) of chlorine is due to the fact that in ordinary chlorine atom, Cl-37 and Cl-35 are present in the ratio of 1 : 3.
 $\therefore$ Average atomic mass of Cl
$$= \frac{3 \times 35 + 1 \times 37}{4} = 35.5 \text{ amu}$$
- (b) ${}_{24}\text{Cr} = [\text{Ar}]3d^5, 4s^1$ $\text{Cr}^{3+} = [\text{Ar}]3d^3$
 ${}_{26}\text{Fe} = [\text{Ar}]3d^6, 4s^2$ $\text{Fe}^{3+} = [\text{Ar}]3d^5$
 ${}_{25}\text{Mn} = [\text{Ar}]3d^5, 4s^2$ $\text{Mn}^{2+} = [\text{Ar}]3d^5$
 ${}_{27}\text{Co} = [\text{Ar}]3d^7, 4s^2$ $\text{Co}^{3+} = [\text{Ar}]3d^6$
 ${}_{21}\text{Sc} = [\text{Ar}]3d^1, 4s^2$ $\text{Sc}^{3+} = [\text{Ar}]$
Thus, Fe^{3+} and Mn^{2+} have the same electronic configuration.
- (d) For the two electrons of $2s$ orbital, the value of m_s is between $+\frac{1}{2}$ and $-\frac{1}{2}$
- (b) From de-Broglie equation wavelength,
$$\lambda = \frac{h}{mv}$$

For same speed of different particles, $\lambda \propto \frac{1}{m}$
As h is constant, greater the mass of matter waves, lesser is wavelength and vice-versa. Among these matter waves, alpha particle (He^{2+}) has higher mass, therefore, shortest wavelength.

NEET/AIPMT (2013-2017) Questions

$$\begin{aligned}
 17. \quad (b) \quad E &= \frac{hc}{\lambda} \times N_A \\
 &= \frac{6.62 \times 10^{-27} \times 3 \times 10^{10} \times 6.02 \times 10^{23}}{\lambda} \\
 &= \frac{1.19 \times 10^8}{\lambda} \text{ ergs mol}^{-1}
 \end{aligned}$$

18. (c) Energy of an electron at infinite distance from the nucleus is zero. As an electron approaches the nucleus, the electron attraction increases and hence the energy of electron decreases and thus becomes negative. Thus as the value of n decreases, *i.e.* lower the orbit is, more negative is the energy of the electron in it.
19. (c) $n = 3 \rightarrow 3^{\text{rd}}$ shell
 $l = 1 \rightarrow p$ sub shell.
 $m = -1$ is possible for two electrons present in an orbital.

$$20. \quad (b) \quad c = v\lambda$$

$$\lambda = \frac{c}{v} = \frac{3 \times 10^{17}}{6 \times 10^{15}} = 50 \text{ nm}$$

21. (a) Given: $n = 3, l = 1, m = 0$
Hence orbital is $3p$

-1	0	+1

hence the number of orbital identified by $m = 0$ can be one only.

22. (d) $E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{45 \times 10^{-9}}$
 $= 4.42 \times 10^{-18} \text{ J}$
23. (d) Two electrons occupying the same orbital should have opposite spins *i.e.* they differ in spin quantum number.
24. (c) For hydrogen like atoms energy of $2s$ -orbital and $2p$ -orbital is equal.

Chapter

3

Classification of Elements and Periodicity in Properties

DEVELOPMENT OF PERIODIC TABLE

The elements have been classified into groups for a systematic study of their properties. Various attempts have been made by scientists from the early 1800's. The first classification was made by **Dobereiner** who formulated 'Triads'. It was followed by **Newland's 'Law of octaves'**. The next development that came was **Mendeleev's periodic table** which classified elements on the basis of their atomic masses.

Moseley showed that atomic number is a more fundamental property of an element than its atomic mass. The Mendeleev's periodic law was then modified to a new law called **Modern Periodic law**, according to which '*The physical and chemical properties of the elements are periodic functions of their atomic numbers*'.

Long form of periodic table is based upon the Modern Periodic law. This is also known as Bohr's table as it is based on Bohr's scheme for the arrangement of various electrons around the nucleus.

The horizontal rows of the periodic table are called 'Periods' while the vertical columns are called 'Groups'. There are 7 periods and 18 groups in the periodic table.

Merits of Long Form of Periodic Table

- (i) **Positions of Isotopes and Isobars** - Modern periodic table is based on atomic numbers. Therefore, various isotopes of the same element will occupy the same position in the periodic table. Isobars have to be placed at different positions.
- (ii) The positions of actinoids and lanthanoids is more clear now because these have been placed in group 3 and due to paucity of space, these are written at the bottom of the periodic table.

NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER > 100

A systematic nomenclature has been derived to directly name the element from its atomic number using numerical roots for 0 and numbers 1-9. The roots are put together in order of digits which make up the atomic number and 'ium' is added at the end.

Ex : Name of element with atomic number 101 is Unnilunium, 102 is unnilbium, 103 is unniltrium, etc. and their symbols are Unu, Unb, Unt.

Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

ELECTRONIC CONFIGURATION OF ELEMENTS AND PERIODIC TABLE

An element's location in the periodic table reflects the quantum numbers of the last orbital filled.

Electronic Configuration in Periods

- (i) The period indicates the value of n for the outermost or valence shell
- (ii) The number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled.
- (iii) There are 2 elements in 1st period; 8 in the 2nd; 8 in the 3rd; 18 in the 4th; 18 in the 5th; 32 in 6th and 7th period is incomplete.

Groupwise Electronic Configuration

Elements in same vertical column or group have similar valence shell electronic configurations, the same number of e^- s in outer orbitals and similar properties.

For ex: all the group 1 elements have ns^1 valence shell electronic configuration.

s-, p-, d- AND f- BLOCK ELEMENTS

Elements can be classified into four blocks: *s*-block, *p*-block, *d*-block and *f*-block depending upon the type of atomic orbitals that being filled with electrons.

The s-block Elements

- (i) General electronic configuration is ns^{1-2}
- (ii) Group 1 and Group 2 elements are s-block elements because they have ns^1 and ns^2 outermost electronic configuration.

- (iii) They are all reactive metals with low ionisation energy. They lose the outermost e^{-1} s readily to form +1 ion (grp 1) or +2 ion (grp 2).
Their compounds are predominantly ionic (except Li and Bi).
- (iv) Group 1 elements are known as alkali metals because they react with water to form alkali. Group 2 elements are known as alkaline earth metals because their oxides react with water to form alkali and these are found in the soil or earth. The total number of s -block elements are 14.

The p-block Elements

- (i) General electronic configuration is $ns^2 np^{1-6}$
- (ii) They comprise of elements from group 13 to 18.
- (iii) Group 16 elements are called chalcogens while group 17 elements are called halogens.
- (iv) Group 18 elements are the noble gases due to completely filled valence shell. As a result, they are less reactive,
- (v) The non-metallic character increases as we move from left to right across a period. Down the group metallic character increases.
- (vi) The p -block elements together with s -block elements are called Representative elements.

The d-block Elements

- (i) General electronic configuration is $(n-1)d^{1-10} ns^{0-2}$
- (ii) They comprise of group 3 to 12. They are all metals.
- (iii) They mostly form coloured ions, exhibit variable oxidation states paramagnetism and are used as catalysts.
- (iv) They form a bridge between chemically active metals of s -block and less active metals of group 13 and 14 and thus are called 'Transition Elements'.
- (v) Zn, Cd and Hg though are d -block elements but do not known as transition elements because in these elements d -orbitals are fully filled.

The f-block Elements

- (i) General electronic configuration is $(n-2)f^{1-14} (n-1) d^{0-1} ns^2$
- (ii) They comprise of the two rows of elements at the bottom of periodic Table, called the Lanthanoids and Actinoids.
- (iii) These two series of elements are called Inner transition elements.
- (iv) They are all metals. The chemistry of early actinoids is more complicated than corresponding lanthanoids due to larger number of oxidation state possible for actinoid elements
- (v) The elements after uranium are called Transuranium elements.

Metals, Non-Metals and Metalloids

The elements can be divided into Metals and Non-metals.

Metals

- (i) They appear on the left hand side of periodic table.
- (ii) They are usually solids at room temperature (except Hg which is a liquid at room temperature)
- (iii) They have high m.pts and b.pts, are good conductors of heat and electricity and are malleable and ductile.

Non-metals

- (i) They are located at the top right hand side of the periodic table.
- (ii) They are usually solids or gases at room temperature with low m.pts and b.pts.
- (iii) They are poor conductors of heat and electricity.
- (iv) They are brittle and are neither malleable nor ductile.

Metalloids

The elements which lie on the borderline between metals and non-metals show properties that are characteristic of both metals and non-metals. They are called semi-metals or metalloids.

PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

Atomic Radius

It is defined as half the distance between the nuclei of two bonded atoms. It refers to both covalent and metallic radius depending on whether the element is metal or non-metal.

Atomic radii decreases across a period because e^{-1} s are being added into same valence shell so that the effective nuclear charge increases as the atomic number increases resulting in increased attraction of e^{-1} s to the nucleus.

In a group, atomic radius increases. This is because down the group, principal quantum number (n) increases and e^{-} is being added into new shell. As a result valence e^{-1} s are farther from the nucleus. Thus, nuclear attraction decreases and therefore size increases.

Ionic Radius

The removal of an e^{-} from an atom results in the formation of cation whereas gain of an e^{-} leads to an anion.

Ionic radii of elements exhibit the same trend as atomic radii.

A cation is smaller than its parent atom because it has fewer e^{-1} s while its nuclear charge remains the same.

The size of anion is larger than parent atom because addition of one or more e^{-1} s results in increased repulsion among e^{-1} s and a decrease in effective nuclear charge.

Isoelectronic species have different radii due to their different nuclear charges. Cation with greater positive charge has smaller radius due to greater effective nuclear charge. Anion with greater negative charge will have larger radius because the net repulsion of the e^{-1} s will outweigh the nuclear charge and the ion expands in size.

Ionization Enthalpy (IE)

It is the amount of energy required to convert gaseous neutral atom into cation, i.e. $X(g) \longrightarrow X^{+}(g) + e^{-}$

Ionization energy is always positive because energy is always required to remove e^{-1} s from an atom.

$IE_3 > IE_2 > IE_1$ This is because it is more difficult to remove an e^{-} from a positively charged species than from a neutral atom. Down the group, atomic size increases and IE decreases. While across a period, atomic size decreases and IE increases.

Factors governing the Ionization energy

- (i) **Nuclear charge:** IE increases with increases in nuclear charge.
- (ii) **Atomic size:** IE decreases as atomic radius decreases.
- (iii) **Penetrating effect of e^{-1} s:** IE increases as penetration effect of e^{-1} s increases. Within the same shell, penetration effect decreases in the order : $s > p > d > f$. Thus, IE to knock out $s - e^{-}$ will be higher than $p - e^{-}$ of the same shell.
- (iv) **Shielding or screening effect of inner shell e^{-1} s:** As shielding or screening effect of inner e^{-1} s. increases, IE decreases.
- (v) **Effect of exactly half-filled or completely filled orbitals:** More stable the electronic configuration, greater is the IE. This is because of extra stability associated with exactly half-filled or completely filled orbitals due to which more energy is required to remove the e^{-} . This is the reason why IE of N is more than that of O.

- (vi) Noble gases, being stable with completely filled orbital have the highest IE in their respective periods.

Electron Gain Enthalpy (EGE)

It is defined as the energy released when a neutral isolated gaseous atom accepts an extra e^- to form gaseous negative ion, i.e., anion, i.e.

$$X(g) + e^- \longrightarrow X^-(g)$$

After the addition of one e^- , the atom becomes negatively charged and 2nd e^- is to be added to a negatively charged ion. But the addition of 2nd e^- is opposed by electrostatic repulsion and hence energy has to be supplied for addition of 2nd e^- . Thus, 2nd electron gain enthalpy of an element is positive.

Factors on which EGE depends

- Atomic size:** As size increases EGE becomes less negative.
- Nuclear charge:** As nuclear charge increases, EGE becomes more negative.
- Electronic configuration:** Elements having exactly half-filled or completely filled orbitals are very stable and have large positive electron gain enthalpy because they do not accept additional e^- easily.

Variation of EGE in periodic table

- Down the group, atomic size increases, EGE becomes less negative. Across a period, atomic size decreases, nuclear charge increases and EGE becomes more negative.
- Halogens have very high negative EGE because they attain stable noble gas electronic configuration by accepting an e^- .
- Noble gases have large positive EGE because the e^- has to enter the next higher shell leading to a very unstable electronic configuration.
- EGE of O or F is less negative than the succeeding element S or Cl. This is because when an e^- is added to O or F, the added e^- goes to smaller $n = 2$ quantum level and suffers significant repulsion from other e^- s in this level. For $n = 3$ level (S or Cl), added e^- occupies a larger region of space and $e^- - e^-$ repulsion is much less.

Electronegativity

It is the tendency of an atom of the element to attract the shared pair of e^- s towards itself in a covalent bond. It is represented by X.

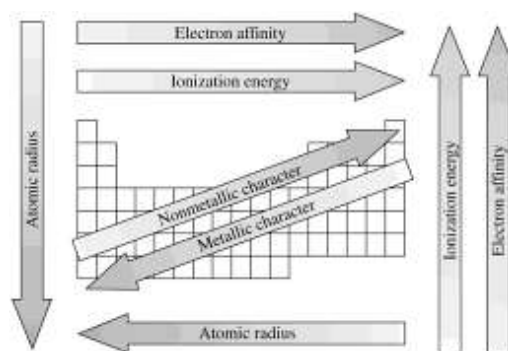
The electronegativity of any given element is not constant but depends on the following factors:

- State of hybridization:** sp -hybridized carbon is more electronegative than sp^2 hybridized which in turn is more electronegative than sp^3 hybridized carbon.
- O.S. of the element:** As O.S. of the element increases, electronegativity increases.
- Nature of substituents attached to the atom:** For ex: C-atom in CF_3I is more electronegative than in CH_3I .

Variation of electronegativity in periodic table

- Down the group, atomic radius increases, electronegativity decreases
Across a period, atomic radius and nuclear charge increases, electronegativity increases.
- F is the most electronegative element and caesium is the least electronegative element.

SUMMARY OF TRENDS IN PERIODIC PROPERTIES OF ELEMENTS.



PERIODIC TRENDS AND CHEMICAL REACTIVITY

Chemical reactivity is highest at the two extremes of a period and is lowest in the centre.

Nature of Oxides

If difference of the two electronegativities ($X_O - X_A$) is 2.3 or more then oxide will be basic in nature. Similarly if value of $X_O - X_A$ is slightly lower than 2.3 then oxide will be amphoteric and if value of $X_O - X_A$ is highly lower than 2.3 then oxide will be of acidic nature.

Nature of Hydroxides

According to **Gallis**, if electronegativity of A in a hydroxide (AOH) is more than 1.7 then it will be acidic in nature whereas it will be basic in nature if electronegativity is less than 1.7

Note : Compounds formed from two nonmetals are called binary compounds. Name of more electronegative element is written at the end and 'ide' is suffixed to it. The name of less electronegative element is written before the name of more electronegative element of the formula.

Periodicity of Valence or Oxidation State

O.S. of an element in a particular compound is defined as the charge acquired by its atom on the basis of electronegativity of other atoms in the molecule. The valence of representative elements is usually equal to no. of e^- s in outermost shell.

Variation of oxidation state in periodic table

Across a period, no. of valence e^- s increases from 1 to 8. The valence of elements first increases from 1 to 4 and then decreases to zero.

Down the group, no. of valence e^- s remain the same, and therefore, all elements in a group exhibit the same valence.

Noble gases are zerovalent, i.e., their valence is zero because they are chemically inert.

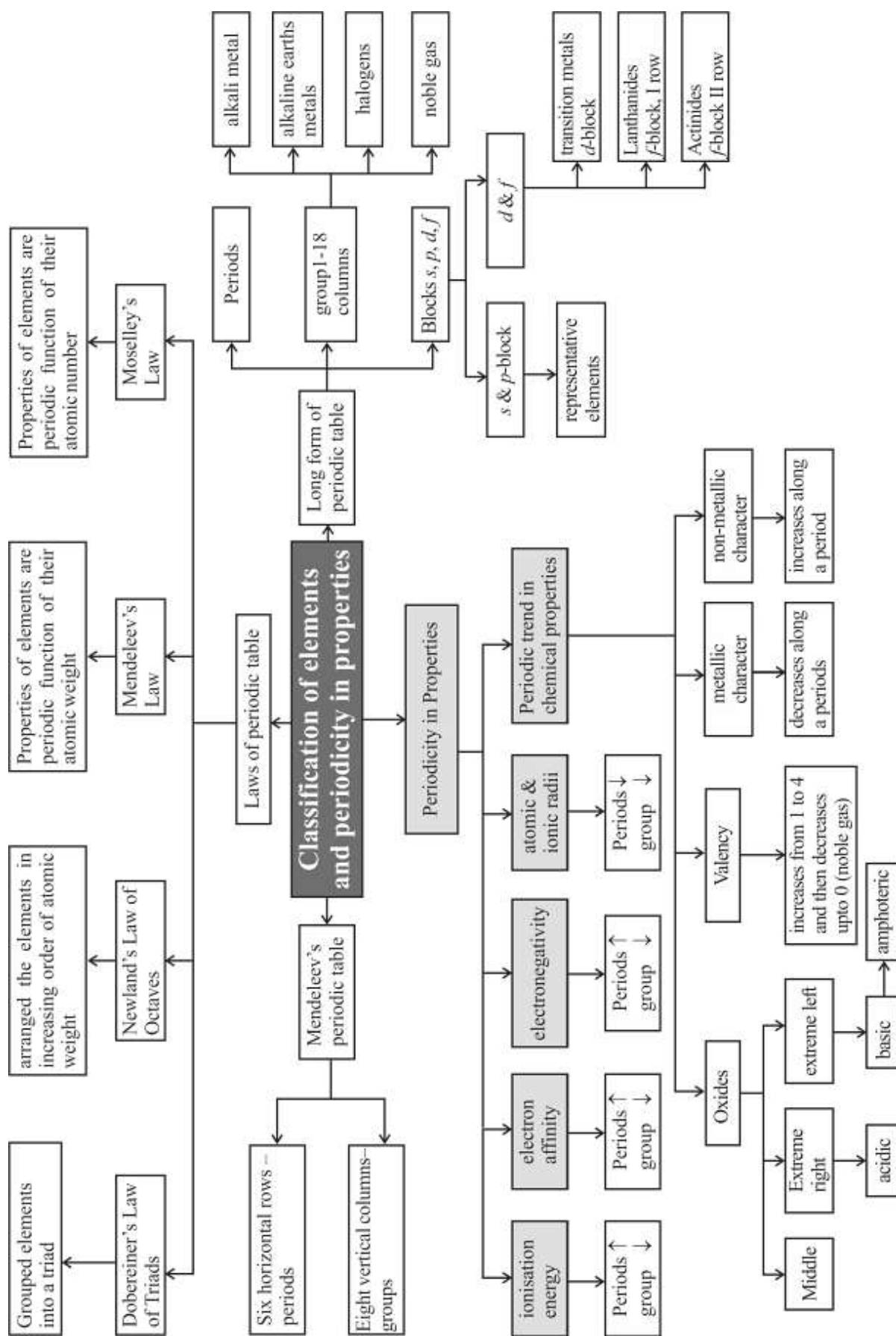
ANOMALOUS PROPERTIES OF SECOND PERIOD ELEMENTS

The first element of each of the groups 1 (Li) and 2 (Be) and groups 13-17 (B to F) differs in many respects from other members of its group. Moreover, the behaviour of Li and Be is more similar with the 2nd element of following group i.e. Mg and Al. This sort of similarity is referred to as diagonal relationship in periodic properties.

The anomalous behaviour of these elements is attributed to their (i) small size (ii) large charge / radius ratio (iii) high electronegativity (iv) non-availability of orbitals due to which they cannot expand their covalence beyond 4.

For example : Because of smaller size and higher electronegativity first member of p-block elements displays greater ability to form $p\pi-p\pi$ multiple bonds to itself ($C \equiv C$, $C \equiv N$, $N \equiv N$) and to other 2nd period elements ($C = O$, $C = N$, $C \equiv N$, $N = O$) compared to subsequent members of same group.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- Which group of periodic table contains no metal:
 - IA
 - IIIA
 - VIIA
 - VIII
- Which of the following is the atomic number of metal?
 - 32
 - 34
 - 36
 - 38
- Which one of these is basic?
 - SiO_2
 - SO_2
 - CO_2
 - Na_2O
- Most acidic oxide is:
 - Na_2O
 - ZnO
 - MgO
 - P_2O_5
- Which of the following metals shows allotropy?
 - Ca
 - Pb
 - Sn
 - K
- The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^3$. What is the atomic number of the element, which is just below the above element in the periodic table?
 - 33
 - 34
 - 36
 - 49
- An atom has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$, you will place it in which group?
 - Fifth
 - Fifteenth
 - Second
 - Third
- Which one of the following is an amphoteric oxide?
 - Na_2O
 - SO_2
 - B_2O_3
 - ZnO
- The screening effect of 'd' electrons is
 - Much less than s- electrons
 - Much more than s- electrons
 - Equal to s- electrons
 - Equal to p- electrons
- The statement that is not correct for the periodic classification of element is
 - the properties of elements are the periodic functions of their atomic numbers.
 - non-metallic elements are lesser in number than metallic elements.
 - the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number.
 - for transition elements the d-subshells are filled with electrons monotonically with increase in atomic number.
- The elements in which 4f orbitals are progressively filled up are called as
 - Actinoids
 - Transition elements
 - Lanthanoids
 - Halogens
- Who developed long form of the periodic table?
 - Lothar Meyer
 - Neils Bohr
 - Mendeleev
 - Moseley
- An element X occurs in short period having configuration $ns^2 np^1$. The formula and nature of its oxide is
 - XO_3 , basic
 - XO_3 , acidic
 - X_2O_3 , amphoteric
 - X_2O_3 , basic
- The statement that is not true for the long form of the periodic table is
 - it reflects the sequence of filling electrons in the order of sub-energy levels s, p, d and f.
 - it helps to predict the stable valence states of the elements
 - it reflects trends in physical and chemical properties of the elements
 - it helps to predict the relative ionicity of the bond between any two elements.
- Among the following elements, the one having the highest ionisation energy is.
 - $[\text{Ar}]3d^{10}, 4s^2 4p^3$
 - $[\text{Ne}]3s^2 3p^1$
 - $[\text{Ne}]3s^2 3p^3$
 - $[\text{Ne}]3s^2 3p^2$
- Polarisation power of a cation increases when
 - size of the cation increases
 - charge of the cation increases
 - charge of the cation decreases
 - it has no relation with its charge or size
- Which one of the following is not a transition metal?
 - Mn
 - Cr
 - Cu
 - Cd
- Which is chemically most active non-metal?
 - S
 - O
 - F
 - N
- Which of the following is non-metallic?
 - B
 - Be
 - Mg
 - Al
- The only non-metal which is liquid at ordinary temperature is
 - Hg
 - Br_2
 - NH_3
 - None of the above
- Amphoteric-oxide combinations are in
 - $\text{ZnO}, \text{K}_2\text{O}, \text{SO}_3$
 - $\text{ZnO}, \text{P}_2\text{O}_5, \text{Cl}_2\text{O}_7$
 - $\text{SnO}_2, \text{Al}_2\text{O}_3, \text{ZnO}$
 - $\text{PbO}_2, \text{SnO}_2, \text{SO}_3$
- The correct order of ionization energies is
 - $\text{Zn} < \text{Cd} < \text{Hg}$
 - $\text{Hg} < \text{Cd} < \text{Zn}$
 - $\text{Ar} > \text{Ne} > \text{He}$
 - $\text{Cs} < \text{Rb} < \text{Na}$
- Which one of the following has largest size?
 - Al
 - Al^{3+}
 - Al^+
 - Al^{2+}
- The ionisation potential order for which set is correct?
 - $\text{Cs} < \text{Li} < \text{K}$
 - $\text{Cs} > \text{Li} > \text{B}$
 - $\text{Li} > \text{K} > \text{Cs}$
 - $\text{B} > \text{Li} > \text{K}$
- Which one has least ionisation potential?
 - Ne
 - N
 - O
 - F
- Which one of the following is smallest in size?
 - N^{3-}
 - O^{2-}
 - Na^+
 - F^-

27. The ionization energy of nitrogen atom is more than that of oxygen atom because of
 (a) greater attraction of electrons by the nucleus.
 (b) smaller size of nitrogen atom.
 (c) more penetrating effect
 (d) due to half filled p orbital
28. Sequence of acidic character is
 (a) $\text{N}_2\text{O}_5 > \text{SO}_2 > \text{CO} > \text{CO}_2$ (b) $\text{N}_2\text{O}_5 > \text{SO}_2 > \text{CO}_2 > \text{CO}$
 (c) $\text{SO}_2 > \text{CO}_2 > \text{CO} > \text{N}_2\text{O}_5$ (d) $\text{SO}_2 > \text{N}_2\text{O}_5 > \text{CO} > \text{CO}_2$
29. Which is a metalloid?
 (a) Manganese (b) Phosphorus
 (c) Oxygen (d) Arsenic
30. Na^+ , Mg^{2+} , Al^{3+} and Si^{4+} ions are isoelectronic. The value of ionic radii of these ions would be in the order:
 (a) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Si}^{4+}$
 (b) $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+} < \text{Si}^{4+}$
 (c) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} < \text{Si}^{4+}$
 (d) $\text{Na}^+ < \text{Mg}^{2+} > \text{Al}^{3+} > \text{Si}^{4+}$
31. Maximum ionisation potential is of:
 (a) Ca (b) Na (c) Be (d) Mg
32. Correct order of first IP among following elements Be, B, C, N, O is
 (a) $\text{B} < \text{Be} < \text{C} < \text{O} < \text{N}$ (b) $\text{B} < \text{Be} < \text{C} < \text{N} < \text{O}$
 (c) $\text{Be} < \text{B} < \text{C} < \text{N} < \text{O}$ (d) $\text{Be} < \text{B} < \text{C} < \text{O} < \text{N}$
33. Which one of the following ions has the highest value of ionic radius?
 (a) O^{2-} (b) B^{3+} (c) Li^+ (d) F^-
34. An element having electronic configuration $1s^2, 2s^2 2p^6, 3s^2 3p^1$ will form
 (a) neutral oxide (b) acidic oxide
 (c) basic oxide (d) amphoteric oxide
35. The first ionisation potential in electron volts of nitrogen and oxygen atoms are respectively given by
 (a) 14.6, 13.6 (b) 13.6, 14.6
 (c) 13.6, 13.6 (d) 14.6, 14.6
36. The correct order of radii is
 (a) $\text{N} < \text{Be} < \text{B}$ (b) $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$
 (c) $\text{N} < \text{Li} < \text{K}$ (d) $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}^{4+}$
37. First ionization potential will be maximum for
 (a) uranium (b) hydrogen
 (c) lithium (d) iron
38. Chloride ion and potassium ion are isoelectronic. Then
 (a) their sizes are same
 (b) Cl^- ion is bigger than K^+ ion
 (c) K^+ ion is relatively bigger
 (d) their sizes depend on either cation or anion
39. Ionic radii of
 (a) $\text{Ti}^{4+} < \text{Mn}^{2+}$ (b) $^{35}\text{Cl}^- < ^{37}\text{Cl}^-$
 (c) $\text{K}^+ > \text{Cl}^-$ (d) $\text{P}^{3+} > \text{P}^{5+}$
40. When an electron is removed from an atom, its energy
 (a) increases (b) decreases
 (c) remains the same (d) none of these
41. Which of the following has minimum melting point?
 (a) CsF (b) HCl (c) HF (d) LiF
42. The correct order of ionization energy for carbon, nitrogen and oxygen atoms is:
 (a) $\text{C} > \text{N} > \text{O}$ (b) $\text{C} > \text{N} < \text{O}$
 (c) $\text{C} < \text{N} > \text{O}$ (d) $\text{C} < \text{N} < \text{O}$
43. Which of the following pairs of atomic numbers represents elements belonging to the same group?
 (a) 11 and 20 (b) 12 and 30
 (c) 13 and 31 (d) 14 and 33
44. The correct order according to size is
 (a) $\text{O} > \text{O}^- > \text{O}^{2-}$ (b) $\text{O}^- > \text{O}^{2-} > \text{O}$
 (c) $\text{O}^{2-} > \text{O}^- > \text{O}$ (d) $\text{O} > \text{O}^{2-} > \text{O}^-$
45. Which of the following element has maximum, first ionisation potential?
 (a) V (b) Ti (c) Cr (d) Mn
46. The outer electronic configuration of transition elements is
 (a) $(n-1)s^2 nd^{1-5}$
 (b) $(n+1)s^2 nd^{1-5}$
 (c) $(n-1)s^2 p^6 (n-1)d^{1-10}, ns^{0-2}$
 (d) $ns^2 (n+1)d^{1-10}$
47. If 19 is the atomic number of an element, then this element will be
 (a) a metal with +3 oxidation state
 (b) a metal with +1 oxidation state
 (c) an inert gas
 (d) a metal with -3 oxidation state
48. Highest energy will be absorbed to eject out the electron in the configuration
 (a) $1s^2 2s^2 2p^1$ (b) $1s^2 2s^2 2p^3$
 (c) $1s^2 2s^2 2p^2$ (d) $1s^2 2s^2 2p^4$
49. In which of the following process highest energy is absorbed?
 (a) $\text{Cu} \rightarrow \text{Cu}^+$ (b) $\text{Br} \rightarrow \text{Br}^-$
 (c) $\text{I} \rightarrow \text{I}^-$ (d) $\text{Li} \rightarrow \text{Li}^+$
50. Which of the following gaseous atoms has highest value of IE?
 (a) P (b) Si
 (c) Mg (d) Al
51. Which ionisation potential (IP) in the following equations involves the greatest amount of energy?
 (a) $\text{Na} \rightarrow \text{Na}^+ + e^-$ (b) $\text{K}^+ \rightarrow \text{K}^{2+} + e^-$
 (c) $\text{C}^{2+} \rightarrow \text{C}^{3+} + e^-$ (d) $\text{Ca}^+ \rightarrow \text{Ca}^{2+} + e^-$
52. Arrange S, P, As in order of increasing ionisation energy
 (a) $\text{S} < \text{P} < \text{As}$ (b) $\text{P} < \text{S} < \text{As}$
 (c) $\text{As} < \text{S} < \text{P}$ (d) $\text{As} < \text{P} < \text{S}$
53. Among the following options, the sequence of increasing first ionisation potential will be
 (a) $\text{B} < \text{C} < \text{N}$ (b) $\text{B} > \text{C} > \text{N}$
 (c) $\text{C} < \text{B} < \text{N}$ (d) $\text{N} > \text{C} > \text{B}$
54. As per the modern periodic law, the physical and chemical properties of elements are periodic functions of their
 (a) Atomic volume
 (b) Electronic configuration
 (c) Atomic weight
 (d) Atomic size
55. Eka-aluminium and Eka-silicon are known as
 (a) Gallium and Germanium
 (b) Aluminium and Silicon
 (c) Iron and Sulphur
 (d) Neutron and Magnesium

56. The correct order of reactivity of halogens is
 (a) $F > Cl > Br > I$ (b) $F < Cl > Br < I$
 (c) $F < Cl < Br < I$ (d) $F < Cl < Br > I$
57. Which one of the following represents the electronic configuration of the most electropositive element?
 (a) $[He] 2s^1$ (b) $[Xe] 6s^1$
 (c) $[He] 2s^2$ (d) $[Xe] 6s^2$
58. A group 16 element exists in the monoatomic state in the metallic state. It also exists in two crystalline forms. The metal is
 (a) S (b) Po (c) Se (d) Te
59. Electron affinity is positive when :
 (a) O changes into O^-
 (b) O^- changes into O^{2-}
 (c) O changes into O^+
 (d) electron affinity is always negative
60. Electron affinity is maximum for
 (a) Cl (b) F (c) Br (d) I
61. Pauling's electronegativity values for elements are useful in predicting
 (a) polarity of the molecules
 (b) position in the E.M.F. series
 (c) coordination number
 (d) dipole moments.
62. Which of the following is most electronegative?
 (a) Lead (b) Silicon
 (c) Carbon (d) Tin
63. Variable valency is generally exhibited by
 (a) representative elements (b) transition elements
 (c) non-metallic elements (d) metallic elements
64. On going from right to left in a period in the periodic table, the electronegativity of the elements
 (a) increases
 (b) decreases
 (c) remains unchanged
 (d) decreases first then increases
65. Which one of the following has the highest electronegativity?
 (a) Br (b) Cl (c) P (d) Si
66. Fluorine, chlorine, bromine and iodine are placed in the same group 17 of the periodic table because :
 (a) they are nonmetals
 (b) they are electronegative
 (c) their atoms are generally univalent
 (d) they have 7 electrons in the outer-most shell of their atom
67. Which is the correct order of electronegativity?
 (a) $F > N < O > C$ (b) $F > N > O > C$
 (c) $F > N > O < C$ (d) $F < N < O = C$
68. The electron affinity for the inert gases is
 (a) zero (b) high
 (c) negative (d) positive
69. Which of the following species has the highest electron affinity?
 (a) F (b) O (c) O^- (d) Na^+
70. An atom with high electronegativity has
 (a) large size
 (b) high ionisation potential
 (c) low electron affinity
 (d) low ionisation potential
71. The largest size of the ion is :
 (a) Cl^- (b) Ca^{++} (c) K^+ (d) S^{--}
72. Which of the following is the most electronegative?
 (a) F (b) He (c) Ne (d) Na
73. The outermost electronic configuration of the most electronegative element is
 (a) $ns^2 np^3$ (b) $ns^2 np^4$ (c) $ns^2 np^5$ (d) $ns^2 np^6$
74. Which of the following sequence correctly represents the decreasing acidic nature of oxides?
 (a) $Li_2O > BeO > B_2O_3 > CO_2 > N_2O_3$
 (b) $N_2O_3 > CO_2 > B_2O_3 > BeO > Li_2O$
 (c) $CO_2 > N_2O_3 > B_2O_3 > BeO > Li_2O$
 (d) $B_2O_3 > CO_2 > N_2O_3 > Li_2O > BeO$
75. Which transition involves maximum amount of energy?
 (a) $M^-(g) \longrightarrow M(g) + e$
 (b) $M^-(g) \longrightarrow M^+(g) + 2e$
 (c) $M^+(g) \longrightarrow M^{2+}(g) + e$
 (d) $M^{2+}(g) \longrightarrow M^{3+}(g) + e$

EXERCISE - 2

Applied Questions

1. Which of the following can not be isoelectronic?
 (a) two different cations (b) two different anions
 (c) cation and anion (d) two different atoms
2. The species with a radius less than that of Ne is
 (a) Mg^{2+} (b) F^- (c) O^{2-} (d) K^+
3. The correct order of acidic strength :
 (a) $Cl_2O_7 > SO_2 > P_4O_{10}$ (b) $K_2O > CaO > MgO$
 (c) $CO_2 > N_2O_5 > SO_3$ (d) $Na_2O > MgO > Al_2O_3$
4. Electron affinity of X would be equal to
 (a) electron affinity of X^-
 (b) ionization energy of X
 (c) ionization energy of X^- with sign reversed
 (d) none of these
5. Which group is called buffer group of the periodic table?
 (a) I (b) VII
 (c) VIII (d) Zero
6. The pair of elements having approximately equal ionisation potential is
 (a) Al, Ga (b) Al, Si
 (c) Al, Mg (d) Al, B
7. Which electronic configuration of an element has abnormally high difference between second and third ionization energy?
 (a) $1s^2, 2s^2, 2p^6, 3s^1$ (b) $1s^2, 2s^2, 2p^6, 3s^1, 3p^1$
 (c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$ (d) $1s^2, 2s^2, 2p^6, 3s^2$

8. Which of the following order is wrong?
 (a) $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3$ – Acidic
 (b) $\text{Li} < \text{Be} < \text{B} < \text{C}$ – First IP
 (c) $\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O}$ – Basic
 (d) $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ – Ionic radius
9. For which of the following processes, enthalpy change is positive
 (a) $\text{F}_{(\text{g})} + \text{e}^- \rightarrow \text{F}_{(\text{g})}^-$ (b) $\text{Cl}_{(\text{g})} + \text{e}^- \rightarrow \text{Cl}_{(\text{g})}^-$
 (c) $\text{O}_{(\text{g})} + 2\text{e}^- \rightarrow \text{O}_{(\text{g})}^{2-}$ (d) $\text{H}_{(\text{g})} + \text{e}^- \rightarrow \text{H}_{(\text{g})}^-$
10. Arrange the elements with the following electronic configurations in increasing order of electron affinity
 (i) $1s^2 s^2 2p^5$ (ii) $1s^2 2s^2 2p^4$
 (iii) $1s^2 2s^2 2p^6 3s^2 3p^4$ (iv) $1s^2 2s^2 2p^6 3s^2 3p^5$
 (a) (ii) < (iii) < (i) < (iv) (b) (iii) < (ii) < (iv) < (i)
 (c) (iii) < (ii) < (i) < (iv) (d) (ii) < (iii) < (iv) < (i)
11. Among Al_2O_3 , SiO_2 , P_2O_3 and SO_2 the correct order of acid strength is
 (a) $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{SO}_2 < \text{P}_2\text{O}_3$
 (b) $\text{SiO}_2 < \text{SO}_2 < \text{Al}_2\text{O}_3 < \text{P}_2\text{O}_3$
 (c) $\text{SO}_2 < \text{P}_2\text{O}_3 < \text{SiO}_2 < \text{Al}_2\text{O}_3$
 (d) $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{P}_2\text{O}_3 < \text{SO}_2$
12. The formation of the oxide ion $\text{O}_{(\text{g})}^{2-}$ requires first an exothermic and then an endothermic step as shown below :
 $\text{O}_{(\text{g})} + \text{e}^- = \text{O}_{(\text{g})}^- \Delta H^\circ = -142 \text{ kJmol}^{-1}$
 $\text{O}_{(\text{g})}^- + \text{e}^- = \text{O}_{(\text{g})}^{2-} \Delta H^\circ = 844 \text{ kJmol}^{-1}$
 This is because
 (a) O^- ion will tend to resist the addition of another electron
 (b) Oxygen has high electron affinity
 (c) Oxygen is more electronegative
 (d) O^- ion has comparatively larger size than oxygen atom
13. In which of the following arrangements, the order is NOT according to the property indicated against it?
 (a) $\text{Li} < \text{Na} < \text{K} < \text{Rb}$:
Increasing metallic radius
 (b) $\text{I} < \text{Br} < \text{F} < \text{Cl}$:
Increasing electron gain enthalpy (with negative sign)
 (c) $\text{B} < \text{C} < \text{N} < \text{O}$
Increasing first ionization enthalpy
 (d) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$
Increasing ionic size
14. Quite a large jump between the values of second and third ionization potentials of an atom would correspond to the electronic configuration
 (a) $1s^2 2s^2 2p^6$ (b) $1s^2 2s^2 2p^6 3s^2$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^1$ (d) $1s^2 2s^2 2p^6 3s^2 3p^2$
15. Consider the following changes
 $A \rightarrow A^+ + \text{e}^- : E_1$ and $A^+ \rightarrow A^{2+} + \text{e}^- : E_2$
 The energy required to pull out the two electrons are E_1 and E_2 respectively. The correct relationship between two energies would be
 (a) $E_1 < E_2$ (b) $E_1 = E_2$
 (c) $E_1 > E_2$ (d) $E_1 \geq E_2$
16. The incorrect statement among the following is
 (a) The first ionization potential of Al is less than the first ionization potential of Mg
 (b) The second ionization potential of Mg is greater than the second ionization potential of Na
 (c) The first ionization potential of Na is less than the first ionization potential of Mg
 (d) The third ionization potential of Mg is greater than the third ionization potential of Al.
17. Successive addition of electronic shells in case of elements of 17th group causes a increase in
 (a) electronegativity
 (b) ionization energy
 (c) ease of formation of unipositive ion
 (d) oxidizing power
18. The second ionization potential of an element M is the energy required to
 (a) remove one mole of electrons from one mole of gaseous cations of the element
 (b) remove one mole of electrons from one mole of gaseous anions
 (c) remove one mole of electrons from one mole of monovalent gaseous cations of the element
 (d) remove 2 moles of electrons from one mole of gaseous atoms
19. Which of the following ions has the most negative value of enthalpy of interaction with water?
 (a) NH_4^+ (b) OH^- (c) H^+ (d) F^-
20. s-electrons of the valence shell of some elements show reluctance in bond formation. Such elements are --- and belong to --- :
 (a) lighter, s-block (b) heavier, d-block
 (c) heavier, f-block (d) heavier, p-block
21. Which of the following cations acts as an oxidizing agent?
 (a) Ga^{3+} (b) In^{3+} (c) Tl^{1+} (d) Tl^{3+}
22. The first ionization potential of Na, Mg, Al and Si are in the order
 (a) $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$ (b) $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$
 (c) $\text{Na} < \text{Mg} < \text{Al} > \text{Si}$ (d) $\text{Na} > \text{Mg} > \text{Al} < \text{Si}$
23. Correct order of polarising power is
 (a) $\text{Cs}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$ (b) $\text{K}^+ < \text{Cs}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$
 (c) $\text{Cs}^+ < \text{K}^+ < \text{Al}^{3+} < \text{Mg}^{2+}$ (d) $\text{K}^+ < \text{Cs}^+ < \text{Al}^{3+} < \text{Mg}^{2+}$
24. In general, the ionization potentials of elements decreases as one proceeds in the periodic table
 (a) bottom $\rightarrow$ top and right $\rightarrow$ left
 (b) top $\rightarrow$ bottom and right $\rightarrow$ left
 (c) bottom $\rightarrow$ top and left $\rightarrow$ right
 (d) top $\rightarrow$ bottom and left $\rightarrow$ right
25. Which of the following properties of elements does not exhibit the periodicity?
 (a) Ionization potential (b) Electronegativity
 (c) Electronic configuration (d) Neutron to proton ratio

26. Identify the correct order of the size of the following:
 (a) $\text{Ca}^{2+} < \text{K}^+ < \text{Ar} < \text{Cl}^- < \text{S}^{2-}$
 (b) $\text{Ar} < \text{Ca}^{2+} < \text{K}^+ < \text{Cl}^- < \text{S}^{2-}$
 (c) $\text{Ca}^{2+} < \text{Ar} < \text{K}^+ < \text{Cl}^- < \text{S}^{2-}$
 (d) $\text{Ca}^{2+} < \text{K}^+ < \text{Ar} < \text{S}^{2-} < \text{Cl}^-$
27. Which one of the following ionic species has the greatest proton affinity to form stable compound?
 (a) NH_2^- (b) F^-
 (c) I^- (d) HS^-
28. The stability of +1 oxidation state increases in the sequence:
 (a) $\text{Tl} < \text{In} < \text{Ga} < \text{Al}$ (b) $\text{In} < \text{Tl} < \text{Ga} < \text{Al}$
 (c) $\text{Ga} < \text{In} < \text{Al} < \text{Tl}$ (d) $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$
29. Amongst the elements with following electronic configurations, which one of them may have the highest ionization energy?
 (a) $\text{Ne}[3s^2 3p^2]$ (b) $\text{Ar}[3d^{10} 4s^2 4p^3]$
 (c) $\text{Ne}[3s^2 3p^1]$ (d) $\text{Ne}[3s^2 3p^3]$
30. Among the elements Ca, Mg, P and Cl, the order of increasing atomic radii is:
 (a) $\text{Ca} < \text{Mg} < \text{P} < \text{Cl}$ (b) $\text{Mg} < \text{Ca} < \text{Cl} < \text{P}$
 (c) $\text{Cl} < \text{P} < \text{Mg} < \text{Ca}$ (d) $\text{P} < \text{Cl} < \text{Ca} < \text{Mg}$
31. What is the value of electron gain enthalpy of Na^+ if IE_1 of $\text{Na} = 5.1 \text{ eV}$?
 (a) -5.1 eV (b) -10.2 eV
 (c) $+2.55 \text{ eV}$ (d) $+10.2 \text{ eV}$
32. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture?
 (a) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens
 (b) In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group
 (c) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group
 (d) In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group
33. In which of the following arrangements, the sequence is *not* strictly according to the property written against it?
 (a) $\text{HF} < \text{HCl} < \text{HBr}$, HI: increasing acid strength
 (b) $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$: increasing basic strength
 (c) $\text{B} < \text{C} < \text{O} < \text{N}$: increasing first ionization enthalpy
 (d) $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$: increasing oxidising power
34. The correct sequence which shows decreasing order of the ionic radii of the elements is
 (a) $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+ > \text{F}^- > \text{O}^{2-}$
 (b) $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{O}^{2-} > \text{F}^-$
 (c) $\text{Na}^+ > \text{F}^- > \text{Mg}^{2+} > \text{O}^{2-} > \text{Al}^{3+}$
 (d) $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$
35. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is:
 (a) $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (b) $\text{Cl} > \text{F} > \text{Br} > \text{I}$
 (c) $\text{Br} > \text{Cl} > \text{I} > \text{F}$ (d) $\text{I} > \text{Br} > \text{Cl} > \text{F}$
36. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar?
 (a) $\text{Ca} < \text{S} < \text{Ba} < \text{Se} < \text{Ar}$ (b) $\text{S} < \text{Se} < \text{Ca} < \text{Ba} < \text{Ar}$
 (c) $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$ (d) $\text{Ca} < \text{Ba} < \text{S} < \text{Se} < \text{Ar}$
37. An element of atomic weight 40 has 2, 8, 8, 2 as the electronic configuration. Which one of the following statements regarding this element is not correct
 (a) it belongs to II group of the periodic table
 (b) it has 20 neutrons
 (c) the formula of its oxide is MO_2
 (d) it belongs to 4th period of the periodic table
38. Which of the following is not the correct order for the stated property?
 (a) $\text{Ba} > \text{Sr} > \text{Mg}$; atomic radius
 (b) $\text{F} > \text{O} > \text{N}$: first ionization enthalpy
 (c) $\text{Cl} > \text{F} > \text{I}$; electron affinity
 (d) $\text{O} > \text{Se} > \text{Te}$; electronegativity
39. Which of the following sets has strongest tendency to form anions?
 (a) Ga, In, Tl (b) Na, Mg, Al
 (c) N, O, F (d) V, Cr, Mn
40. One of the characteristic properties of non-metals is that they
 (a) Are reducing agents
 (b) Form basic oxides
 (c) Form cations by electron gain
 (d) Are electronegative
41. In which of the following electronic configuration an atom has the lowest ionisation enthalpy?
 (a) $1s^2 2s^2 2p^3$ (b) $1s^2 2s^2 2p^5 3s^1$
 (c) $1s^2 2s^2 2p^6$ (d) $1s^2 2s^2 2p^5$
42. Which of the following represents the correct order of increasing electron gain enthalpy with negative sign for the elements O, S, F and Cl?
 (a) $\text{Cl} < \text{F} < \text{O} < \text{S}$ (b) $\text{O} < \text{S} < \text{F} < \text{Cl}$
 (c) $\text{F} < \text{S} < \text{O} < \text{Cl}$ (d) $\text{S} < \text{O} < \text{Cl} < \text{F}$
43. Which is the correct order of ionic sizes (At. No. : Ce = 58, Sn = 50, Yb = 70 and Lu = 71)?
 (a) $\text{Ce} > \text{Sn} > \text{Yb} > \text{Lu}$ (b) $\text{Sn} > \text{Ce} > \text{Yb} > \text{Lu}$
 (c) $\text{Lu} > \text{Yb} > \text{Sn} > \text{Ce}$ (d) $\text{Sn} > \text{Yb} > \text{Ce} > \text{Lu}$
44. The increasing order of the ionic radii of the given isoelectronic species is:
 (a) $\text{Cl}^-, \text{Ca}^{2+}, \text{K}^+, \text{S}^{2-}$ (b) $\text{S}^{2-}, \text{Cl}^-, \text{Ca}^{2+}, \text{K}^+$
 (c) $\text{Ca}^{2+}, \text{K}^+, \text{Cl}^-, \text{S}^{2-}$ (d) $\text{K}^+, \text{S}^{2-}, \text{Ca}^{2+}, \text{Cl}^-$
45. Atom of which of the following elements has the greatest ability to attract electrons?
 (a) Silicon (b) Sulphur
 (c) Sodium (d) Nitrogen
46. The correct order of decreasing electronegativity values among the elements I-beryllium, II-oxygen, III-nitrogen and IV-magnesium is
 (a) $\text{II} > \text{III} > \text{I} > \text{IV}$ (b) $\text{III} > \text{IV} > \text{II} > \text{I}$
 (c) $\text{I} > \text{II} > \text{III} > \text{IV}$ (d) $\text{II} > \text{III} > \text{IV} > \text{I}$
47. The element with positive electron gain enthalpy is
 (a) hydrogen (b) sodium
 (c) oxygen (d) neon

48. Consider the following statements
- The radius of an anion is larger than that of the parent atom.
 - The ionization energy generally increases with increasing atomic number in a period.
 - The electronegativity of an element is the tendency of an isolated atom to attract an electron.
- Which of the above statements is/are correct?
- I alone
 - II alone
 - I and II
 - II and III
49. The element with atomic number 117 has not been discovered yet. In which family would you place this element if discovered?
- Alkali metals
 - Alkaline earth metals
 - Halogens
 - Noble gases
50. The set representing the correct order for first ionisation potential is
- $K > Na > Li$
 - $Be > Mg > Ca$
 - $B > C > N$
 - $Ge > Si > C$

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Consider the isoelectronic species, Na^+ , Mg^{2+} , F^- and O^{2-} . The correct order of increasing length of their radii is
 - $F^- < O^{2-} < Mg^{2+} < Na^+$
 - $Mg^{2+} < Na^+ < F^- < O^{2-}$
 - $O^{2-} < F^- < Na^+ < Mg^{2+}$
 - $O^{2-} < F^- < Mg^{2+} < Na^+$
- Which of the following is not an actinoid?
 - Curium ($Z = 96$)
 - Californium ($Z = 98$)
 - Uranium ($Z = 92$)
 - Terbium ($Z = 65$)
- The order of screening effect of electrons of s, p, d and f orbitals of a given shell of an atom on its outer shell electrons is
 - $s > p > d > f$
 - $f > d > p > s$
 - $p < d < s > f$
 - $f > p > s > d$
- The first ionisation enthalpies of Na, Mg, Al and Si are in the order
 - $Na < Mg > Al < Si$
 - $Na > Mg > Al > Si$
 - $Na < Mg < Al < Si$
 - $Na > Mg > Al < Si$
- The electronic configuration of gadolinium (Atomic number 64) is
 - $[Xe] 4f^3 5d^5 6s^2$
 - $[Xe] 4f^7 5d^2 6s^1$
 - $[Xe] 4f^7 5d^1 6s^2$
 - $[Xe] 4f^8 5d^6 6s^2$
- The statement that is not correct for periodic classification of elements is
 - the properties of elements are periodic function of their atomic numbers.
 - non-metallic elements are less in number than metallic elements.
 - for transition elements, the 3d-orbitals are filled with electrons after 3p-orbitals and before 4s-orbitals.
 - the first ionisation enthalpies of elements generally increase with increase in atomic number as we go along a period.
- Among halogens, the correct order of amount of energy released in electron gain (electron gain enthalpy) is
 - $F > Cl > Br > I$
 - $F < Cl < Br < I$
 - $F < Cl > Br > I$
 - $F < Cl < Br < I$
- The period number in the long form of the periodic table is equal to
 - magnetic quantum number of any element of the period
 - atomic number of any element of the period
 - maximum principal quantum number of any element of the period
 - maximum azimuthal quantum number of any element of the period
- The elements in which electrons are progressively filled in 4f-orbital are called
 - actinoids
 - transition elements
 - lanthanoids
 - halogens
- Which of the following is the correct order of size of the given species
 - $I > I^- > I^+$
 - $I^+ > I^- > I$
 - $I > I^+ > I^-$
 - $I^- > I > I^+$
- The formation of oxide ion $O^{2-}(g)$, from oxygen atom requires first an exothermic and then an endothermic step as shown below

$$O(g) + e^- \rightarrow O^-(g); \Delta H^\circ = -141 \text{ kJ mol}^{-1}$$

$$O^-(g) + e^- \rightarrow O^{2-}(g); \Delta H^\circ = +780 \text{ kJ mol}^{-1}$$

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that

 - oxygen is more electronegative
 - addition of electron in oxygen results in larger size of the ion
 - electron repulsion outweighs the stability gained by achieving noble gas configuration
 - O^- ion has comparatively smaller size than oxygen atom
- Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option.
In the modern periodic table, elements are arranged in order of increasing atomic numbers which is related to the electronic configuration. Depending upon the type of orbitals receiving the last electron, the elements in the periodic table have been divided into four blocks, viz s, p, d and f.
The modern periodic table consists of 7 periods and 18 groups. Each period begins with the filling of a new energy shell. In accordance with the Aufbau principle, the seven periods (1 to 7) have 2, 8, 8, 18, 18, 32 and 32 elements respectively.

The seventh period is still incomplete. To avoid the periodic table being too long, the two series of *f*-block elements, called lanthanoids and actinoids are placed at the bottom of the main body of the periodic table.

- (i) The element with atomic number 57 belongs to
 (a) *s*-block (b) *p*-block
 (c) *d*-block (d) *f*-block
- (ii) The last element of the *p*-block in 6th period is represented by the outermost electronic configuration.
 (a) $7s^2 7p^6$ (b) $5f^{14} 6d^{10} 7s^2 7p^0$
 (c) $4f^{14} 5d^{10} 6s^2 6p^6$ (d) $4f^{14} 5d^{10} 6s^2 6p^4$
- (iii) Which of the elements whose atomic numbers are given below, cannot be accommodated in the present set up of the long form of the periodic table?
 (a) 107 (b) 118
 (c) 126 (d) 102
- (iv) The electronic configuration of the element which is just above the element with atomic number 43 in the same group is
 (a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
 (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^3 4p^6$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
 (d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
- (v) The elements with atomic numbers 35, 53 and 85 are all
 (a) noble gases (b) halogens
 (c) heavy metals (d) light metals
13. Electronic configuration of four elements A, B, C and D are given below
 A. $1s^2 2s^2 2p^6$ B. $1s^2 2s^2 2p^4$
 C. $1s^2 2s^2 2p^6 3s^1$ D. $1s^2 2s^2 2p^5$
 Which of the following is the correct order of increasing tendency to gain electron?
 (a) $A < C < B < D$ (b) $A < B < C < D$
 (c) $D < B < C < A$ (d) $D < A < B < C$

NEET/AIPMT (2013-2017) Questions

14. Which one of the following arrangements represents the correct order of least negative to most negative electron gain enthalpy for C, Ca, Al, F and O? [NEET Kar. 2013]
 (a) $Ca < Al < C < O < F$
 (b) $Al < Ca < O < C < F$
 (c) $Al < O < C < Ca < F$
 (d) $C < F < O < Al < Ca$
15. Which of the following orders of ionic radii is correctly represented ? [2014]
 (a) $H^- > H^+ > H$ (b) $Na^+ > F^- > O^{2-}$
 (c) $F^- > O^{2-} > Na^+$ (d) $Al^{3+} > Mg^{2+} > N^{3-}$
16. The species Ar, K^+ and Ca^{2+} contain the same number of electrons. In which order do their radii increase ? [2015]
 (a) $Ca^{2+} < Ar < K^+$ (b) $Ca^{2+} < K^+ < Ar$
 (c) $K^+ < Ar < Ca^{2+}$ (d) $Ar < K^+ < Ca^{2+}$
17. The formation of the oxide ion $O^{2-}(g)$, from oxygen atom requires first an exothermic and then an endothermic step as shown below :
 $O(g) + e^- \rightarrow O^-(g); \Delta_f H^\ominus = -141 \text{ kJ mol}^{-1}$
 $O^-(g) + e^- \rightarrow O^{2-}(g); \Delta_f H^\ominus = +780 \text{ kJ mol}^{-1}$
 Thus process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that [2015 RS]
 (a) Electron repulsion outweighs the stability gained by achieving noble gas configuration
 (b) O^- ion has comparatively smaller size than oxygen atom
 (c) Oxygen is more electronegative
 (d) Addition of electron in oxygen results in larger size of the ion.
18. In which of the following options the order of arrangement does not agree with the variation of property indicated against it ? [2016]
 (a) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)
 (b) $B < C < N < O$ (increasing first ionisation enthalpy)
 (c) $I < Br < Cl < F$ (increasing electron gain enthalpy)
 (d) $Li < Na < K < Rb$ (increasing metallic radius)
19. The element Z = 114 has been discovered recently. It will belong to which of the following family/group and electronic configuration ? [2017]
 (a) Carbon family, $[Rn] 5f^{14} 6d^{10} 7s^2 7p^2$
 (b) Oxygen family, $[Rn] 5f^{14} 6d^{10} 7s^2 7p^4$
 (c) Nitrogen family, $[Rn] 5f^{14} 6d^{10} 7s^2 7p^6$
 (d) Halogen family, $[Rn] 5f^{14} 6d^{10} 7s^2 7p^5$

Hints & Solutions

EXERCISE - 1

- (c) Group IA and III A contain mostly metals. Group VIII contains transition elements which are metals. Group VII A contains mostly non-metals (F, Cl, Br).
- (d) Elements having 1, 2 or 3 electrons in its last shell act as metals.
 $32 = [\text{Ar}] 3d^{10} 4s^2 p^2$
 $34 = [\text{Ar}] 3d^{10} 4s^2 p^4$
 $36 = [\text{Ar}] 3d^{10} 4s^2 p^6$
 $38 = [\text{Ar}] 3d^{10}, 4s^2 p^6, 5s^2$
- (d) Basicity of oxides decreases in a period from left to right. Na_2O is basic oxide, CO_2 , SiO_2 and SO_2 are acidic oxides.
 Alternatively, oxides of metals (e.g., Na_2O) are basic, while oxides of non-metals (SO_2 , SiO_2 and CO_2) are acidic.
- (d) Oxides of non metals are acidic in nature. P is a non-metal and its oxides are acidic. Rest of the oxides are basic because they are oxides of metals.
- (c) Allotropy is characteristic property of group 14 elements. All elements of group 14, except Pb, show allotropy.
 Sn has three allotropic forms grey tin, white tin and rhombic.
- (a) Atomic number of the given element is 15 and it belongs to 5th group. Therefore atomic number of the element below the above element = $15 + 18 = 33$.
- (a) The electronic configuration clearly suggest that it is a d-block element (having configuration $(n-1)d^{1-10} ns^{0-2}$) which starts from III B and goes till II B. Hence with d^3 configuration it would be classified in the fifth group.
- (d) Na_2O (basic), SO_2 and B_2O_3 (acidic) and ZnO is amphoteric.
- (a) The screening effect follows the order $s > p > d > f$.
- (d) The electrons are not filled in d-subshell monotonically with increase in atomic number among transition elements.
- (c)
- (b)
- (c) $ns^2 p^1$ is the electronic configuration of III A period. Al_2O_3 is amphoteric oxide.
- (b)
- (c) I. E. increases across a period and decreases down in a group. So, element with electronic configuration $[\text{Ne}] 3s^2 3p^3$ will have the highest I.E. among the given choices.

	I.E. increases →			
	grp III A	grp IV A	grp V A	
period 3	$[\text{Ne}]3s^2 3p^1$	$[\text{Ne}]3s^2 3p^2$	$[\text{Ne}]3s^2 3p^3$	I.E. decreases ↓
period 4			$[\text{Ar}]3d^1 4s^2 4p^3$	

- (b) The tendency of a cation to distort the electron cloud of an anion when it is approaching the anion, is called polarisation power of cation. As polarisation power of cation increases, the covalent character increases. According to Fajan's rule high charge and small size of cation will favour covalency. So, polarisation power of a cation increases with charge of the cation.
- (d) Cd is not a transition metal among the given options because it do not have incomplete d-subshell either in its atomic state $[\text{Cd} = 5d^{10} 4s^2]$ or in its common oxidation state ($\text{Cd}^{2+} = 5d^{10} 4s^0$).
- (c) F_2 has highest electronegativity, so it is chemically most active non metal.
- (a) Metallic character decreases down group and increases along a period.
- (b)
- (c) Basicity of oxides decreases in a period and increases in a group.
 $\therefore \text{SnO}_2, \text{Al}_2\text{O}_3$ and ZnO are amphoteric oxides.
- (d)
- (a) A cation is always smaller in size as compared to corresponding neutral atom. Greater the magnitude of charge, smaller will be size of ion. Following is the correct order of decreasing size $\text{Al}^{3+} < \text{Al}^{2+} < \text{Al}^+ < \text{Al}$.
 $\therefore \text{Al}$ has largest size.
- (c) While moving down in a group, effective nuclear attraction decreases due to addition of new orbits. As a result ionisation potential decreases. Hence, the correct order is $\text{Li} > \text{K} > \text{Cs}$.
- (c) Ionisation potential increases while moving in a period.

Group	V	VI	VII	VIII
Element	N	O	F	Ne

Oxygen (group 6) has low ionisation potential than N (group 5) because of stable configuration of nitrogen (half filled p -orbital)
- (c) They are isoelectronic species.

	N^{3-}	O^{2-}	Na^+	F^-
No. of electrons	10	10	10	10
No. of protons	7	8	11	9

$\therefore$ Attractive forces are highest in Na^+ .
 $\therefore \text{Na}^+$ is smallest in size.

27. (d) According to the general trend of I.E. in a period, it is expected that oxygen atom has higher I.E. than nitrogen atom but nitrogen atom has more stable half filled p -orbitals due to which it has higher I.E. than oxygen atom.
28. (b) The acidic character of non metal oxides increases across a period from left to right and decreases down a group. So, acidic character will follow the order:
oxide of nitrogen > oxides of sulfur > oxides of carbon.
Among oxides of carbon acidic character increases with the oxidation number of carbon. So, $^{+4}\text{CO}_2$ is more acidic than CO . Hence the sequence of acidic character is $\text{N}_2\text{O}_5 > \text{SO}_2 > \text{CO}_2 > \text{CO}$
29. (d) Arsenic is the only metalloid among the given options. Its small amounts are even very harmful for humans.
30. (a)

Species	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}
Protons	11	12	13	14
Electrons	10	10	10	10

Size of isoelectronic cations decreases with increase in magnitude of nuclear charge
 $\therefore$ Order of decreasing size is $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Si}^{4+}$
31. (c) Ionisation potential is amount of energy required to take outermost loosely bonded electron from isolated gaseous atom. Its value decreases in a group and increases along a period. Thus, here Be has highest ionisation potential.
32. (a) $\text{Be} - 1s^2 2s^2$; $\text{B} - 1s^2 2s^2 2p^1$; $\text{C} - 1s^2 2s^2 2p^2$; $\text{N} - 1s^2 2s^2 2p^3$; $\text{O} - 1s^2 2s^2 2p^4$. IP increases along the period. But IP of $\text{Be} > \text{B}$. Further IP of $\text{O} < \text{N}$ because atoms with fully or partly filled orbitals are most stable and hence have high ionisation energy.
33. (a) O^{2-} and F^- are isoelectronic. Hence have same number of shells, therefore greater the nuclear charge smaller will be the size i.e., $\text{O}^{2-} > \text{F}^-$
 further Li^+ and B^{3+} are isoelectronic. therefore
 $\text{Li}^+ > \text{B}^{3+}$
 Hence the correct order of atomic size is.
 $\text{O}^{2-} > \text{F}^- > \text{Li}^+ > \text{B}^{3+}$
34. (d) The given electronic configuration represents that it has 3 valency electrons or it can show a maximum oxidation state of +3 and element with intermediate oxidation states form amphoteric oxides.
35. (a) Ionisation potential of nitrogen is more than that of oxygen. This is because nitrogen has more stable half-filled p -orbitals. ($\text{N} = 1s^2, 2s^2, 2p^3$, $\text{O} = 1s^2, 2s^2, 2p^4$)
36. (b)
37. (b) Due to presence of most penetrating s -electron, hydrogen (1s) shows maximum IP out of list.
38. (b)
39. (d) P^{5+} has more effective nuclear charge and smaller size than P^{3+} .
40. (a) Energy is supplied in order to remove electron from atoms. So energy of atom increases when electron is removed from atom.
41. (b) Ionic compounds have high melting point. Greater the ionic character, more is melting point.
 HCl has least ionic character because of maximum electronegativity difference between the two constituent elements, H and Cl among CsF , HCl , HF and LiF
 $\therefore \text{HCl}$ has minimum melting point.
42. (c) The ionization energy increases with decrease in size. Further the element having stable configuration has higher ionisation energy than expected. Hence the ionization energy of nitrogen ($Z = 7$) is more than oxygen ($Z = 8$) and carbon ($Z = 6$) because it has half-filled p -orbitals.
 $^6\text{C} = 1s^2 2s^2 2p^2$; $^7\text{N} = 1s^2 2s^2 2p^3$; $^8\text{O} = 1s^2 2s^2 2p^4$
 Hence the correct order should be $\text{C} < \text{N} > \text{O}$
43. (c)
44. (c)
- (i) The anion is always larger in size as compared to corresponding neutral atom.
- (ii) Greater the magnitude of negative charge, larger will be the size.
 Therefore, the correct order of size is $\text{O}^{2-} > \text{O}^- > \text{O}$
45. (d)
46. (c) $(n-1)s^2 p^6 (n-1)d^{1-10} ns^{0-2}$ represents the correct electronic configuration of transition elements among the given choices.
47. (b) As atomic number, number 19 falls within group I of modern periodic table so it is an alkali metal with +1 oxidation state.
48. (b) Due to high stability of half-filled orbitals.
49. (a) In Cu it has completely filled d -orbital so highest energy is absorbed when it converts to Cu^+ ion.
50. (a) Since, stable half filled configuration.
51. (b) $\text{K}^+ \rightarrow \text{K}^2 + e^-$. Since e^- is to be removed from stable configuration.
52. (c)
53. (a) 1st I.P. increases from left to right in a period.
54. (b)
55. (a)
56. (a) We know that atomic no. of fluorine (F), chlorine (Cl), Bromine (Br) and Iodine (I) are 9, 17, 35 and 53 respectively. Therefore, correct order of reactivity of halogens is $\text{F} > \text{Cl} > \text{Br} > \text{I}$
57. (b) Electropositive nature increases down the group and decreases across the period.
58. (b) Polonium is only true metal in group 16. It has two crystalline forms α -form which is cubic and β -form which is rhombohedral.

59. (a) Electron affinity is said to be positive when an atom has spontaneous tendency to accept an electron. When O changes to O^- , energy is released. So, this change has positive electron affinity while all other given changes required to be forced i.e., these require energy to occur.
60. (a) Electron affinity is energy released when electron is added to isolated gaseous atom. Its value decreases down the group. So electron affinity of F should be highest among halogens but due to its smaller size electron affinity of Cl is more than F.
 $\therefore$ Cl has highest electron affinity.
61. (a) Pauling scale of electronegativity was helpful in predicting
 (i) Nature of bond between two atoms
 (ii) Stability of bond
 by calculating the difference in electronegativities polarity of bond can be calculated.
62. (c) 63. (b) 64. (b)
65. (b) Electronegativity decreases down the group and increases along a period. Cl lies in 17th group hence more electronegative than P and Si; further it lies above Br, hence more electronegative than Br.
66. (d) Fluorine, chlorine, bromine and iodine are placed in the same group 17 because they have 7 electrons in the outermost shell.
67. (a)
68. (a) Zero, because of the stable electronic configuration the noble gases do not show any force of attraction towards the incoming electron.
69. (a) Halogens have the highest e^- affinity.
70. (b) An atom with high electronegativity has high IP.
71. (c) Chlorine and sulphur are in period three. Potassium and calcium are in period four. As K has radius more than calcium, K^+ ion will have largest size.
72. (a) F, because of its smallest size.
73. (c) Halogens are most electronegative.
74. (b) On passing from left to right in a period acidic character of the normal oxides of the elements increases with increase in electronegativity.
75. (d) The energy involved is ionisation energy (I.E.). Further the 3rd ionisation energy will be greater than the 2nd and 1st.
6. (a) In case of Ga there are 10d electrons in the penultimate energy shell which shield the nuclear charge less effectively, the outer electron is held firmly by nucleus. As a result, the ionisation energy remains nearly the same as that of aluminium inspite of the fact that atomic size increases.
7. (d) Abnormally high difference between 2nd and 3rd ionization energy means that the element has two valence electrons, i.e., configuration (d)
8. (b) Along the period, I.P. generally increases but not regularly. Be and B are exceptions. First I.P. increases in moving from left to right in a period, but I.P. of B is lower than Be.
9. (a) Gaining of an electron by a gaseous atom is usually an exothermic process. Gain of second electron by negatively charged species feels a strong repulsion and the energy of the system increases.
10. (a)
11. (d) As the size increases the basic nature of oxides changes to acidic nature i.e., acidic nature increases.
- $$SO_2 > P_2O_3 > SiO_2 > Al_2O_3$$
- Acidic Weak Amphoteric
 acidic
- SO_2 and P_2O_3 are acidic as their corresponding acids H_2SO_3 and H_3PO_3 are strong acids.
12. (a) O^- ion exerts a force of repulsion on the incoming electron. The energy is required to overcome it.
13. (c) In a period the value of ionisation potential increases from left to right with breaks where the atoms have some what stable configuration. In this case N has half filled stable orbitals. Hence has highest ionisation energy. Thus the correct order is $B < C < O < N$ and not as given in option (c)
14. (b) 3rd ionization involves removal of electron from inert gas configuration $1s^2 2s^2 2p^6$, hence there would be a large jump between 2nd and 3rd ionization energies.
15. (a) IE_1 is always less than IE_2 .
16. (b) IE_2 of Mg is lower than that of Na because in case of Mg^+ , 3s-electron has to be removed whereas in case of Na^+ , an electron is removed from the stable inert gas configuration which is difficult.
17. (c) 18. (c)
19. (c) Amongst the ions carrying same charge, the smallest one will have the greatest hydration energy (most negative).
20. (d)
21. (d) Tl shows the inert pair effect. Hence Tl^+ oxidation state is more stable than Tl^{3+} .
22. (a) 23. (a) 24. (b) 25. (d)
26. (a) For isoelectronic species, size of anion increases as negative charge increases whereas size of cation decreases with increase in positive charge. Further ionic radii of anions is more than that of cations. Thus the correct order is $Ca^{++} < K^+ < Ar < Cl^- < S^{--}$
27. (a) Proton affinity decreases in moving across the period from left to right due to increase in charge, within a group the proton affinities decreases from top to bottom. Nitrogen family > Oxygen family > Halogens

EXERCISE - 2

1. (d) 2. (a)
3. (a) Acidic character of oxide $\propto$ Non-metallic nature of element.
 Non-metallic character increases along the period. Hence order of acidic character is
 $Cl_2O_7 > SO_2 > P_4O_{10}$.
4. (c) $X_{(g)} + e^- \rightarrow X^-_{(g)} + x \text{ kJ} \dots\dots(i)$
 $X^-_{(g)} \rightarrow X_{(g)} - x \text{ kJ} \dots\dots(ii)$
5. (d) Zero group is also called as buffer group because it is placed between highly electropositive metals (group 1) and highly electronegative non-metals (group 17).

28. (d) The stability of +1 oxidation state increases from aluminium to thallium i.e. $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$
29. (d) The smaller the atomic size, larger is the value of ionisation potential. Further the atoms having half filled or fully filled orbitals are comparatively more stable, hence more energy is required to remove the electron from such atoms.
30. (c) ${}_{12}^{24}\text{Mg}$ ${}_{15}^{31}\text{P}$ ${}_{17}^{35}\text{Cl}$ ${}_{20}^{40}\text{Ca}$
 160p 110 99 $197(\text{pm})$
 $\text{Cl} < \text{P} < \text{Mg} < \text{Ca}$
31. (a) IE_1 of Na = – Electron gain enthalpy of $\text{Na}^+ = -5.1\text{ eV}$.
32. (b) The alkali metals are highly reactive because their first ionisation potential is very low and hence they have great tendency to lose electron to form unipositive ion.
 On moving down group- I from Li to Cs ionisation enthalpy decreases hence the reactivity increases. The halogens are most reactive elements due to their low bond dissociation energy, high electron affinity and high enthalpy of hydration of halide ion. However their reactivity decreases with increase in atomic number
33. (b) In hydrides of 15th group elements, basic character decreases on descending the group i.e.
 $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$.
34. (d) All the given species contains 10 e^- each i.e. isoelectronic.
 For isoelectronic species anion having high negative charge is largest in size and the cation having high positive charge is smallest.
35. (b) As we move down in a group electron gain enthalpy becomes less negative because the size of the atom increases and the distance of added electron from the nucleus increases. Negative electron gain enthalpy of F is less than Cl. This is due to the fact that when an electron is added to F, the added electron goes to the smaller $n = 2$ energy level and experiences significant repulsion from the other electrons present in this level. In Cl, the electron goes to the larger $n = 3$ energy level and consequently occupies a larger region of space leading to much less electron–electron repulsion. So the correct order is $\text{Cl} > \text{F} > \text{Br} > \text{I}$.
36. (c) On moving along a period from left to right I.E. increases and on moving down a group I.E. decreases. hence correct order is : $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$
37. (c) Its valency is 2. So it will form MO type compound.
38. (b) On moving along the period, ionization enthalpy increases.
 In second period, the order of ionization enthalpy should be as follows : $\text{F} > \text{O} > \text{N}$
 But N has half-filled structure, therefore, it is more stable than O. That's why its ionization enthalpy is higher than O. Thus, the correct order of IE is $\text{F} > \text{N} > \text{O}$.
39. (c) N, O and F (p-block elements) are highly electronegative non metals and will have the strongest tendency to form anions by gaining electrons from metal atoms.
40. (a) Non metals form oxides with oxygen and thus reduce oxides of metals behaving as reducing agents.
41. (b)
42. (b) $\text{O} < \text{S} < \text{F} < \text{Cl}$
 Electron gain enthalpy – 141, –200, –333, –349 kJ mol^{-1}
43. (b) Correct order of ionic size is $\text{Sn} > \text{Ce} > \text{Yb} > \text{Lu}$.
44. (c)
45. (d) Halogens have very high values of electron gain enthalpies.
46. (a) Electronegativity values of given elements are as follows:
 $\text{Be} - 1.5 \text{ (I)}$ $\text{Mg} - 1.2 \text{ (IV)}$
 $\text{O} - 3.5 \text{ (II)}$ $\text{N} - 3.0 \text{ (III)}$
 i.e. $\text{II} > \text{III} > \text{I} > \text{IV}$
47. (d) Noble gases have positive values of electron gain enthalpy because the anion is higher in energy than the isolated atom and electron.
48. (c) The tendency of an atom in a compound to attract a pair of bonded electrons towards itself is known as electronegativity of the atom.
49. (c)
50. (b) The correct order of first ionisation energy is represented by
 $\text{Be} > \text{Mg} > \text{Ca}$
 Since on moving down a group atomic size increases due to addition of one extra shell, hence I.E decreases.

EXERCISE - 3

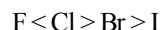
Exemplar Questions

1. (b) In case of isoelectronic species

$$\text{ionic radii} \propto \frac{1}{\text{atomic number}}$$
 $\therefore$ The correct order of increasing ionic radii will be :
 Ionic radii $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-}$
 Atomic number (12) (11) (9) (8)
2. (d) Elements with atomic number, $Z = 90$ to 103 are called actinoids. Terbium belongs to lanthanoids.
3. (a) For a given shell, screening effect decreases in the order : $s > p > d > f$.
4. (a) Electronic configuration for the given elements will be :
 $\text{Na} = [\text{Ne}]3s^1$, $\text{Mg} = [\text{Ne}]3s^2$, $\text{Al} = [\text{Ne}]3s^23p^1$,
 $\text{Si} = [\text{Ne}]3s^23p^2$
 Ionisation enthalpy increases along a period but I.E of Mg is higher than Al because of completely filled $3s$ orbital in Mg.
5. (c) The electronic configuration of Gd ($Z = 64$) is
 $[\text{Xe}]4f^75d^16s^2$.
6. (c) In case of transition element, the order of filling of electrons in various orbital is $3p < 4s < 3d$. Thus, $3d$ orbital is filled only when $4s$ orbital gets completely filled.

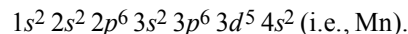
7. (c) As we move in a group from Cl to I, the electron gain enthalpy (i.e., energy released in electron gain) become less and less negative due to corresponding increase in the atomic size.

However, the electron gain enthalpy of F is less negative than that of Cl due to its small size. Thus, the negative electron gain enthalpy among halogens follows the order :



8. (c) As each period starts with the filling of electrons in a new principal quantum number, so, the period number in the long form of the periodic table refers to the maximum principal quantum number (n) of any element in the period.
9. (c) The elements in which electrons are filled in $4f$ -orbital are called lanthanoids. Lanthanoids consist of elements from $Z = 58$ (cerium) to 71 (lutetium).
10. (d) Generally, cations are smaller in size while anions are bigger in size than the neutral atom.
11. (c) O^{2-} has noble gas configuration and isoelectronic with neon but its formation is unfavourable due to strong electronic repulsion between the negatively charged O^- ion and the electron being added.
Thus, the electron repulsion will be more than the stability gained by achieving noble gas configuration.
12. (i)(c) The element with atomic number 57 belongs to d -block element as the last electron enters into the $5d$ -orbital against the aufbau principle. This anomalous behaviour can be explained on the basis of greater stability of the xenon (inert gas) core.
After barium ($Z = 56$), the addition of the next electron should occur in $4f$ -orbital in accordance with aufbau principle. This will however, tend to destabilize the xenon core ($Z = 54$), $[Kr] (4d^{10} 4f^0 5s^2 5p^6 5d^0)$ since the $4f$ -orbitals lie inside the core. Therefore, the 57th electron prefers to enter $5d$ -orbital which lies outside the xenon core and whose energy is only slightly higher than that of $4f$ -orbital. Thus, the outer electronic configuration of La ($Z = 57$) is $5d^1 6s^2$ rather than the expected $4f^1 6s^2$.
- (ii)(c) Each period starts with the filling of electrons in a new principal energy shell. Therefore, 6th period starts with the filling of $6s$ -orbital and ends when $6p$ -orbitals are completely filled.
Thus, the outermost electronic configuration of the last element of the p -block in the 6th period is represented by $6s^2 4f^{14} 5d^{10} 6p^6$ or $4f^{14} 5d^{10} 6s^2 6p^6$.
- (iii)(c) The long form of the periodic table contain element with atomic number 1 to 118.
- (iv)(a) The fifth period begins with Rb ($Z = 37$) and ends at Xe ($Z = 54$). Thus, the element with $Z = 43$ lies in the 5th period. Since, the 4th period has 18 elements, thus, the atomic number of the element which lies immediately above the element with atomic number 43 will be $43 - 18 = 25$.

The electronic configuration of the element with $Z = 25$ is



- (v) (b) The elements with atomic numbers 35 ($36 - 1$), 53 ($54 - 1$) and 85 ($86 - 1$), lie in a group before noble gases, i.e., belongs to halogens (group 17).
13. (a) Electronic configuration of given elements indicate that A is a noble gas (i.e., Ne), B is oxygen, C is sodium metal and D is fluorine.
- (i) Noble gases have no tendency to gain electrons since all their orbitals are completely filled.
 $\therefore$ element A will have the least electron gain enthalpy.
- (ii) Element D has one electron less and element B has two electrons less than the corresponding noble gas configuration, hence, element D will have the highest electron gain enthalpy in comparison to element B.
- (iii) Since, element C has one electron in the s -orbital and need one more electron to complete its configuration, therefore, electron gain enthalpy of C is less than that of element B. So, we can conclude that the electron gain enthalpies of the four elements increases in the order : $A < C < B < D$.

NEET/AIPMT (2013-2017) Questions

14. (a) As the nuclear charge increases, the force of attraction between the nucleus and the incoming electron increases and hence the electron gain enthalpy becomes more negative, hence the correct order is
 $Ca < Al < C < O < F$
15. (N) All answers are incorrect.
16. (b) In isoelectronic species the radius decrease with increase in nuclear charge hence increasing order of radius is
 $Ca^{+2} < K^+ < Ar$
17. (a) Incoming electrons occupy the smaller $n = 2$ shell, also negative charge on oxygen (O^-) is another factor due to which incoming electron feel repulsion.
Hence electron repulsion outweigh the stability gained by achieving noble gas configuration.
18. (b&c) The correct order is $B < C < O < N$
Generally Ionisation energy increases across a period. But here first I.E. of O is less than the first I.E. of N. This is due to the half-filled $2p$ orbital in N ($1s^2, 2s^2, 2p^3$) which is more stable than the $2p$ orbital in O ($1s^2, 2s^2, 2p^4$)
- (c) The correct order of electron affinity is
 $I < Br < F < Cl$
Halogens have high electron affinities which decreases on moving down the group. However, fluorine has lower value than chlorine which is due to its small size and repulsion between the electron added and electrons already present.
19. (a) $Z = 114$ belong to Group 14, carbon family
Electronic configuration = $[Rn]5f^{14}6d^{10}7s^27p^2$

Chapter

4

Chemical Bonding and Molecular Structure

The attraction force which holds various constituents (atoms, ions, etc) together in different chemical species is called a chemical bond.

KOSSEL - LEWIS APPROACH TO CHEMICAL BONDING

- Lewis postulated that atoms achieve stable octet when they are linked by chemical bonds.
- The outer shell electrons are called valence electrons and it is these electrons which take part in chemical bonding.
- The valence electrons are represented by putting dots around the symbol of the element. These are called Lewis symbols. For ex: $\text{Li}\cdot$, $\cdot\ddot{\text{Be}}\cdot$, $\cdot\ddot{\text{B}}\cdot$, etc.
- Kossel provided the basis for ion formation by electron transfer and formation of ionic crystalline compounds.

IONIC AND COVALENT BOND

Ionic or Electrovalent Bond

The bond formed as a result of electrostatic attraction between positive and negative ions is called ionic bond. Ionic bonds are formed readily between elements with low IE and elements with high -ve value of electron gain enthalpy.

Factors favouring the formation of ionic bond :

- Ionisation energy (IE)
- Electron affinity
- Lattice energy

Note : A qualitative measure of the stability of an ionic compound is provided by its lattice enthalpy which is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions

Covalent Bond and Lewis Structures

The bond formed as a result of sharing of electrons between elements is called covalent bond. When electrons shared by bonded atoms are contributed entirely by one of the bonded atoms bond formed is known as a coordinate bond. Lewis dot structures provide a picture of bonding in molecules and ions in terms of shared pair of electrons and the octet rule.

Covalency : It is defined as the number of electrons contributed by an atom of the element for sharing with other atoms so as to achieve noble gas configuration.

FORMAL CHARGE AND RESONANCE

Formal Charge

It is the difference between the number of valence electrons in an isolated atom and no of electrons assigned to that atom in Lewis structure.

$$\begin{aligned} \text{Formal change (F.C)} \\ \text{on an atom in} \\ \text{Lewis structure} &= \left(\begin{array}{l} \text{Total no. of valence} \\ \text{electrons in the free} \\ \text{atom} \end{array} \right) - \left[\begin{array}{l} \text{Total no. of} \\ \text{non - bonding} \\ \text{electrons (lone pairs)} \end{array} \right] - \frac{1}{2} \left[\begin{array}{l} \text{Total no. of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right] \end{aligned}$$

Note : Among the valence electrons, those pair of electrons which are involved in bonding are called bond pair of electrons while those which are not involved in bonding are called lone pair of electrons.

Resonance

It has been found that the observed properties of certain molecules cannot be satisfactorily explained by one structure. The molecule is then supposed to have many structures, each of which can explain most of the properties but not all. This phenomenon is called resonance.

BOND PARAMETERS

- Bond length :** It is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. The covalent radius is half of the distance from the centre of nucleus of one atom to the centre of nucleus of the other atom provided bonded atoms will be of same element in a molecule.

The van der Waal's radius represents the overall size of the atom which includes its valence shell in a non-bonded situation.

Van der Waal's radius > Covalent radius

- Bond angle :** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule / complex ion.
- Bond Enthalpy :** It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. Its unit is kJ mol^{-1} . Larger the bond dissociation enthalpy, stronger is the bond.

- (iv) **Bond order** : It is given by the number of bonds between two atoms in a molecule. Isoelectronic molecules and ions have identical bond order. For ex: F_2 and O_2^{2-} have B.O. = 1.

In general,

$$\text{Bond order} \propto \text{Bond Enthalpy} \propto \frac{1}{\text{Bond length}}$$

POLARITY OF BONDS AND DIPOLE MOMENT

When covalent bond is formed between two similar atoms like H_2 , O_2 , Cl_2 , N_2 etc, the shared pair of electrons is equally attracted by two atoms. As a result, electrons pair is exactly situated between the two atoms. Such a bond is called non-polar covalent bond.

In heteronuclear molecules like HF, the shared pair of electrons gets shifted towards the more electronegative element (here F), resulting in polarity in bond. Such a bond is called polar covalent bond. This polarisation of the bond gives rise to a dipole moment given by:

Dipole moment (μ) = charge (q) $\times$ distance of separation (d). It is represented as $\overrightarrow{H-F}$. Dipole moment is a vector quantity

Covalent Character in Ionic Compounds

Just as covalent bonds have partial ionic character, ionic bonds have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajan in terms of following rules:

- Smaller the cation and larger the anion, greater is the covalent character of the ionic bond.
- Greater the charge on cation, greater is the covalent character of the ionic bond.
- For cations of same size and charge, the one with electronic configuration $ns^2np^6nd^{10}$ is more polarising than the one with noble gas configuration ns^2np^6 .

The covalent character of an ionic bond is explained on the basis of polarisation. The cation polarises the anion, pulling the electronic charge towards itself and thereby increasing electronic charge between the two. This is what happens in a covalent bond, i.e. build up of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of polarisation of the anion determine the percent covalent character of the ionic bond.

Applications of Dipole Moment

- (i) **In determining the polarity of bonds :**

$$\text{As } \mu = q \times d,$$

- (ii) **In the calculation of ionic character :**

i.e., % ionic character

$$= \frac{\text{Observed dipole moment}}{\text{Dipole moment considering 100\% ionic character}} \times 100$$

- (iii) **Determination of shape or symmetry of molecules:**

Note : In A—B molecule

$$\text{Ionic nature} \propto X_A - X_B$$

% Ionic character = 0 when $X_A = X_B$ (100% covalent bond)

% Ionic character = 0 – 15% Non polar covalent bond

% Ionic character = 15 – 50% Polar covalent bond

% Ionic character = > 50% Ionic bond

THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The main postulates of this theory are:

- The geometry of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom
- Pairs of electrons in valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair
- Where two or more resonance structures can represent a molecule, VSEPR model is applicable to any such structure. The decreasing order of repulsive interaction of electron pairs is

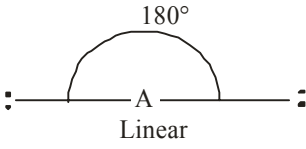
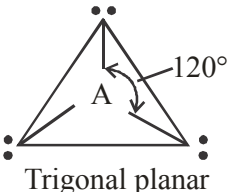
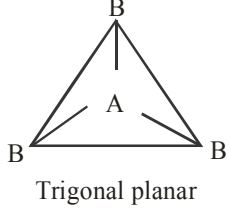
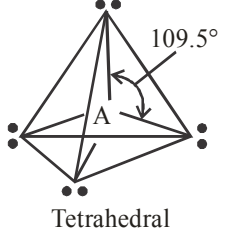
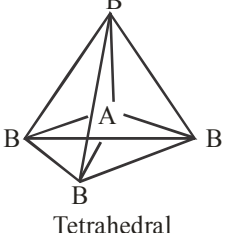
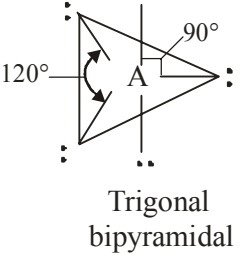
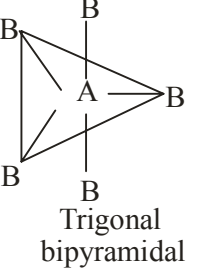
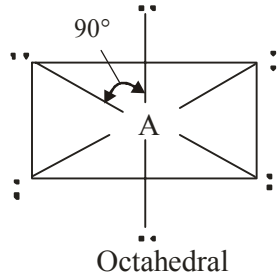
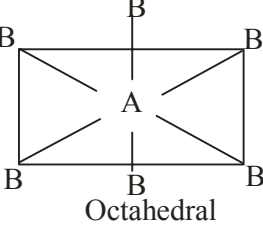
$$lp - lp > lp - bp > bp - bp$$

Where lp $\rightarrow$ lone pair and bp $\rightarrow$ bond pair

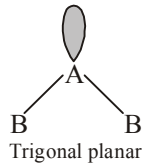
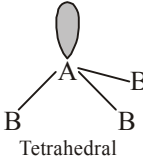
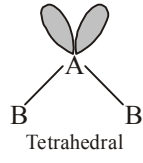
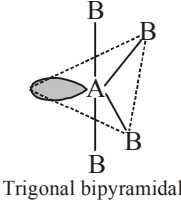
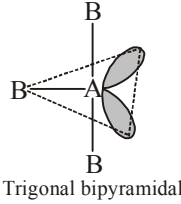
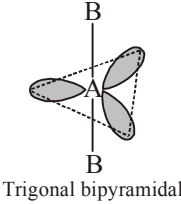
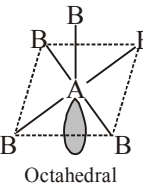
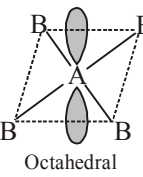
For prediction of geometrical shape of molecules, we divided molecules in two categories :

- molecules in which central atom has no lone pair(s)
- molecules in which central atom has one or more lone pair(s).

Geometry of molecules when central atom has no lone pair of electrons.

No. of electron pairs	Arrangement of electron pairs	Molecular Geometry	Examples
2		$B - A - B$ Linear	BeF_2 , $HgCl_2$
3			BF_3 , $AlCl_3$
4			CH_4 , SiF_4
5			PCl_5 , AsF_5
6			SF_6

Geometry of molecules when central atom has one or more lone pair of electrons

Molecule type	No. of bonding pairs	No. of lone pairs	Total electron pairs	Arrangement of electron pairs	Shape (geometry)	Example
AB_2L	2	1	3	 Trigonal planar	Bent or V shaped	$SO_2, O_3, SnCl_2$
AB_3L	3	1	4	 Tetrahedral	Pyramidal	NH_3
AB_2L_2	2	2	4	 Tetrahedral	V shaped	H_2O
AB_4L	4	1	5	 Trigonal bipyramidal	See saw	SF_4
AB_3L_2	3	2	5	 Trigonal bipyramidal	T shaped	ClF_3
AB_2L_3	2	3	5	 Trigonal bipyramidal	Linear	XeF_2
AB_5L	5	1	6	 Octahedral	Square pyramidal	BrF_5
AB_4L_2	4	2	6	 Octahedral	Square planar	XeF_4

VALENCE BOND THEORY (VBT)

- (i) This theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridisation of atomic orbitals and the principles of variation and superposition.
- (ii) According to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of e^{-1} s present in the valence shell having opposite spins greater is the overlap, stronger is the bond formed between the atoms.
- (iii) Co-axial overlapping $\rightarrow$ extent of overlapping more $\rightarrow$ high bond strength
Collateral overlapping $\rightarrow$ extent of overlapping less $\rightarrow$ low bond strength
In Co-axial overlapping, extent of overlapping is $p-p < s-p < s-s$
- (iv) VBT explains the formation and directional properties of bonds in polyatomic molecules like CH_4 , NH_3 , etc. in terms of overlap and hybridisation of atomic orbitals.
- (v) Two types of bonds are formed on account of overlapping.
(a) Sigma (σ) bond (b) Pi (π) bond

Sigma bond (σ)	Pi bond (π)
(i) It is formed by end to end (head on) overlap of bonding orbitals along internuclear axis. (ii) This bond is formed by overlapping of s with s, s with p (along axis) and p with p orbitals. (iii) Stronger and less reactive. (iv) Can be independently exist (v) The groups or atoms can undergo bond rotation about single sigma (σ) bonds	(i) It is formed by sideways overlapping, perpendicular to internuclear axis. (ii) This bond is formed by overlap of p-p orbitals above and below the plane of participating atoms. (iii) Less strong and more reactive. (iv) Always exist along with a σ bond (v) Due to resistance to rotation around the π bond the groups attached to it are not free to rotate.

HYBRIDISATION

According to Pauling, the atomic orbitals combine to form a new set of equivalent orbitals known as hybrid orbitals. It is these hybrid orbitals which are used in bond formation. The phenomenon is known as hybridisation.

Features of Hybridisation

- (i) The number of hybrid orbitals is equal to the number of atomic orbitals that get hybridised.
- (ii) The hybridised orbitals are always equal in energy and shape.
- (iii) The hybrid orbitals are more effective in forming stable bonds than pure atomic orbitals.
- (iv) The type of hybridisation indicates the geometry of molecules.

Conditions of Hybridisation

- (i) The orbitals present in valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.

- (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Types of Hybridisation

Depending upon the type and number of orbitals involved in intermixing, the hybridization can be of various types namely sp , sp^2 , sp^3 , sp^3d , dsp^2 , sp^3d^2 , sp^3d^3 .

Method for Finding the Type of Hybridisation

The structure of any molecule can be predicted on the basis of hybridization which in turn can be known by the following general formulation :

$$H = \frac{1}{2}(V + M - C + A)$$

where H = Number of orbitals involved in hybridization viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridization will be sp , sp^2 , sp^3 , sp^3d , sp^3d^2 , sp^3d^3 respectively.

V = Number of electrons in valence shell of the central atom,

M = Number of monovalent atoms,

C = Charge on cation,

A = Charge on anion.

Shape of molecule ion	Hybridisation Type	Atomic orbitals	Examples
Linear	sp	$s + p$	BeCl_2 , C_2H_2 , CO_2 , HgCl_2 ,
Trigonal planar	sp^2	$s + p(2)$	SnCl_2 , CO_3^{2-}
Tetrahedral	sp^3	$s + p(3)$	CH_4 , H_2O , NH_3
Square planar	dsp^2	$d + s + p(2)$	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PtCl}_2]^{2-}$
Trigonal bipyramidal	sp^3d	$s + p(3) + d$	PF_5 , PCl_5
Square pyramidal	sp^3d^2	$s + p(3) + d(2)$	BrF_5
Octahedral	sp^3d^2 , d^2sp^3	$s + p(3) + d(2)$, $d(2) + s + p(3)$	SF_6 , $[\text{CrF}_6]^{3-}$
Pentagonal bipyramidal	sp^3d^3	$s + p(3) + d(3)$	IF_7

MOLECULAR ORBITAL THEORY

Important Features of MOT

- The electrons in a molecule are present in various molecular orbitals (MO's) as the electrons of atoms are present in various atomic orbitals (AO's).
- The atomic orbitals of comparable energies and proper symmetry combine to form MO's.
- An electron in a MO is influenced by two or more nuclei depending upon no. of atoms in molecule. Thus, a MO is polycentric.
- The no. of MO's formed is equal to the number of combining AO's. When two AO's combine, two MO's are formed. One is bonding MO (BMO) and the other is antibonding MO (ABMO).
- BMO has lower energy and higher stability than corresponding ABMO.
- The MO's are filled in accordance with Aufbau's principle, obeying the Pauli's exclusion principle and Hund's rule.

Conditions for Atomic Orbitals to Form M.O.

- The combining AO's must have same or nearly same energy.
- The combining AO's must have same symmetry about the molecular axis.
- The combining AO's must overlap to the maximum extent.

Types of MO

σ -MO's of diatomic molecules are designated as σ (sigma), π (pi), δ (delta) etc. σ -MO's are symmetrical around bond-axis while π -MO's are not symmetrical.

Filling of Electrons in MO's

- For O_2 and F_2 , the increasing order of energies of various MO's is :
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$
- For Li_2 , Be_2 , B_2 , C_2 , N_2 the increasing order of energies of various MO's is :
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$
 The main difference between the two types of sequences in energy level is that for molecules O_2 , F_2 , the $\sigma 2p_z$ M.O. is lower in energy than $\pi 2p_x$ and $\pi 2p_y$.

Electronic Configuration and Molecular Behaviour

The distribution of electrons among various MO's is called electronic configuration of the molecule. It gives important information about the molecule as discussed below:

(i) Stability of molecules :

If $N_b > N_a$, molecule is stable

If $N_b < N_a$, molecule is unstable

Where $N_b \rightarrow$ No. of electrons in BMO

Where $N_a \rightarrow$ No. of electrons in ABMO

(ii) Bond order (B. O.)

$$B. O. = \frac{1}{2} (N_b - N_a)$$

$\therefore$ +ve B.O. (i.e. $N_b > N_a$) means stable molecule whereas -ve B.O. (i.e. $N_a > N_b$) means unstable molecule.

(iii) **Nature of bond :** B. O. values of 1, 2 or 3 correspond to single, double and triple bonds. According to MOT even a fractional bond order is possible.

(iv) **Bond length (BL) :** $BL \propto 1/B.O.$

Bonding in Few Molecules/Ions

(i) **He₂ :** EC is $\sigma 1s^2 \sigma^* 1s^2$.

$$\therefore B.O. = \frac{1}{2} (2 - 2) = 0$$

He₂ does not exist.

(ii) **C₂ :** EC is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$.
 $(\pi 2p_x^2 = \pi 2p_y^2)$

$$\therefore B.O. = \frac{1}{2} (8 - 4) = 2$$

It is diamagnetic due to absence of unpaired electron(s)

(iii) **O₂ :** EC is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2$
 $\left(\pi 2p_x^2 \right) \left(\pi^* 2p_x^1 \right)$
 $\left(\pi 2p_y^2 \right) \left(\pi^* 2p_y^1 \right)$

$$\therefore B.O. = \frac{1}{2} (10 - 6) = 2$$

It is paramagnetic due to unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$.

(iv) **H₂⁻ :**
 M.O. configuration - $(\sigma 1s)^2 (\sigma^* 1s)^1$

Paramagnetic

$$\text{Bond order} = \frac{1}{2} [2 - 1] = \frac{1}{2}$$

(v) **N₂⁺ :**
 M.O. configuration
 $= (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^1$
 Paramagnetic

$$\text{Bond order} = \frac{1}{2} [9 - 4] = 2.5$$

(vi) **O₂⁺ :**
 M.O. configuration
 $= KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^1$

$$\text{Bond order} = \frac{1}{2} [8 - 3] = 2.5$$

(vii) **O₂⁻ :**
 M.O. configuration
 $= KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^2 (\pi^* 2p_y)^1$

$$\text{Paramagnetic, Bond order} = \frac{1}{2} [8 - 5] = 1.5$$

HYDROGEN BONDING

It is defined as an attractive force which binds H-atom of one molecule with the electronegative atom (F, O or N) of another molecule. The magnitude of H-bonding depends on the physical state of the compound, it is maximum in solid state and minimum in gaseous state.

Types of H-bonding :

- (i) **Intermolecular H-bond** : H-bond formed between two different molecules of same or different compounds.

These are of two types :

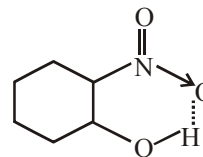
- (a) **Homo intermolecular** : H-bond between molecules of same compounds

Example : $\text{H}-\text{F} \cdots \cdots \text{H}-\text{F} \cdots \cdots \text{H}-\text{F}$

- (b) **Hetero intermolecular** : H-bond between molecules of different compounds

Example : Solution of alcohol and water.

- (ii) **Intramolecular H-bond** : Formed when H-atom is in between two highly electronegative (F, O, N) atoms present within the same molecule. For example in o-nitrophenol i.e.



Effect of H-bond on Physical Properties:

- (i) **Melting point and boiling point** :— Due to intermolecular H-bonding, M.P. & B.P. of compounds increases.
- (ii) **Molecular weight** : Increases due to H-bonding
- (iii) **Solubility** :
- (a) **Intermolecular H-bonding** —Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to H-bonding.
- (b) **Intramolecular H-bonding** : It decreases solubility as it forms chelate by H-bonding, so H-atom is not free for other molecule.
- (iv) **Viscosity and surface tension** — H-bond associates molecules together so viscosity and surface tension increases.

Chemical Bonding and Molecular Structure

- Molecular orbital Theory**
 - atomic orbital merge into molecular orbitals as atoms are moved towards each other
 - bonding & antibonding molecular orbitals
 - difference between no. of bonding & non bonding pairs
 - defines bond order
 - Hydrogen bond
 - attractive force formed between H atom of one molecule with the electronegative atom of another molecule
 - Hybridization
 - s-s overlapping
 - s-p overlapping
 - p-p overlapping
 - Ex - sp, sp², sp³, dsp², sp³d, sp³d², sp²-sp³
 - Intermixing of the orbitals of slightly different energies
 - Formation of bond by orbitals overlapping
 - side wise overlap
 - pi bond
 - head on overlap
 - Sigma bond
 - VBT
 - Predicts stability of molecules
 - Predicts magnetic behaviour of molecules
- VSEPR Theory**
 - predict geometry of molecules having
 - Bond pair & lone pair both
 - Ex - NH₃, H₂O, SO₂ etc
 - Bond pair only
 - Ex - BF₃, CH₄, PCl₅, SF₆ etc
- Bond parameters**
 - Bond length (equilibrium distance between the nuclei of two bonded atoms in a molecule)
 - Covalent radius
 - Van der waals radius
 - Bond Angle (angle between orbital containing bonding electron pairs around the central atom in a molecule, complex ion)
- Ionic Bond**
 - (Complete transfer of electron from one atom to other atom)
 - Formed between the elements of low I.E. and negative value of E.A.
 - Lattice Enthalpy (energy required to completely separate one mole of a solid ionic compound into gaseous constituents)
- Covalent Bond**
 - (Sharing of electron pair between the atoms)
 - Lewis dot structure (represents bonding in molecules & ions in terms of shared pairs of electrons and the octet-rule)
 - Formal Charge (difference between the number of valence electrons of that atom in an isolated or free state & no. of electrons assigned to that atom in the lewis structure)
- Polarity of Bonds** : due to difference in electro negativities of bonded atoms
 - Dipole moment ($\mu = q \times d$)
- Bond enthalpy** (energy required to break one mole of bond)
- Bond order** (number of bonds between two atoms in a molecule)
- Resonance structure** e.g. O₃, CO₃⁻ & CO₂ molecule

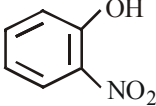
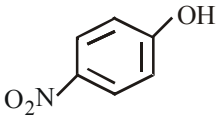
EXERCISE - 1

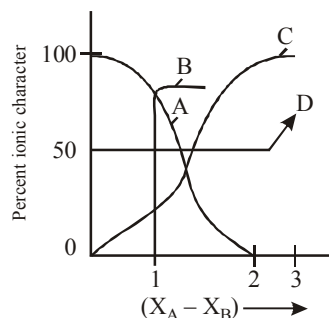
Conceptual Questions

- The following group does not contain a dative bond
(a) NO_2 (b) N_2Cl
(c) NC^- (d) all of these
- Which of the following pairs will form the most stable ionic bond?
(a) Na and Cl (b) Mg and F
(c) Li and F (d) Na and F
- Which of the following conceivable structures for CCl_4 will have a zero dipole moment?
(a) Irregular tetrahedron
(b) Square planar
(c) Square pyramid (carbon at apex)
(d) None of these
- Among the following which compound will show the highest lattice energy?
(a) KF (b) NaF (c) CsF (d) RbF
- The compound which contains both ionic and covalent bond:
(a) KCl (b) KCN (c) CH_4 (d) H_2
- Which one of the following contains a co-ordinate covalent bond?
(a) H_2O (b) HCl (c) BaCl_2 (d) N_2H_5^+
- The strength of bonds formed by s-s and p-p, s-p overlap in the order of
(a) $\text{s-p} > \text{s-s} > \text{p-p}$ (b) $\text{p-p} > \text{s-s} > \text{s-p}$
(c) $\text{s-s} > \text{p-p} > \text{s-p}$ (d) $\text{s-s} > \text{s-p} > \text{p-p}$
- The types of bonds present in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are only
(a) electrovalent, covalent and co-ordinate covalent bonds
(b) electrovalent, covalent and hydrogen bond
(c) electrovalent and covalent bonds
(d) electrovalent and co-ordinate covalent bonds
- Which of the following combination will form an electrovalent bond?
(a) P and Cl (b) NH_3 and BF_3
(c) H and Ca (d) H and S
- Which one of the following will dissolve in water most readily?
(a) I_2 (b) BaCO_3 (c) KF (d) PbI_2
- When a metal atom combines with non-metal atom, the non-metal atom will
(a) lose electrons and decrease in size
(b) lose electrons and increase in size
(c) gain electrons and decrease in size
(d) gain electrons and increase in size
- Indicate the nature of bonding in CCl_4 and CaH_2
(a) Covalent in CCl_4 and electrovalent in CaH_2
(b) Electrovalent in both CCl_4 and CaH_2
(c) Covalent in both CCl_4 and CaH_2
(d) Electrovalent in CCl_4 and covalent in CaH_2
- What is the correct mode of hybridisation of the central atom in the following compounds?

NO_2^-	SF_6	PF_6^-
(a) sp	sp^2	sp^3
(b) sp^2	sp^3d	sp^3d^2
(c) sp^2	sp^3	d^2sp^3
(d) sp^3	sp^3	sp^3d^2
- In PO_4^{3-} ion, the formal charge on each oxygen atom and P—O bond order respectively are
(a) $-0.75, 0.6$ (b) $-0.75, 1.0$
(c) $-0.75, 1.25$ (d) $-3, 1.25$
- Which of the following hydrogen bonds are strongest in vapour phase?
(a) $\text{HF} \cdots \text{HF}$ (b) $\text{HF} \cdots \text{HCl}$
(c) $\text{HCl} \cdots \text{HCl}$ (d) $\text{HF} \cdots \text{HI}$
- As the s-character of hybridised orbital increases, the bond angle
(a) increase (b) decrease
(c) becomes zero (d) does not change
- Among the following the electron deficient compound is
(a) BCl_3 (b) CCl_4 (c) PCl_5 (d) BeCl_2
- How many sigma bonds are there in P_4O_{10} ?
(a) 4 (b) 8
(c) 12 (d) 16
- The number of possible resonance structures for CO_3^{2-} is
(a) 2 (b) 3 (c) 6 (d) 9
- The strongest hydrogen bond is:
(a) $\text{O}-\text{H} \cdots \text{S}$ (b) $\text{S}-\text{H} \cdots \text{O}$
(c) $\text{F}-\text{H} \cdots \text{F}$ (d) $\text{F}-\text{H} \cdots \text{O}$
- Which of the following has the highest dipole moment?

(a) $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{array}$	(b) $\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{CH}_3 \quad \text{H} \end{array}$
(c) $\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{CH}_3 \quad \text{H} \end{array}$	(d) $\begin{array}{c} \text{Cl} \quad \text{CH}_3 \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{CH}_3 \quad \text{Cl} \end{array}$
- In the cyanide ion, the formal negative charge is on
(a) C (b) N
(c) Both C and N (d) Resonate between C and N
- Of the following hydrides which one has the lowest boiling point?
(a) AsH_3 (b) SbH_3 (c) PH_3 (d) NH_3
- Resonance structures can be written for
(a) O_3 (b) NH_3 (c) CH_4 (d) H_2O
- Which one of the following is the correct order of interactions?
(a) covalent < hydrogen bonding < van der Waals < dipole-dipole
(b) van der Waals < hydrogen bonding < dipole-dipole < covalent
(c) van der Waals < dipole-dipole < hydrogen bonding < covalent
(d) dipole-dipole < van der Waals < hydrogen bonding < covalent
- Which one of the following molecules will form a linear polymeric structure due to hydrogen bonding?
(a) NH_3 (b) H_2O (c) HCl (d) HF

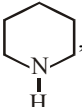
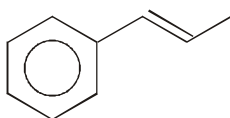
27. Among the following, the species having square planar geometry for central atom are
 (i) XeF_4 (ii) SF_4
 (iii) $[\text{NiCl}_4]^{2-}$ (iv) $[\text{PtCl}_4]^{2-}$
 (a) (i) and (iv) (b) (i) and (ii)
 (c) (ii) and (iii) (d) (iii) and (iv)
28. In $[\text{Ag}(\text{CN})_2]^-$, the number of π bonds is :
 (a) 2 (b) 3
 (c) 4 (d) 6
29. Which of the following does not contain any coordinate bond?
 (a) H_3O^+ (b) BF_4^-
 (c) HF_2^- (d) SO_2^-
30. Hydrogen bonding could not affect the boiling point of :
 (a) CH_3OH (b) HI (c) H_2O (d) NH_3
31. The low density of ice compared to water is due to :
 (a) induced dipole-induced dipole interactions
 (b) dipole-induced dipole interactions
 (c) hydrogen bonding interactions
 (d) dipole-dipole interactions
32. Intramolecular hydrogen bonding is found in :
 (a) *p*-nitrophenol (b) *m*-nitrophenol
 (c) *o*-nitrophenol (d) phenol
33. The vapour pressure of  is higher than  due to
 (a) dipole moment (b) dipole-dipole interaction
 (c) H-bonding (d) lattice structure
34. The bond length between C-C bond in sp^2 hybridised molecule is :
 (a) 1.2 Å (b) 1.39 Å
 (c) 1.33 Å (d) 1.54 Å
35. Which one of the following pairs of molecules will have permanent dipole moments for both members ?
 (a) NO_2 and CO_2 (b) NO_2 and O_3
 (c) SiF_4 and CO_2 (d) SiF_4 and NO_2
36. The correct sequence of increasing covalent character is represented by
 (a) $\text{LiCl} < \text{NaCl} < \text{BeCl}_2$ (b) $\text{BeCl}_2 < \text{LiCl} < \text{NaCl}$
 (c) $\text{NaCl} < \text{LiCl} < \text{BeCl}_2$ (d) $\text{BeCl}_2 < \text{NaCl} < \text{LiCl}$
37. Which of the following would have a permanent dipole moment?
 (a) SiF_4 (b) SF_4 (c) XeF_4 (d) BF_3
38. Dipole moment is shown by :
 (a) *cis*-1, 2-dichloroethene
 (b) *trans*-1, 2-dichloroethene
 (c) *trans*-2, 3-dichloro-2 pentene
 (d) Both (a) and (c)
39. The correct order of hybridisation of the central atom in the following species :
 NH_3 , $[\text{PtCl}_4]^{2-}$, PCl_2 and BCl_3 is
 (a) dsp^2 , dsp^3 , sp^2 , sp^3 (b) sp^3 , dsp^2 , dsp^3 , sp^2
 (c) dsp^2 , sp^2 , sp^3 , dsp^3 (d) dsp^2 , sp^3 , sp^2 , sp^3
40. Which of the following salt shows maximum covalent character?
 (a) AlCl_3 (b) MgCl_2 (c) CsCl (d) LaCl_3
41. Pauling's electronegativity values for elements are useful in predicting :
 (a) polarity of bonds in molecules
 (b) ionic and covalent nature of bonds
 (c) coordination number
 (d) Both (a) and (b)
42. Identify the non polar molecule in the following compounds:
 (a) H_2 (b) HCl
 (c) HF and HBr (d) HBr
43. Which of the following substances has the greatest ionic character ?
 (a) Cl_2O (b) NCl_3 (c) PbCl_2 (d) BaCl_2
44. Methanol and ethanol are miscible in water due to
 (a) Covalent character
 (b) Hydrogen bonding character
 (c) Oxygen bonding character
 (d) None of the above
45. As compared to covalent compounds, electrovalent compounds generally have
 (a) Low melting points and low boiling points
 (b) Low melting points and high boiling points
 (c) High melting points and low boiling points
 (d) High melting points and high boiling points
46. Which bond angle θ would result in the maximum dipole moment for the triatomic molecule YXY
 (a) $\theta = 90^\circ$ (b) $\theta = 120^\circ$
 (c) $\theta = 150^\circ$ (d) $\theta = 180^\circ$
47. Which does not show resonance :
 (a) Benzene (b) Aniline
 (c) Ethylamine (d) Toluene
48. Polarisability of halide ions increases in the order
 (a) F^- , I^- , Br^- , Cl^- (b) Cl^- , Br^- , I^- , F^-
 (c) I^- , Br^- , Cl^- , F^- (d) F^- , Cl^- , Br^- , I^-
49. For AB bond if percent ionic character is plotted against electronegativity difference ($X_A - X_B$), the shape of the curve would look like



The correct curve is

- (a) (A) (b) (B) (c) (C) (d) (D)
50. In which of the following compound electrovalent, covalent and co-ordinate bonds are present?
 (a) NH_4Cl (b) CCl_4 (c) CaCl_2 (d) H_2O
51. Following are the molecules or ions of the type AH_3 where A is the central atom. In which of them does the central atom A use its sp^2 hybrid orbitals to form A-H bonds ?
 (a) PH_3 (b) NH_3 (c) CH_3^+ (d) CH_3^-

52. Equilateral shape has
(a) sp hybridisation (b) sp^2 hybridisation
(c) sp^3 hybridisation (d) None of these
53. Which one of the following has the shortest carbon carbon bond length ?
(a) Benzene (b) Ethene (c) Ethyne (d) Ethane
54. Which of the following does not have a tetrahedral structure?
(a) BH_4^- (b) BH_3 (c) NH_4^+ (d) CH_4
55. The bond length in LiF will be
(a) less than that of NaF (b) more than that of KF
(c) equal to that of KF (d) equal to that of NaF
56. Which of the following molecules does not have a linear arrangement of atoms ?
(a) H_2S (b) C_2H_2 (c) BeH_2 (d) CO_2
57. In which one of the following molecules the central atom said to adopt sp^2 hybridization?
(a) BeF_2 (b) BF_3 (c) C_2H_2 (d) NH_3
58. In an octahedral structure, the pair of d orbitals involved in d^2sp^3 hybridization is
(a) $d_{x^2-y^2}, d_{z^2}$ (b) $d_{xz}, d_{x^2-y^2}$
(c) d_{z^2}, d_{xz} (d) d_{xy}, d_{yz}
59. Which of the following shows linear structure?
(a) Ethane (b) Ethene (c) Acetylene (d) CCl_4
60. The element X [$1s^2, 2s^2 2p^6, 3s^2 3p^5$] reacts with Y (atomic no. = 1) to form
(a) XY_2 (b) X_2Y (c) XY (d) None
61. Which one of the following does not follow octate rule?
(a) PF_3 (b) BF_3 (c) CO_2 (d) CCl_4
62. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimize
(a) lone pair - bond pair repulsion only
(b) bond pair - bond pair repulsion only
(c) lone pair - lone pair repulsion and lone pair - bond pair repulsion
(d) lone pair - lone pair repulsion only
63. Match List I and List II and pick out correct matching codes from the given choices :
- | List I
Compound | List II
Structure |
|--------------------|-------------------------|
| A. ClF_3 | 1. Square planar |
| B. PCl_5 | 2. Tetrahedral |
| C. IF_5 | 3. Trigonal bipyramidal |
| D. CCl_4 | 4. Square pyramidal |
| E. XeF_4 | 5. T-shaped |
- Codes
(a) A-5, B-4, C-3, D-2, E-1 (b) A-5, B-3, C-4, D-2, E-1
(c) A-5, B-3, C-4, D-1, E-2 (d) A-4, B-3, C-5, D-2, E-1
64. Bond order in benzene is :
(a) 1 (b) 2
(c) 1.5 (d) none of these
65. The decreasing values of bond angles from NH_3 (106°) to SbH_3 (101°) down group-15 of the periodic table is due to
(a) decreasing lp-bp repulsion
(b) decreasing electronegativity
(c) increasing bp-bp repulsion
(d) increasing lp-bp repulsion
66. Hybridization present in ClF_3 is :
(a) sp^2 (b) sp^3 (c) dsp^2 (d) sp^3d
67. Which one of the following has the pyramidal shape?
(a) CO_3^{2-} (b) SO_3 (c) BF_3 (d) PF_3
68. Fluorine molecule is formed by
(a) the axial p - p orbital overlap
(b) the sideways p - p orbital overlap
(c) the s - s orbital overlap
(d) the s - p orbital overlap
69. In NO_3^- ion number of bond pair and lone pair of electrons on nitrogen atom respectively are
(a) 2, 2 (b) 3, 1 (c) 1, 3 (d) 4, 0
70. Among the following the pair in which the two species are **not** isostructural is
(a) SiF_4 and SF_4 (b) IO_3^- and XeO_3
(c) BH_4^- and NH_4^+ (d) PF_6^- and SF_6
71. N_2 and O_2 are converted into monoanions, N_2^- and O_2^- respectively. Which of the following statements is wrong ?
(a) In N_2^- , N - N bond weakens
(b) In O_2^- , O - O bond order increases
(c) In O_2^- , O - O bond order decreases
(d) N_2^- becomes paramagnetic
72. In a regular octahedral molecule, MX_6 the number of X - M - X bonds at 180° is
(a) three (b) two (c) six (d) four
73. Which of the following molecules has trigonal planar geometry?
(a) BF_3 (b) NH_3 (c) PCl_3 (d) IF_3
74. The pair of species having identical shapes for molecules of both species is
(a) XeF_2, CO_2 (b) BF_3, PCl_3
(c) PF_5, IF_5 (d) CF_4, SF_4
75. Which contains both polar and non - polar bonds?
(a) NH_4Cl (b) HCN
(c) H_2O_2 (d) CH_4
76. The values of electronegativity of atoms A and B are 1.20 and 4.0 respectively. The percentage of ionic character of A - B bond is
(a) 50% (b) 72.24% (c) 55.3% (d) 43%
77. The electronegativities of F, Cl, Br and I are 4.0, 3.0, 2.8, 2.5 respectively. The hydrogen halide with a high percentage of ionic character is
(a) HF (b) HCl (c) HBr (d) HI
78. Which one of the following has the regular tetrahedral structure ?
(a) BF_4^- (b) SF_4
(c) XeF_4 (d) $[Ni(CN)_4]^{2-}$
(Atomic nos. : B = 5, S = 16, Ni = 28, Xe = 54)
79. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is
(a) PH_3 (b) NH_3 (c) CH_3^+ (d) SbH_3
80. Which molecule is planar ?
(a) SF_4 (b) XeF_4 (c) NF_3 (d) SiF_4

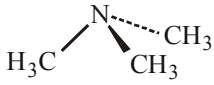
81. Amongst the following, the molecule/ion that is linear is :
 (a) SO_2 (b) CO_2 (c) ClO_2^- (d) NO_2^-
82. The trigonal bipyramidal geometry is obtained from the hybridisation :
 (a) dsp^3 or sp^3d (b) dsp^2 or sp^2d
 (c) d^2sp^3 or sp^3d^2 (d) None of these
83. The true statements from the following are
 1. PH_5 and BiCl_5 do not exist
 2. $p\pi - d\pi$ bond is present in SO_2
 3. Electrons travel at the speed of light
 4. SeF_4 and CH_4 have same shape
 5. I_3^+ has bent geometry
 (a) 1, 3 (b) 1, 2, 5
 (c) 1, 3, 5 (d) 1, 2, 4
84. The hybrid state of S in SO_3 is similar to that of
 (a) C in C_2H_2 (b) C in C_2H_4
 (c) C in CH_4 (d) C in CO_2
85. Which of the following set contains species having same angle around the central atom?
 (a) SF_4 , CH_4 , NH_3 (b) NF_3 , BCl_3 , NH_3
 (c) BF_3 , NF_3 , AlCl_3 (d) BF_3 , BCl_3 , BBR_3
86. The compound MX_4 is tetrahedral. The number of $\angle \text{XMX}$ formed in the compound are
 (a) Three (b) Four
 (c) Five (d) Six
87. The bond angle between two hybrid orbitals is 105° . The percentage of s-character of hybrid orbital is between
 (a) 50-55% (b) 9-12%
 (c) 22-23% (d) 11-12%
88. Which of the following has the shortest C-C bond length?
 (a) $\text{C}_2\text{H}_5\text{OH}$ (b) C_2H_6
 (c) C_2H_2 (d) C_2H_4
89. In piperidine , the hybrid state assumed by N is
 (a) sp (b) sp^2 (c) sp^3 (d) dsp^2
90. The compound 1, 2 - butadiene has
 (a) only sp hybridized carbon atoms
 (b) only sp^2 hybridized carbon atoms
 (c) both sp and sp^2 hybridized carbon atoms
 (d) sp , sp^2 and sp^3 hybridized carbon atoms
91. In the following molecule, the two carbon atoms marked by asterisk (*) possess the following type of hybridized orbitals
 $\text{H}_3\text{C}-\text{C}^* \equiv \text{C}^*-\text{CH}_3$
 (a) sp^3 orbital (b) sp^2 orbital
 (c) sp orbital (d) sp^3 and sp respectively
92. Which has the least bond angle
 (a) NH_3 (b) BeF_2 (c) H_2O (d) CH_4
93. The shape of SO_4^{2-} ion is
 (a) square planar (b) tetrahedral
 (c) trigonal bipyramidal (d) hexagonal
94. The largest bond angle is in
 (a) AsH_3 (b) NH_3 (c) H_2O (d) PH_3
95. Which one has a pyramidal structure
 (a) CH_4 (b) NH_3 (c) H_2O (d) CO_2
96. Each carbon in carbon suboxide (C_3O_2) is
 (a) sp^2 - hybridized
 (b) sp^3 - hybridized
 (c) sp - hybridized
 (d) sp^2 - hybridized but linked with one co-ordinate bond
97. Which statement is NOT correct ?
 (a) A sigma bond is weaker than a π -bond.
 (b) A sigma bond is stronger than a π -bond.
 (c) A double bond is stronger than a single bond.
 (d) A double bond is shorter than a single bond.
98. Linear combination of two hybridized orbitals belonging to two atoms and each having one electron leads to a
 (a) sigma bond
 (b) double bond
 (c) co-ordinate covalent bond
 (d) Pi bond.
99. Main axis of a diatomic molecule is z, molecular orbital p_x and p_y overlap to form which of the following orbital?
 (a) π - molecular orbital (b) σ - molecular orbital
 (c) δ - molecular orbital (d) No bond will be formed
100. The number of anti-bonding electron pairs in O_2^{2-} molecular ion on the basis of molecular orbital theory is, (Atomic number of O is 8)
 (a) 5 (b) 2 (c) 3 (d) 4
101. In which of the following species is the underlined carbon having sp^3 - hybridisation ?
 (a) $\text{CH}_3-\underline{\text{C}}\text{OOH}$ (b) $\text{CH}_3-\underline{\text{C}}\text{H}_2\text{OH}$
 (c) $\text{CH}_3-\underline{\text{C}}\text{OCH}_3$ (d) $\text{CH}_2=\underline{\text{C}}\text{H}-\text{CH}_3$
102. Which of the following statements is not correct for sigma and pi-bonds formed between two carbon atoms?
 (a) Sigma-bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard
 (b) Sigma-bond is stronger than a pi-bond
 (c) Bond energies of sigma- and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol, respectively
 (d) Free rotation of atoms about a sigma-bond is allowed but not in case of a pi-bond
103. The bond order in N_2^+ is
 (a) 1.5 (b) 3.0 (c) 2.5 (d) 2.0
104. How many σ - and π -bonds are there in?

 (a) $14\sigma, 8\pi$ (b) $18\sigma, 8\pi$ (c) $19\sigma, 4\pi$ (d) $14\sigma, 2\pi$
105. Which of the following has $p\pi - d\pi$ bonding ?
 (a) NO_3^- (b) SO_3^{2-} (c) BO_3^{3-} (d) CO_3^{2-}
106. How many σ and π bonds are present in toluene?
 (a) $3\pi+8\sigma$ (b) $3\pi+10\sigma$
 (c) $3\pi+15\sigma$ (d) $6\pi+3\sigma$
107. The calculated bond order in O_2^- ion is
 (a) 1 (b) 1.5 (c) 2 (d) 2.5
108. The molecular electronic configuration of H_2^- ion is?
 (a) $(\sigma 1s)^2$ (b) $(\sigma 1s)^2(\sigma^* 1s)^2$
 (c) $(\sigma 1s)^2(\sigma^* 1s)^1$ (d) $(\sigma 1s)^3$
109. In pyrophosphoric acid, $\text{H}_2\text{P}_2\text{O}_7$, number of σ and $d\pi - p\pi$ bonds are respectively
 (a) 8 and 2 (b) 6 and 2
 (c) 12 and zero (d) 12 and 2

110. Arrange the following ions in the order of decreasing X – O bond length, where X is the central atom in
- ClO_4^- , SO_4^{2-} , PO_4^{3-} , SiO_4^{4-}
 - SiO_4^{4-} , PO_4^{3-} , SO_4^{2-} , ClO_4^-
 - SiO_4^{4-} , PO_4^{3-} , ClO_4^- , SO_4^{2-}
 - SiO_4^{4-} , SO_4^{2-} , PO_4^{3-} , ClO_4^-
111. In the change of NO^+ to NO , the electron is added to
- σ - orbital
 - π - orbital
 - σ^* - orbital
 - π^* - orbital
112. Which of the following represents the given mode of hybridisation $\text{sp}^2 - \text{sp}^2 - \text{sp} - \text{sp}$ from left to right ?
- $\text{H}_2\text{C} = \text{CH} - \text{C} \equiv \text{N}$
 - $\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$
 - $\text{H}_2\text{C} = \text{C} = \text{C} = \text{CH}_2$
 - $\text{H}_2\text{C} = \text{C} = \text{C} = \text{CH}_2$
113. In O_2^- , O_2 and O_2^{2-} molecular species, the total number of antibonding electrons respectively are
- 7, 6, 8
 - 1, 0, 2
 - 6, 6, 6
 - 8, 6, 8
114. If N_x is the number of bonding orbitals of an atom and N_y is the number of antibonding orbitals, then the molecule/atom will be stable if
- $N_x > N_y$
 - $N_x = N_y$
 - $N_x < N_y$
 - $N_x \leq N_y$
115. Which of the following is the correct electron dot structure of N_2O molecule?
- $\text{:N} = \text{N} = \ddot{\text{O}}\text{:}$
 - $\text{:N} = \overset{+}{\text{N}} = \ddot{\text{O}}\text{:}^-$
 - $\ddot{\text{N}} = \ddot{\text{N}} = \ddot{\text{O}}\text{:}$
 - $\text{:N} = \text{N} = \ddot{\text{O}}\text{:}$
116. The correct statement with regard to H_2^+ and H_2^- is
- Both H_2^+ and H_2^- do not exist
 - H_2^- is more stable than H_2^+
 - H_2^+ is more stable than H_2^-
 - Both H_2^+ and H_2^- are equally stable
117. In which of the following pairs hydrogen-bonding is not possible ?
- NH_3 , NH_3
 - NH_3 , CH_4
 - H_2O , CH_3OCH_3
 - CH_3OH , CH_3OCH_3
118. Dipole moment of CO_2 is zero which implies that
- Carbon and oxygen have equal electronegativities
 - Carbon has no polar bond
 - CO_2 is a linear molecule
 - Carbon has bond moments of zero value
119. In which of the following pairs, the two species are iso-structure?
- SO_3^{2-} and NO_3^-
 - BF_3 and NF_3
 - BrO_3^- and XeO_3
 - SF_4 and XeF_4
120. Four diatomic species are listed below in different sequences. Which of these presents the *correct* order of their increasing bond order ?
- $\text{O}_2^- < \text{NO} < \text{C}_2^{2-} < \text{He}_2^+$
 - $\text{NO} < \text{C}_2^{2-} < \text{O}_2^- < \text{He}_2^+$
 - $\text{C}_2^{2-} < \text{He}_2^+ < \text{NO} < \text{O}_2^-$
 - $\text{He}_2^+ < \text{O}_2^- < \text{NO} < \text{C}_2^{2-}$
121. What is the dominant intermolecular force or bond that must be overcome in converting liquid CH_3OH to a gas?
- Dipole-dipole interactions
 - Covalent bonds
 - London dispersion forces
 - Hydrogen bonding
122. In which one of the following species the central atom has the type of hybridization which is not the same as that present in the other three?
- SF_4
 - I_3^-
 - SbCl_5^{2-}
 - PCl_5
123. Some of the properties of the two species, NO_3^- and H_3O^+ are described below. Which one of them is correct?
- Similar in hybridization for the central atom with different structures.
 - Dissimilar in hybridization for the central atom with different structures.
 - Isostructural with same hybridization for the central atom.
 - Isostructural with different hybridization for the central atom.
124. In which of the following molecules the central atom does not have sp^3 hybridization?
- NH_4^+
 - CH_4
 - SF_4
 - BF_4^-
125. Which one of the following species does not exist under normal conditions?
- Be_2^+
 - Be_2
 - B_2
 - Li_2

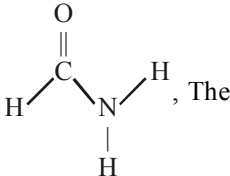
EXERCISE - 2

Applied Questions

- In the anion HCOO^- the two carbon - oxygen bonds are found to be of equal length. What is the reason for it ?
 - Electronic orbitals of carbon atom are hybridised
 - The $\text{C}=\text{O}$ bond is weaker than the $\text{C}-\text{O}$ bond
 - The anion HCOO^- has two resonating structures
 - The anion is obtained by removal of a proton from the acid molecule
- In compounds of type ECl_3 , where $\text{E} = \text{B}, \text{P}, \text{As}$ or Bi , the angles $\text{Cl}-\text{E}-\text{Cl}$ for different E are in the order.
 - $\text{B} > \text{P} = \text{As} = \text{Bi}$
 - $\text{B} > \text{P} > \text{As} > \text{Bi}$
 - $\text{B} < \text{P} = \text{As} = \text{Bi}$
 - $\text{B} < \text{P} < \text{As} < \text{Bi}$
- Molecular shapes of SF_4 , CF_4 and XeF_4 are
 - the same, with 2, 0 and 1 lone pairs of electrons respectively
 - the same, with 1, 1 and 1 lone pairs of electrons respectively
 - different, with 0, 1 and 2 lone pairs of electrons respectively
 - different, with 1, 0 and 2 lone pairs of electrons respectively
- The molecules BF_3 and NF_3 are both covalent compounds, but BF_3 is non polar whereas NF_3 is polar. The reason for this is
 - atomic size of Boron is larger than nitrogen
 - Boron is metal while nitrogen is gas
 - $\text{B}-\text{F}$ bonds are non-polar while $\text{N}-\text{F}$ bonds are polar
 - BF_3 is planar but NF_3 is pyramidal
- The common features among the species CN^- , CO and NO^+ are
 - bond order three and isoelectronic
 - bond order three and weak field ligands
 - isoelectronic and weak field ligands
 - None of these
- The correct order of bond energies in NO , NO^+ and NO^- is:
 - $\text{NO}^- > \text{NO} > \text{NO}^+$
 - $\text{NO} > \text{NO}^- > \text{NO}^+$
 - $\text{NO}^+ > \text{NO} > \text{NO}^-$
 - $\text{NO}^+ > \text{NO}^- > \text{NO}$
- A σ bonded molecule MX_3 is T-shaped. The number of non bonded pair of electrons is
 - 0
 - 2
 - 1
 - can be predicted only if atomic number is known
- Experiment shows that H_2O has a dipole moment while CO_2 has not. Point out the structures which best illustrate these facts
 - $\text{O}=\text{C}=\text{O}$; $\text{H}-\text{O}-\text{H}$
 - $\text{O}=\text{C}=\text{O}$; $\text{H}-\text{O}-\text{H}$
 - $\text{O}=\text{C}=\text{O}$; $\text{H}-\text{H}-\text{O}$
 - $\text{O}=\text{C}=\text{O}$; $\text{O}-\text{H}$
- The enolic form of a acetone contains
 - 9 sigma bonds, 1 pi bond and 2 lone pairs
 - 8 sigma bonds, 2 pi bonds and 2 lone pairs
 - 10 sigma bonds, 1 pi bond and 1 lone pair
 - 9 sigma bonds, 2 pi bonds and 1 lone pair
- In which case hydrogen bond will not be observed
 - H_3O_2^-
 - H_2O
 - H_5O_2^+
 - H_3O^+
- Which one of the following formulae does not correctly represent the bonding capacities of the two atoms involved?
 - $\left[\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{P}-\text{H} \\ | \\ \text{H} \end{array} \right]^+$
 - $\text{F}-\text{O}-\text{F}$
 - $\text{O} \leftarrow \text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}-\text{H} \end{array}$
 - $\text{H}-\text{C}=\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}-\text{H} \end{array}$
- Trimethylamine is a pyramidal molecule



and formamide is a planar molecule



The hybridisation of Nitrogen in both is

 - sp^2, sp^2
 - sp^3, sp^2
 - sp^3, sp^3
 - sp^2, sp
- If climbing of water droplets is made to occur on a coated microscope slide, the slide would have to be coated in which of the following way

Polar
A

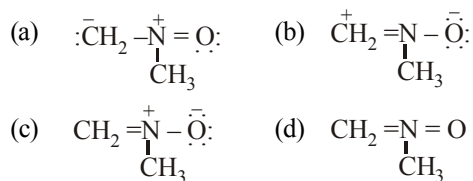
Non Polar
B

POLAR
↑
NON POLAR
C

NON POLAR
↑
POLAR
D

 - A
 - B
 - C
 - D
- Mark the incorrect statement in the following
 - The bond order in the species O_2 , O_2^+ and O_2^- decreases as $\text{O}_2^+ > \text{O}_2 > \text{O}_2^-$
 - The bond energy in a diatomic molecule always increases when an electron is lost
 - Electrons in antibonding M.O. contribute to repulsion between two atoms.
 - With increase in bond order, bond length decreases and bond strength increases

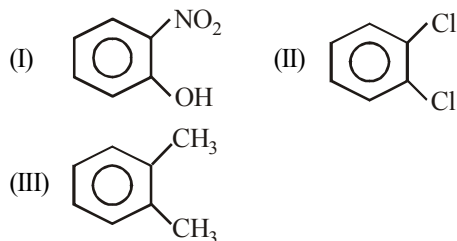
15. Which of the following is not expected to be resonance structure ?



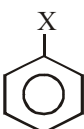
16. The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol because

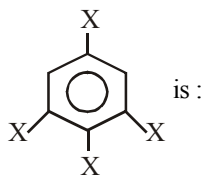
- (a) NO_2 group at *p*-position behave in a different way from that at *o*-position.
 (b) intramolecular hydrogen bonding exists in *p*-nitrophenol
 (c) there is intermolecular hydrogen bonding in *p*-nitrophenol
 (d) *p*-nitrophenol has a higher molecular weight than *o*-nitrophenol.

17. Which is the correct order of dipole moments of the compounds :



- (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{II} > \text{I} > \text{III}$
 (c) $\text{III} > \text{I} > \text{II}$ (d) $\text{III} > \text{II} > \text{I}$

18. The dipole moment of  is 1.5 D. The dipole moment of



- (a) 1 D (b) 1.5 D
 (c) 2.25 D (d) 3 D

19. The BCl_3 is a planar molecule whereas NCl_3 is pyramidal because

- (a) B-Cl bond is more polar than N-Cl bond
 (b) N-Cl bond is more covalent than B-Cl bond
 (c) nitrogen atom is smaller than boron atom
 (d) BCl_3 has no lone pair but NCl_3 has a lone pair of electrons

20. Dipole moment of *p*-nitroaniline, when compared to nitrobenzene (X) and aniline (Y) will be :

- (a) smaller than both (X) and (Y)
 (b) greater than both (X) and (Y)
 (c) greater than (Y) but smaller than (X)
 (d) equal to zero

21. The cylindrical shape of an alkyne is due to the fact that it has

- (a) three sigma C - C bonds

- (b) two sigma C - C and one ' π ' C - C bonds
 (c) three ' π ' C - C bonds
 (d) one sigma C - C and two ' π ' C - C bonds

22. N_2 and O_2 are converted into monocations, N_2^+ and O_2^+ respectively. Which of the following statements is wrong ?

- (a) In N_2^+ , the N—N bond weakens
 (b) In O_2^+ , the O—O bond order increases
 (c) In O_2^+ , paramagnetism decreases
 (d) N_2^+ becomes diamagnetic

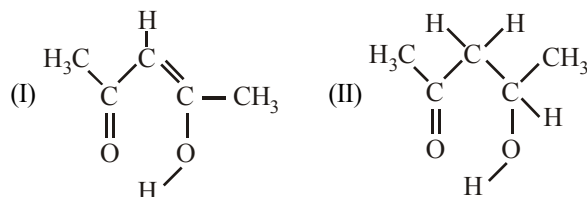
23. The AsF_5 molecule is trigonal bipyramidal. The hybrid orbitals used by the As atom for bonding are

- (a) $d_{x^2-y^2}, d_z^2, s, p_x, p_y$ (b) d_{xy}, s, p_x, p_y, p_z
 (c) s, p_x, p_y, p_z, d_z^2 (d) $d_{x^2-y^2}, s, p_x, p_y, p_z$

24. The dipole moments of diatomic molecules AB and CD are 10.41 D and 10.27 D, respectively while their bond distances are 2.82 and 2.67 Å, respectively. This indicates that

- (a) bonding is 100% ionic in both the molecules
 (b) AB has more ionic bond character than CD
 (c) AB has lesser ionic bond character than CD
 (d) bonding is nearly covalent in both the molecules

25. Consider the two molecules :



Which of the following statements about them is true ?

- (a) II is capable of forming intramolecular hydrogen bonding whereas I is not
 (b) Both are capable of forming equally stable intramolecular hydrogen bonding
 (c) I is likely to form more stable intramolecular hydrogen bonding than II
 (d) Both of them cannot form intramolecular hydrogen bonding

26. The hybridization of P in PO_4^{3-} is the same as of

- (a) S in SO_3 (b) N in NO_3^-
 (c) I in ICl_2^+ (d) I in ICl_4^-

27. The relationship between the dissociation energy of N_2 and N_2^+ is :

- (a) Dissociation energy of $\text{N}_2^+ >$ dissociation energy of N_2
 (b) Dissociation energy of $\text{N}_2 =$ dissociation energy of N_2^+
 (c) Dissociation energy of $\text{N}_2 >$ dissociation energy of N_2^+
 (d) Dissociation energy of N_2 can either be lower or higher than the dissociation energy of N_2^+

28. In X--H---Y , X and Y both are electronegative elements

- (a) thus electron density on X will increase and on H will decrease
 (b) in both electron density will decrease
 (c) in both electron density will increase and on H will decrease
 (d) thus electron density will decrease on X and will increase on H

29. The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2D). This is because
- in NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions
 - in NH_3 as well as NF_3 the atomic dipole and bond dipole are in opposite directions
 - in NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3 these are in the same direction
 - in NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the same direction
30. In the process : $\text{XH}_3 + \text{H}^+ \longrightarrow \text{XH}_4^+$, (X being N, P, As and Sb), the maximum increase in the bond angle will be in case of
- NH_3
 - PH_3
 - AsH_3
 - SbH_3
31. On changing N_2 to N_2^+ , the dissociation energy of N–N bond and on changing O_2 to O_2^+ the dissociation energy of O–O bond....
- increases, decreases
 - decreases, increases
 - decreases in both cases
 - increases in both cases
32. H_2O is dipolar, whereas BeF_2 is not. It is because
- the electronegativity of F is greater than that of O
 - H_2O involves hydrogen bonding whereas BeF_2 is a discrete molecule
 - H_2O is linear and BeF_2 is angular
 - H_2O is angular and BeF_2 is linear
33. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species ?
- Bond length in NO^+ is equal to that in NO
 - Bond length in NO is greater than in NO^+
 - Bond length in NO^+ is greater than in NO
 - Bond length is unpredictable
34. Which is correct about the directional orientation of the orbital?
- $p > sp$
 - $p < sp$
 - $p = sp$
 - none of these
35. Pb^{4+} is less stable than Sn^{4+} . It is because of
- Higher value of $\text{IE}_1 + \text{IE}_2 + \text{IE}_3 + \text{IE}_4$ for Pb than Sn
 - Lesser polarising power of Pb^{4+} than Sn^{4+}
 - Inert pair effect in Pb
 - None of these
36. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+
- Paramagnetic and Bond order $< \text{O}_2$
 - Paramagnetic and Bond order $> \text{O}_2$
 - Diamagnetic and Bond order $< \text{O}_2$
 - Diamagnetic and Bond order $> \text{O}_2$
37. Select the most stable cation
- NH_4^+
 - CH_5^+
 - OH_3^+
 - FH_2^+
38. Which of the following represents the correct order of Cl–O bond lengths in ClO^- , ClO_2^- , ClO_3^- , ClO_4^- ?
- $\text{ClO}_4^- = \text{ClO}_3^- = \text{ClO}_2^- = \text{ClO}^-$
 - $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$
 - $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^- < \text{ClO}^-$
 - $\text{ClO}_3^- < \text{ClO}_4^- < \text{ClO}_2^- < \text{ClO}^-$
39. The correct order of increasing bond angles in the following triatomic species is :
- $\text{NO}_2^- < \text{NO}_2^+ < \text{NO}_2$
 - $\text{NO}_2^- < \text{NO}_2 < \text{NO}_2^+$
 - $\text{NO}_2^+ < \text{NO}_2 < \text{NO}_2^-$
 - $\text{NO}_2^+ < \text{NO}_2^- < \text{NO}_2$
40. In which of the following molecules / ions BF_3 , NO_2^- , NH_2^- and H_2O , the central atom is sp^2 hybridized ?
- NH_2^- and H_2O
 - NO_2^- and H_2O
 - BF_3 and NO_2^-
 - NO_2^- and NH_2^-
41. According to MO theory which of the following lists ranks the nitrogen species in terms of increasing bond order?
- $\text{N}_2^{2-} < \text{N}_2^- < \text{N}_2$
 - $\text{N}_2 < \text{N}_2^{2-} < \text{N}_2^-$
 - $\text{N}_2^- < \text{N}_2^{2-} < \text{N}_2$
 - $\text{N}_2^- < \text{N}_2 < \text{N}_2^{2-}$
42. Which of the two ions from the list given below have the geometry that is explained by the same hybridization of orbitals, NO_2^- , NO_3^- , NH_2^- , NH_4^+ , SCN^- ?
- NO_2^- and NO_3^-
 - NH_2^- and NO_3^-
 - SCN^- and NH_2^-
 - NO_2^- and NH_2^-
43. Which of the following has the minimum bond length ?
- O_2^+
 - O_2^-
 - O_2^{2-}
 - O_2
44. The pairs of species of oxygen and their magnetic behaviours are noted below. Which of the following presents the correct description ?
- $\text{O}_2^-, \text{O}_2^{2-}$ – Both diamagnetic
 - $\text{O}_2^+, \text{O}_2^{2-}$ – Both paramagnetic
 - O_2^+, O_2 – Both paramagnetic
 - None of these
45. Which one of the following pairs is isostructural (i.e., having the same shape and hybridization) ?
- $[\text{BCl}_3 \text{ and } \text{BrCl}_3^-]$
 - $[\text{NH}_3 \text{ and } \text{NO}_3^-]$
 - $[\text{NF}_3 \text{ and } \text{BF}_3]$
 - $[\text{BF}_4^- \text{ and } \text{NH}_4^+]$
46. Bond order of 1.5 is shown by :
- O_2^+
 - O_2^-
 - O_2^{2-}
 - O_2
47. Which of the following hydrogen bonds is the strongest?
- $\text{O}-\text{H} \cdots \text{F}$
 - $\text{O}-\text{H} \cdots \text{H}$
 - $\text{F}-\text{H} \cdots \text{F}$
 - $\text{O}-\text{H} \cdots \text{O}$
48. The bond dissociation energy of B–F in BF_3 is 646 kJ mol^{-1} whereas that of C–F in CF_4 is 515 kJ mol^{-1} . The correct reason for higher B–F bond dissociation energy as compared to that of C–F is
- stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4 .
 - significant $p\pi-p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4 .
 - lower degree of $p\pi-p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4 .
 - smaller size of B–atom as compared to that of C–atom.

49. The number of types of bonds between two carbon atoms in calcium carbide is
 (a) One sigma, One pi (b) Two sigma, one pi
 (c) Two sigma, two pi (d) One sigma, two pi
50. In which of the following pairs the two species are not isostructural ?
 (a) CO_3^{2-} and NO_3^- (b) PCl_4^+ and SiCl_4
 (c) PF_5 and BrF_5 (d) AlF_6^{3-} and SF_6
51. Among the following, the paramagnetic compound is
 (a) Na_2O_2 (b) O_3
 (c) N_2O (d) KO_2
52. The species having bond order different from that in CO is
 (a) NO^- (b) NO^+
 (c) CN^- (d) N_2
53. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is :
 (a) 1 and diamagnetic (b) 0 and diamagnetic
 (c) 1 and paramagnetic (d) 0 and paramagnetic
54. The species having pyramidal shape is :
 (a) SO_3 (b) BrF_3
 (c) SiO_3^{2-} (d) OsF_2
55. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^- , CN^- and H_2O , respectively, are
 (a) octahedral, tetrahedral and square planar
 (b) tetrahedral, square planar and octahedral
 (c) square planar, tetrahedral and octahedral
 (d) octahedral, square planar and octahedral
56. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) :
 (a) sp and sp^3 (b) sp and sp^2
 (c) only sp^3 (d) sp^2 and sp^3
57. Which one of the following molecules is expected to exhibit diamagnetic behaviour ?
 (a) C_2 (b) N_2
 (c) O_2 (d) S_2
58. Which of the following is the wrong statement ?
 (a) ONCl and ONO^- are not isoelectronic.
 (b) O_3 molecule is bent
 (c) Ozone is violet-black in solid state
 (d) Ozone is diamagnetic gas.
59. In which of the following pairs of molecules/ions, both the species are not likely to exist ?
 (a) H_2^+ , He_2^{2-} (b) H_2^- , He_2^{2-}
 (c) H_2^{2+} , He_2 (d) H_2^- , He_2^+
60. Stability of the species Li_2 , Li_2^- and Li_2^+ increases in the order of :
 (a) $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$ (b) $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$
 (c) $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$ (d) $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$
61. Considering the state of hybridization of carbon atoms, find out the molecule among the following which is linear ?
 (a) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 (b) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$
 (c) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$
 (d) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
62. Which of the following species contains three bond pairs and one lone pair around the central atom ?
 (a) H_2O (b) BF_3 (c) NH_2^- (d) PCl_3
63. The pair of species with the same bond order is :
 (a) O_2^{2-} , B_2 (b) O_2^+ , NO^+
 (c) NO , CO (d) N_2 , O_2
64. Which of the following species exhibits the diamagnetic behaviour ?
 (a) NO (b) O_2^{2-} (c) O_2^+ (d) O_2
65. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+ , Ca^{2+} , Mg^{2+} , Be^{2+} ?
 (a) $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+} < \text{K}^+$
 (b) $\text{Mg}^{2+} < \text{Be}^{2+} < \text{K}^+ < \text{Ca}^{2+}$
 (c) $\text{Be}^{2+} < \text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$
 (d) $\text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$
66. In which of the following ionization processes, the bond order has increased and the magnetic behaviour has changed ?
 (a) $\text{N}_2 \rightarrow \text{N}_2^+$ (b) $\text{C}_2 \rightarrow \text{C}_2^+$
 (c) $\text{NO} \rightarrow \text{NO}^+$ (d) $\text{O}_2 \rightarrow \text{O}_2^+$
67. Which one of the following pairs of species have the same bond order ?
 (a) CN^- and NO^+ (b) CN^- and CN^+
 (c) O_2^- and CN^- (d) NO^+ and CN^+
68. The molecule having smallest bond angle is :
 (a) NCl_3 (b) AsCl_3
 (c) SbCl_3 (d) PCl_3
69. The electronegativities of four atoms labeled as D, E, F and G are as follows. $D = 3.8$, $E = 3.3$, $F = 2.8$ and $G = 1.3$. If the atoms form the molecules DE, DG, EG and DF, the order of arrangement of these molecules in the increasing order of covalent bond character is
 (a) $\text{DG} < \text{EG} < \text{DF} < \text{DE}$ (b) $\text{DF} < \text{DG} < \text{DE} < \text{EG}$
 (c) $\text{DG} < \text{DF} < \text{EG} < \text{DE}$ (d) $\text{DE} < \text{EG} < \text{DG} < \text{DF}$
70. Which one of the following is the correct statement ?
 (a) O_2 molecule has bond order 2 and is diamagnetic
 (b) N_2 molecule has bond order 3 and is paramagnetic
 (c) H_2 molecule has bond order zero and is diamagnetic
 (d) C_2 molecule has bond order 2 and is diamagnetic
71. Among the following molecules : SO_2 , SF_4 , ClF_3 , BrF_5 and XeF_4 , which of the following shapes does not describe any of the molecules mentioned ?
 (a) Bent (b) Trigonal bipyramidal
 (c) See-saw (d) T-shape
72. The type of hybridization in xenon atom and the number of lone pairs present on xenon atom in xenon hexafluoride molecule are respectively
 (a) sp^3d^3 , one (b) sp^3d^3 , two
 (c) sp^3d^3 , two (d) sp^3d^2 , zero
- DIRECTIONS for Qs. 73 to 75: These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1

- (b) Statement -1 is True, Statement -2 is True ; Statement-2 is NOT a correct explanation for Statement - 1
 (c) Statement - 1 is True, Statement- 2 is False
 (d) Statement -1 is False, Statement -2 is True
73. **Statement-1** : Ice is less dense than liquid water.
Statement-2 : There are vacant spaces between hydrogen bonded water molecules in ice.

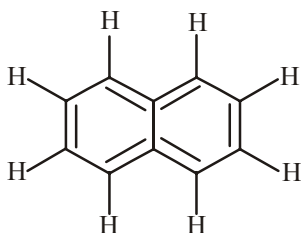
74. **Statement-1** : A resonance hybrid is always more stable than any of its canonical structures.
Statement-2 : This stability is due to delocalization of electrons.
75. **Statement-1** : *o* and *p*-nitrophenols can be separated by steam distillation.
Statement-2 : *o*-nitrophenol have intramolecular hydrogen bonding while *p*-nitrophenol exists as associated molecules.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Isostructural species are those which have the same shape and hybridisation. Among the given species identify the isostructural pairs.
 (a) $[\text{NF}_3 \text{ and } \text{BF}_3]$ (b) $[\text{BF}_4^- \text{ and } \text{NH}_4^+]$
 (c) $[\text{BCl}_3 \text{ and } \text{BrCl}_3]$ (d) $[\text{NH}_3 \text{ and } \text{NO}_3^-]$
- Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?
 (a) CO_2 (b) HI
 (c) H_2O (d) SO_2
- The types of hybrid orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ respectively are expected to be
 (a) sp , sp^3 and sp^2 (b) sp , sp^2 and sp^3
 (c) sp^2 , sp and sp^3 (d) sp^2 , sp^3 and sp
- Hydrogen bonds are formed in many compounds e.g., H_2O , HF , NH_3 . The boiling point of such compounds depends to an extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points above compounds is
 (a) $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$ (b) $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$
 (c) $\text{NH}_3 > \text{HF} > \text{H}_2\text{O}$ (d) $\text{NH}_3 > \text{H}_2\text{O} > \text{HF}$
- In PO_4^{3-} ion the formal charge on the oxygen atom of P-O bond is
 (a) +1 (b) -1
 (c) -0.75 (d) +0.75
- In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are
 (a) 2, 2 (b) 3, 1
 (c) 1, 3 (d) 4, 0
- Which of the following species has tetrahedral geometry?
 (a) BH_4^- (b) NH_2^-
 (c) CO_3^{2-} (d) H_3O^+
- Number of π bonds and σ bonds in the following structure is



- (a) 6, 19 (b) 4, 20
 (c) 5, 19 (d) 5, 20
- Which molecule/ion out of the following does not contain unpaired electrons?
 (a) N_2^+ (b) O_2
 (c) O_2^{2-} (d) B_2
- In which of the following molecule/ion all the bonds are not equal?
 (a) XeF_4 (b) BF_4^-
 (c) C_2H_4 (d) SiF_4
- In which of the following substances will hydrogen bond be strongest?
 (a) HCl (b) H_2O
 (c) HI (d) H_2S
- If the electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$, the four electrons involved in chemical bond formation will be
 (a) $3p^6$ (b) $3p^6, 4s^2$
 (c) $3p^6, 3d^2$ (d) $3d^2, 4s^2$
- Which of the following angle corresponds to sp^2 hybridisation?
 (a) 90° (b) 120°
 (c) 180° (d) 109°

Direction (Q. no. 14-17) The electronic configurations of the elements A, B and C are given below. Answer the questions from 14 to 17 on the basis of these configurations.

A	$1s^2$	$2s^2$	$2p^6$		
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
C	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

- Stable form of A may be represented by the formula
 (a) A (b) A_2
 (c) A_3 (d) A_4
- Stable form of C may be represented by the formula
 (a) C (b) C_2
 (c) C_3 (d) C_4
- The molecular formula of the compound formed from B and C will be
 (a) BC (b) B_2C
 (c) BC_2 (d) BC_3
- The bond between B and C will be
 (a) ionic (b) covalent
 (c) hydrogen (d) coordinate

18. Which of the following order of energies of molecular orbitals of N_2 is correct?
 (a) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
 (b) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
 (c) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
 (d) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
19. Which of the following statement is not correct from the view point of molecular orbital theory?
 (a) Be_2 is not a stable molecule
 (b) He_2 is not stable but He_2^+ is expected to exist
 (c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period
 (d) The order of energies of molecular orbitals in N_2 molecule is
 $\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y) < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$
20. Which of the following options represents the correct bond order?
 (a) $O_2^- > O_2 > O_2^+$ (b) $O_2^- < O_2 < O_2^+$
 (c) $O_2^- > O_2 < O_2^+$ (d) $O_2^- < O_2 > O_2^+$
21. The electronic configuration of the outer most shell of the most electronegative element is
 (a) $2s^2 2p^5$ (b) $3s^2 3p^5$
 (c) $4s^2 4p^5$ (d) $5s^2 5p^5$
22. Amongst the following elements whose electronic configuration are given below, the one having the highest ionisation enthalpy is
 (a) $[Ne]3s^2 3p^1$ (b) $[Ne]3s^2 3p^3$
 (c) $[Ne]3s^2 3p^2$ (d) $[Ar]3d^{10} 4s^2 4p^3$
23. Which of the following is a polar molecule? [NEET Kar. 2013]
 (a) SF_4 (b) SiF_4
 (c) XeF_4 (d) BF_3
24. The outer orbitals of C in ethene molecule can be considered to be hybridized to give three equivalent sp^2 orbitals. The total number of sigma (σ) and pi (π) bonds in ethene molecule is [NEET Kar. 2013]
 (a) 1 sigma (σ) and 2 pi (π) bonds
 (b) 3 sigma (σ) and 2 pi (π) bonds
 (c) 4 sigma (σ) and 1 pi (π) bonds
 (d) 5 sigma (σ) and 1 pi (π) bonds
25. In which of the following ionisation processes the bond energy increases and the magnetic behaviour changes from paramagnetic to diamagnetic? [NEET Kar. 2013]
 (a) $N_2 \rightarrow N_2^+$ (b) $O_2 \rightarrow O_2^+$
 (c) $C_2 \rightarrow C_2^+$ (d) $NO \rightarrow NO^+$
26. The pair of species that has the same bond order in the following is: [NEET Kar. 2013]
 (a) O_2, B_2 (b) CO, NO^+
 (c) NO^-, CN^- (d) O_2, N_2
27. In which of the following pair both the species have sp^3 hybridization? [NEET Kar. 2013]
 (a) H_2S, BF_3 (b) SiF_4, BeH_2
 (c) NF_3, H_2O (d) NF_3, BF_3
28. XeF_2 is isostructural with [2013]
 (a) ICl_2^- (b) $SbCl_3$
 (c) $BaCl_2$ (d) TeF_2
29. Which of the following is paramagnetic? [2013]
 (a) O_2^- (b) CN^-
 (c) NO^+ (d) CO
30. Which one of the following molecules contains no π bond? [2013]
 (a) H_2O (b) SO_2
 (c) NO_2 (d) CO_2
31. Which of the following is electron - deficient? [2013]
 (a) $(SiH_3)_2$ (b) $(BH_3)_2$
 (c) PH_3 (d) $(CH_3)_2$
32. Be^{2+} is isoelectronic with which of the following ions? [2014]
 (a) H^+ (b) Li^+
 (c) Na^+ (d) Mg^{2+}
33. Which of the following molecules has the maximum dipole moment? [2014]
 (a) CO_2 (b) CH_4
 (c) NH_3 (d) NF_3
34. Which one of the following species has plane triangular shape? [2014]
 (a) N_3^- (b) NO_3^-
 (c) NO_2^- (d) CO_2
35. The correct bond order in the following species is: [2015]
 (a) $O_2^{2+} < O_2^- < O_2^+$ (b) $O_2^+ < O_2^- < O_2^{2+}$
 (c) $O_2^- < O_2^+ < O_2^{2+}$ (d) $O_2^{2+} < O_2^+ < O_2^-$
36. Which of the following pairs of ions are isoelectronic and isostructural? [2015]
 (a) ClO_3^-, CO_3^{2-} (b) SO_3^{2-}, NO_3^-
 (c) ClO_3^-, SO_3^{2-} (d) CO_3^{2-}, SO_3^{2-}
37. Which of the following options represents the correct bond order? [2015]
 (a) $O_2^- < O_2 < O_2^+$ (b) $O_2^- > O_2 < O_2^+$
 (c) $O_2^- < O_2 > O_2^+$ (d) $O_2^- > O_2 > O_2^+$
38. Maximum bond angle at nitrogen is present in which of the following? [2015]
 (a) NO_2^- (b) NO_2^+
 (c) NO_3^- (d) NO_2
39. Which of the following species contains equal number of σ - and π -bonds: [2015]
 (a) XeO_4 (b) $(CN)_2$
 (c) $CH_2(CN)_2$ (d) HCO_3^-

NEET/AIPMT (2013-2017) Questions

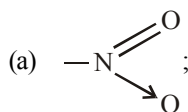
40. Decreasing order of stability of O_2 , O_2^- , O_2^+ and O_2^{2-} is :
 (a) $O_2^+ > O_2 > O_2^- > O_2^{2-}$ [2015 RS]
 (b) $O_2^{2-} > O_2^- > O_2 > O_2^+$
 (c) $O_2 > O_2^+ > O_2^{2-} > O_2^-$
 (d) $O_2^- > O_2^{2-} > O_2^+ > O_2$
41. In which of the following pairs, both the species are not isostructural ? [2015 RS]
 (a) $SiCl_4, PCl_4^+$
 (b) diamond, silicon carbide
 (c) NH_3, PH_3
 (d) XeF_4, XeO_4
42. The hybridization involved in complex $[Ni(CN)_4]^{2-}$ is (At. No. Ni = 28) [2015 RS]
 (a) dsp^2 (b) sp^3
 (c) d^2sp^2 (d) d^2sp^3
43. Consider the molecules CH_4 , NH_3 and H_2O . Which of the given statements is false? [2016]
 (a) The H–C–H bond angle in CH_4 , the H–N–H bond angle in NH_3 , and the H–O–H bond angle in H_2O are all greater than 90°
 (b) The H–O–H bond angle in H_2O is larger than the H–C–H bond angle in CH_4 .
 (c) The H–O–H bond angle in H_2O is smaller than the H–N–H bond angle in NH_3 .
 (d) The H–C–H bond angle in CH_4 is larger than the H–N–H bond angle in NH_3 .
44. Predict the correct order among the following : [2016]
 (a) lone pair - lone pair > lone pair - bond pair > bond pair - bond pair
 (b) lone pair - lone pair > bond pair - bond pair > lone pair - bond pair
 (c) bond pair - bond pair > lone pair - bond pair > lone pair - lone pair
 (d) lone pair - bond pair > bond pair - bond pair > lone pair - lone pair
45. Which of the following pairs of compounds is isoelectronic and isostructural ? [2017]
 (a) TeI_2, XeF_2 (b) IBr_2^-, XeF_2
 (c) IF_3, XeF_2 (d) $BeCl_2, XeF_2$
46. The species, having bond angles of 120° is :- [2017]
 (a) ClF_3 (b) NCl_3
 (c) BCl_3 (d) PH_3
47. Which of the following pairs of species have the same bond order ? [2017]
 (a) O_2, NO^+ (b) CN^-, CO
 (c) N_2, O_2^- (d) CO, NO

Hints & Solutions

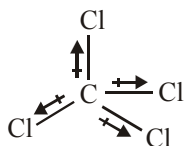
EXERCISE - 1

1. (b) Dative bond is formed between two atoms when the electrons of shared pair are contributed solely by one of the two atoms and it is directed toward that atom which do not contribute the electrons. It is represented by an arrow on the bond which is directed towards the electron recipient atom.

So, $-\text{N}^+ \equiv \text{NCl}^-$ is the only group among the given options which does not contain a dative bond.

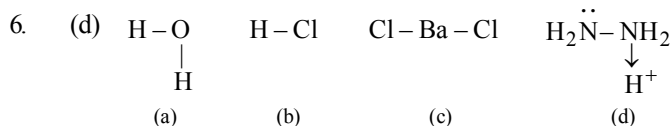


2. (b) The stability of the ionic bond depends upon the lattice energy which is expected to be more between Mg and F due to +2 charge on Mg atom.
3. (d) In CCl_4 , each C-Cl bond is polar but due to the very symmetrical tetrahedral arrangement they exactly cancel each other and hence CCl_4 have zero dipole moment.



So, none on these i.e. option (d) is correct choice.

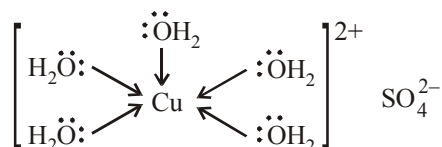
4. (b) For compounds containing cations of same charge, lattice energy increases as the size of the cation decrease. Thus, NaF has highest lattice energy. The size of cations is in the order $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$
5. (b) In KCN, K^+ and CN^- have ionic bond and $\text{C} \equiv \text{N}$ has covalent bond.



7. (d) The strength of a bond depends upon the extent of overlapping. s-s and s-p overlapping results in the formation of σ bond but extent of overlapping along internuclear axis is more in case of s-s overlapping than in s-p. p-p overlapping may result in σ bond if overlapping takes place along internuclear axis or may result in π -bond if sideways overlapping takes place. In any case the extent of overlapping is lesser in p-p than that of the other two, s-s and s-p. Hence the correct order is

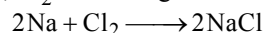
$$s-s > s-p > p-p.$$

8. (d) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ can be represented as

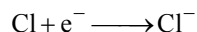
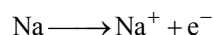


So, in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ one electrovalent bond, 5 coordinate bonds and covalent bonds are present.

9. (c) Higher the difference in electronegativity between the two atoms, more will be electrovalent character of the bond. Among given choices, calcium and hydrogen have maximum difference in their electronegativities.
10. (c) KF being highly ionic compound will dissolve most readily in water. (Like dissolves like).
11. (d) When a metal for example Na combines with a non metal e.g., Cl_2 . Following reaction occurs



In this process Na loses one electron to form Na^+ and Cl accepts one electron to form Cl^-



Therefore, in this process Cl gain electrons and hence its size increases.

12. (a)
13. (b) Hybridisation of the central atom in compound is given by

$$H = \frac{1}{2}[V + M - C + A]$$

where V = no. of valency electrons in central metal atom,

M = no. of monovalent atoms surrounding the central atom,

C = charge on cation and A = charge on anion

- For NO_2^- , $H = \frac{1}{2}[5 + 0 - 0 + 1] = 3$

sp^2 hybridisation

- For SF_4 , $H = \frac{1}{2}[6 + 4 - 0 + 0] = 5$

sp^3d hybridisation

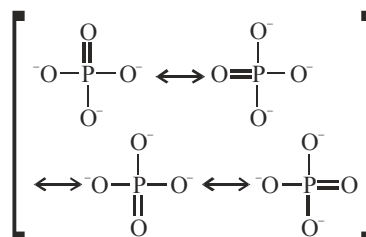
- For PF_6^- , $H = \frac{1}{2}[5 + 6 - 0 + 1] = 6$

sp^3d^2 hybridisation.

So, option (a) is correct choice.

14. (c) Bond order between P-O

$$= \frac{\text{no. of bonds in all possible direction}}{\text{total no. of resonating structures}} = \frac{5}{4} = 1.25$$

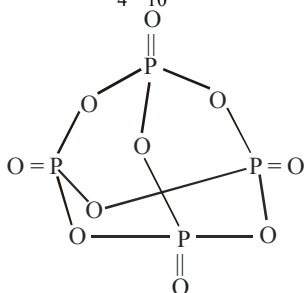


$$\text{Formal charge on oxygen} = -\frac{3}{4} = -0.75$$

15. (a) A compound having element with highest electronegativity will form strongest hydrogen bond.
16. (a) Bond angle increases with increase in s-character of hybridised orbital. The table given below shows the hybridised orbitals, their % s-character and bond angles.

Hybridised orbitals	% s-character	Bond angle
sp^3	25	109.5°
sp^2	33	120°
sp	50	180°

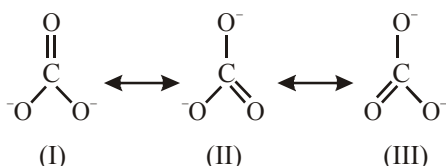
17. (a) Boron in BCl_3 has 6 electrons in outermost shell. Hence BCl_3 is an electron deficient compound.
18. (d) The structure of P_4O_{10} is



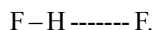
The number of σ bonds in it = 16

[Note: Single bonds are σ -bonds. Double bond consists of 1 σ and 1 π bond].

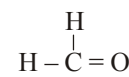
19. (b) There are three resonance structures of CO_3^{2-} ion.



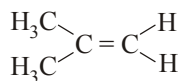
20. (c) Higher the electronegativity of the other atom, greater is the strength of hydrogen bond. Strongest hydrogen bond is between H and F.



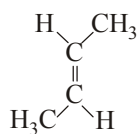
21. (a) Greater the difference in electronegativity between the two atoms, larger will be polarity and hence dipole moment. Thus (a) has maximum dipole moment.



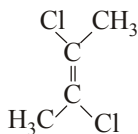
(a)
(C-O bond is more polar)



(b)
(very less polar)



(c)



(d)

Symmetrical molecules ($\mu = 0$)

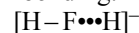
22. (b) In CN^- ion formal negative charge is on nitrogen atom due to lone pair of electrons.

23. (c) NH_3 undergoes H-bonding and hence has the highest b.p. Among the remaining hydrides i.e. PH_3 , AsH_3 and SbH_3 as we move from PH_3 to BiH_3 , the molecular mass increases. As a result the van der Waals forces of attraction increase and the boiling point increases regularly from PH_3 to BiH_3 .

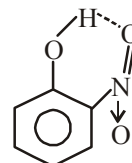
24. (a) Resonating structures can be written only for such molecules in which multiple bonds are present, eg, O_3



25. (c)
26. (d) HF forms linear polymeric structure due to hydrogen bonding.
27. (a) Square Planar Structure: XeF_4 and $[PtCl_4]^{2-}$
28. (c) In one $C \equiv N$, No. of π bonds = 2
So in $[Ag(CN_2)]^-$, No. of π bonds = $2 \times 2 = 4$
29. (c) HF_2 is the only compound among the given options which does not contain any coordinate bond because it has hydrogen bonding.

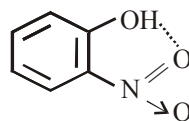


30. (b) The compounds having O or F or N along with hydrogen show hydrogen bonding and have high boiling points. So HI does not form hydrogen bonds and its boiling point is not affected.
31. (c) Ice has many hydrogen bonds which give rise to a cage-like structure of water molecules. This structure possesses larger volume and thus makes the density of ice low.
32. (c) Intramolecular hydrogen bonding is formed (within molecule) when the two groups capable of forming H-bonding are very near to each other.

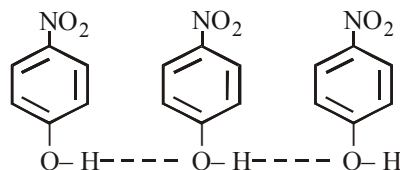


o-Nitrophenol

33. (c) *ortho*-Nitrophenol has intramolecular H-bonding



and *para*-nitrophenol has intermolecular H-bonding.



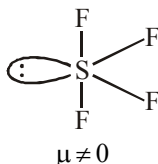
hence *o*-Nitrophenol is more volatile than *p*-Nitrophenol. Intermolecular H-bonds are stronger than intramolecular H-bonds.

34. (c) The bond length between carbon & carbon in sp^2 hybridisation (double bond) is $1.33 \text{ \AA}$.
35. (b) Both NO_2 and O_3 have an angular shape and hence will have a net dipole moment.

36. (c) As difference of electronegativity increases % ionic character increases and covalent character decreases i.e., electronegativity difference decreases covalent character increases.

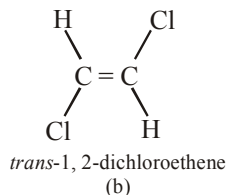
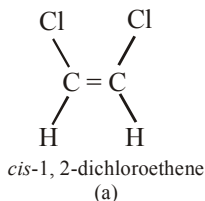
Further greater the charge on the cation and smaller the size more will be its polarising power. Hence covalent character increases.

37. (b) SF_4 has permanent dipole moment. SF_4 has sp^3d hybridization and see saw shape (irregular geometry).

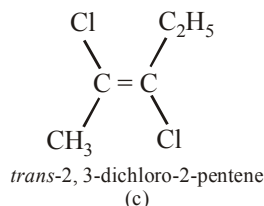


Whereas XeF_4 shows square planar geometry SiF_4 has tetrahedral shape and BF_3 has triangular planar shape. All these are symmetric molecules. Hence $\mu = 0$.

38. (d) Dipole moment is a vector quantity, hence dipole moment of a symmetrical molecule is zero.



Symmetrical hence
dipole moment = 0

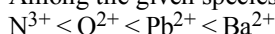


$\therefore$ (a) and (c), both show dipole moment.

39. (b) In NH_3 sp^3 hybridisation is found.
40. (a) According to Fajan's rule, as the charge on the cation increases, and size decreases, its tendency to polarise the anion increases. This brings more and more covalent nature to electrovalent compounds. Hence AlCl_3 shows maximum covalent character.
41. (d)
42. (a) In H_2 , both atoms are identical, so the molecule is non polar.
43. (d) According to Fajan's rule :

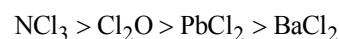
$$\text{Covalent character} \propto \frac{1}{\text{size of cation}} \\ \propto \text{size of anion}$$

Among the given species order of size of cations



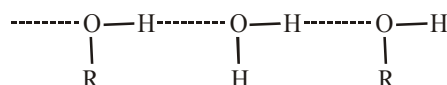
order of size of anions $\text{O}^{2-} > \text{Cl}^-$.

Hence the order of covalent character is



BaCl_2 is most ionic in nature.

44. (b) A substance is said to be soluble in water if it is capable of forming hydrogen bonds with water molecules as in methanol and ethanol.

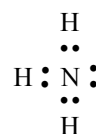


Hydrogen bonding between alcohol and water.

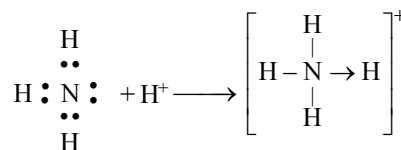
However, this hydrogen bonding is restricted when alkyl group of alcohol has four or more carbon atoms.

45. (d) Ionic compounds generally have high melting and boiling points because of the strong electrostatic force of attraction between oppositely charged ions. Consequently, a considerable amount of energy is required to overcome strong attractive inter-ionic forces and to break down the crystal lattice.
46. (a) The dipole moment of two dipoles inclined at an angle θ is given by the equation $\mu = \sqrt{X^2 + Y^2 + 2XY \cos \theta}$
 $\cos 90^\circ = 0$. Since the angle increases from $90^\circ - 180^\circ$, the value of $\cos \theta$ becomes more and more -ve and hence resultant decreases. Thus, dipole moment is maximum when $\theta = 90^\circ$.

47. (c) Benzene and the compounds having benzene ring show resonance. Hence, ethylamine does not show resonance.
48. (d) In case of anions having same charge as the size of anion increases, polarisability of anion also increases.
49. (c) Percent ionic character is given by following equation.
 $\% \text{ of ionic character} = 16(X_A - X_B) + 3.5(X_A - X_B)^2$
 From the above relation, it is clear that as soon as $(X_A - X_B)$ increases, % ionic character will also increase. Therefore, curve C show a correct path.
50. (a) Covalent bonds are formed by sharing of electrons. N forms 3 covalent bonds with 3 hydrogens.

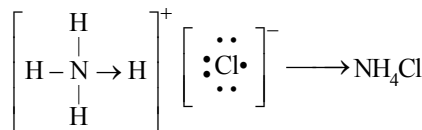


This leaves one lone pair of electron free which can be donated to H^+ to form ammonium ion NH_4^+ . This is called coordinate bond.



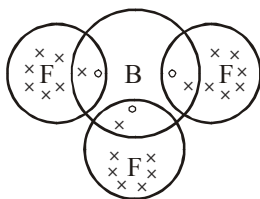
Covalent bonds are shown by straight line & coordinate by an arrow.

This NH_4^+ cation can gain electrons from Cl^- to form a electrovalent bond.

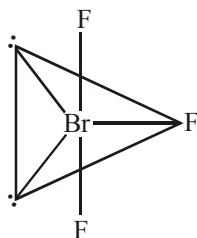


51. (c) CH_3^+ has sp^2 hybridization because s orbital has one electron and p orbitals of central atom C have only two electrons. Therefore s and 2p orbitals participate in hybridization.

52. (b) Equilateral or triangular planar shape involves sp^2 hybridization.
53. (c) The bond length decreases in the order $sp^3 > sp^2 > sp$. Because of the triple bond, the carbon-carbon bond distance in ethyne is shortest.
54. (b) BH_3 has sp^2 hybridization and hence does not have tetrahedral structure while all others have tetrahedral structures.
55. (a) We know that size of Na^+ ion is greater than Li^+ ion. Since bond length is directly proportional to atomic radius. Therefore, the bond length in LiF is less than that of NaF .
Option (a) is correct.
56. (a) For linear arrangement of atoms the hybridisation should be sp (linear shape, 180° angle). Only H_2S has sp^3 -hybridization and two lone pair of electrons on sulphur atom hence has angular shape while C_2H_2 , BeH_2 and CO_2 all involve sp -hybridization and hence have linear arrangement of atoms.
57. (b) BF_3 involves sp^2 -hybridization.
58. (a) Only those d orbitals whose lobes are directed along X, Y and Z directions hybridise with s and p orbitals. In other three d orbitals namely d_{xy} , d_{yz} and d_{xz} , the lobes are at an angle of 45° from both axis, hence the extent of their overlap with s and p orbitals is much lesser than $d_{x^2-y^2}$ and d_{z^2} orbitals.
59. (c) Acetylene has sp hybridization and linear structure $CH \equiv CH$
Hence, option (c) is correct.
60. (c) X is deficient of e^- . Y has $1e^-$ only. Therefore, Y is hydrogen. It forms covalent bond with X (halogen) by sharing 2 valence electrons
- $$:\ddot{X}::Y$$
61. (b) BF_3 does not follow octate rule because central atom, boron lacks an electron pair. Thus, it also acts as Lewis acid.



62. (c)

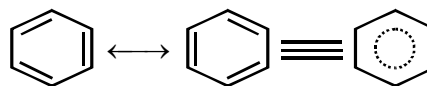


In BrF_3 , both bond pairs as well as lone pairs of electrons are present. Due to the presence of lone pairs of electrons (lp) in the valence shell, the bond angle is contracted and the molecule takes the T-shape. This is due to greater repulsion between two lone pairs or between a lone pair and a bond pair than between the two bond pairs.

63. (b)

List I Compound	List II Structure
(A) ClF_3	T-shaped
(B) PCl_5	Trigonal bipyramidal
(C) IF_5	Square pyramidal
(D) CCl_4	Tetrahedral
(E) XeF_4	Square planar

64. (c) Benzene has the following resonance structures—



Hence, its bond order is

$$\frac{\text{no of possible resonating structures}}{2} = 1.5.$$

65. (b) The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
107°	94°	92°	91°	90°

This can also be explained by the fact that as the size of central atom increases and its electronegativity decreases. Thus distance between bond pairs of electron increases and bp-bp repulsion decreases. As a result bond angle decrease from NH_3 to BiH_3 .

66. (d) Hybridisation present in a molecule can be findout by the following formula.

$$H = \frac{1}{2}(V + M - C + A)$$

Where V = no. of electrons in valence shell of central atom

M = no. of singly charged atoms

C = charge on cation

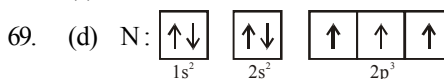
A = charge on anion

$$\text{So, } H(\text{in } ClF_3) = \frac{1}{2}[7 + 3 - 0 + 0] = 5$$

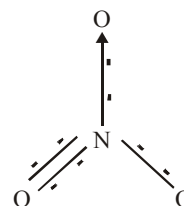
$\Rightarrow sp^3d$ Hybridisation

67. (d) PF_3 has pyramidal shape. Phosphorus exist in sp^3 hybridization state hence it exist in tetrahedral shape. But due to presence of lone pair its shape is pyramidal.

68. (a)



To form NO_3^- , nitrogen uses one p -electron for π -bond formation two p -electrons for σ -bond formation. $2s$ electrons are used for coordinate bond formation. Thus there is no lone pair on nitrogen but four bond pairs



70. (a) Shape (structure) of a species can be predicted on the basis of hybridisation of its central atom, which in turn can be known by determining the number of hybrid

bonds (H). Thus $H = \frac{1}{2}(V + X - C + A)$

For SiF_4 : $H = \frac{1}{2}(4 + 4 - 0 + 0) = 4$; sp^3

(Tetrahedral structure)

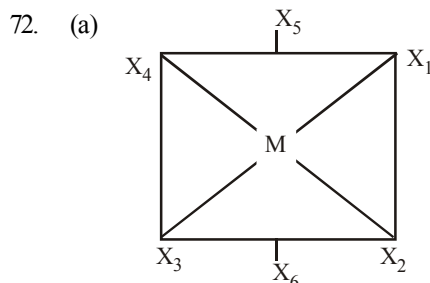
For SF_4 : $H = \frac{1}{2}(6 + 4 - 0 + 0) = 5$; sp^3d

(See saw structure due to presence of one lp of electrons on central atom)

Hence the two compounds have different structures

71. (c) Species	N_2	O_2	N_2^-	O_2^-
Bond order	3	2	2.5	1.5

The O-O bond in O_2^- decreases



Thus here bond angles between

$$X_4 - M - X_2 = 180^\circ$$

$$X_1 - M - X_3 = 180^\circ$$

$$X_5 - M - X_6 = 180^\circ$$

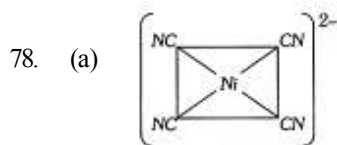
73. (a) BF_3 is sp^2 hybridised. So, it is trigonal planar. NH_3 , PCl_3 has sp^3 hybridisation hence has trigonal pyramidal shape. IF_3 has sp^3d hybridisation and has T-shape.

74. (a) Both XeF_2 and CO_2 have a linear structure.
 $\text{F} - \text{Xe} - \text{F}$ $\text{O} = \text{C} = \text{O}$

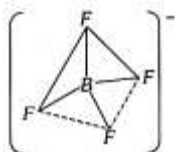
75. (c)

76. (b) Electronegativity difference is $4.0 - 1.20 = 2.8$ percentage ionic character is 72.24% when the electronegativity difference is 1.7, the % ionic character is approx 51%.

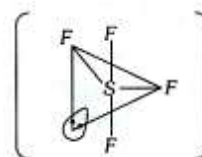
77. (a) Ionic character follows the order $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$



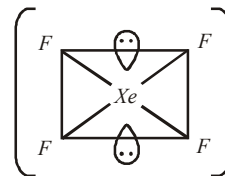
$[\text{Ni}(\text{CN})_4]^{2-}$ (dsp^2 square planar),



BF_4^- (sp^3 tetrahedral),



SF_4 (sp^3d see saw shaped)



XeF_4 (sp^3d^2 square planar),

79. (c) From amongst given species PH_3 , NH_3 and SbH_3 are all sp^3 hybridised. Their central atom has both bond pair as well as lone pair of electrons. The lone pair occupies the fourth orbital. CH_3^+ has only three pairs of electrons so it is sp^2 hybridised.

80. (b) Geometry of compounds can be determined by hybridisation, which in turn can be known by the following relation.

Hybridisation (H) = $\frac{1}{2}$ [No. of electrons in valence shell of central atom + No. of monovalent atoms - charge on cation + charge on anion]

- (i) SF_4 : $H = \frac{1}{2}(6 + 4 - 0 + 0) = 5$

sp^3d (trigonal bipyramidal but actual geometry is see saw due to presence of one lone pair of electrons).

- (ii) XeF_4 : $H = \frac{1}{2}(8 + 4 - 0 + 0) = 6$

sp^3d^2 (Octahedral but actually square planar due to presence of two lone pairs of electrons)

- (iii) NF_3 : $H = \frac{1}{2}(5 + 3 - 0 + 0) = 4$

sp^3 (tetrahedral but distorted due to one lone pair of electrons)

- (iv) SiF_4 : $H = \frac{1}{2}(4 + 4 - 0 + 0) = 4$

sp^3 (tetrahedral)

81. (b) Molecule or ion having sp hybridisation and no lone pair of electrons is linear.

Hybridisation = $\frac{1}{2}$ [No. of e^- in valence shell of central atom + No. monovalent atoms + Charge on anion - Charge on cation]

- (a) SO_2

$$H = \frac{1}{2}(6 + 0 + 0 - 0)$$

$$= 3 \quad sp^2 \text{ (trigonal planar shape)}$$

- (b) CO_2

$$H = \frac{1}{2} (4 + 0 + 0 - 0) = 2 \text{ } sp \text{ (linear shape)}$$



$$H = \frac{1}{2} (7 + 0 + 1 - 0) = 4 \text{ } sp^3 \text{ (tetrahedral)}$$



$$H = \frac{1}{2} (5 + 0 + 1 - 0) = 3 \text{ } sp^2 \text{ (trigonal planar)}$$

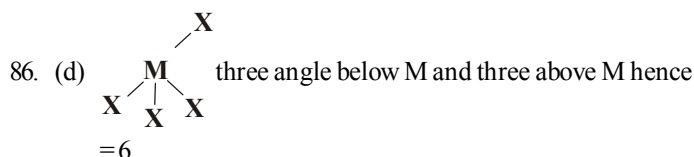
$\therefore \text{CO}_2$ has linear shape.

82. (a) According to VSEPR theory, trigonal bipyramidal geometry results from sp^3d or dsp^3 hybridisation. dsp^2 hybridisation results in square planar geometry, while d^2sp^3 leads to octahedral shape.
83. (b) SeF_4 has distorted tetrahedral geometry while, CH_4 has tetrahedral geometry.

84. (b)

Molecule	Hybridization
SO_3	sp^2
C_2H_2	sp
C_2H_4	sp^2
CH_4	sp^3
CO_2	sp

85. (d)



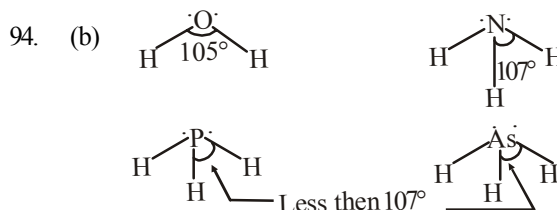
87. (c) s -character $\propto$ bond angle
For 25% s character (as in sp^3 hybrid orbital), bond angle is 109.5° , for 33.3% s character (as in sp^2 hybrid orbital), bond angle is 120° and for 50% s character (as in sp hybrid orbital), bond angle is 180° .
Similarly, when the bond angle decreases below 109.5° , the s -character will decrease accordingly.
Decreasing in angle = $120^\circ - 109.5^\circ = 10.5^\circ$
Decrease in s -character = $33.3 - 25 = 8.3$
Actual decrease in bond angle = $109.5^\circ - 105^\circ = 4.5^\circ$
Expected decrease in s -character

$$= \frac{8.3}{10.5} \times 4.5 = 3.56\%$$

Thus, the s -character should decrease by about 3.56% i.e., s -character = $25 - 3.56 = 21.44\%$

88. (c) Because of the triple bond the carbon - carbon bond distance in ethyne is shortest.
89. (c) Hybridisation of N = $\frac{1}{2} [5 + 3 + 0 - 0] = 4$ hence sp^3
90. (d) $\text{CH}_2=\text{C}=\text{CH}-\text{CH}_3$ 1, 2 -butadiene.
91. (c)
92. (c) H_2O , NH_3 and CH_4 all are sp^3 hybridized due to lp-lp repulsions, bond angle in H_2O (104.5°) is lower than in NH_3 (107°) which have one lp and CH_4 ($109^\circ 28'$) which have no lp BeF_2 on the other hand, has sp hybridization and hence has a bond angle of 180° .

93. (b) SO_4^{2-} ion is tetrahedral since hybridization of S is sp^3 .



95. (b) NH_3 has pyramidal structure, as nitrogen is sp^3 hybridised. This is due to the presence of lone pair of electrons on N atom.
96. (c) $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$ is sp hybridised
97. (a) A σ -bond is stronger than a π -bond hence option (a) is not correct. Sigma (σ) bonds are formed by head on overlap of unhybridised s - s , p - p or s - p orbitals and hybridised orbitals (sp , sp^2 , sp^3 , sp^3d and sp^3d^2) hence σ bonds are strong bonds. Whereas Pi (π)-bonds are formed by sideways overlap of unhybridised p - and d -orbitals hence π bonds are weak bonds.
98. (a) Linear combination of two hybridized orbitals leads to the formation of sigma bond.
99. (a) For π -overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei.

100. (d) Total no. of electrons in $\text{O}_2^{2-} = 16 + 2 = 18$

Distribution of electrons in molecular orbital

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

Antibonding electrons = 8 (4 pairs)

101. (b) In $\text{CH}_3\text{CH}_2\text{OH}$ underlined C is forming 4 σ bonds, hence sp^3 hybridisation. In others it is sp^2 hybridised (due to 3 σ bonds).

102. (c) As sigma bond is stronger than the π (pi) bond, so it must be having higher bond energy than π (pi) bond.

103. (c) $\text{N}_2^+ = 7 + 7 - 1 = 13$ electrons

Configuration is

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^1$$

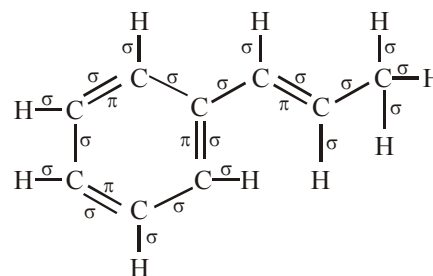
Bond order =

$$\frac{1}{2} \left(\begin{array}{l} \text{No. of } e^- \text{ s in bonding} \\ \text{molecular orbital} \end{array} - \begin{array}{l} \text{No. of } e^- \text{ s in antibonding} \\ \text{molecular orbital} \end{array} \right)$$

$$= \frac{1}{2} (9 - 4) = \frac{1}{2} \times 5 = 2.5$$

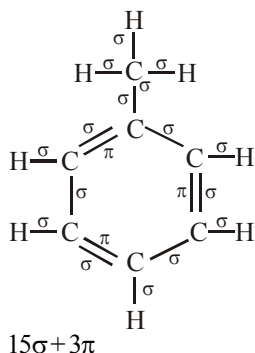
104. (b) Only d of S and p of O can be involved in π bonding.

105. (c) The first bond between any two C atoms having multiple bonds is σ and rest are π bonds. Draw detailed structure of compound and find the total bonds in it



$\therefore$ 19 σ bonds and 4 π bonds.

106. (c)



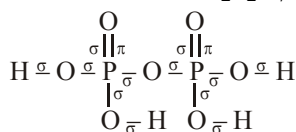
15σ + 3π

107. (b) $O_2^- = 16 + 1 = 17$ Molecular orbital configuration of O_2^- (superoxide ion).

$$KK\sigma 2s^2\sigma^* 2s^2\sigma 2p_z^2\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

$$\text{Bond order} = \frac{8-5}{2} = \frac{3}{2} = 1.5$$

108. (c)

109. (d) Bond structure of $H_2P_2O_7$ is following

12σ, 2dπ - pπ bonds.

110. (b) More will be the electronegativity of X lesser will be the bond length of X-O bond.

111. (d) M.O. configuration of NO^+ is :

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$$

and M.O. configuration of NO is :

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$$

112. (a) $CH_2 = CH - C \equiv N$ 3 σ bonds (sp^2 hybridisation); 2 σ bonds (sp - hybridisation) $C_1 = 3$ σ bonds, $C_2 = 3$ σ bonds, $C_3 = 2$ σ bonds

113. (a) Molecular orbital electronic configuration of these species are :

$$O_2^-(17e^-) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

$$O_2(16e^-) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

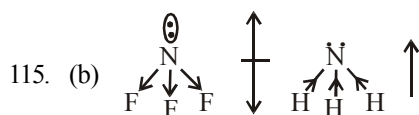
$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$$

$$O_2^{2-}(18e^-) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

Hence number of antibonding electrons are 7, 6 and 8 respectively.

114. (a)

 $:N \equiv N - \ddot{O}:$ octet of each atom is complete.116. (c) $H_2^+ : (\sigma 1s^1)$

$$\therefore \text{B.O.} = \frac{1}{2}(1-0) = \frac{1}{2}$$

$$H_2^- : (\sigma 1s^2)(\sigma^* 1s^1)$$

$$\therefore \text{B.O.} = \frac{1}{2}(2-1) = \frac{1}{2}$$

Even though the bond order of H_2^+ and H_2^- are equal but H_2^+ is more stable than H_2^- as in the latter, an electron is present in the antibonding ($\sigma^* 1s$) orbital of higher energy.

117. (b) In H - bonding atoms involved are F, O and N.

118. (c) $O^{\delta-} = C^{\delta+} = O^{\delta-}$ linear molecule hence $\mu = 0$.119. (c) Both BrO_3^- and XeO_3 have sp^3 hybridization but due to presence of one lp of electrons they have trigonal pyramidal geometry.

120. (d) Calculating the bond order of various species.

$$O_2^- : KK\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$$

$$\text{B.O.} = \frac{1}{2}(N_b - N_a)$$

$$= \frac{8-5}{2} \text{ or } 1.5$$

$$NO = KK\sigma 2s^2, \sigma^* 2s^2, 6\sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1$$

$$\text{B.O.} = \frac{N_b - N_a}{2} = \frac{8-3}{2} \text{ or } 2.5$$

$$= C_2^{2-} : KK\sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$$

$$\text{B.O.} = \frac{N_b - N_a}{2} = \frac{8-2}{2} \text{ or } 3$$

$$He_2^{2+} = \sigma 1s^2 \sigma^* 1s^1$$

$$\text{B.O.} = \frac{N_b - N_a}{2} = \frac{2-1}{2} \text{ or } 0.5$$

From these values we conclude that the correct order of increasing bond order is

$$He_2^{2+} < O_2^- < NO < C_2^{2-}$$

121. (d) Due to intermolecular hydrogen bonding in methanol, it exist as associated molecule.

122. (c) For $SbCl_5^{2-}$, $H = \frac{5+5+2}{2} = 6$ means sp^3d^2 hybridization IF_3 , SF_4 , and PCl_5 ; all have sp^3d hybridization.123. (b) In NO_3^- , nitrogen have sp^2 hybridisation, thus planar in shape. In H_3O^+ , oxygen is in sp^3 hybridisation, thus tetrahedral geometry is expected but due to presence of one lp of electrons on central oxygen atom it is pyramidal in shape.

124. (c) NH_4^+ : sp^3 hybridisation
 CH_4 : sp^3 hybridisation
 SF_4 : sp^3d hybridisation
 BF_4^- : sp^3 hybridisation

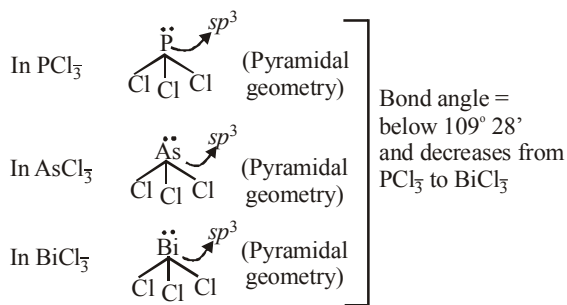
125. (b) Bond order of $\text{Be}_2 = 0$, hence Be_2 cannot exist.

EXERCISE - 2

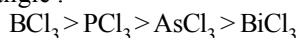
1. (c) $\text{H}-\text{C} \begin{array}{c} \text{O} \\ \text{O} \end{array} \longleftrightarrow \text{H}-\text{C} \begin{array}{c} \text{O} \\ \text{O} \end{array} \longleftrightarrow$ or Resonance

hybrid $\left[\text{H}-\text{C} \begin{array}{c} \text{O} \\ \text{O} \end{array} \right]^-$ due to resonance C - O bond length is the same.

2. (b) BiCl_3 : $\text{Cl}-\text{Bi} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array}$; sp^2 - Hybridisation (Trigonal geometry); Bond angle = 120°



In these, order of bond angle :



3. (d) $\text{H} = \frac{1}{2} \left[\begin{array}{ccc} \text{No. of electrons} & \text{No. of mono-} & \text{charge} \\ \text{in valence shell} & \text{valent atoms} & \text{on} \\ \text{of central atom} & & \text{anion} \end{array} + \begin{array}{ccc} \text{charge} & & \\ \text{on} & & \\ \text{cation} & & \end{array} \right]$

For SF_4 :

$$= \frac{1}{2} (6 + 4 + 0 - 0) = 5$$

S is sp^3d hybridised in SF_4 . Thus SF_4 has 5 hybrid orbitals out of which only four are used to form bonds with four F atoms leaving one lone pair of electrons on sulphur.

For CF_4 : $\text{H} = \frac{1}{2} [4 + 4 + 0 - 0] = 4$ $\therefore sp^3$ hybridisation

Since all the four orbitals of carbon are involved in bond formation, no lone pair is present on C atom

For XeF_4 : $\text{H} = \frac{1}{2} (8 + 4 + 0 - 0) = 6$, $\therefore sp^3d^2$

hybridization of the six hybrid orbitals, out of which only four form bonds with F atoms, leaving behind two lone pairs of electrons on Xe.

4. (d) The shape of BF_3 is trigonal planar $\begin{array}{c} \delta^- \\ \text{F} \\ \delta^- \end{array} \text{B} \begin{array}{c} \delta^+ \\ \text{F} \\ \delta^- \end{array}$ and $\mu = 0$ hence it is non polar. The shape of NF_3 is pyramidal $\begin{array}{c} \delta^+ \\ \text{N} \\ \delta^- \end{array} \text{F} \begin{array}{c} \delta^- \\ \text{F} \\ \delta^- \end{array}$ and $\mu \neq 0$ hence it is polar.

5. (a) Number of electrons in each species are
 $\text{CN}^- = 6 + 7 + 1 = 14$
 $\text{CO} = 6 + 8 = 14$
 $\text{NO}^+ = 7 + 8 - 1 = 14$
Each of the species has 14 electrons which are distributed in MOs as below
For CO and CN^-

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \{ \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2 \}$$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

For NO^+

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2$$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

6. (c) Bond energy $\propto$ Bond order
Bond order can be determined by MO configuration.
 NO : No. of electrons = $7 + 8 = 15$

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1$$

$$\therefore \text{Bond order} = \frac{10 - 5}{2} = 2.5$$

NO^+ : No. of electrons = $15 - 1 = 14$

Delete $\pi^* 2p_x^1$ from NO configuration

$$\therefore \text{Bond order} = \frac{10 - 4}{2} = 3$$

NO^- : No. of electrons = $15 + 1 = 16$

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2,$$

$$\pi^* 2p_x^1 = \pi^* 2p_y^1$$

$$\therefore \text{Bond order} = \frac{10 - 6}{2} = 2$$

$\therefore$ Bond order; hence bond strength

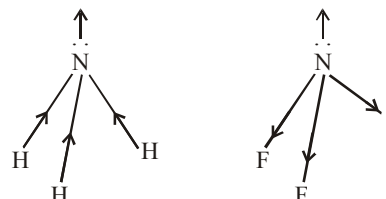
$$\text{NO}^+ > \text{NO} > \text{NO}^-$$

7. (b) For T-shape geometry the molecule must have 3 bonded pair and 2 lone pair of electrons.
8. (a) Structure of CO_2 is linear $\text{O}=\text{C}=\text{O}$ while that of

H_2O is  i.e., bent structure so in CO_2 resultant dipole moment is zero while that of H_2O has significant value.

9. (a) $\text{CH}_3 - \text{C} \begin{array}{c} \text{O} \\ \text{O} \end{array} = \text{CH}_2$ has 9 σ , 1 π and 2 lone pairs.

10. (d) H_3O_2^- species H bonding in H_2O
- (i) $\left[\begin{array}{c} \text{O}-\text{H} \cdots \text{O}-\text{H} \\ | \\ \text{H} \end{array} \right]^-$ (ii) $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{O}-\text{H} \cdots \text{O}-\text{H} \end{array}$
- (iii) H_5O_2^+ (H-bonding) (iv) H_3O^+ (no H-bonding)
- $\left[\begin{array}{c} \text{H} \quad \text{O} \cdots \text{H}-\text{O} \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \right]^+$ $\left[\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{O} \cdots \text{H} \\ | \\ \text{H} \end{array} \right]^+$
11. (d) $\text{H}-\text{C}=\text{C}^*-\text{O}-\text{H}$
 The star marked carbon has a valency of 5 and hence this formula is not correct.
12. (b) In amine the nitrogen is sp^3 hybridised and in amide the nitrogen is sp^2 hybridised.
13. (c) Since water is polar in nature and like dissolves like, the coating must be nonpolar to polar manner.
14. (b) The removal of an electron from a diatomic molecule may increase the bond order as in the conversion $\text{O}_2(2) \longrightarrow \text{O}_2^+(2.5)$ or decrease the bond order as in the conversion, $\text{N}_2(3.0) \longrightarrow \text{N}_2^+(2.5)$. As a result, the bond energy may increase or decrease. Thus, statement (b) is incorrect.
15. (d) Nitrogen can not be pentavalent as it has no d -orbitals.
16. (c) The b.p. of p -nitrophenol is higher than that of o -nitrophenol because in p -nitrophenol there is intermolecular H-bonding but in o -nitrophenol it is intramolecular H-bonding.
17. (a) The group moments of $-\text{NO}_2$, $-\text{OH}$, $-\text{Cl}$ and $-\text{CH}_3$ respectively are 3.98, 1.6, 1.55 and 0.4D.
18. (b) Resultant of two C-X dipoles in 1, 4 positions is zero. The resultant of other two C-X dipoles in 3, 5 positions
 $= \sqrt{1.5^2 + 1.5^2 + 2 \times 1.5 \times 1.5 \cos 120^\circ} = 1.5D$
19. (d) As there is no lone pair on boron in BCl_3 therefore no repulsion takes place. But there is a lone pair on nitrogen in NCl_3 . Therefore repulsion takes place. Thus BCl_3 is planar molecule but NCl_3 is a pyramidal molecule.
20. (b) Group moment of $-\text{NO}_2$ is $-3.98D$ (acting towards the benzene ring) and that of $-\text{NH}_2$ is $+1.5D$ (acting away from the group). Hence moments of both the groups in p -positions will act in the same direction.
21. (d) In alkynes the hybridisation is sp i.e., each carbon atom undergoes sp hybridisation of one s and one p orbital to form two sp -hybrid orbitals. Out of which one overlaps to form C-C σ bond and other overlaps with half filled orbital of H forming σ -bond. The other two $2p$ -orbitals remain unhybridised and form two π -bonds via sidewise overlapping.
 Hence two π bond and one sigma bond between C—C lead to cylindrical shape.
22. (d) N_2^+ is paramagnetic
 $\sigma 1s^2, \sigma^* 1s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^1$
23. (c) The electronic configuration of As is
 $\text{As} = \underbrace{[\text{Ar}] 3d^{10} 4s^1 4p_x^1 4p_y^1 4p_z^1 4d^1}_{\downarrow sp^3 d \text{ hybridisation}}$
 Thus the hybridisation involved in the AsF_5 molecule is trigonal bipyramidal. So, the hybrid orbitals used are s, p_x, p_y, p_z, d_z^2 .
24. (c) As dipole moment = electric charge $\times$ bond length
 D. M. of AB molecule
 $= 4.8 \times 10^{-10} \times 2.82 \times 10^{-8} = 13.53D$
 D.M. of CD molecule
 $= 4.8 \times 10^{-10} \times 2.67 \times 10^{-8} = 12.81D$
 Now % ionic character
 $= \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of pure ionic compound}} \times 100$
 then % ionic character in
 $\text{AB} = \frac{10.41}{13.53} \times 100 = 76.94\%$
 % ionic character in
 $\text{CD} = \frac{10.27}{12.81} \times 100 = 80.17\%$
25. (c) Structure I has two resonance forms, which make the hydrogen bonding more stable. The II molecule has no such resonance stabilization.
26. (c) Number of hybrid orbitals of P in $\text{PO}_4^{3-} = \frac{1}{2} [5 + 0 + 3] = 4 (sp^3)$
 No. of hybrid orbitals of N in $\text{NO}_3^- = \frac{1}{2} [5 + 0 + 1] = 3 (sp^2)$
 No. of hybrid orbitals of $\text{I}^+ (5s^2 5p_x^2 5p_y^1 5p_z^1) : (sp^3)^2 (sp^3)^1 (sp^3)^1$
 I-atom in excited state : $5s^2 5p^4 5d_{z^2}^1 5d_{x^2-y^2}^0$
 I-atom is $sp^3 d^2$ hybridised state in $\text{ICl}_4^- : (sp^3 d^2) (sp^3 d^2) (sp^3 d^2)^1 (sp^3 d^2)^1 (sp^3 d^2)^0$ - Two lps occupy the axial positions of octahedron and the shape of ICl_4^- becomes square planar.
27. (c) Dissociation energy of any molecule depends upon its bond order. Bond order in N_2 molecule is 3 while bond order in N_2^+ is 2.5. Further we know that more the Bond order, more is the stability and more is the bond dissociation energy.
28. (c) In $\text{X}-\text{H} \cdots \text{Y}$, X and Y both are electronegative elements (i.e. attracts the electron pair) then electron density on X and Y will increase and on H will decrease.
29. (a) In NH_3 the atomic dipole (orbital dipole due to lone pair) and bond dipole are in the same direction whereas in NF_3 these are in opposite direction so in the former case they are added up whereas in the latter case net result is reduction of dipole moment. It has been shown in the following figure :



30. (d) The bond angles HXH vary in the order : $\text{NH}_3 > \text{PH}_3$
 $\text{AsH}_3 > \text{SbH}_3$. In the formation of XH_4^+ , the bond angle
 HXH increases to $109^\circ 28'$. Hence, maximum increase
 in the bond angle will be for SbH_3 .
31. (b) On changing N_2 to N_2^+ , B.O. decreases from 3 to 2.5
 whereas on changing O_2 to O_2^+ , B.O. increases from 2
 to 2.5. In former case, the bond dissociation energy
 decreases and in the latter case, it increases.
32. (d) In a linear symmetrical molecule like BeF_2 , the bond
 angle between three atoms is 180° , hence the polarity
 due to one bond is cancelled by the equal polarity due
 to other bond, while it is not so in angular molecules,
 like H_2O .
33. (b) Now since bond order of NO^+ (3) is higher than that of
 NO (2.5). Thus bond length of NO^+ will be shorter.
34. (b) The p -orbital has equal sized lobes whereas an sp
 hybrid orbital has more probability density on one side.
 Hence, sp orbital is more directional in character.
35. (c) ns^2 electrons in the heavier elements, like lead, remain
 paired and do not take part in bonding. Thus, Pb^{2+} is
 more stable than Pb^{4+} .
36. (b) $\text{O}_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\left\{ \begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right\}, \left\{ \begin{array}{l} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{array} \right\}$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

(two unpaired electrons in antibonding molecular orbital)

$$\text{O}_2^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \left\{ \begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right\}, \left\{ \begin{array}{l} \pi^* 2p_x^1 \\ \pi^* 2p_y^0 \end{array} \right\}$$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

(One unpaired electron in antibonding molecular orbital)

Hence O_2 as well as O_2^+ both are paramagnetic, and

bond order of O_2^+ is greater than that of O_2 .

37. (a) Its conjugate base (i.e. NH_3) is most stable.

38. (c) The b.o in $\text{Cl}-\text{O}^-$ is 1
 The b.o in $\text{O}=\text{Cl}-\text{O}^-$ is 1.5

$$\text{The b.o. in } \text{O}=\text{Cl}=\text{O} \text{ is } \frac{5}{3} = 1.66$$

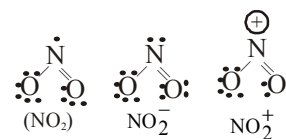
$$\begin{array}{c} \text{O} \\ | \\ \text{O}^- \end{array}$$

$$\text{The b.o. in } \text{O}=\text{Cl}(\text{O})-\text{O}^- \text{ is } \frac{7}{4} = 1.75$$

$$\begin{array}{c} \text{O} \\ || \\ \text{O} \end{array}$$

The bond length increases as b.o. decreases.

39. (b) From the structure of three species we can determine
 the number of lone pair electron(s) on central atom (i.e.
 N atom) and thus the bond angle.



We know that higher the number of lone pair electron(s)
 on central atom, greater is the lp – lp repulsion. Thus
 smaller is bond angle.

The correct order of bond angle is

$\text{NO}_2^- < \text{NO}_2 < \text{NO}_2^+$ i.e., option (b) is correct.

40. (c) On determining hybridisation from $H = 1/2(V + M - C + A)$.
 The hybridisation of BF_3 , NO_2^- , NH_2^- and H_2O are
 sp^2 , sp^2 , sp^3 and sp^3 respectively.

41. (a) Molecular orbital configuration of

$$\text{N}_2^{2-} = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, -$$

$$\left\{ \begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right\}, \sigma 2p_z^2, \left\{ \begin{array}{l} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{array} \right\}$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

$$\text{N}_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \left\{ \begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right\}, \sigma 2p_z^2, \left\{ \begin{array}{l} \pi^* 2p_x^1 \\ \pi^* 2p_y^0 \end{array} \right\}$$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

$$\text{N}_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \left\{ \begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right\}, \sigma 2p_z^2$$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

$\therefore$ The correct order is $= \text{N}_2^{2-} < \text{N}_2^- < \text{N}_2$

42. (a) Hybridisation $= \frac{1}{2}$ [No. of valence electrons of central
 atom + No. of monovalent atoms attached to it +
 Negative charge if any – Positive charge if any]

$$\text{NO}_2^- \quad H = \frac{1}{2}[5 + 0 + 1 - 0] = 3 = sp^2$$

$$\text{NO}_3^- \quad H = \frac{1}{2}[5 + 0 + 1 - 0] = 3 = sp^2$$

$$\text{NH}_2^- \quad H = \frac{1}{2}[5 + 2 + 1 + 0] = 4 = sp^3$$

$$\text{NH}_4^+ \quad H = \frac{1}{2}[5 + 4 + 0 - 1] = 4 = sp^3$$

$\text{SCN}^- = sp$

i.e., NO_2^- and NO_3^- have same hybridisation.

43. (a) $\text{O}_2 (16) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$$

$$\text{B.O.} = \frac{1}{2}(\text{N}_b - \text{N}_a) = \frac{1}{2}(10 - 6) = 2$$

$$\text{O}_2^+ (15) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^0$$

$$\text{B.O.} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 5) = 2.5$$

$$\text{O}_2^- (17) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$$

$$\text{B.O.} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 7) = 1.5$$

$$\text{O}_2^{2-} (18) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

$$\text{B.O.} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 8) = 1$$

Since, the bond length decreases as the bond order increases, hence, O_2^+ have least bond length.

44. (c) MOT configurations of O_2 and O_2^+ :

$$\text{O}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$$

$$(\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$$

Number of unpaired electrons = 1, so paramagnetic.

$$\text{O}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$$

$$(\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$$

Number of unpaired electrons = 2, so paramagnetic.

45. (d) BF_4^- hybridisation sp^3 , tetrahedral structure.

NH_4^+ hybridisation sp^3 , tetrahedral structure.

46. (b) $(\text{O}_2) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = \frac{4}{2} = 2$$

$$(\text{O}_2^+ \text{ ion}) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 5}{2} = \frac{5}{2} = 2\frac{1}{2}$$

$$(\text{O}_2^-) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$$

$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10 - 7}{2} = \frac{3}{2} = 1\frac{1}{2}$$

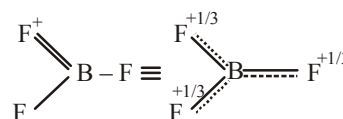
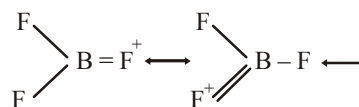
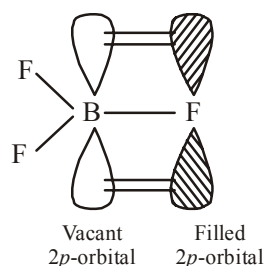
$$(\text{O}_2^{2-}) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 8}{2} = \frac{2}{2} = 1$$

47. (c) Greater the difference between electro-negativity of bonded atoms, stronger will be the bond. Since F is most electronegative hence F—H F is the strongest bond.

48. (b) The delocalised $p\pi - p\pi$ bonding between filled p -orbital of F and vacant p -orbital of B leads to shortening of B—F bond length which results in higher bond dissociation energy of the B—F bond.



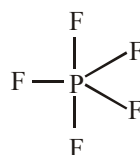
49. (d) Calcium carbide exists as Ca^{2+} and C_2^{2-} . According to the molecular orbital model, C_2^{2-} should have molecular orbital configuration :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$$

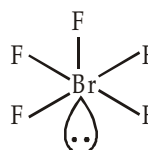
$$\{\pi 2p_x^2 = \pi 2p_y^2\}, \sigma 2p_z^2$$

Thus M.O. configuration suggests that it contains one σ & 2π bonds.

50. (c) PF_5 trigonal bipyramidal



BrF_5 square pyramidal (distorted due to presence of one lp of electrons on central atom)



51. (d) (i) In Na_2O_2 , we have O_2^{2-} ion. Number of valence electrons of the two oxygen in O_2^{2-} ion = $8 \times 2 + 2 = 18$ which are present as follows

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \{\pi 2p_x^2 = \pi 2p_y^2,$$

$$\{\pi^* 2p_x^2 = \pi^* 2p_y^2\}$$

$\therefore$ Number of unpaired electrons = 0, hence, O_2^{2-} is diamagnetic.

- (ii) No. of valence electrons of all atoms in

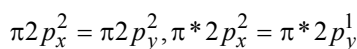
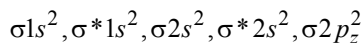
$$\text{O}_3 = 6 \times 3 = 18.$$

Thus, it also, does not have any unpaired electron, hence it is diamagnetic.

- (iii) No. of valence electrons of all atoms in N_2O

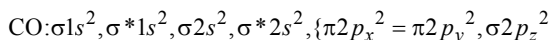
$$= 2 \times 5 + 6 = 16. \text{ Hence, here also all electrons are paired. So it is diamagnetic.}$$

- (iv) In KO_2 , we have O_2^- . No. of valence electrons of all atoms in $\text{O}_2^- = 2 \times 8 + 1 = 17$,

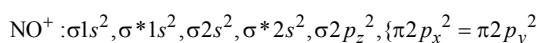


Thus it has one unpaired electron, hence it is paramagnetic.

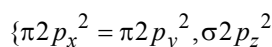
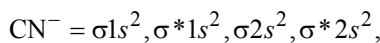
52. (a) Molecular electronic configuration of



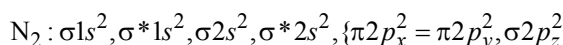
$$\text{Therefore, bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$



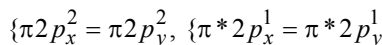
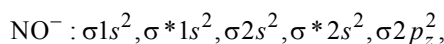
$$\text{Bond order} = \frac{10 - 4}{2} = 3$$



$$\text{Bond order} = \frac{10 - 4}{2} = 3$$



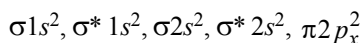
$$\text{Bond order} = \frac{10 - 4}{2} = 3$$



$$\text{Bond order} = \frac{10 - 6}{2} = 2$$

$\therefore \text{NO}^-$ has different bond order from that in CO.

53. (a) Molecular orbital configuration of B_2 (10) as per the condition given in question will be



$$\text{Bond order of } \text{B}_2 = \frac{6 - 4}{2} = 1.$$

B_2 will be diamagnetic.

54. (d) $\text{OSF}_2: \text{H} = \frac{6 + 2}{2} = 4.$

It has 1 lone pair.



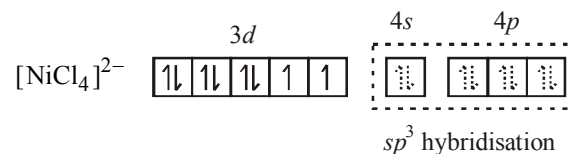
(Shape is trigonal pyramidal)

The shapes of SO_3 , BrF_3 and SiO_3^{2-} are trigonal planar respectively.

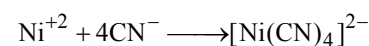
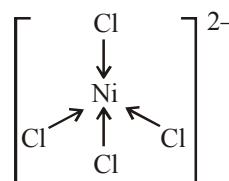
55. (b) $\text{Ni}^{+2} + 4\text{Cl}^- \longrightarrow [\text{NiCl}_4]^{2-}$
 sp^3

$[\text{NiCl}_4]^{2-} = 3d^8$ configuration with nickel in +2 oxidation state, Cl^- being weak field ligand does not compel for pairing of electrons.

So,

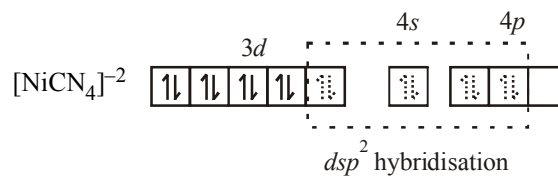


Hence, complex has tetrahedral geometry

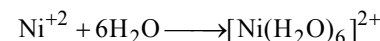
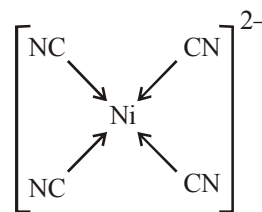


$[\text{Ni}(\text{CN})_4]^{2-} = 3d^8$ configuration with nickel in +2 oxidation state, CN^- being strong field ligand compels for pairing of electrons.

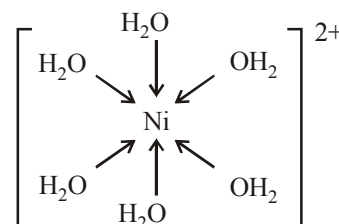
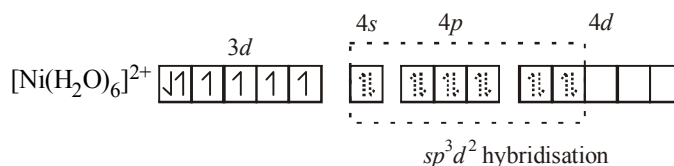
So,



Hence, complex has square planar geometry.



$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} = 3d^8$ configuration with nickel in +2 oxidation state. As with $3d^8$ configuration two d -orbitals are not available for d^2sp^3 hybridisation. So, hybridisation of Ni (II) is sp^3d^2 and Ni (II) with six co-ordination will have octahedral geometry.



56. (b) Allene (C_3H_4) is $H_2C \overset{sp^2}{=} \overset{sp}{C} = \overset{sp^2}{CH_2}$

57. (a) & (b) The molecular orbital structures of C_2 and N_2 are

$$N_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2$$

$$C_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_y^2 \pi 2p_z^2$$

Both N_2 and C_2 have paired electrons, hence they are diamagnetic.

58. All options are correct,

(a) $ONCl = 8 + 7 + 17 = 32e^-$
 $ONO^- = 8 + 7 + 8 + 1 = 24e^-$ } not isoelectronic

(b)  The central atom is sp^2 hybridized with one lone pair.

(c) It is a pale blue gas. At -249.7° , it forms violet black crystals.

(d) It is diamagnetic in nature due to absence of unpaired electrons.

59. (c) $H_2^{2+} = \sigma 1s^0 \sigma^* 1s^0$

$$\text{Bond order for } H_2^{2+} = \frac{1}{2}(0 - 0) = 0$$

$$He_2 = \sigma 1s^2 \sigma^* 1s^2$$

$$\text{Bond order for } He_2 = \frac{1}{2}(2 - 2) = 0$$

so both H_2^{2+} and He_2 does not exist.

60. (b) $Li_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2$

$$\therefore \text{Bond order} = \frac{1}{2}(4 - 2) = 1$$

$$Li_2^+ = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^1$$

$$\text{B.O.} = \frac{1}{2}(3 - 2) = 0.5$$

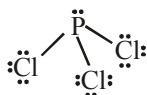
$$Li_2^- = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^1$$

$$\text{B.O.} = \frac{1}{2}(4 - 3) = 0.5$$

The bond order of Li_2^+ and Li_2^- is same but Li_2^+ is more stable than Li_2^- because Li_2^+ is smaller in size and has 2 electrons in antibonding orbitals whereas Li_2^- has 3 electrons in antibonding orbitals. Hence Li_2^+ is more stable than Li_2^- .

61. (b) $H_3C \overset{sp^3}{-} \overset{sp}{C} \equiv \overset{sp}{C} - \overset{sp^3}{CH_3}$
 linear due to sp hybridized C atom.

62. (d) PCl_3



63. (a) Both O_2^- and B_2 has bond order equal to 1.

$$B_2 (10) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 \pi 2p_y^1$$

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{6 - 4}{2} = \frac{2}{2} = 1$$

B_2 is known in the gas phase

$$O_2^{2-} = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$$

$$\text{Bond order} = \frac{1}{2}(10 - 8) = 1$$

64. (b) Diamagnetic species have no unpaired electrons

$$O_2^{2-} \Rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\{\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2\}$$

Whereas paramagnetic species has one or more unpaired electrons as in

$$O_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \{\pi 2p_x^2 = \pi 2p_y^2,$$

$$\{\pi^* 2p_x^1 = \pi^* 2p_y^1 = 2 \text{ unpaired electrons}\}$$

$$O_2^+ \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^0 = 1 \text{ unpaired electron}$$

$$NO \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^0 = 1 \text{ unpaired electron}$$

65. (d) Smaller the size and higher the charge more will be the polarising power of cation. Since the order of the size of cation is $K^+ > Ca^{++} > Mg^{++} > Be^{++}$. So the correct order of polarising power is $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

66. (c) (i) N_2 : bond order = 3, diamagnetic
 N_2^- : bond order = 2.5, paramagnetic

(ii) C_2 : bond order = 2, diamagnetic
 C_2^+ : bond order = 1.5, paramagnetic

(iii) NO : bond order = 2.5, paramagnetic
 NO^+ : bond order = 3, diamagnetic

(iv) O_2 : bond order = 2, paramagnetic
 O_2^+ : bond order = 2.5, paramagnetic

67. (a) For any species to have same bond order we can expect them to have same number of electrons. Calculating the number of electrons in various species.

$$O_2^- (8 + 8 + 1 = 17); CN^- (6 + 7 + 1 = 14)$$

$$NO^+ (7 + 8 - 1 = 14); CN^+ (6 + 7 - 1 = 12)$$

We find CN^- and NO^+ both have 14 electrons and bond order 3.

68. (c) All the members form volatile halides of the type AX_3 . All halides are pyramidal in shape. The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

69. (a) Compound having maximum electronegativity difference is more ionic. Hence the correct order is $DG < EG < DF < DE$

70. (d)

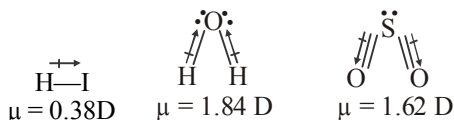
71. (b) SO_2 – bent
 SF_4 – see-saw
 ClF_3 – T-shape
 BrF_5 – square pyramidal
 XeF_4 – square planar.

72. (a) XeF_4 having one lone pair of electron show distorted pentagonal bipyramidal shape and sp^3d^3 hybridisation
73. (a) It is correct that during formation of ice from water there are vacant spaces between hydrogen bonded molecules of ice. Ice has a cage like structure. Due to this reason ice is less dense than liquid water. Hence both statement-1 and statement-2 are true and statement-2 is correct explanation of statement-1.
74. (a)
75. (a) *o* and *p*-nitrophenols can be separated by steam distillation because *o*-nitrophenol is steam volatile due to presence of weak intramolecular hydrogen bonding whereas *p*-nitrophenol contains intermolecular hydrogen bonding. Here, both statement-1 and statement-2 are correct and statement-2 is correct explanation of statement-1.

EXERCISE - 3

Exemplar Questions

1. (b) BF_4^- and NH_4^+ both the species are tetrahedral and sp^3 hybridised.
2. (c) CO_2 being symmetrical has zero dipole moment. Amongst HI , SO_2 and H_2O . H_2O exhibit the highest dipole moment as the central atom in H_2O contains 2 lone pairs.



3. (b) Applying the formula to find the hybridisation of central atom (nitrogen) :

$$\frac{1}{2} [\text{No. of valence } e^- \text{ of central atom} +$$

no. of monovalent atoms attached to it +
(-ve) charge if any - (+ve) charge if any]

$$\text{For, } \text{NO}_2^+ = \frac{1}{2} [5 + 0 + 0 - 1] = 2 \Rightarrow sp\text{-hybridised}$$

$$\text{NO}_3^- = \frac{1}{2} [5 + 0 + 1 - 0] = 3 \Rightarrow sp^2\text{-hybridised}$$

$$\text{NH}_4^+ = \frac{1}{2} [5 + 4 + 0 - 1] = 4 \Rightarrow sp^3\text{-hybridised}$$

4. (b) Strength of H-bonding is in the order :
 $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$

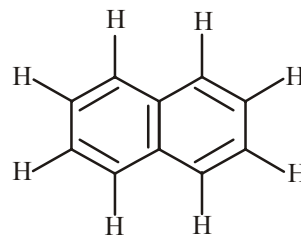
Also, each H_2O molecule is linked to four other H_2O molecules through H-bonds while each HF molecule is linked only to two other HF molecules.

Hence, decreasing order of b.p. will be : $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$

5. (c) In PO_4^{3-} ion, formal charge on each O-atom of P - O

$$\text{bond} = \frac{\text{Total charge}}{\text{Number of O atom}} = -\frac{3}{4} = -0.75$$

6. (d) In NO_3^- ion,
number of bond pairs (or shared pairs) = 4
number of lone pairs = 0
7. (a) $\text{BH}_4^- \Rightarrow 4$ bond pairs and 0 lone pair $\rightarrow sp^3$ hybridised.
 $\therefore$ Tetrahedral geometry
8. (c) The correct structure of the given compound will be as follows :



Now, there are 5 π -bonds and 19 σ -bonds are present in the above molecule.

9. (c) The electronic configuration of the given molecules are :

$$\text{N}_2^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi p_y^2, \sigma 2p_z^1; \quad 1 \text{ unpaired } e^-$$

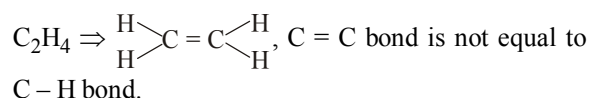
$$\text{O}_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \quad \pi^* 2p_x^1 \approx \pi^* 2p_y^1; \quad 2 \text{ unpaired } e^-s$$

$$\text{O}_2^{2-} = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \quad \pi^* 2p_x^2 \approx \pi^* 2p_y^2; \quad \text{no unpaired } e^-s$$

$$\text{B}_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi 2p_y^1; \quad 2 \text{ unpaired } e^-s$$

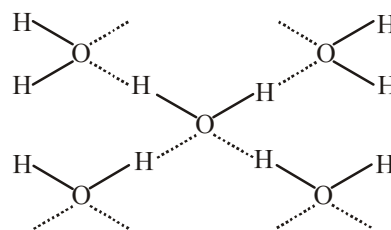
10. (c) $\text{XeF}_4 \Rightarrow$ square planar, all bonds are equal.

$$\text{BF}_4^- \Rightarrow \text{tetrahedral, all bonds are equal.}$$



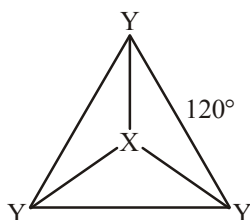
$$\text{SiF}_4 \Rightarrow \text{tetrahedral, all bonds are equal.}$$

11. (b) HCl , HI and H_2S do not form H-bonds. Only H_2O forms hydrogen bonds and each H_2O molecule is linked with four H_2O molecules.



12. (d) The given electronic configuration shows that the element belongs to *d*-block of the periodic table and known to be a transition element. In transition elements, electrons of *ns* and (*n* - 1)*d* subshell take part in bond formation.

13. (b) For sp^2 hybridisation, generally the geometry is usually taken to be triangular planar.



Thus, bond angle should be 120° .

14. (a) The given electronic configuration of A shows that it is a noble gas because the octet is complete and hence it will be the stable form.
15. (b) The electronic configuration of C represent chlorine. Its stable form is Cl_2 i.e., C_2 .
16. (d) The electronic configuration show that B represents phosphorus and C represents chlorine. The stable compound formed will be PCl_3 i.e., BC_3 .
17. (b) The bond between B and C will be covalent as both B and C are non-metal atoms.
18. (a) The correct increasing order of energies of molecular orbitals of N_2 is :
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x \approx \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$
19. (d) (a) $\text{Be}_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 1s^2, \sigma^* 2s^2$

$$(\text{B.O.}) = \frac{1}{2} [\text{Number of bonding electrons } (N_b) - \text{Number of anti-bonding electrons } N_a]$$

$$= \frac{4 - 4}{2} = 0$$

Bond order of Be_2 is zero thus, it does not exist.

- (b) $\text{He}_2 = \sigma 1s^2, \sigma^* 1s^2$

$$\text{B.O.} = \frac{2 - 2}{2} = 0$$

Now, $\text{He}_2^+ = \sigma 1s^2, \sigma^* 1s^1$

$$\text{B.O.} = \frac{2 - 1}{2} = 0.5$$

As the bond order is not zero, He_2^+ molecule is expected to exist.

- (c) N_2 ($7 + 7 = 14$) = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

$$\text{B.O.} = \frac{10 - 4}{2} = 3$$

Thus, dinitrogen (N_2) molecule contain triple bond and as bond order = 3 while no molecule of second period have more than double bond. Thus, bond strength of N_2 its maximum amongst the homonuclear diatomic molecules belonging to the second period.

- (d) The correct order of energies of molecular orbitals in N_2 molecule is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x \approx \pi 2p_y) < \sigma 2p_z < \pi^* 2p_x \approx \pi^* 2p_y < \sigma^* 2p_z$$

20. (b) E.C of O_2 :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2,$$

$$\pi^* 2p_x^1 \approx \pi^* 2p_y^1$$

$$\text{B.O.} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 6) = 2$$

E.C of O_2^+ :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2,$$

$$\pi^* 2p_x^1 \approx \pi^* 2p_y^0$$

$$\text{B.O.} = \frac{1}{2} (10 - 5) = 2.5$$

E.C of O_2^- :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2,$$

$$\pi^* 2p_x^2 \approx \pi^* 2p_y^1$$

$$\text{Bond order} = \frac{1}{2} (10 - 7) = 1.5$$

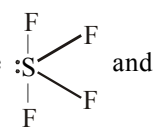
Hence, the correct order of bond order will be :

$$\text{O}_2^- < \text{O}_2 < \text{O}_2^+$$

21. (a) Out of the given electronic configuration $2s^2 2p^5$ represents fluorine which is the most electronegative element while $3s^2 3p^5$, $4s^2 4p^5$ and $5s^2 5p^5$ represents chlorine, bromine and iodine respectively.
22. (b) The electronic configuration of (b) and (d) have exactly half-filled p -orbitals but (b) being smaller in size than (d) will have the highest ionisation enthalpy.

NEET/AIPMT (2013-2017) Questions

23. (a) SF_4 has 4 bond pairs and 1 lone pair of electrons, sp^3d

hybridisation leads to irregular shape  and resultant $\mu \neq 0$.

24. (d) $\text{H} - \overset{\sigma}{\underset{\text{H}}{\text{C}}} - \overset{\pi}{\text{C}} = \overset{\sigma}{\underset{\text{H}}{\text{C}}} - \text{H}$

25. (d) (a) $\text{N}_2 \longrightarrow \text{N}_2^+$
 B.O. 3 2.5

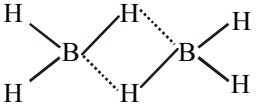
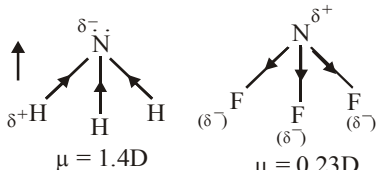
Bond energy decreases

Magnetic behaviour changes from diamagnetic to paramagnetic

- (b) $\text{O}_2 \longrightarrow \text{O}_2^+$
 B.O. 2 2.5

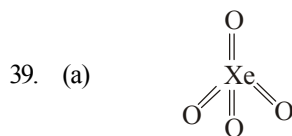
Bond energy increases

Magnetic behaviour does not change.

- $C_2 \longrightarrow C_2^+$
 (c) B.O. 2 2.5
 Bond energy decreases
 Magnetic behaviour changes from diamagnetic to paramagnetic
 $NO \longrightarrow NO^+$
 (d) B.O. 2 2.5
 bond energy increases
 Magnetic behaviour changes from paramagnetic to diamagnetic
26. (b) No. of electrons in $CO = 6 + 8 = 14$
 No. of electrons in $NO^+ = 7 + 8 - 1 = 14$
 $\therefore CO$ and NO^+ are isoelectronic species.
 Isoelectronic species have identical bond order.
27. (c) Applying VSEPR theory, both NF_3 and H_2O are sp^3 hybridized.
28. (a) $F-\ddot{X}e:-F$ sp^3d and Linear
 $Cl-\ddot{I}:-Cl$ sp^3d and Linear
29. (a) Molecular orbital configuration of O_2^- is
 $O_2^- (17) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$
 $\sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$
30. (a) $H \overset{\sigma}{\underset{\sigma}{\text{O}}} H$ $O \leftarrow S \overset{\sigma}{\underset{\pi}{=}} O$ $O \leftarrow N \overset{\sigma}{\underset{\pi}{=}} O$ $O \overset{\sigma}{\underset{\pi}{=}} C \overset{\sigma}{\underset{\pi}{=}} O$
31. (b) $(BH_3)_2$ or (B_2H_6)

 It contains two 3 centre - 2 electron bonds and present above and below the plane of molecules compounds which do not have sufficient number of electrons to form normal covalent bonds are called electron deficient molecules.
32. (b) $Be^{2+} = (4 - 2) = 2$
 is isoelectronic with $Li^+ (3 - 1 = 2)$
 Since both have same number of electrons in their outermost shell.
33. (c) Dipole moment of $NH_3 > NF_3$

 $\mu = 1.4D$ $\mu = 0.23D$
 (F is more electronegative than N)
34. (b) Hybridization of $NO_3^- = \frac{1}{2}(5 + 0 + 1 - 0)$
 $= \frac{6}{2} = 3 = sp^2$ hence geometry is trigonal planner.
 NO_2^- (nitrite ion) also has sp^2 hybridization and gives a trigonal planner geometry but because there are only

two outer atoms, the molecular geometry is bent with $\angle 120^\circ$ bond angles.

35. (c) O_2^+ ion - Total number of electrons $(16 - 1) = 15$.
 Electronic configuration
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2$
 $< \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1$
 $\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 5}{2} = \frac{5}{2} = 2\frac{1}{2}$
 O_2^- (Super oxide ion): Total number of electrons $(16 + 1) = 17$.
 Electronic configuration
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2$
 $< \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^2 = \pi^* 2p_z^2$
 $\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10 - 7}{2} = \frac{3}{2} = 1\frac{1}{2}$
 O_2^{2+} ion: Total number of electrons
 $= (16 - 2) = 14$ Electronic configuration
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2$
 $\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10 - 4}{2} = \frac{6}{2} = 3$
 So bond order: $O_2^- < O_2^+ < O_2^{2+}$
36. (c) ClO_3^- and SO_3^{2-} both have same number of electrons (42) and central atom in each being sp^3 hybridised. Both are having one lone pair on central atom hence they are pyramidal.
37. (a) Oxygen molecule (O_2) - Total number of electrons = 16 and electronic configuration is
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2$
 $< \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1 = \pi^* 2p_z^1$
 $\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = \frac{4}{2} = 2$
 O_2^+ ion - Total number of electrons $(16 - 1) = 15$.
 Electronic configuration
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2$
 $< \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1$
 $\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 5}{2} = \frac{5}{2} = 2\frac{1}{2}$
 O_2^- (Super oxide ion) Total number of electrons $(16 + 1) = 17$. Electronic configuration
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2$
 $< \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^2 = \pi^* 2p_z^2$
 $\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10 - 7}{2} = \frac{3}{2} = 1\frac{1}{2}$
38. (b) NO_2^+ has sp hybridisation so it is linear with bond angle $= 180^\circ$.



Number of σ bonds = 4
Number of π bonds = 2

40. (a) According to molecular orbital theory as bond order decreases stability of the molecule decreases

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

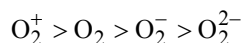
$$\text{Bond order for } \text{O}_2^+ = \frac{1}{2}(10 - 5) = 2.5$$

$$\text{Bond order for } \text{O}_2 = \frac{1}{2}(10 - 6) = 2$$

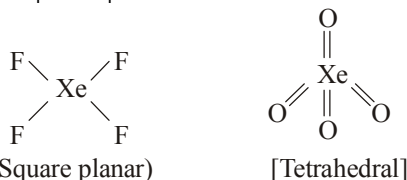
$$\text{Bond order for } \text{O}_2^- = \frac{1}{2}(10 - 7) = 1.5$$

$$\text{Bond order for } \text{O}_2^{2-} = \frac{1}{2}(10 - 8) = 1.0$$

hence the correct order is

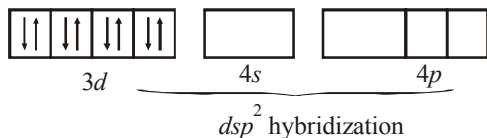


41. (d) $\text{XeF}_4, \text{XeO}_4$



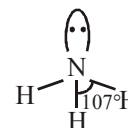
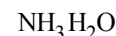
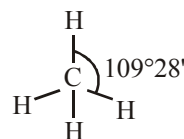
42. (a) $\text{Ni}^{2+} = [\text{Ar}]^{18} 4s^0 3d^8$

Valence bond theory can be used to predict shape.



(In presence of ligand, pairing of electron occurs)
 $\therefore$ Square planar.

43. (b) CH_4

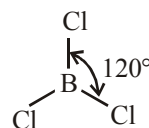


Tetrahedral;

Trigonal Bent
pyramidal

Note: The geometry of H_2O should have been tetrahedral if there are all bond pairs. But due to presence of two lone pairs the shape is distorted tetrahedral. Hence bond angle reduced to 104.5° from 109.5° .

44. (a) According to VSEPR theory order of repulsion in between lp – lp, lp – bp and bp – bp is as under
 $\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$
45. (b) $\text{IBr}_2^-, \text{XeF}_2$
Total number of valence electrons are equal in both the species and both the species exhibit linear shape.
46. (c) BCl_3 is trigonal planar and hence the bond angle is 120° .



47. (b) CN^- and CO have same no. of electrons and have same bond order equal to 3.

Chapter

5

States of Matter

INTERMOLECULAR FORCES AND THERMAL ENERGY

Intermolecular Forces:

These are the forces of attraction and repulsion between interacting particles. (The term does not include electrostatic forces or forces between covalent bonds).

Attractive intermolecular forces are called van der Waals forces. The different types of van der Waals forces are discussed below:

- (i) **Dispersion forces or London forces:** The forces of attraction between induced momentary dipoles are called London forces. These forces arise when the electron cloud of the molecule is distorted momentarily, thus generating a momentary dipole which in turn induces dipole in the neighbouring molecules. These are then attracted to each other. They are important only at short distances and their magnitude depends on the polarisability of the particle.
- (ii) **Dipole-Dipole forces :** These forces act between molecules possessing permanent dipole. The positive pole of one molecule is attracted towards the negative pole of the other molecule.
- The magnitude of these forces depends on the polarity of molecules which, in turn, depends on the electronegativities of the atoms present in the molecule. The attractive forces decrease with increase of distance between dipoles.
- (iii) **Dipole-Induced dipole forces :** They operate between molecules having permanent dipole and molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on electrically neutral molecule by deforming its electronic cloud.
- (iv) **Hydrogen bond :** It is a special case of dipole - dipole interactions. It arises in molecules in which highly polar N-H, O-H or H-F bonds are present.

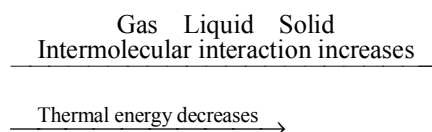
Strength of the H-bond depends on the coulombic interaction between lone pair of electrons of electronegative atom of one molecule and H-atom of the other molecule.

Thermal Energy

It is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to temperature of substance. It is a measure of average KE of particles.

Intermolecular Forces Vs Thermal Energy

Intermolecular forces tend to keep molecules together while thermal energy tends to keep them apart. The three states of matter are the result of balance between intermolecular forces and thermal energy of molecules. The predominance of thermal energy and molecular interaction energy of a substance in the three states is depicted as follows:



GASEOUS STATE

The gaseous state is characterized by the following physical properties:

- Gases are highly compressible.
- They exert pressure equally in all the directions.
- Gases have much lower density than solids and liquids.
- The volume and shape of gases are not fixed. They assume volume and shape of the container.
- Gases mix evenly and completely in all proportions.

Gas Laws

Boyle's law: According to this law, at constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.

Mathematically,

$$P \propto \frac{1}{V} \quad (\text{at constant } T \text{ and } n)$$

$$\Rightarrow P = \frac{k}{V} \quad (k \rightarrow \text{constant of proportionality})$$

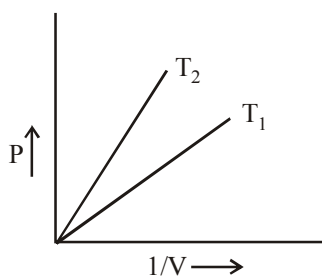
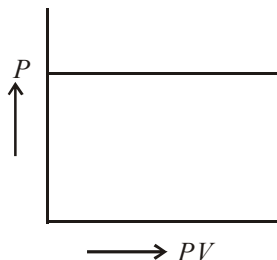
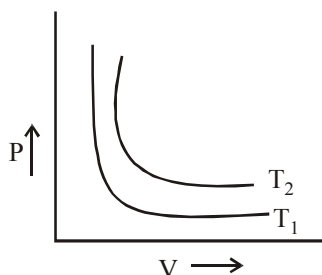
$$\Rightarrow PV = k$$

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure P_1 undergoes expansion, so that volume becomes V_2 and pressure becomes P_2 , then according to Boyle's law :

$$P_1 V_1 = P_2 V_2 = \text{constant}$$

$$\Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

Graphically, Boyle's law can be represented as:



Charles's law : According to this law, pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature, i.e.,

$$V \propto T \text{ or } V = kT$$

Other way of representing it is following:

For each degree change of temperature, the volume of sample of a gas changes by the fraction of $1/273.15$ of its volume at 0°C .

$$V_t = V_0 + \frac{t}{273.15} V_0$$

$$\Rightarrow V_t = V_0 \left(1 + \frac{t}{273.15} \right) = V_0 \left(\frac{273.15 + t}{273.15} \right)$$

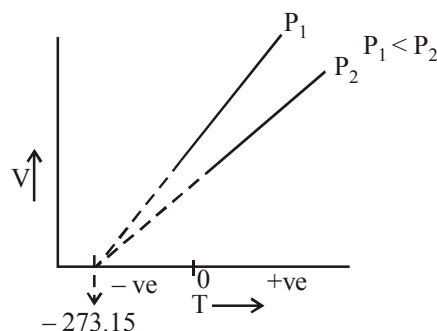
$$\Rightarrow V_t = V_0 \left(\frac{T_t}{T_0} \right) \Rightarrow \frac{V_t}{V_0} = \frac{T_t}{T_0}$$

Where $T_0 = 273.15$ and is called Kelvin temperature or Absolute temperature

$$\therefore \boxed{0^\circ\text{C} = 273.15\text{K}}$$

At -273.15°C , volume of a gas will be zero. This means that the gas will not exist. This temperature at which gases are supposed to occupy zero volume is called Absolute zero.

Graphically, it is represented as:



Gay lussac's law : It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature, i.e.

$$P \propto T$$

$$\text{or, } \frac{P}{T} = \text{constant} = k$$

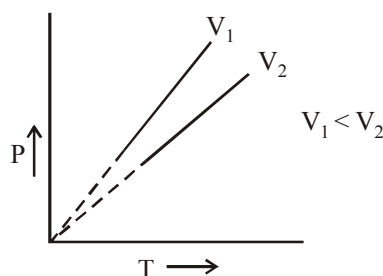
Hence, if the pressure of a gas P_1 at temperature T_1 changes to P_2 at T_2 , volume remaining constant, we have

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{constant}$$

$$\text{or, } \log P - \log T = \text{constant}$$

$$P_t = P_0 \left(1 + \frac{t}{273.15} \right)$$

Graphically,



Avogadro law : It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

$$\text{i.e. } V \propto n, \text{ where } n \rightarrow \text{Number of molecules of gas}$$

$$V = kn$$

Thus, one mole of each gas at standard temperature and pressure will have same volume. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (10^5 Pa) pressure.

$$\text{As } n = \frac{m}{M} \text{ where, } m \rightarrow \text{given mass, } M \rightarrow \text{molar mass}$$

$$\therefore V = k \frac{m}{M} \Rightarrow M = k \frac{m}{V} = k d$$

$$\Rightarrow V \propto d \quad \text{where, } d \rightarrow \text{density of gas}$$

Ideal gas equation : A gas that follows Boyle's law, Charles's law and Avogadro law strictly is called an ideal gas. Combining the three laws, we can get the ideal gas equation as discussed below:

$$\text{Boyle's law : } V \propto \frac{1}{P} \text{ at constant } T \text{ and } n$$

$$\text{Charles's law : } V \propto T \text{ at constant } P \text{ and } n$$

Avogadro law : $V \propto n$ at constant P and T

$$\therefore V \propto \frac{nT}{P}$$

$$\Rightarrow V = \frac{RnT}{P}$$

or, $PV = nRT$ Ideal Gas equation or Equation of State.

R=Universal gas constant

$$R = \frac{PV}{nT} = \frac{(10^5 \text{ Pa})(22.71 \times 10^{-3} \text{ m}^3)}{(1 \text{ mol})(273.15 \text{ K})}$$

$$= 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}.$$

$$= 8.314 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1}.$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}.$$

If T, P and V of a fixed amount of gas vary from T_1 , V_1 and P_1 to T_2 , V_2 and P_2 , then

$$\frac{P_1 V_1}{T_1} = nR \text{ and } \frac{P_2 V_2}{T_2} = nR$$

$$\text{or } \left[\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \right] \text{ combined gas Law}$$

Density and Molar Mass of Gaseous Substance from Ideal Gas Equation,

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{m}{MV} = \frac{P}{RT} \quad \left(\because n = \frac{m}{M} \right)$$

$$\frac{d}{M} = \frac{P}{RT}$$

$$M = \frac{dRT}{P}$$

Dalton's Law of Partial Pressures : According to this law, the total pressure exerted by a mixture of non-reactive gases is equal to the sum of partial pressures of individual gases, i.e.

$$P_{\text{Total}} = P_1 + P_2 + P_3 + \dots \text{ (at constant T and V)}$$

Pressure exerted by saturated water vapour is called aqueous tension.

$$\therefore P_{\text{dry gas}} = P_{\text{Total}} - \text{Aq. tension}$$

Partial pressure in terms of mole fraction

$$P_1 = x_1 P_{\text{Total}}$$

$$P_2 = x_2 P_{\text{Total}}$$

$$\text{In general, } P = x P_{\text{Total}}$$

where $x \rightarrow$ mole fraction; $P \rightarrow$ partial pressure

Graham's Law of Diffusion or Effusion : According to this law, at constant temperature and pressure, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its density and is directly proportional to its pressure.

$$\text{Rate of diffusion } (r) \propto \frac{P}{\sqrt{d}}$$

$$\frac{r_1}{r_2} = \frac{p_1}{p_2} \sqrt{\frac{d_2}{d_1}}$$

As pressure is constant

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Where r_1 & r_2 are rates of diffusion of two gases and d_1 & d_2 are densities.

$\therefore 2 \times \text{vapour density} = \text{Molecular mass}$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Where M_1 & M_2 are the molecular masses of two gases.

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

KINETIC MOLECULAR THEORY OF GASES

This theory attempts to elucidate the behaviour of gases. The assumptions or postulates of this theory are:

- Gases consist of large number of identical particles which are very small and far apart so that the actual volume of molecules is negligible in comparison to empty space between them. This explains the compressibility of gases.
- There is no force of attraction between the particles of a gas at ordinary T and P. This is why gases can expand and occupy all the space available to them.
- Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed position, a gas would have had a fixed shape, which is not so.
- Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
- Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after collision remains the same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant.
- At any particular time, the different particles of the gas have different speeds and hence different kinetic energies.
- The average KE of gas molecules is directly proportional to the absolute temperature.

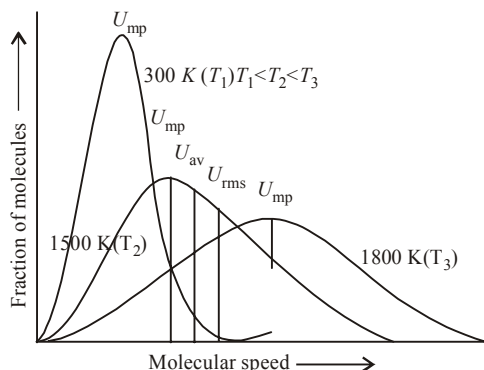
MAXWELL'S DISTRIBUTION OF MOLECULAR SPEEDS/ENERGIES

Maxwell and Boltzmann, however, showed that as a result of collisions, though some molecules are speeded up, some others are slowed down and hence the fractions of molecules possessing particular speed remains constant at constant temperature. This is called Maxwell-Boltzmann distributions.

Maxwell gave distribution curves of molecular speeds for CO_2 at different temperatures.

Special features of the curve are :

- Fraction of molecules with too high or too low speeds is very small.
- No molecules has zero velocity.
- Initially the fraction of molecules increases with velocity till the peak of the curve which pertains to most probable velocity and thereafter it falls with increase in velocity.



Speed Related to Gaseous State

(a) Root mean square speed (RMS speed) -

$$u = \frac{\sqrt{u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2}}{n}$$

$$C = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

(b) Average speed (AVS) :

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi m}}$$

$$\text{Average speed} = .9213 \times \text{RMS speed}$$

$$\text{RMS speed} = 1.085 \times \text{Average speed}$$

(c) Most probable speed (MPS) :

$$\text{Most probable speed} = \sqrt{\frac{2RT}{M}}$$

$$\text{MPS} = .816 \times \text{RMS} ; \text{RMS} = 1.224 \text{ MPS}$$

Relation between the three types of velocities

$$\alpha : v : u$$

$$\sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$\sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$1.414 : 1.595 : 1.732$$

$$1 : 1.128 : 1.234 \quad \text{i.e., } \alpha < v < u.$$

DEVIATION FROM IDEAL GAS BEHAVIOUR : REAL GASES

A gas that follows Boyle's law, Charle's law and Avogadro law strictly is called an ideal gas. Such a gas is hypothetical. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. This is discussed as follows:

Two questions arise :

- Why do gases deviate from ideality?
- Under what conditions gases deviate from ideality?

Gases deviate from ideality because two assumptions of kinetic theory do not hold good:

- There is no force of attraction between molecules of a gas.
- Volume of molecules of a gas is negligible compared to volume of the gas.

Equation of State for Real Gases (Van der Waals Equation)

Correction for pressure : Real gases show deviations from ideal gas law because molecules interact with each other. At high pressures, molecules of gas are very close to each other. Molecular interactions start operating. As a result, pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

Hence, corrected pressure :

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2} \quad a \rightarrow \text{constant}$$

Volume correction : The volume occupied by the molecules also becomes significant at high pressure when the molecules are quite close together because instead of moving in volume V , these are now restricted to volume $(V - nb)$ where nb is approximately the volume occupied by molecules themselves.

i.e., corrected volume = $(V - nb)$

Thus, taking into account the corrections for P and V , we have

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

van der Waals equation $a, b \rightarrow$ van der Waals constants

units of 'a' $\rightarrow$ atm. litre² mole⁻²

units of 'b' $\rightarrow$ litres mole⁻¹

Value of 'a' is a measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

Also, at very low temperature, intermolecular forces become significant. Thus, real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible.

As b is the effective volume of the gas molecules, the constant value of b for any gas over a wide range of temperature and pressure indicates that the gas molecules are incompressible.

Study of Deviation

The deviation from ideal behaviour can be measured in terms of compressibility factor Z which is given by

$$Z = \frac{PV}{nRT}$$

For ideal gas, $Z = 1$ at all temperatures and pressures.

At very low pressure, all gases have $Z = 1$ and behave ideally. At high pressure, all gases have $Z > 1$. They are difficult to compress. At intermediate pressure, most gases have $Z < 1$.

The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point. At low pressure and high temperature, gases show ideal behaviour.

The temperature at which a real gas obeys ideal gas laws over an appreciable range of pressure is called **Boyle temperature or Boyle point** T_B . T_B and two van der Waal's constants are related as below

$$T_B = \frac{a}{bR}$$

Liquifaction of Gases

Critical temperature (T_c) of a gas is the highest temperature at which liquifaction of the gas first occurs.

Liquifaction of gas requires cooling as well as considerable compression. Compression brings the molecules in close vicinity and cooling slows down the movement of molecules. Therefore, intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquifies.

Critical Constants

(i) **Critical temperature (T_c)** : The temperature above which gas cannot be liquefied whatever pressure is applied is called

$$\text{critical temperature } T_c = \frac{8a}{27bR}$$

(ii) **Critical pressure (P_c)** : The minimum pressure required to liquefy a gas at its critical temperature is called critical

$$\text{pressure. } P_c = \frac{a}{27b^2}$$

(iii) **Critical volume (V_c)** : The volume occupied by one mole of a gas at the critical temperature and critical pressure is called critical volume.

$$V_c = 3b$$

There is continuity between gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognise this continuity. A liquid can be viewed as a very dense gas. Liquid and gas can be distinguished only when the fluid is below its critical temperature, since in that case liquid and gas are in equilibrium and a surface separating the two phases is visible. At critical temperature, liquid passes into gaseous state imperceptibly and continuously, the surface separating two phases disappears. A gas below T_c can be liquified by applying pressure, and is called vapour of the substance.

LIQUID STATE

Molecules in liquids are so close that there is very little empty space between them and under normal conditions, liquids are denser than gases.

Their molecules are held together by attractive intermolecular forces. They have definite volume and the molecules can move past one another freely and thus liquids can flow, can be poured and can assume the shape of the container.

Some physical properties of liquids are:

(i) Vapour Pressure

It is the pressure exerted by the vapours in equilibrium with the liquid. The temperature at which vapour pressure of liquid is equal to external pressure is called boiling point of the liquid.

At 1 atm, it is the normal boiling point and at 1 bar, it is standard boiling point. At high altitudes, atmospheric pressure is low. Therefore, liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at lower temperature on hills, pressure cooker is used for cooking food.

(ii) Surface Tension

A molecule in the bulk of the liquid experiences equal intermolecular forces from all sides but the molecule on the surface experiences a net attractive force towards the interior of the liquid. This phenomena is called surface tension.

It is defined as the force acting at right angles to the surface along 1 cm length of the surface. Thus, the units of surface tension are dynes per cm (or Nm^{-1} in SI system).

Due to net downward force at the surface, liquids tend to have minimum number of molecules at their surface. If surface of liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. The energy required to increase the surface area of the liquid by one unit is called surface energy.

Magnitude of surface tension of a liquid depends on attractive forces between molecules. As temperature increases, attractive forces decreases and thus, surface tension also decreases.

Since a sphere has minimum surface area and lowest energy state of a liquid is when surface area is minimum, therefore, mercury drops are spherical in shape. Liquid tends to rise (or fall) in capillary because of surface tension.

(iii) Viscosity

It is a measure of resistance to flow which arises due to internal friction between layers of fluid as they slip past one another while liquid flows.

A force is required to maintain the flow of layers. It is given

by: $F = \eta A \frac{du}{dz}$ where $A \rightarrow$ area of contact $\frac{du}{dz} \rightarrow$ velocity gradient $\eta \rightarrow$ coefficient of viscosity.

SI unit of η is 1 N sm^{-2} and its cgs unit is poise

Viscosity of liquids decreases as temperature increases because at high temperature, molecules have high KE and can overcome intermolecular forces to slip past one another between the layers.

Greater viscosity, more slowly the liquid flows. H-bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids.

CONCEPT MAP

Intermolecular Interactions Dispersion or London Forces: (act between induced momentary dipoles)
Dipole-Dipole Force: (act between molecules possessing permanent dipoles)
Dipole-Induced Dipole Forces: (act between molecules having permanent dipole and molecules lacking it)
Hydrogen Bonding: (It is a special case of dipole-dipole interactions)

Kinetic Theory of Gases.
 All the gases are made up of molecules moving randomly in all the directions.
 $K.E = \frac{3}{2} RT$, $c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$
 Average speed $= \sqrt{\frac{8RT}{\pi M}} = 0.9213 \times \text{rms speed}$
 Most probable speed $= \sqrt{\frac{2RT}{M}}$
 MPs = $816 \times \text{RMS}$

Behaviour of Real Gases
 Two faulty assumptions of kinetic theory lead van der Waal to modify ideal gas equation as,
 $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
 Compressibility factor $Z = \frac{PV}{nRT}$
 For ideal gas $Z = 1$; For real gas $Z \neq 1$
 $Z > 1$ the gas shows +ve deviation
 $Z < 1$ the gas shows -ve deviation

Gas Laws
Boyle's Law: $V \propto 1/P$
 $P_1 V_1 = P_2 V_2$, $P \propto d$
Charles's Law: $V \propto T$
 $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay Lussac's Law: $P \propto T$
 $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Avogadro's Law: $V = Kn$
 $M = Kd$
Graham's Law: $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

Ideal Gas Equation: $PV = nRT$
 Value of $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $0.0822 \text{ atm K}^{-1} \text{ mol}^{-1}$, $8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$ and $8.314 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1}$
 Equation of state:
 $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
 Dalton's Law $P_{\text{Total}} = P_1 + P_2 + P_3 + \dots$, (at const. T, V)

STATES OF MATTER

Liquefaction of Gases

$T_C = \frac{8a}{27bR}$ (temperature above which gas can not be liquified)
 $P_C = \frac{a}{27b^2}$ (minimum pressure required to liquify a gas at its critical temperature)
 $V_C = 3b$ (Volume occupied by one mole of gas at T_C and P_C)

Liquid State: Intermolecular forces are stronger than gaseous state and have definite volume.
Vapour pressure: Pressure exerted by the vapour in equilibrium with the liquid at that temperature. It increases with increase in temperature.
Surface Tension: Force acting at right angles to the surface along 1 cm length of the surface. Unit dynes per cm or Nm^{-1} SI System. It decreases with increase in temperature.
Viscosity: It is a measure of resistance to flow which arises due to internal friction between layers of fluid as they slip past one another as the liquid flows.

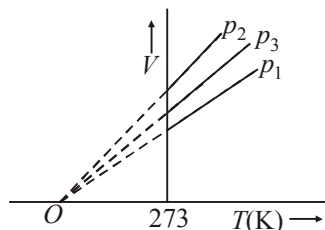
EXERCISE - 1

Conceptual Questions

- Correct gas equation is :
 - $\frac{V_1 T_2}{P_1} = \frac{V_2 T_1}{P_2}$
 - $\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$
 - $\frac{P_1 T_2}{V_1} = \frac{P_2 V_2}{T_2}$
 - $\frac{V_1 V_2}{T_1 T_2} = P_1 P_2$
- A gas of volume of 15 ml at 300 K and 740 mm of Hg. Find the temperature if volume becomes 10 ml at 760 mm pressure of Hg.
 - 209 K
 - 200 K
 - 205 K
 - 275 K
- The K.E. for 14 g of nitrogen gas at 127°C is nearly (molecular mass of nitrogen is 28 g/mole) and gas constant is 8.31 J/mol K)
 - 8.3 kJ
 - 4.15 kJ
 - 2.5 kJ
 - 3.3 kJ
- At constant temperature, for a given mass of an ideal gas
 - the ratio of pressure and volume always remains constant.
 - volume always remains constant.
 - pressure always remains constant.
 - the product of pressure and volume always remains constant.
- The molecular weight of two gases are 100 and 81 respectively. Their rates of diffusions are in the ratio:
 - 81 : 100
 - 100 : 81
 - 10 : 9
 - 9 : 10
- Which is not true in case of an ideal gas ?
 - It cannot be converted into a liquid
 - There is no interaction between the molecules
 - All molecules of the gas move with same speed
 - At a given temperature, PV is proportional to the amount of the gas
- The correct value of the gas constant ' R ' is close to :
 - 0.082 litre-atmosphere K
 - 0.082 litre-atmosphere $K^{-1} \text{ mol}^{-1}$
 - 0.082 litre-atmosphere $^{-1} \text{ K mol}^{-1}$
 - 0.082 litre $^{-1}$ atmosphere $^{-1} \text{ K mol}$
- In two separate bulbs containing ideal gases A and B respectively, the density of gas A is twice of that of gas B, while mol wt. of gas A is half of that of gas B at the same temperature, pressure. P_A/P_B will be:
 - 1
 - 4
 - 1/4
 - 1/2
- Under what conditions will a pure sample of ideal gas not only exhibit a pressure of 1 atm, but also a concentration of 2 moles per litre?
 - At STP
 - When volume is 22.4 litre
 - At 6.1 K
 - When R has no unit
- Select one correct statement. In the gas equation, $PV = nRT$
 - n is the number of molecules of a gas
 - V denotes volume of one mole of the gas
 - n moles of the gas have a volume V
 - P is the pressure of the gas when only one mole of gas is present.
- 500 ml of nitrogen at 27°C is cooled to -5°C at the same pressure. The new volume becomes
 - 326.32 ml
 - 446.66 ml
 - 546.32 ml
 - 771.56 ml
- 600 c.c. of a gas at a pressure of 750 mm of Hg is compressed to 500 c.c. Taking the temperature to remain constant, the increase in pressure, is
 - 150 mm of Hg
 - 250 mm of Hg
 - 350 mm of Hg
 - 450 mm of Hg
- From a heated mixture of nitrogen, oxygen and carbon, two compounds (out of the many obtained) are isolated. The rates of diffusion of the two isolated compounds are almost identical. The two compounds are
 - N_2O and CO_2
 - CO and NO
 - CO_2 and NO_2
 - N_2O and CO
- The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be
 - 4
 - 2
 - 1
 - 0.5
- Gas equation $PV = nRT$ is obeyed by
 - Only isothermal process
 - Only adiabatic process
 - Both (a) and (b)
 - None of these
- Densities of two gases are in the ratio 1:2 and their temperatures are in the ratio 2:1 then the ratio of their respective pressures is
 - 1:1
 - 1:2
 - 2:1
 - 4:1
- A cylinder of 5 L capacity, filled with air at NTP is connected with another evacuated cylinder of 30 L of capacity. The resultant air pressure in both the cylinders will
 - 10.8 cm of Hg
 - 14.9 cm of Hg
 - 21.8 cm of Hg
 - 38.8 cm of Hg
- Volume occupied by a gas at one atmospheric pressure and 0°C is V mL. Its volume at 273 K will be
 - V ml
 - $V/2$ ml
 - $2V$
 - None of these
- Van der Waal's equation

$$\left[P + \frac{a}{V^2} \right] (V - b) = nRT$$
 is applicable for :
 - Ideal gas
 - Non-ideal gas
 - Both (a) and (b)
 - None of these

20. Which one of the following indicates the value of the gas constant R ?
 (a) $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ (b) $8.3 \text{ cal K}^{-1} \text{ mol}^{-1}$
 (c) $0.0821 \text{ lit K}^{-1} \text{ mol}^{-1}$ (d) $1.987 \text{ Joules K}^{-1} \text{ mol}^{-1}$
21. 16 g of oxygen and 3 g of hydrogen are mixed and kept at 760 mm of Hg pressure and 0°C . The total volume occupied by the mixture will be nearly
 (a) 22.4 litres (b) 33.6 litres (c) 448 litres (d) 44800 ml
22. If P is pressure and ρ is density of a gas, then P and ρ are related as
 (a) $P \propto \rho$ (b) $P \propto (1/\rho)$
 (c) $P \propto \rho^2$ (d) $P \propto (1/\rho^2)$
23. Pure hydrogen sulphide is stored in a tank of 100 litre capacity at 20°C and 2 atm pressure. The mass of the gas will be
 (a) 34 g (b) 340 g (c) 282.68 g (d) 28.24 g
24. If three unreactive gases having partial pressures P_A , P_B and P_C and their moles are 1, 2 and 3 respectively then their total pressure will be
 (a) $P = P_A + P_B + P_C$ (b) $P = \frac{P_A + P_B + P_C}{6}$
 (c) $P = \frac{\sqrt{P_A + P_B + P_C}}{3}$ (d) None of these
25. When a substance is dissolved in a solvent, the vapour pressure of solvent decreases. It brings:
 (a) a decrease in boiling point of solution
 (b) an increase in boiling point of the solution
 (c) a decrease in freezing point of the solution
 (d) an increase in freezing point of the solution
26. Dalton's law of partial pressure will not apply to which of the following mixture of gases
 (a) H_2 and SO_2 (b) H_2 and Cl_2
 (c) H_2 and CO_2 (d) CO_2 and Cl_2
27. A gas diffuses $1/5$ times as fast as hydrogen. Its molecular weight is
 (a) 50 (b) 25 (c) $25\sqrt{2}$ (d) $50\sqrt{2}$
28. Dominance of strong repulsive forces among the molecules of the gas (Z = compressibility factor):
 (a) Depends on Z and indicated by $Z = 1$
 (b) Depends on Z and indicated by $Z > 1$
 (c) Depends on Z and indicated by $Z < 1$
 (d) Is independent of Z .
29. The volume-temperature graphs of a given mass of an ideal gas at constant pressure are shown below.



What is the correct order of pressures ?

- (a) $P_1 > P_3 > P_2$ (b) $P_1 > P_2 > P_3$
 (c) $P_2 > P_3 > P_1$ (d) $P_2 > P_1 > P_3$

30. Equal weights of methane and hydrogen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by hydrogen is :
 (a) $\frac{1}{2}$ (b) $\frac{8}{9}$ (c) $\frac{1}{9}$ (d) $\frac{16}{17}$
31. The rate of diffusion of methane at a given temperature is twice that of a gas X . The molecular weight of X is
 (a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0
32. X mL of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is :
 (a) 10 seconds : He (b) 20 seconds : O_2
 (c) 25 seconds : CO (d) 55 seconds : CO_2
33. The inversion temperature T_i (K) of hydrogen is (given van der Waal's constants a and b are $0.244 \text{ atm L}^2 \text{ mol}^{-2}$ and 0.027 L mol^{-1} respectively)
 (a) 440 (b) 220 (c) 110 (d) 330
34. The ratio between most probable velocity, mean velocity and r.m.s velocity is :
 (a) $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$ (b) $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$
 (c) $1 : 2 : 3$ (d) $1 : \sqrt{2} : \sqrt{3}$
35. Root mean square velocity of a gas molecule is proportional to
 (a) $m^{1/2}$ (b) m^0 (c) $m^{-1/2}$ (d) m
36. Which of the following is not a property of liquid state?
 (a) Intermolecular force of attraction in a liquid is quite large
 (b) All liquids accompanied by cooling on evaporation
 (c) Lower the boiling point of a liquid, greater is its vapour pressure at room temperature
 (d) A liquid boils at high temperature at the top of a mountain than at the sea level
37. In a closed flask of 5 litres, 1.0 g of H_2 is heated from 300 to 600 K. Which statement is not correct?
 (a) Pressure of the gas increases
 (b) The rate of collision increases
 (c) The number of moles of gas increases
 (d) The energy of gaseous molecules increases
38. Internal energy and pressure of a gas per unit volume are related as :
 (a) $P = \frac{2}{3}E$ (b) $P = \frac{3}{2}E$ (c) $P = \frac{1}{2}E$ (d) $P = 2E$
39. Which of the following gases will have highest rate of diffusion?
 (a) CO_2 (b) NH_3
 (c) O_2 (d) N_2
40. The temperature of the gas is raised from 27°C to 927°C , the root mean square velocity is
 (a) $\sqrt{927/27}$ time the earlier value
 (b) same as before
 (c) halved
 (d) doubled

41. Which of the following expressions correctly represents the relationship between the average molar kinetic energy, $\overline{KE}$, of CO and N_2 molecules at the same temperature ?
- $\overline{KE}_{CO} < \overline{KE}_{N_2}$
 - $\overline{KE}_{CO} > \overline{KE}_{N_2}$
 - $\overline{KE}_{CO} = \overline{KE}_{N_2}$
 - cannot be predicted unless volumes of the gases are given
42. The inversion temperature for van der Waal's gas is :
- $T_i = \frac{a}{(Rb)}$
 - $T_i = \left(\frac{2a}{Rb} \right)$
 - $T_i = 0.5 T$
 - $T_i = \frac{a}{2(R/b)}$
43. Root mean square velocity of a molecule is 1000 m/s. The average velocity of the molecule is :
- 455.55 m/s
 - 675.55 m/s
 - 921.58 m/s
 - 1221.58 m/s
44. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels
- in a wavy path
 - in a straight line path
 - with an accelerated velocity
 - in a circular path
45. As the temperature is raised from 20°C to 40°C , the average kinetic energy of neon atoms changes by a factor of which of the following ?
- $\frac{313}{293}$
 - $\sqrt{(313/293)}$
 - $\frac{1}{2}$
 - 2
46. When universal gas constant (R) is divided by Avogadro no. (N_0), then the value of R/N_0 is equivalent to
- Rydberg's constant
 - Boltzmann's constant
 - Planck's constant
 - Van der waal's constant
47. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is
- 1.086 : 1
 - 1 : 1.086
 - 2 : 1.086
 - 1.086 : 2
48. The rms speed at NTP of a gas can be calculated from the expression :
- $\sqrt{3P/d}$
 - $\sqrt{3PV/M}$
 - $\sqrt{3RT/M}$
 - All of these
49. Ratio of molecular weights of A and B is $\frac{4}{25}$ then ratio of rates of diffusion will be :
- 5 : 1
 - 5 : 2
 - 25 : 3
 - 25 : 4
50. When the temperature of an ideal gas is increased from 27°C to 927°C , the kinetic energy will be :
- same
 - eight times
 - four times
 - twice
51. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is,
- 4
 - 2
 - 1
 - $1/4$
52. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as
- d^2
 - d
 - $\sqrt{d}$
 - $1/\sqrt{d}$
53. The root mean square velocity of one mole of a monoatomic gas having molar mass M is $u_{r.m.s.}$. The relation between the average kinetic energy (E) of the gas and $u_{r.m.s.}$ is
- $u_{r.m.s.} = \sqrt{\frac{3E}{2M}}$
 - $u_{r.m.s.} = \sqrt{\frac{2E}{3M}}$
 - $u_{r.m.s.} = \sqrt{\frac{2E}{M}}$
 - $u_{r.m.s.} = \sqrt{\frac{E}{3M}}$
54. The total pressure of a mixture of two gases is :
- The sum of the partial pressures
 - The difference between the partial pressures
 - The product of the partial pressures
 - The ratio of the partial pressures.
55. An ideal gas can't be liquefied because
- its critical temperature is always above 0°C
 - Its molecules are relatively smaller in size
 - it solidifies before becoming a liquid
 - forces between its molecules are negligible
56. When is deviation more in the behaviour of a gas from the ideal gas equation $PV = nRT$?
- At high temperature and low pressure
 - At low temperature and high pressure
 - At high temperature and high pressure
 - At low temperature and low pressure
57. Some moles of O_2 diffuse through a small opening in 18 s. Same number of moles of an unknown gas diffuse through the same opening in 45 s. molecular weight of the unknown gas is :
- $32 \times \frac{45^2}{18^2}$
 - $32 \times \frac{18^2}{45^2}$
 - $32 \times \frac{45}{18}$
 - $32^2 \times \frac{18}{45}$
58. At which one of the following temperature-pressure conditions the deviation of a gas from ideal behaviour is expected to be minimum?
- 350 K and 3 atm.
 - 550 K and 1 atm.
 - 250 K and 4 atm.
 - 450 K and 2 atm.
59. In van der Waal's equation of state of the gas law, the constant 'b' is a measure of
- volume occupied by the molecules
 - intermolecular attraction
 - intermolecular repulsions
 - intermolecular collisions per unit volume

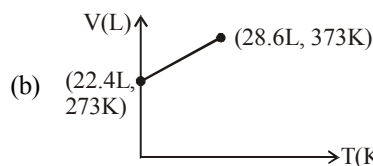
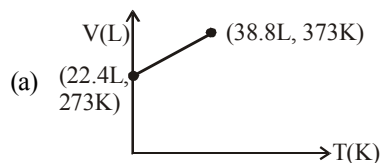
60. At what centigrade temperature will the volume of gas becomes $2x$, if the volume of this gas is ' x ' at 0°C at constant pressure?
 (a) 0°C (b) 237°C
 (c) 273°C (d) 546°C
61. Value of universal gas constant (R) depends upon
 (a) Number of moles of gas
 (b) Volume of gas
 (c) Temperature of gas
 (d) None of these
62. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is
 (a) critical temperature (b) Boyle temperature
 (c) inversion temperature (d) reduced temperature
63. In van der Waal's equation of state for a non-ideal gas, the term that accounts for intermolecular forces is
 (a) $(V-b)$ (b) RT
 (c) $\left(P + \frac{a}{V^2}\right)$ (d) $(RT)^{-1}$
64. The compressibility factor for an ideal gas is
 (a) 1.5 (b) 1.0 (c) 2.0 (d) ∞
65. Graph between P and V at constant temperature is
 (a) straight
 (b) curved increasing
 (c) straight line with slope
 (d) none of these
66. A gas described by van der Waal's equation
 (i) behaves similar to an ideal gas in the limit of large molar volume
 (ii) behaves similar to an ideal gas in the limit of large pressure
 (iii) is characterised by van der Waal's coefficients that are dependent on the identity of the gas but are independent of the temperature
 (iv) has the pressure that is lower than the pressure exerted by the same gas behaving ideally
 (a) (i) and (ii) (b) (i) and (iii)
 (c) (i), (ii) and (iii) (d) (ii) and (iv)
67. Rate of diffusion of NH_3 is twice that of X . What is the molecular mass of X ?
 (a) 68 (b) 48
 (c) 12 (d) 8
68. Gas deviates from ideal gas nature because molecules
 (a) are colourless
 (b) attract each other
 (c) contain covalent bond
 (d) show Brownian movement.
69. The van der Waal's constant ' a ' for four gases P, Q, R and S are 4.17, 3.59, 6.71 and $3.8 \text{ atm L}^2 \text{ mol}^{-2}$ respectively. Therefore, the ascending order of their liquefaction is
 (a) $R < P < S < Q$ (b) $Q < S < R < P$
 (c) $Q < S < P < R$ (d) $R < P < Q < S$
70. At low pressure the van der Waal's equation is reduced to
 (a) $Z = \frac{pV_m}{RT} = 1 - \frac{ap}{RT}$ (b) $Z = \frac{pV_m}{RT} = 1 + \frac{b}{RT} p$
 (c) $pV_m = RT$ (d) $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RT}$
71. Same mass of CH_4 and H_2 is taken in container, The partial pressure caused by H_2 is
 (a) $\frac{8}{9}$ (b) $\frac{1}{9}$
 (c) $\frac{1}{2}$ (d) 1
72. In which molecule the van der Waal's force is likely to be the most important in determining the m.pt. and b.pt.?
 (a) H_2S (b) Br_2
 (c) HCl (d) CO
73. Soap helps in cleaning clothes, because
 (a) chemical of soap change
 (b) it increases the surface tension of the solution
 (c) it absorbs the dirt
 (d) it lowers the surface tension of the solution
74. The r.m.s Velocity of hydrogen is $\sqrt{7}$ times the r.m.s velocity of nitrogen. If T is the temperature of the gas, then
 (a) $T(\text{H}_2) = T(\text{N}_2)$ (b) $T(\text{H}_2) > T(\text{N}_2)$
 (c) $T(\text{H}_2) < T(\text{N}_2)$ (d) $T(\text{H}_2) = \sqrt{7}T(\text{N}_2)$
75. If temperature increases, the surface tension of a liquid
 (a) increases
 (b) decreases
 (c) remains the same
 (d) increases then decreases

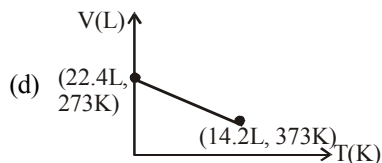
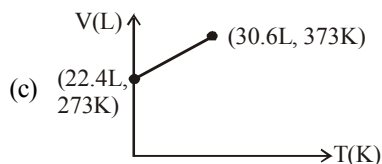
EXERCISE - 2

Applied Questions

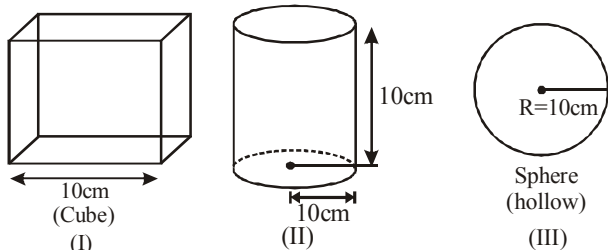
1. The molecular velocities of two gases at the same temperature are u_1 and u_2 . Their masses are m_1 and m_2 respectively. Which of the following expression is correct.
 (a) $m_1/u_1^2 = m_2/u_2^2$ (b) $m_1u_1 = m_2u_2$
 (c) $m_1/u_1 = m_2/u_2$ (d) $m_1u_1^2 = m_2u_2^2$
2. Reducing the pressure from 1.0 atm to 0.5 atm would change the number of molecules in one mole of ammonia to
 (a) 25% of its initial value (b) 50% of its initial value
 (c) 75% of its initial value (d) None of the above
3. Under what conditions will a pure sample of an ideal gas not only exhibit a pressure of 1 atm but also a concentration of $1 \text{ mole litre}^{-1}$? ($R = 0.082 \text{ litre atm mol}^{-1} \text{ deg}^{-1}$)

- (a) At STP
(b) When $V = 22.4$ litres
(c) When $T = 12$ K
(d) Impossible under any conditions
4. The average kinetic energy of 28 g CO at, 300 K is E kcal. The average kinetic energy of 2 g H_2 at the same temperature would be..... kcal.
(a) E (b) $14E$
(c) $1/14E$ (d) $28E$
5. Cyclopropane and oxygen at partial pressures 170 torr and 570 torr respectively are mixed in a gas cylinder. What is the ratio of the number of moles of cyclopropane to the number of moles of oxygen ($n_{C_3H_6}/n_{O_2}$)?
(a) $\frac{170 \times 42}{570 \times 32} = 0.39$ (b) $\frac{170}{42} \div \left(\frac{170}{42} + \frac{570}{32} \right) \approx 0.19$
(c) $\frac{170}{740} = 0.23$ (d) $\frac{170}{570} = 0.30$
6. 14 g of N_2 and 36 g of ozone are at the same pressure and temperature. Their volumes will be related as
(a) $2V_{N_2} = 3V_{O_3}$ (b) $3V_{N_2} = 2V_{O_3}$
(c) $3V_{N_2} = 4V_{O_3}$ (d) $4V_{N_2} = 3V_{O_3}$
7. If 500 ml of gas A at 400 torr and 666.6 ml of B at 600 torr are placed in a 3 litre flask, the pressure of the system will be
(a) 200 torr (b) 100 torr (c) 550 torr (d) 366 torr
8. The beans are cooked earlier in pressure cooker, because
(a) boiling point increases with increasing pressure
(b) boiling point decreases with increasing pressure
(c) internal energy is not lost while cooking in pressure cooker
(d) extra pressure of pressure cooker, softens the beans
9. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules
(a) are above the inversion temperature
(b) exert no attractive forces on each other
(c) do work equal to loss in kinetic energy
(d) collide without loss of energy
10. The reciprocal of compressibility factor of a real gas in the critical state is
(a) $\frac{3}{8}$ (b) $\frac{3}{4}$ (c) $\frac{8}{3}$ (d) $\frac{1}{3}$
11. Use of hot air balloons in sports and meteorological observations is an application of
(a) Boyle's law (b) Charle's law
(c) Kelvin's law (d) Gay-Lussac's law
12. Air at sea level is dense. This is a practical application of
(a) Boyle's law (b) Charle's law
(c) Kelvin's law (d) Brown's law
13. Consider a real gas placed in a container. If the intermolecular attractions are supposed to disappear suddenly which of the following would happen?
(a) The pressure decreases
(b) The pressure increases
(c) The pressure remains unchanged
(d) The gas collapses
14. Calculate the total pressure in a 10.0 L cylinder which contains 0.4 g helium, 1.6 g oxygen and 1.4 g nitrogen at 27°C .
(a) 0.492 atm (b) 49.2 atm
(c) 4.52 atm (d) 0.0492 atm
15. When helium is allowed to expand into vacuum, heating effect is observed. Its reason is that
(a) helium is an ideal gas
(b) helium is an inert gas
(c) the inversion temperature of helium is very low
(d) the boiling point of helium is the lowest amongst the elements
16. Diffusion of helium gas is four times faster than
(a) CO_2 (b) SO_2 (c) NO_2 (d) O_2
17. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends the white ammonium chloride ring first formed will be
(a) at the centre of the tube.
(b) near the hydrogen chloride bottle.
(c) near the ammonia bottle.
(d) throughout the length of the tube.
18. The ratio $\frac{a}{b}$ (a and b being the van der Waal's constants of real gases) has the dimensions of
(a) atm mol^{-1} (b) L mol^{-1}
(c) atm L mol^{-1} (d) atm L mol^{-2}
19. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3} , then the volume occupied by water molecules in 1 litre of steam at that temperature is
(a) 6 cm^3 (b) 60 cm^3 (c) 0.6 cm^3 (d) 0.06 cm^3
20. If V is the volume of one molecule of gas under given conditions, the van der Waal's constant b is
(a) $4V$ (b) $\frac{4V}{N_0}$
(c) $\frac{N_0}{4V}$ (d) $4/N_0$
21. Which of the following volume (V) - temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?





22. If for two gases of molecular masses M_A and M_B at temperatures T_A and T_B , $T_A M_B = T_B M_A$, then which of the following properties has the same magnitude for both the gases
- (a) Pressure (b) Density
(c) Molar K.E. (d) rms velocity
23. Positive deviation from ideal behaviour takes place because of
- (a) molecular interaction between atoms and $PV/nRT > 1$
(b) molecular interaction between atoms and $PV/nRT < 1$
(c) finite size of atoms and $PV/nRT > 1$
(d) finite size of atoms and $PV/nRT < 1$
24. At what temperature the average speed of helium molecule will be the same as that of oxygen molecule at 527°C
- (a) 100 K (b) 200 K (c) 273 K (d) 400 K
25. There are three closed containers in which equal amount of the gas are filled.



If all the containers are placed at the same temperatures, then find the incorrect options –

- (a) Pressure of the gas is minimum in (III) container
(b) Pressure of the gas is equal in I and II container
(c) Pressure of the gas is maximum in (I)
(d) The ratio of pressure in II and III container is 4 : 3
26. The compressibility factor $Z = \frac{PV}{RT}$ for 1 mol of a real gas is greater than unity at a pressure of 1 atm and 273.15 K. The molar volume of the gas at STP will be
- (a) less than 22.4 L (b) greater than 22.4 L
(c) equal to 22.4 L (d) none of these
27. The van der Waals's constants for gases A, B and C are as follows
- | Gas | a (L ² atm mol ⁻²) | b (L mol ⁻¹) |
|-----|---|--------------------------|
| A | 0.024 | 0.027 |
| B | 4.17 | 0.037 |
| C | 3.59 | 0.043 |

Based upon the above data, which of the following statements is correct?

- (i) The gas B has the highest critical temperature

- (ii) The gas A has minimum departure from the ideal behavior
(iii) The gas C has largest molecular volume
- (a) (i) (b) (i) and (ii)
(c) (ii) and (iii) (d) all the three
28. The pressure of 11gm of a gas which is placed in a 4 litres container at 127°C is 2 atm, then the gas would be
(Take : $R = 0.08 \text{ litre atm K}^{-1} \text{ mol}^{-1}$)
- (a) N_2O (b) CO_2
(c) NO_2 (d) Both (a) and (b) possible
29. A mixture of two gases A and B in the mole ratio 2 : 3 is kept in a 2 litre vessel. A second 3L vessel has the same two gases in the mole ratio 3 : 5. Both gas mixtures have the same temperature and same total pressure. They are allowed to intermix and the final temperature and the total pressure are the same as the initial values, the final volume being 5 litres. Given that the molar masses are M_A and M_B . What is the mean molar mass of the final mixture?
- (a) $\frac{5M_A + 8M_B}{13}$ (b) $\frac{77M_A + 123M_B}{200}$
(c) $\frac{123M_A + 77M_B}{250}$ (d) $\frac{123M_A + 77M_B}{150}$
30. Two flasks A and B of equal volumes maintained at temperatures 300K and 600K contain equal mass of H_2 and CH_4 respectively. The ratio of total translational kinetic energy of gas in flask A to that in flask B is
- (a) unity (b) 2 (c) 4 (d) 0.25
31. By what factor does the average velocity of a gaseous molecule increase when the temperature (in Kelvin) is doubled?
- (a) 2.0 (b) 2.8 (c) 4.0 (d) 1.4
32. A bubble of air is underwater at temperature 15°C and the pressure 1.5 bar. If the bubble rises to the surface where the temperature is 25°C and the pressure is 1.0 bar, what will happen to the volume of the bubble?
- (a) Volume will become greater by a factor of 1.6.
(b) Volume will become greater by a factor of 1.1.
(c) Volume will become smaller by a factor of 0.70.
(d) Volume will become greater by a factor of 2.5.
33. 50 mL of each gas A and of gas B takes 150 and 200 seconds respectively for effusing through a pin hole under the similar condition. If molecular mass of gas B is 36, the molecular mass of gas A will be :
- (a) 96 (b) 128 (c) 20.25 (d) 64
34. When r , P and M represent rate of diffusion, pressure and molecular mass, respectively, then the ratio of the rates of diffusion (r_A/r_B) of two gases A and B, is given as :
- (a) $(P_A/P_B)(M_B/M_A)^{1/2}$ (b) $(P_A/P_B)^{1/2}(M_B/M_A)$
(c) $(P_A/P_B)(M_A/M_B)^{1/2}$ (d) $(P_A/P_B)^{1/2}(M_A/M_B)$
35. The compressibility factor for a real gas at high pressure is :
- (a) $1 + \frac{RT}{pb}$ (b) 1
(c) $1 + \frac{pb}{RT}$ (d) $1 - \frac{pb}{RT}$

36. At constant volume and temperature conditions, the rate of diffusion D_A and D_B of gases A and B having densities ρ_A and ρ_B are related by the expression.

$$(a) D_A = \left[D_B \frac{\rho_A}{\rho_B} \right]^{1/2} \quad (b) D_A = \left[D_B \frac{\rho_B}{\rho_A} \right]^{1/2}$$

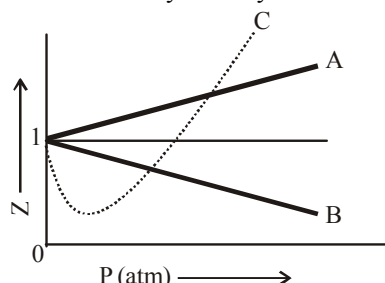
$$(c) D_A = D_B \left(\frac{\rho_A}{\rho_B} \right)^{1/2} \quad (d) D_A = D_B \left(\frac{\rho_B}{\rho_A} \right)^{1/2}$$

37. The compression factor (compressibility factor) for 1 mole of a van der Waal's gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate the van der Waal's constant 'a'.

- (a) $0.253 \text{ L}^2\text{mol}^{-2}\text{atm}$ (b) $0.53 \text{ L}^2\text{mol}^{-2}\text{atm}$
(c) $1.853 \text{ L}^2\text{mol}^{-2}\text{atm}$ (d) $1.253 \text{ L}^2\text{mol}^{-2}\text{atm}$

38. The given graph represents the variation of Z

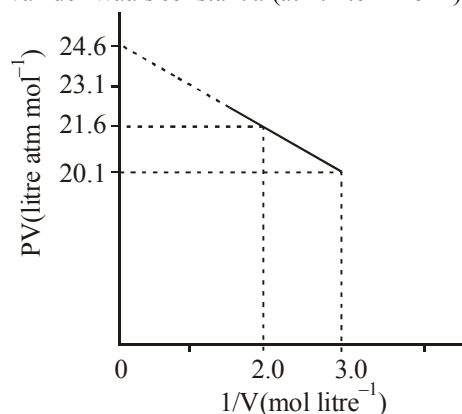
(compressibility factor $= \frac{PV}{nRT}$) versus P , for three real gases A, B and C. Identify the only incorrect statement



- (a) For the gas A, $a = 0$ and its dependence on P is linear at all pressure.
(b) For the gas B, $b = 0$ and its dependence on P is linear at all pressure
(c) For the gas C, which is typical real gas for which neither a nor $b = 0$. By knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated
(d) At high pressure, the slope is positive for all real gases
39. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is

- (a) nb (b) $\frac{an^2}{V^2}$ (c) $-\frac{an^2}{V^2}$ (d) $-nb$

40. For one mole of a van der Waals gas when $b = 0$ and $T = 300 \text{ K}$, the PV vs. $1/V$ plot is shown below. The value of the van der Waals constant a ($\text{atm} \cdot \text{liter}^2 \text{mol}^{-2}$) is :



- (a) 1.0 (b) 4.5 (c) 1.5 (d) 3.0

41. For gaseous state, if most probable speed is denoted by C^* , average speed by $\bar{C}$ and mean square speed by C , then for a large number of molecules the ratios of these speeds are :

- (a) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$
(b) $C^* : \bar{C} : C = 1.128 : 1.225 : 1$
(c) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$
(d) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$

42. Small droplets of a liquid are usually more spherical in shape than larger drops of the same liquid because

- (a) force of surface tension is equal and opposite to the force of gravity
(b) force of surface tension predominates the force of gravity
(c) force of gravity predominates the force of surface tension
(d) force of gravity and force of surface tension act in the same direction and are equal

43. A weather balloon filled with hydrogen at 1 atm and 27°C has volume equal to 12000 litres. On ascending it reaches a place where the temperature is -23°C and pressure is 0.5 atm. The volume of the balloon is

- (a) 24000 litres (b) 20000 litres
(c) 10000 litres (d) 12000 litres

44. The pressure exerted by 6.0g of methane gas in a 0.03 m^3 vessel at 129°C is (Atomic masses : $\text{C} = 12.01$, $\text{H} = 1.01$ and $R = 8.314 \text{ Kpa dm}^3\text{K}^{-1}\text{mol}^{-1}$)

- (a) 31684 Pa (b) 215216 Pa
(c) 13409 Pa (d) 41777 Pa

45. Two gases A and B having the same volume diffuse through a porous partition in 20 and 10 seconds respectively. The molecular mass of A is 49 u. Molecular mass of B will be :

- (a) 50.00 u (b) 12.25 u (c) 6.50 u (d) 25.00 u

46. A gaseous mixture was prepared by taking equal mole of CO and N_2 . If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen (N_2) in the mixture is :

- (a) 0.5 atm (b) 0.8 atm (c) 0.9 atm (d) 1 atm

47. Which one of the following statements is NOT true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?

- (a) The area under the distribution curve remains the same as under the lower temperature
(b) The distribution becomes broader
(c) The fraction of the molecules with the most probable speed increases
(d) The most probable speed increases

DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

48. **Statement-1** : Jet aeroplane flying at high altitude need pressurization of the cabin.

Statement-2 : Oxygen is not present at higher altitude.

49. **Statement-1** : 1 mol of H_2 and O_2 each occupy 22.4 L of volume at $0^\circ C$ and 1 bar pressure.

Statement-2 : Molar volume for all gases at the same temperature and pressure has the same volume.

50. **Statement-1** : Greater the value of van der Waal's constant ' a ' greater is the liquefaction of gas.

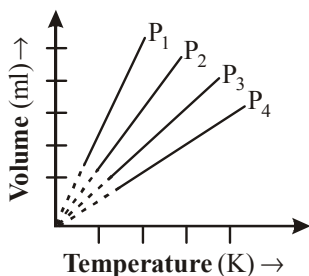
Statement-2 : ' a ' indirectly measures the magnitude of attractive forces between the molecules.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- A person living in Shimla observed that cooking food without using pressure cooker takes more time. The reason for this observation is that at high altitude
 - pressure increases
 - temperature decreases
 - pressure decreases
 - temperature increases
- Which of the following property of water can be used to explain the spherical shape of rain droplets?
 - Viscosity
 - Surface tension
 - Critical phenomena
 - Pressure
- A plot of volume (V) versus temperature (T) for a gas at constant pressure is a straight line passing through the origin. The plots at different values of pressure are shown in figure. Which of the following order of pressure is correct for this gas?



- $P_1 > P_2 > P_3 > P_4$
 - $P_1 = P_2 = P_3 = P_4$
 - $P_1 < P_2 < P_3 < P_4$
 - $P_1 < P_2 = P_3 < P_4$
- The interaction energy of London force is inversely proportional to sixth power of the distance between two interacting particles but their magnitude depends upon
 - charge of interacting particles
 - mass of interacting particles
 - polarisability of interacting particles
 - strength of permanent dipoles in the particles
 - Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is
 - more than unit electronic charge
 - equal to unit electronic charge
 - less than unit electronic charge
 - double the unit electronic charge
 - The pressure of a 1 : 4 mixture of dihydrogen and dioxygen enclosed in a vessel is one atmosphere. What would be the partial pressure of dioxygen?
 - $0.8 \times 10^5 \text{ atm}$
 - 0.008 Nm^{-2}
 - $8 \times 10^4 \text{ Nm}^{-2}$
 - 0.25 atm

- As the temperature increases average kinetic energy of molecules increases. What would be the effect of increase of temperature on pressure provided the volume is constant?
 - Increases
 - Decreases
 - Remains same
 - Becomes half
- Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the particles. Following are the critical temperatures of some gases.

Gases	H_2	He	O_2	N_2
Critical temperature in Kelvin	33.2	5.3	154.3	126

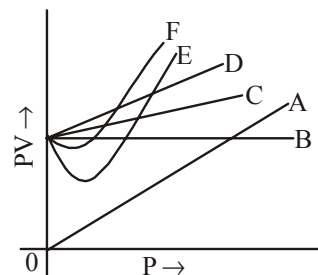
From the above data what would be the order of liquefaction of these gases? Start writing the order from the gas liquefying first

- H_2, He, O_2, N_2
 - He, O_2, H_2, N_2
 - N_2, O_2, He, H_2
 - O_2, N_2, H_2, He
- What is SI unit of viscosity coefficient (η)?
 - Pascal
 - Nsm^{-2}
 - km^{-2}s
 - Nm^{-2}
 - Atmospheric pressures recorded in different cities are as follows

Cities	Shimla	Bengaluru	Delhi	Mumbai
p in N/m^2	1.01×10^5	1.2×10^5	1.02×10^5	1.21×10^5

Consider the above data and mark the place at which liquid will boil first.

- Shimla
 - Bengaluru
 - Delhi
 - Mumbai
- Which curve in figure represents the curve of ideal gas?



- Only B
- C and D
- E and F
- A and B

12. Increase in kinetic energy can overcome intermolecular forces of attraction. How will the viscosity of liquid be affected by the increase in temperature?
(a) Increase
(b) No effect
(c) Decrease
(d) No regular pattern will be followed
13. How does the surface tension of a liquid vary with increase in temperature?
(a) Remains same
(b) Decreases
(c) Increases
(d) No regular pattern is followed
- NEET/AIPMT (2013-2017) Questions**
14. Maximum deviation from ideal gas is expected from :
(a) $\text{N}_2(\text{g})$ (b) $\text{CH}_4(\text{g})$ [2013]
(c) $\text{NH}_3(\text{g})$ (d) $\text{H}_2(\text{g})$
15. Dipole-induced dipole interactions are present in which of the following pairs : [2013]
(a) Cl_2 and CCl_4
(b) HCl and He atoms
(c) SiF_4 and He atoms
(d) H_2O and alcohol
16. What is the density of N_2 gas at 227°C and 5.00 atm pressure? ($R = 0.0821 \text{ atm K}^{-1} \text{ mol}^{-1}$) [NEET Kar. 2013]
(a) 0.29 g/ml (b) 1.40 g/ml
(c) 2.81 g/ml (d) 3.41 g/ml
17. Equal masses of H_2 , O_2 and methane have been taken in a container of volume V at temperature 27°C in identical conditions. The ratio of the volumes of gases $\text{H}_2 : \text{O}_2 : \text{methane}$ would be : [2014]
(a) 8 : 16 : 1 (b) 16 : 8 : 1
(c) 16 : 1 : 2 (d) 8 : 1 : 2
18. A gas such as carbon monoxide would be most likely to obey the ideal gas law at : [2015 RS]
(a) high temperatures and low pressures.
(b) low temperatures and high pressures.
(c) high temperatures and low pressures.
(d) low temperatures and low pressures.
19. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape ? [2016]
(a) $1/8$ (b) $1/4$
(c) $3/8$ (d) $1/2$

Hints & Solutions

EXERCISE - 1

- (b) $\frac{PV}{T} = \text{constant}$ or $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
 $\Rightarrow \frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$
- (c) Given: $P_1 = 740 \text{ mm of Hg}$; $V_1 = 15 \text{ mL}$; $T_1 = 300 \text{ K}$ and $P_2 = 760 \text{ mm of Hg}$; $V_2 = 10 \text{ mL}$; $T_2 = ?$
 Using gas equation,
 $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
 $\Rightarrow \frac{740 \times 15}{300} = \frac{760 \times 10}{T_2}$
 $\Rightarrow T_2 = \frac{760 \times 10 \times 300}{740 \times 15} = 205.405 \approx 205 \text{ K}$
- (c) K.E of n moles of N_2 gas = $\frac{3}{2} nRT$
 Here $n = \frac{14}{28} = \frac{1}{2}$ moles
 $R = 8.31 \text{ J/mol/K}$
 $T = 127^\circ\text{C} = 400 \text{ K}$
 $\therefore \text{K.E} = \frac{3}{2} \times \frac{1}{2} \times 8.31 \times 400 \text{ J}$
 $= 2493.0 \text{ J} = 2.493 \text{ kJ} \approx 2.5 \text{ kJ}$
- (d) According to Boyle's law at constant temperature,
 $V \propto \frac{1}{P}$ or $PV = \text{constant}$
- (d) According to Graham's law of diffusion,
 $r \propto \sqrt{\frac{1}{M}}$
 where r is rate of diffusion of gas and M is its molecular weight
 So, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{r_1}{r_2} = \sqrt{\frac{81}{100}} = \frac{9}{10}$
 $\Rightarrow r_1 : r_2 = 9 : 10$
- (c) Molecules in an ideal gas move with different speeds.
- (b) $R = 0.082 \text{ litre atm K}^{-1} \text{ mole}^{-1}$.
- (b) For an ideal gas, $PV = nRT$
 $\Rightarrow P = \frac{n}{V} RT = \frac{mRT}{MV} = \frac{dRT}{M} \left(\frac{m}{V} = \text{density (say } d) \right)$
 $\text{So, } \frac{P_A}{P_B} = \frac{d_A M_B}{d_B M_A} = \frac{(2d_B) \times M_B}{d_B (M_B/2)} = 4$
- (c) Given $P = 1 \text{ atm}$, $n = 2 \text{ mole}$, $V = 1 \text{ L}$

Let at $T \text{ K}$ the given sample will exhibit pressure of 1 atm and a concentration of 2 M .

For an ideal gas, $PV = nRT$

$$\Rightarrow (1 \text{ atm})(1 \text{ L})$$

$$= (2 \text{ mol})(0.0821 \text{ mol}^{-1} \text{ L atm K}^{-1})T$$

$$\Rightarrow T = \frac{1}{2(0.0821)} \text{ K} = 6.0901 \text{ K} \approx 6.1 \text{ K}$$

So, $T = 6.1 \text{ K}$ is the required condition.

- (c) In the equation $PV = nRT$, n moles of the gas have volume V .
- (b) Given initial volume (V_1) = 500 ml ; Initial temperature (T_1) = $27^\circ\text{C} = 300 \text{ K}$ and final temperature (T_2) = $-5^\circ\text{C} = 268 \text{ K}$.

$$\text{From Charle's law: } \frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } \frac{500}{300} = \frac{V_2}{268}$$

Where V_2 = New volume of gas

$$V_2 = \frac{500}{300} \times 268 = 446.66 \text{ ml.}$$

- (a) Given initial volume (V_1) = 600 c.c. ; Initial pressure (P_1) = 750 mm of Hg and final volume (V_2) = 500 c.c. according to Boyle's law,
 $P_1 V_1 = P_2 V_2$
 or $750 \times 600 = P_2 \times 500$

$$\text{or } P_2 = \frac{750 \times 600}{500} = 900 \text{ mm of Hg}$$

Therefore increase of pressure = $(900 - 750) = 150 \text{ mm of Hg}$

- (a) Rate of diffusion depend upon molecular weight

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow r_1 = r_2 \text{ if } M_1 = M_2$$

Hence, compounds are N_2O and CO_2 as both have same molar mass.

- (b) Use Grahams' law of diffusion

$$\frac{r_{\text{He}}}{r_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \sqrt{\frac{16}{4}} = 2$$

- (c) $PV = nRT$ is for an ideal gas which follows both isothermal and adiabatic processes.

$$16. (a) P \propto d \text{ and } T, \frac{P_1}{P_2} = \frac{d_1 T_1}{d_2 T_2} = \frac{1}{2} \times \frac{2}{1} \Rightarrow P_1 : P_2 = 1 : 1$$

- (a) The gas inside the cylinder of 5 L capacity has pressure $76 \text{ cm of Hg (NTP)}$

The new volume for the gas = $(30 + 5) \text{ L} = 35 \text{ L}$.

$$\text{According to Boyle's law: } P_1 V_1 = P_2 V_2$$

$$76 \times 5 = P_2 \times 35$$

$$\therefore P_2 = \frac{76 \times 5}{35} = 10.85 \approx 10.8 \text{ cm of Hg}$$

18. (a) 0°C is equivalent to 273°K i.e., conditions are same so volume will be V ml.
19. (b) Vander Waal's equation is applicable for real (non-ideal) gases.
20. (a) $8.31 \text{ J.K}^{-1} \text{ mol}^{-1}$
 $1 \text{ cal} = 4.2 \text{ J}$
 $\therefore \frac{8.31}{4.2} \text{ cal.K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal.K}^{-1} \text{ mol}^{-1}$
21. (d) $n \text{ of } \text{O}_2 = \frac{16}{32} = \frac{1}{2}$
 $n \text{ of } \text{H}_2 = \frac{3}{2}$
 Total no. of moles $= \frac{3}{2} + \frac{1}{2} = 2$
 $V = \frac{nRT}{P} = \frac{2 \times 0.082 \times 273}{1} = 44.8 \text{ lit} = 44800 \text{ ml}$
22. (a) $P \propto \frac{1}{V}$ and $\frac{m}{V} = \rho$; $\frac{1}{V} = \frac{\rho}{m}$
 So, $P \propto \frac{\rho}{m}$ i.e. Pressure $\propto \rho$
23. (c) $n = \frac{PV}{RT} = \frac{m}{M}$
 $m = \frac{MPV}{RT} = \frac{34 \times 2 \times 100}{0.082 \times 293} = 282.68 \text{ gm}$
24. (a)
25. (a) When vapour pressure decreases, boiling point increases correspondingly.
26. (b) Because H_2 & Cl_2 gases may react with each other to produce HCl gas hence Dalton's law is not applicable.
27. (a) $r_g = \frac{1}{5} r_{\text{H}_2}$
 $\frac{M_g}{M_{\text{H}_2}} = \left[\frac{r_{\text{H}_2}}{r_g} \right]^2 = (5)^2 = 25$; $M_g = 2 \times 25 = 50$
28. (b) Repulsive force will decrease the compressibility factor i.e. so, value of $Z > 1$ as
 $Z = \frac{PV}{RT}$
 Due to repulsion value of PV will be greater than RT so $Z > 1$.
29. (a) From the graph we can see the correct order of pressures $p_1 > p_3 > p_2$
30. (b) Pressure exerted by hydrogen will be proportional to its mole fraction.
 Mole fraction of $\text{H}_2 = \frac{\frac{w}{2}}{\frac{w}{16} + \frac{w}{2}} = \frac{8}{9}$
31. (a) $\frac{r_{\text{CH}_4}}{r_x} = 2 = \sqrt{\frac{M_x}{M_{\text{CH}_4}}} = \sqrt{\frac{M_x}{16}}$, or $M_x = 64$
32. (b) Under identical conditions, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$
 As rate of diffusion is also inversely proportional to time, we will have, $\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$
 (a) Thus, For He , $t_2 = \sqrt{\frac{4}{2}}(5s) = 5\sqrt{2}s \neq 10s$;
 (b) For O_2 , $t_2 = \sqrt{\frac{32}{2}}(5s) = 20s$
 (c) For CO , $t_2 = \sqrt{\frac{28}{2}}(5s) \neq 25s$;
 (d) For CO_2 , $t_2 = \sqrt{\frac{44}{2}}(5s) \neq 55s$
33. (b) Gases become cooler during Joule Thomson's expansion only if they are below a certain temperature known as inversion temperature (T_i). The inversion temperature is characteristic of each gas and is given by
 $T_i = \frac{2a}{bR}$, where R is gas constant
 Given $a = 0.244 \text{ atm L}^2 \text{ mol}^{-2}$
 $b = 0.027 \text{ L mol}^{-1}$
 $R = 0.0821 \text{ L atm deg}^{-1} \text{ mol}^{-1}$
 $\therefore T_i = \frac{2 \times 0.244}{0.027 \times 0.0821} = 220 \text{ K}$
34. (a) Most probable velocity $= \sqrt{\frac{2RT}{M}}$
 Average velocity $= \sqrt{\frac{8RT}{\pi M}}$
 Root mean square velocity $= \sqrt{\frac{3RT}{M}}$
 $\therefore$ Most probable : Average : Root mean square velocity
 $= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$
35. (c) According to kinetic gas equation
 $PV = \frac{1}{3} mNu^2$, u = root mean square velocity
 $\Rightarrow u^2 = \frac{3PV}{mN}$ or $u \propto \frac{1}{\sqrt{m}}$ i.e. $u \propto m^{-\frac{1}{2}}$
36. (d) A liquid boils at lower temperature at the top of a mountain.
37. (c) Here volume is constant. Again the mass of H_2 is fixed so the number of moles of the gas do not change. As temperature increases the pressure also increases. The rate of collision among the gas molecules and their energy also increases.
38. (a) $PV = \frac{1}{3} mnu^2 = \frac{1}{3} Mu^2$
 $= \frac{2}{3} \cdot \frac{1}{2} Mu^2 = \frac{2}{3} E$ or $P = \frac{2}{3} E$ per unit vol.

39. (b) Rate of diffusion

$$\propto \frac{1}{\sqrt{\text{density}}} \propto \frac{1}{\sqrt{\text{molality}}}$$

NH_3 has the highest rate of diffusion as it is the lightest molecule.

40. (d)
- $u \propto \sqrt{T}$
- or
- $u_1/u_2 = \sqrt{T_1/T_2}$

$$= \sqrt{\frac{27+273}{927+273}} = \sqrt{\frac{300}{1200}} = \frac{1}{2}$$

$$u_2 = 2u_1$$

41. (c) Average molar kinetic energy =
- $\frac{3}{2}kT$

As temperature is same hence average kinetic energy of CO and N_2 is same.

42. (b) The inversion temp is the temp below which the gas warms up on expansion

$$\text{for, Vander Waal's gas, } T_i = \left(\frac{2a}{Rb} \right).$$

43. (c) R.M.S. velocity =
- $\sqrt{\frac{3RT}{M}}$

Average velocity

$$= \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8}{3\pi}} \times \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{8}{3\pi}} \times \text{R.M.S. velocity}$$

$$= 0.921 \times 1000 = 921 \text{ m/sec}$$

44. (b) According to kinetic theory the gas molecules are in a state of constant rapid motion in all possible directions colliding in a random manner with one another and with the walls of the container and between two successive collisions molecules travel in a straight line path but show haphazard motion due to collisions.

45. (a)
- $\frac{\text{K.E of neon at } 40^\circ\text{C}}{\text{K.E of neon at } 20^\circ\text{C}} = \frac{\frac{3}{2}K \times 313}{\frac{3}{2}K \times 293} = \frac{313}{293}$

46. (b)
- $\frac{R}{N_0}$
- is also known as Boltz mann's constant.

47. (a)
- $u_{rms} : u_{av} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}}$
- or
- $\sqrt{3} : \sqrt{\frac{8}{\pi}} = 1.086 : 1$

48. (d)
- $u_{rms} = \sqrt{\frac{3RT}{M}}$
- (As
- $PV = RT$
-) (i)

By putting this value in eq. (i) we get

$$= \sqrt{\frac{3PV}{M}}$$

$$\text{Now, } \frac{PVM}{M} = RT = PM = dRT = T = \frac{PM}{dR}$$

By substituting T in eq. (i) we get

$$= \sqrt{\frac{3RPM}{dRM}} = \sqrt{\frac{3P}{d}}$$

49. (b) Rate of diffusion
- $\propto \frac{1}{\sqrt{\text{molecular weight}}}$

$$\text{So, ratio of rate of diffusion} = \sqrt{\frac{25}{4}} = \frac{5}{2}$$

50. (c) K.E.
- $\propto T$
- [K.E. of one molecule of monoatomic gas =
- $\frac{3}{2}RT$
-]

As temperature increases to

$$\frac{927+273}{27+273} = \frac{1200}{300} = 4 \text{ times}$$

therefore, Kinetic energy will be increased to 4 times.

51. (c) The expression of root mean square speed is

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

Hence,

$$\frac{u_{rms}(\text{H}_2)}{u_{rms}(\text{O}_2)} = \left[\frac{3R(50\text{K})/(2\text{g mol}^{-1})}{3R(800\text{K})/(32\text{g mol}^{-1})} \right]^{1/2} = 1$$

52. (d)
- $u_{rms} = \sqrt{\frac{3RT}{M}}$
- Using ideal gas equation,

$$PV = nRT = \frac{w}{M} RT; \quad \frac{RT}{M} = \frac{PV}{w} = \frac{P}{d} \text{ where } d \text{ is the density of the gas}$$

$$\therefore u_{rms} = \sqrt{\frac{3P}{d}} \text{ at constant pressure, } u_{rms} \propto \frac{1}{\sqrt{d}}$$

53. (c) Average KE =
- $E = \frac{1}{2} M u_{rms}^2$

$$\therefore u_{rms}^2 = \frac{2E}{M} \text{ or } u_{rms} = \sqrt{\frac{2E}{M}}$$

54. (a) By Dalton's law of partial pressures, the total pressure of a mixture of two gases is the sum of the partial pressures.

55. (d) In the ideal gas, the intermolecular forces of attraction are negligible and hence it cannot be liquefied.

56. (b) At low temperature and high pressure.

57. (a)
- $r_1 = \frac{V}{t_1} = \frac{V}{18}, r_2 = \frac{V}{t_2} = \frac{V}{45}$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{18}{45} = \sqrt{\frac{x}{32}}$$

$$\Rightarrow \sqrt{\frac{x}{32}} = \frac{45}{18} \Rightarrow x = 32 \times \frac{45^2}{18^2}$$

58. (b) At low pressure and high temperature real gas nearly behave like ideal gas. Hence deviation is minimum from ideal behaviour.
 59. (a) In van der Waals equation 'b' is for volume correction
 60. (c) By ideal gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Given that,

$$P_1 = P_2, V_1 = x, V_2 = 2x,$$

$$T_1 = 273 \text{ K}, T_2 = ?$$

On putting value

$$\frac{P_2 x}{273} = \frac{P_2 2x}{T_2}$$

$$T_2 = 2 \times 273 = 546 \text{ K or } 273^\circ\text{C}$$

Hence, option (d) is correct.

61. (d) Value of gas constant depends only upon units of measurement.
 62. (b) The temperature at which a real gas behaves like an ideal gas is called Boyle's temperature or Boyle's point.
 63. (c) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$; Here $\left(P + \frac{a}{V^2}\right)$ represents the intermolecular forces.
 64. (b) The compressibility factor of a gas is defined as

$$Z = \frac{pV_m}{RT}$$

For an ideal gas, $pV_m = RT$. Hence $Z = 1$

65. (d) $P \propto \frac{1}{V}$ (at constant T)
 $\therefore PV = \text{constant}$.
 66. (b)
 (i) At very large molar volume
 $P + \frac{a}{V_m^2} \approx P$ and $V_m - b = V_m$
 (iii) According to van der Waals equation 'a' and 'b' are independent of temperature.
 67. (a) r_1 = rate of diffusion of $\text{NH}_3 = 2R$
 r_2 = rate of diffusion of X = R
 M_1 = Molecular mass of NH_3
 $= 14 + 1 \times 3 = 17$
 $M_2 = ?$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{or } \frac{2R}{R} = \sqrt{\frac{M_2}{17}}$$

$$\text{or } 2 = \sqrt{\frac{M_2}{17}}$$

$$\therefore M_2 = 17 \times 4 = 68$$

68. (b) Due to intermolecular interactions appreciable at high P and low T, the ideal gas deviates from ideal behaviour.
 69. (c) Easily liquefiable gases have greater intermolecular forces which is represented by high value of 'a'. The greater the value of 'a' more will be liquefiability.
 So, the order is $Q < S < P < R$.
 70. (a) When pressure is low 'b' can be neglected, thus

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V}$$

$$\frac{PV}{RT} = \frac{RT}{RT} - \frac{a}{VRT}$$

$$Z = \frac{PV}{RT} = 1 - \frac{a}{VRT}$$

71. (a) Let the mass be x, then moles of CH_4 and H_2 are $\frac{x}{16}$ & $\frac{x}{2}$;

$$\text{Total moles} = \frac{9x}{16}$$

$$p_{\text{H}_2} = \text{mole fraction} \times P = \frac{x/2}{9x/16} \cdot P = \frac{8}{9}P$$

72. (b)
 73. (d) Soap helps to lower the surface tension of solution, thus soap get stick to the dust particles and grease and these are removed by action of water.

$$74. (c) \frac{U_{\text{H}_2}}{U_{\text{N}_2}} = \sqrt{\frac{T_{\text{H}_2}}{T_{\text{N}_2} \times 2}} = \sqrt{7} \Rightarrow \frac{T_{\text{H}_2}}{T_{\text{N}_2}} = \frac{1}{2}$$

$$\Rightarrow T_{\text{N}_2} = 2T_{\text{H}_2}$$

$$\therefore T_{\text{N}_2} > T_{\text{H}_2}$$

75. (b)

EXERCISE - 2

1. (d) $u_{\text{rms}} \propto \sqrt{\frac{1}{M}} : u_1 \propto \sqrt{\frac{1}{m_1}}, u_2 \propto \sqrt{\frac{1}{m_2}} \therefore \frac{u_1^2}{u_2^2} = \frac{m_2}{m_1}$
 2. (d) One mole of a substance contains the number of molecules which is independent of pressure.
 3. (c) $PV = nRT$ or $P = \frac{n}{V} RT = CRT$.
 Hence $1 = 1 \times 0.082 \times T$ is $T = \frac{1}{0.082} = 12\text{K}$
 4. (a) $28\text{g of CO} = \frac{28}{28} = 1 \text{ mole}; 2\text{g H}_2 = \frac{2}{2} = 1 \text{ mole}$

Since the temperature and moles are the same, the average kinetic energy will also be the same.

5. (d) By Ideal gas equation

$$P_1 V = n_1 R T$$

$$n_1 \propto P_1 \text{ and } n_2 \propto P_2$$

$$\frac{n_1}{n_2} = \frac{P_1}{P_2} \Rightarrow \frac{n_1}{n_2} = \frac{170}{570} = 0.30$$

6. (b) At the same conditions of T and P , $V \propto n$

$$n_{N_2} = \frac{14}{28} = \frac{1}{2}; V_{N_2} \propto \frac{1}{2} \quad n_{O_3} = \frac{36}{48} = \frac{3}{4}; V_{O_3} \propto \frac{3}{4}$$

$$\text{Hence, } V_{N_2} / V_{O_3} = \frac{2}{3}, 3V_{N_2} = 2V_{O_3}$$

7. (a) Applying Boyle's law $P_1 V_1 = P_2 V_2$ for both gases

$$\frac{500}{1000} \times 400 = P \times 3 \Rightarrow P = \frac{200}{3}$$

$$600 \times \frac{666.6}{1000} = P' \times 3 \Rightarrow P' = \frac{400}{3}$$

$$\Rightarrow P_T = P + P' = \frac{200}{3} + \frac{400}{3} = \frac{600}{3} = 200 \text{ torr}$$

8. (a) The beans are cooked earlier in pressure cooker because boiling point increases with increasing pressure.

9. (b) No work is required to tear apart the molecules due to the absence of attractive forces in an ideal gas.

10. (c) Critical compressibility factor $Z = \frac{P_c V_c}{R T_c}$

$$P_c = \frac{a}{27} b^2; V_c = 3b, T_c = \frac{8a}{Rb}$$

$$\text{Hence, } Z = \frac{3}{8} \text{ or } \frac{1}{Z} = \frac{8}{3}$$

11. (b) Hot air is lighter due to less density (Charles's law)

$$\left(d = \frac{MP}{RT} \right)$$

12. (a) $d \propto P$, Boyle's law, $\left(d = \frac{MP}{RT} \right)$. At sea level pressure is more, hence density of air is more.

13. (b)

14. (a) Given $T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$

$$V = 10.0 \text{ L}$$

$$\text{Mass of He} = 0.4 \text{ g}$$

$$\text{Mass of oxygen} = 1.6 \text{ g}$$

$$\text{Mass of nitrogen} = 1.4 \text{ g}$$

$$n_{\text{He}} = 0.4/4 = 0.1$$

$$n_{\text{O}_2} = 1.6/32 = 0.05$$

$$n_{\text{N}_2} = 1.4/28 = 0.05$$

$$n_{\text{total}} = n_{\text{He}} + n_{\text{O}_2} + n_{\text{N}_2} = 0.1 + 0.05 + 0.05 = 0.2$$

$$P = \frac{nRT}{V} = \frac{0.2 \times 0.082 \times 300}{10} = 0.492 \text{ atm}$$

15. (c) Since the inversion temperature of helium is very low, hence during the expansion into vacuum, heating effect

is observed.

16. (b) rate of diffusion $\propto \sqrt{\frac{1}{\text{molecular mass}}}$

Let the molecular mass of the gas $X = M_x$

$$\text{Thus } \frac{r_{\text{He}}}{r_x} = 4 = \sqrt{\frac{M_x}{M_{\text{He}}}}$$

$$\text{or } 4 = \sqrt{\frac{M_x}{4}} \text{ or } 16 = \frac{M_x}{4}$$

$$\text{or } M_x = 64$$

The molecular masses of given gases are 44, 64, 46 and 32 respectively. Thus (b) is correct option.

17. (b) Rate of diffusion $\propto \sqrt{\frac{1}{\text{Molecular mass}}}$

$\therefore$ Molecular mass of $\text{HCl} >$ Molecular mass of NH_3

$\therefore$ HCl diffuses at slower rate and white ammonium chloride is first formed near HCl bottle.

18. (c) $a = \frac{PV^2}{n^2}$ ($\text{atm L}^2 \text{ mol}^{-2}$); $b = \text{L mol}^{-1}$;

$$\text{Hence, } \frac{a}{b} = \left(\frac{\text{atm L}^2 \text{ mol}^{-2}}{\text{L mol}^{-1}} \right) = \text{atm L mol}^{-1}$$

19. (c) Mass of 1 L of vapour = volume $\times$ density
 $= 1000 \times 0.0006 = 0.6 \text{ g}$

$$V \text{ of liquid water} = \frac{\text{mass}}{\text{density}} = \frac{0.6}{1} = 0.6 \text{ cm}^3$$

20. (d) van der Waals's constant $b = 4$ times the actual volume of 1 mole molecules $= 4 V N_0$

21. (c) Find the volume by either $V = RT/P$ ($PV = RT$) or $P_1 V_1 = P_2 V_2$ and match it with the values given in graph to find correct answer.
 Volume of 1 mole of an ideal gas at 273 K and 1 atm pressure is 22.4 L and that at 373 K and 1 atm pressure is calculated as ;

$$V = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.58 \text{ L} \approx 30.6 \text{ L}$$

22. (d)

23. (c) For positive deviation: $PV = nRT + nPb$

$$\Rightarrow \frac{PV}{nRT} = 1 + \frac{Pb}{RT}$$

Thus, the factor nPb is responsible for increasing the PV value, above ideal value. b is actually the effective volume of molecules. So, it is the finite size of molecules that leads to the origin of b and hence positive deviation at high pressure.

24. (a) For equal average speeds of two of gases,

$$\sqrt{\frac{T_1}{M_1}} = \sqrt{\frac{T_2}{M_2}}$$

$$T_1 = ?; M_1 = 4; T_2 = 273 + 527 = 800 \text{ K}; M_2 = 32$$

25. (b) n, T same hence $P \propto \frac{1}{V}$,

$$V_1 = 1000 \text{ cm}^3$$

$$V_2 = \pi(10)^2 \times 10 = 1000\pi \text{ cm}^3$$

$$V_3 = \frac{4}{3}\pi(10)^3 = \frac{4}{3}\pi 1000 \text{ cm}^3$$

$\therefore$ Pressure of the gas is minimum in (III) container, pressure of the gas is maximum in (I),

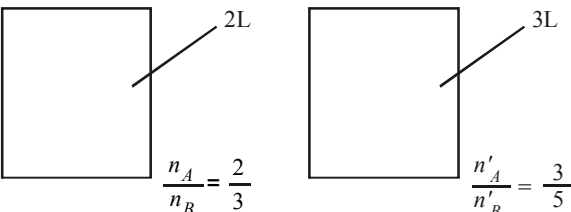
The ratio of pressure in II and III container is 4 : 3

26. (b) The gas is less compressible than ideal gas. Hence, $V_m > 22.4\text{L}$

27. (d) (i) Greater is the van der Waals's constant a , higher would be T_c (easier liquefaction of the gas).
(ii) Smaller the constants a and b , lesser departure from ideal behaviour.
(iii) Greater the constant b , larger is the molecular volume.

28. (d) Calculate molar mass M ,

$$M = \frac{mRT}{PV} = \frac{11 \times 0.08 \times 400}{2 \times 4} = 44$$

29. (b) 

$$\text{Mean molar mass} = \frac{(n_A + n'_A) M_A + (n_B + n'_B) M_B}{n_A + n'_A + n_B + n'_B}$$

30. (c) K.E. = $\frac{3}{2}nRT$; K.E.(H₂) = $\frac{3}{2} \times \frac{w}{2} \times R \times 300$;

$$\text{K.E.}(\text{CH}_4) = \frac{3}{2} \times \frac{w}{16} \times R \times 600$$

$$\text{Hence } \frac{\text{K.E.}(\text{H}_2)}{\text{K.E.}(\text{CH}_4)} = 4$$

31. (d) Average velocity = $\sqrt{\frac{8RT}{\pi M}}$

$$\text{i.e., } v \propto \sqrt{T}$$

$$\therefore \frac{v_2}{v_1} = \sqrt{\frac{2T}{T}} = 1.41$$

32. (a) Given

$$P_1 = 1.5 \text{ bar } T_1 = 273 + 15 = 288 \text{ K } V_1 = V$$

$$P_2 = 1.0 \text{ bar } T_2 = 273 + 25 = 298 \text{ K } V_2 = ?$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{1.5 \times V}{288} = \frac{1 \times V_2}{298}$$

$V_2 = 1.55 V$ i.e., volume of bubble will be almost 1.6 times to initial volume of bubble.

33. (c) $\frac{V_A}{t_A} / \frac{V_B}{t_B} = \sqrt{\frac{M_B}{M_A}}$

$$\Rightarrow \frac{200}{150} = \sqrt{\frac{36}{M_A}} \Rightarrow \frac{4}{3} = \sqrt{\frac{36}{M_A}}$$

$$\Rightarrow \frac{16}{9} = \frac{36}{M_A} \Rightarrow M_A = \frac{81}{4} = 20.25$$

34. (a) $r \propto \frac{p}{\sqrt{m}}$

$$\frac{r_A}{r_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}}$$

35. (c) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ at high pressure $\frac{a}{V^2}$ can be neglected

$$PV - Pb = RT \text{ and } PV = RT + Pb$$

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{Pb}{RT}; Z > 1 \text{ at high pressure}$$

36. (d) $\frac{D_A}{D_B} = \sqrt{\frac{\rho_B}{\rho_A}} = \left[\frac{\rho_B}{\rho_A}\right]^{1/2}; \therefore D_A = D_B \left(\frac{\rho_B}{\rho_A}\right)^{1/2}$

37. (d) We know that

$$Z = \frac{PV}{nRT} \Rightarrow 0.5 = \frac{100 \times V}{1 \times 0.0821 \times 273} \Rightarrow V = 0.112 \text{ lit.}$$

According to van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

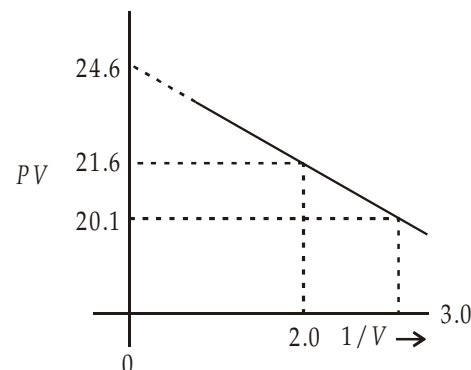
$$\left(100 + \frac{a}{(0.112)^2}\right)(0.112 - 0) = 0.0821 \times 273$$

$$a = 1.253 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$$

38. (b)

39. (b) Correction factor for attractive force for n moles of real gas is given by the term mentioned in (b).

40. (c)



$$\left(P + \frac{a}{V^2}\right)(V) = RT$$

$$PV + a/V = RT$$

$$PV = RT - \frac{a}{V}$$

$$y = RT - a(x)$$

$$\text{So, slope} = -a = \frac{21.6 - 20.1}{2 - 3} = -a = -1.5$$

$$a = 1.5$$

41. (c) Most probable speed (C^*) = $\sqrt{\frac{2RT}{M}}$

$$\text{Average Speed } (\bar{C}) = \sqrt{\frac{8RT}{\pi M}}$$

$$\text{Root mean square velocity } (C) = \sqrt{\frac{3RT}{M}}$$

$$C^* : \bar{C} : C = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.225$$

42. (b)

43. (b) $V_2 = \frac{P_1}{P_2} \cdot \frac{T_2}{T_1} \cdot V_1 = \frac{1}{0.5} \times \frac{250}{300} \times 12000 \text{ lit.} = 20000 \text{ lit.}$

44. (d) $P = \frac{nRT}{V} = \frac{6}{16} \times \frac{8.314 \times 402}{0.03 \times 10^3} \simeq 41777 \text{ Pa}$

45. (b) $\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$

$$\frac{\frac{V}{20}}{\frac{V}{10}} = \sqrt{\frac{M_B}{49}} \Rightarrow \frac{1}{2} = \sqrt{\frac{M_B}{49}}$$

$$M_B = \frac{1}{4} \times 49 = 12.25$$

46. (a) Given $n_{\text{CO}} = n_{\text{N}_2}$

$$P_{\text{CO}} + P_{\text{N}_2} = 1 \text{ atm}$$

$$\text{Partial pressure of a gas} \\ = \text{mole fraction of gas} \times \text{total pressure}$$

$$\therefore P_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{CO}} + n_{\text{N}_2}} \times 1 = \frac{n_{\text{N}_2}}{2n_{\text{N}_2}} \times 1 = \frac{1}{2} = 0.5 \text{ atm.}$$

47. (c) As temperature rises the most probable speed increases and the fraction of molecules possessing most probable speed decreases.

48. (c) The air pressure decreases with increase in altitude. So the partial pressure of oxygen is not sufficient for breathing at higher altitude and thus pressurization is needed to increase the concentration of oxygen.

49. (a) At STP one mole of each gas occupies 22.4 L

50. (a) Considering the attractive forces between gas molecules pressure in ideal gas equation ($PV = nRT$) is corrected by

$$\text{introducing a factor of } \frac{an^2}{V^2} \text{ where 'a' is a van der Waal's constant.}$$

EXERCISE - 3

Exemplar Questions

- (c) At high altitude pressure is low hence boiling point is low due to which things take more time to cook. However, in a pressure cooker, pressure is increased and hence, boiling point increases. Thus, in a pressure cooker food get cook faster i.e. a less period of time.
- (b) The property of surface tension explain the spherical shape of rain droplets. Surface tension tries to decrease the surface area of the liquid to the minimum. The rain droplets are spherical because for a given volume, a sphere has minimum surface area.
- (c) According to Boyle's law at a particular temperature, $PV = \text{constant}$
Thus, $P_1 V_1 = P_2 V_2 = P_3 V_3 = P_4 V_4$
As $V_1 > V_2 > V_3 > V_4$
Therefore, $P_1 < P_2 < P_3 < P_4$
- (c) London dispersion force is a temporary attractive force that results when the electrons in two adjacent atom occupy position that makes the atoms form temporary dipoles. The energy of interaction varies as

$$\frac{1}{(\text{distance between two interacting particles})^6}$$

Larger or more complex are the molecules, greater is the magnitude of London forces. This is obviously due to the fact that the large electron clouds are easily distorted or polarised. Hence, greater the polarisability of the interacting particles, greater is the magnitude of the interaction energy.

- (c) Dipole-dipole forces act between the molecules possessing permanent dipole and ends of dipoles possess 'partial charges'. Partial charges present on ends of a dipole are always less than the unit electronic charge.
- (c) Let the number of moles of dihydrogen and dioxygen be 1 and 4.

$$\text{Mole fraction of } \text{O}_2 = \frac{4}{5}$$

$$\text{Partial pressure of } \text{O}_2 = \text{Mole fraction of } \text{O}_2 \times \text{total pressure of mixture}$$

$$= \frac{4}{5} \times 1 \text{ atm}$$

$$= 0.8 \text{ atm} = 0.8 \times 10^5 \text{ Nm}^{-2} = 8 \times 10^4 \text{ Nm}^{-2}$$

- (a) From Gay-Lussac's law, at constant volume, as the temperature is increased, pressure increases.
- (d) Higher the critical temperature, more easily is the gas get liquified. Hence, order of liquefaction starting with the gas liquefying first will be : $\text{O}_2, \text{N}_2, \text{H}_2, \text{He}$.
- (b) The SI unit of viscosity coefficient (η) in $\text{Nm}^{-2} \text{ s}$ or Nsm^{-2} .

$$\text{As we know that, } f = \eta A \frac{dv}{dx}$$

where, f = force

η = viscosity coefficient

$\frac{dv}{dx}$ = velocity gradient

Substitute SI units of $f = \text{N}$, $dx = \text{m}$, $A = \text{m}^2$ and $v = \text{ms}^{-1}$ in above equation, we get,

$$\eta = \frac{\text{N} \times \text{m}}{\text{m}^2 \times \text{ms}^{-1}} = \text{Nm}^{-2}\text{s}$$

Hence, the SI unit of η is Nsm^{-2}

10. (a) Among all the four cities Shimla has the lowest atmospheric pressure. Since lower the atmospheric pressure, lower is the boiling point. Thus, at Shimla liquid will boil first.
11. (a) For ideal gas $PV = \text{constant}$ at all pressures. Therefore, only B represents ideal gas.
12. (c) Kinetic energy of the molecules of liquid increases with increase of temperature, which can overcome the intermolecular forces. Hence, the liquid starts flowing. In other words the viscosity of a liquid decrease with increase in temperature.
13. (b) The surface tension of liquids generally decreases with increase of temperature and becomes zero at the critical temperature. This is due to the fact that with increase of temperature, the kinetic energy of the molecules increases and therefore, the intermolecular attraction decreases.

NEET/AIPMT (2013-2017) Questions

14. (c) Higher the critical temperature more easily will be the gas liquify. Now since most easily liquifiable gas show larger deviation, NH_3 will show maximum deviation from ideal behaviour.

15. (b) This type of attractive force operates between the polar molecules having permanent dipole and the molecules lacking permanent dipole.
HCl is polar ($\mu \neq 0$) and He is non polar ($\mu = 0$), thus gives dipole-induced dipole interaction.

$$16. (d) \text{Density} = \frac{PM}{RT} = \frac{5 \times 28}{0.0821 \times 500} = 3.41 \text{g/ml}$$

17. (c) According to Avogadro's law "At same temperature and pressure

Volume $\propto$ no. of moles"

$$n_{\text{H}_2} = \frac{w}{2}; \quad n_{\text{O}_2} = \frac{w}{32}; \quad n_{\text{CH}_4} = \frac{w}{16}$$

$$\therefore V_{\text{H}_2} : V_{\text{O}_2} : V_{\text{CH}_4} = n_{\text{H}_2} : n_{\text{O}_2} : n_{\text{CH}_4}$$

$$= \frac{w}{2} : \frac{w}{32} : \frac{w}{16} = 16 : 1 : 2$$

18. (a) At high temperature and low pressure.
19. (a) Given, $n_{\text{H}_2} = n_{\text{O}_2}$ and $t_{\text{H}_2} = t_{\text{O}_2}$
According to Graham's law of diffusion for two different gases.

$$\frac{r_{\text{H}_2}}{r_{\text{O}_2}} = \frac{v_1 / t_1}{v_2 / t_2} \Rightarrow \sqrt{\frac{M_{\text{O}_2}}{M_{\text{H}_2}}} = \sqrt{\frac{32}{2}}$$

$$\frac{1/2}{1/x} = \sqrt{16} = 4$$

$$\frac{x}{2} = 4$$

$$\therefore x = 8$$

$$\therefore \text{Fraction of } \text{O}_2 = 1/8$$

Chapter

6

Thermodynamics

SOME IMPORTANT THERMODYNAMIC TERMS

The System and The Surroundings

System in thermodynamics refers to that part of universe in which observations are made and remaining universe constitute the surroundings.

Universe = system + surroundings

Types of System

- (i) **Open System** : In this system there is exchange of energy and matter between system and its surroundings
- (ii) **Closed System** : In this system there is no exchange of matter, but exchange of energy is possible between system and its surroundings
- (iii) **Isolated System** : In this system there is no exchange of matter and energy between system and surroundings.

State of the System and State Variables

The state of a thermodynamic system is described by its measurable or macroscopic properties. Variables like pressure (P), volume (V) and temperature (T) are called state variables or state functions because their values depend only on state of system and not on how it is reached.

The state of a system is specified by state functions or state variables.

Macroscopic System and Macroscopic Properties

If a system contains a large no. of chemical species, it is called a macroscopic system. The properties of macroscopic system like temperature, pressure, volume, density, melting point, boiling point, etc are called macroscopic properties.

They are further divided into two types :

- (i) **Extensive properties**
They depend on quantity of matter contained in system
Example : mass, volume, heat capacity etc.
- (ii) **Intensive properties** depend only on nature of substance and are independent of amount of substance present in system
Example : temperature, pressure, density, etc.

Thermodynamic Processes

These are said to occur when a system changes from one state to another.

- (i) **Isothermal process** occurs when temperature remains constant throughout the process.
- (ii) **Adiabatic process** occurs when no heat can flow from system to its surroundings and vice-versa.

- (iii) **Isochoric process** occurs when volume of the system is kept constant.
- (iv) **Isobaric process** occurs when pressure of the system is kept constant.
- (v) **Cyclic Process** – The process in which a system proceeds via many intermediate steps and returns to the initial state. Change in internal energy (dE) = 0, change in enthalpy (dH) = 0

Thermodynamic Quantities

Internal energy

The energy stored within a substance is called its internal energy. It is represented by 'U' or 'E'. It is the sum of different types of energies associated with atoms and molecules.

The change in internal energy is given by:

$$\Delta U = U_2 - U_1.$$

where,

U_2 : final state

U_1 : initial state

The internal energy of a system changes when

- (i) heat passes in or out of the system.
- (ii) work is done on or by the system.
- (iii) matter enters or leaves the system.

It is a state function and is an extensive property.

ΔU is negative if energy is evolved and ΔU is positive if energy is absorbed.

Internal energy of one mole of a monoatomic gas at 'T' Kelvin is

$\frac{3}{2} RT$. Internal energy of ideal gas is a function of temperature only.

In isothermal processes (T is constant), $\Delta U = 0$.

Work

There are two types of work in Thermodynamics :

- (i) Electrical work = EMF $\times$ quantity of electricity
- (ii) Pressure – volume work

$$W = -P_{\text{ext}} \Delta V$$

$$(\Delta V = V_2 - V_1 = V_{\text{final}} - V_{\text{initial}})$$

Work done on the system is positive while work done by the system is negative

For free expansion of an ideal gas, $P_{\text{ext}} = 0$, $\therefore W = 0$

Heat

It is a mode of energy exchanged between the system and the surroundings as a result of difference of temperature between them. It is represented by 'q', when heat is given by the system, it

is given negative sign.

When heat is absorbed by the system, it is given positive sign.

Work and heat are not state functions.

FIRST LAW OF THERMODYNAMICS

It is the law of conservation of energy.

According to this law, *energy can neither be created nor destroyed although it may be converted from one form to another*

or

The energy of an isolated system is constant.

Mathematically, $\Delta U = q + W$

where, q = energy absorbed by the system

W = workdone on the system.

SOME IMPORTANT RESULTS

- For isothermal irreversible expansion,
 $q = -W = P_{\text{ext}}(V_2 - V_1)$
- For isothermal reversible expansion or compression from volume V_1 to V_2
 $q = -W = nRT \ln \frac{V_2}{V_1}$
- For isothermal expansion of an ideal gas against vacuum i.e. for free expansion,
 $\Delta U = 0$, $W = 0$, $q = 0$
- Since internal energy of an ideal gas is a function of temperature, for all isothermal processes involving ideal gas, $\Delta U = 0$, whether the process is reversible or irreversible.
- For adiabatic change, $q = 0$, therefore $\Delta U = W_{\text{ad}}$.
- For isochoric process, $W = 0$
 $\therefore \Delta U = q_v + 0$ i.e., heat given to system at constant volume changes internal energy.

ENTHALPY, H

The total heat content of a system at constant pressure is known as its enthalpy

From 1st law of thermodynamics,

$$\Delta U = q + W$$

$$\text{As } W = -P \Delta V$$

$$\therefore q = \Delta U + P \Delta V$$

At constant volume, $\Delta V = 0$, we have

$$q_v = \Delta U$$

At constant pressure, we have

$$q_p = \Delta U + P \Delta V$$

$$\text{or, } q_p = (U_2 - U_1) + P(V_2 - V_1)$$

$$q_p = (U_2 + PV_2) - (U_1 + PV_1) \quad \dots (1)$$

The quantity $(U + PV)$ is called heat content or enthalpy of the system.

$$\therefore H = U + PV$$

$$\text{Also, } H_2 = U_2 + PV_2 \text{ and } H_1 = U_1 + PV_1$$

Putting these values in eq (1),

$$q_p = H_2 - H_1$$

$$\text{or, } q_p = \Delta H$$

$$\text{as } q_p = \Delta U + P \Delta V$$

$$\therefore \Delta H = \Delta U + P \Delta V$$

Enthalpy is a state function and an extensive property.

$$\text{Enthalpy of monoatomic gas} = \frac{5}{2} RT \text{ per mole.}$$

Change in enthalpy of the products and reactants at 298 K and 1 atmospheric pressure is called **standard molar enthalpy change**.

In a cyclic process, i.e. when the system returns to the original state after a number of changes, ΔU or $\Delta H = 0$.

Relationship between heat of reaction at constant pressure and at constant volume

We know $q_p = \Delta H$ and $q_v = \Delta U$,

$$\Delta H = \Delta U + P \Delta V = \Delta U + P(V_2 - V_1) = \Delta U + (PV_2 - PV_1)$$

$$\text{Putting } PV = n_1 RT, PV_2 = n_2 RT,$$

$$\Delta H = \Delta U + (n_2 RT - n_1 RT)$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\text{or, } q_p = q_v + \Delta n_g RT$$

HEAT CAPACITY

It is the amount of heat required to raise the temperature of a system through 1°C . It is given by:

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

$$\therefore q = C \times \Delta T$$

Specific Heat Capacity

It is the amount of heat required to raise the temperature of one gm of substance through 1°C .

$$q = m \times c \times \Delta T \text{ where } m : \text{mass of sample, } c : \text{specific heat}$$

Molar Heat Capacity

It is amount of heat required to raise the temperature of 1 mole of a substance through 1°C .

$$\text{i.e., } C_m = \frac{C}{n}$$

Types of heat capacities or molar heat capacities

- Heat capacity at constant volume (C_v)
At constant volume, $q_v = C_v \Delta T = \Delta U$
- Heat capacity at constant pressure (C_p)
At constant pressure, $q_p = C_p \Delta T = \Delta H$

Relation between C_p and C_v

$$\text{As } \Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(RT)$$

$$\Delta H = \Delta U + R \Delta T$$

$$\therefore C_p \Delta T = C_v \Delta T + R \Delta T$$

$$\Rightarrow C_p = C_v + R$$

$$\text{or, } C_p - C_v = R$$

Relation between ratio C_p/C_v and atomicity of a gas

- For monoatomic gases $C_p/C_v = 1.66$
- For Diatomic gases $C_p/C_v = 1.40$
- For Triatomic gases $C_p/C_v = 1.33$

EXOTHERMIC AND ENDOTHERMIC REACTIONS

Exothermic reactions are those which are accompanied by evolution of heat. ΔH is negative for exothermic reactions

Endothermic reactions are those in which heat is absorbed. ΔH is positive for endothermic reactions.

THERMOCHEMICAL EQUATION

When a balanced chemical equation not only indicates the quantities of different reactants and products but also indicates the amount of heat evolved or absorbed, it is called thermochemical equation.

HEAT OF REACTION OR ENTHALPY OF REACTION OR ENTHALPY CHANGE OF REACTION

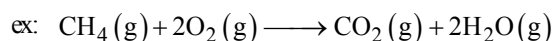
The amount of heat evolved or absorbed in a chemical reaction when the number of moles of reactants as represented by the chemical equation have completely reacted, is called heat of reaction or enthalpy of reaction or enthalpy change of reaction ($\Delta_r H$).

Change in total heat of reaction at 25°C and 1 atm pressure is called standard heat of reaction

Different types of heats/ enthalpies of reaction

(i) Enthalpy of combustion :

It is the heat evolved when 1 mole of substance is completely burnt or oxidised in oxygen. It is represented as $\Delta_c H$.



$\Delta_c H^\circ$ is standard enthalpy of combustion i.e. combustion taking place under standard conditions, i.e., 298 K and 1 bar pressure.

(ii) Enthalpy of formation :

It is the heat change i.e. heat evolved or absorbed when 1 mole of the substance is formed from its elements under given conditions of T and P. It is represented by $\Delta_f H$.

Standard enthalpy of formation arises when the substance is formed in the standard state from its elements, which is also taken in the standard state (i.e. 298 K and 1 bar pressure). It is represented by $\Delta_f H^\circ$

The standard enthalpy change of the reaction is:

$$\Delta_r H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

For elementary substances in standard state, $\Delta_f H^\circ$ is taken as zero.

(iii) Enthalpy of Neutralization

The enthalpy of neutralization of an acid by a base is defined as the heat change when one gram equivalent of the acid is neutralized by a base, the reaction being carried out in dilute aqueous solution.

The enthalpy of neutralization of any strong acid with a strong base or vice-versa, is always the same, i.e. 57.1 kJ.

(iv) Enthalpy of solution

It is defined as the enthalpy change when 1 mole of the substance is dissolved in a specified amount of the solvent. For ionic compounds, enthalpy of solution depends upon lattice enthalpy and hydration enthalpy, i.e.,

$$\Delta_{\text{sol}} H^\circ = \Delta_{\text{lattice}} H^\circ + \Delta_{\text{hyd}} H^\circ$$

For most ionic compounds, $\Delta_{\text{sol}} H^\circ$ is positive and dissociation process is endothermic. Thus, solubility of most salts in water increases with increase in T. If lattice enthalpy of a salt is very high, the dissolution of the compound may not take place at all. For this reason fluorides are less soluble than chlorides.

(v) **Heat of hydration :** The amount of heat released on complete hydration of one mole of an anhydrous substance is called heat of hydration.

(vi) Lattice enthalpy and its calculation

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

Lattice energy is calculated using the Born-Haber Cycle. It is explained by taking the examples of NaCl.

(a) $\text{Na}(\text{s}) \longrightarrow \text{Na}(\text{g})$ i.e., sublimation

$$\Delta_{\text{sub}} H^\circ = 108.4 \text{ kJ mol}^{-1}$$

(b) $\text{Na}(\text{g}) \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$ i.e., ionization of

$$\Delta_i H^\circ = 496 \text{ kJ mol}^{-1}$$

(c) $\frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{Cl}(\text{g})$ i.e., dissociation of Cl

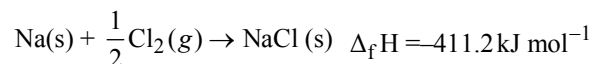
$$\frac{1}{2} \Delta_{\text{bond}} H^\circ = 121 \text{ kJ mol}^{-1}$$

(d) $\text{Cl}(\text{g}) + \text{e}^- \longrightarrow \text{Cl}^-(\text{g})$ i.e. gain of e^- by Cl.

$$\Delta_{\text{EG}} H^\circ = -348.6 \text{ kJ mol}^{-1}$$

(e) $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{Na}^+\text{Cl}^-(\text{s})$

and



This is the Born – Haber Cycle .

Applying Hess's law, we get

$$\Delta_f H^\circ = \Delta_{\text{sub}} H^\circ + \frac{1}{2} \Delta_{\text{bond}} H^\circ + \text{I.E.} + \text{E. A.} + \Delta_{\text{lattice}} H^\circ$$

$$\Delta_{\text{lattice}} H^\circ = 411.2 + 108.4 + 121 + 496 - 348.6 \\ = + 788 \text{ kJ}$$

$$\text{Now, } \Delta_{\text{sol}} H^\circ = \Delta_{\text{lattice}} H^\circ + \Delta_{\text{hyd}} H^\circ$$

$$= + 788 \text{ kJ mol}^{-1} + (- 784 \text{ kJ mol}^{-1})$$

$$= + 4 \text{ kJ mol}^{-1}.$$

(vii) Enthalpy of Atomization

When one mole of a given substance dissociates into gaseous atoms, the enthalpy change accompanying the process is called enthalpy of atomization. It is represented by $\Delta_a H^\circ$.

$$\text{e.g., } \text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g}), \Delta_a H^\circ = 435.0 \text{ kJ mol}^{-1}$$

(viii) Bond Enthalpy or Bond energy

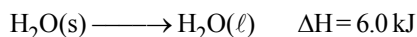
It is the amount of energy released when one mole of bonds are formed from the isolated atom in gaseous state or the amount of energy required to dissociate one mole of bonds present between the atoms in gaseous molecules. It is represented by $\Delta_b H$ or $\Delta_{\text{bond}} H$. It is expressed in kcal/mole $\Delta_r H = \sum \text{B.E. (Reactants)} - \sum \text{B.E. (Products)}$

Enthalpy Changes During Phase Transitions

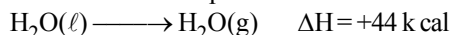
- (i) **Heat of sublimation** : The amount of heat required to change one mole of a solid substance into vapour state is called heat of sublimation.



- (ii) **Heat of fusion** : The amount of heat required to completely change one mole of a solid substance into liquid at its melting point is called heat of fusion.

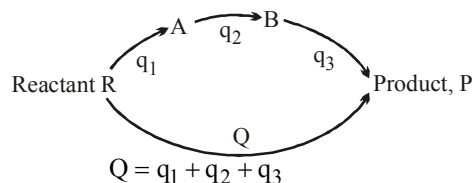


- (iii) **Heat of vapourisation** : The amount of heat required to completely change one mole of a liquid into vapours at its boiling point is called heat of vapourisation.



HESS'S LAW OF CONSTANT HEAT SUMMATION

It states that the total amount of heat evolved or absorbed in a reaction is the same whether the reaction takes place in one step or in a number of steps. In other words, the total amount of heat change in a reaction depends only upon the nature of initial reactants and nature of final products and is independent of the path or manner by which this change is brought about.



SPONTANEITY

A spontaneous process is an irreversible process and may only be reversed by some external agency.

The tendency for a process to occur depends upon two factors:

- tendency for minimum energy
- tendency for maximum randomness

The resultant of the above two tendencies which gives the overall tendency for a process to occur is called driving force of the process.

ENTROPY

It is a measure of randomness or disorder of the system.

Unit of entropy is $\text{JK}^{-1}\text{mol}^{-1}$

Greater the randomness, higher is the entropy.

Entropy change during a process is given by:

$$\Delta S = S_2 - S_1 = \sum S_{\text{product}} - \sum S_{\text{reactant}}$$

ΔS is related to q and T for a reversible process as follows:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

In any process :

$$\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

At equilibrium, entropy of the system is maximum and $\Delta S = 0$

For irreversible process,

$$\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

SECOND LAW OF THERMODYNAMICS

It states that the energy of universe is constant whereas the entropy of universe is continuously increasing and tends to a maximum.

GIBBS FREE ENERGY AND SPONTANEITY

The available amount of energy to the system during the process which can be changed into useful work, is called free energy of the system.

Gibbs energy helps in predicting the spontaneity of a process.

It is denoted by 'G' and is given by

$$G = H - TS$$

The change in Gibbs energy is given by:

$$\Delta G = \Delta H - T\Delta S$$

The decrease in the value of Gibbs free energy during a process is equal to the maximum possible useful work that can be obtained from the system.

According to Gibbs energy equation :

$$\Delta G = \Delta H - T\Delta S$$

It combines both the factors of spontaneity, namely, energy factor ΔH and entropy factor $T\Delta S$

Spontaneity in Terms of Free Energy Change

- If ΔG is negative, the process is spontaneous
- If $\Delta G = 0$, the process does not occur or system is in equilibrium.
- If ΔG is positive, process does not occur in forward direction. It may occur in backward direction.

$$\text{At equilibrium, } \Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$= -RT \ln K = -2.303 RT \log K$$

(K $\rightarrow$ equilibrium constant)

Relation Between ΔG and emf of Cell

$$\Delta G = -nFE_{\text{cell}}$$

where, E_{cell} = emf of the cell

n = number of moles of electrons involved

F = Faraday's constant i.e., 96500 coulomb

If reactants and products are in their standard state,

$$\Delta G^\circ = -nFE^\circ$$

where E° = standard cell potential

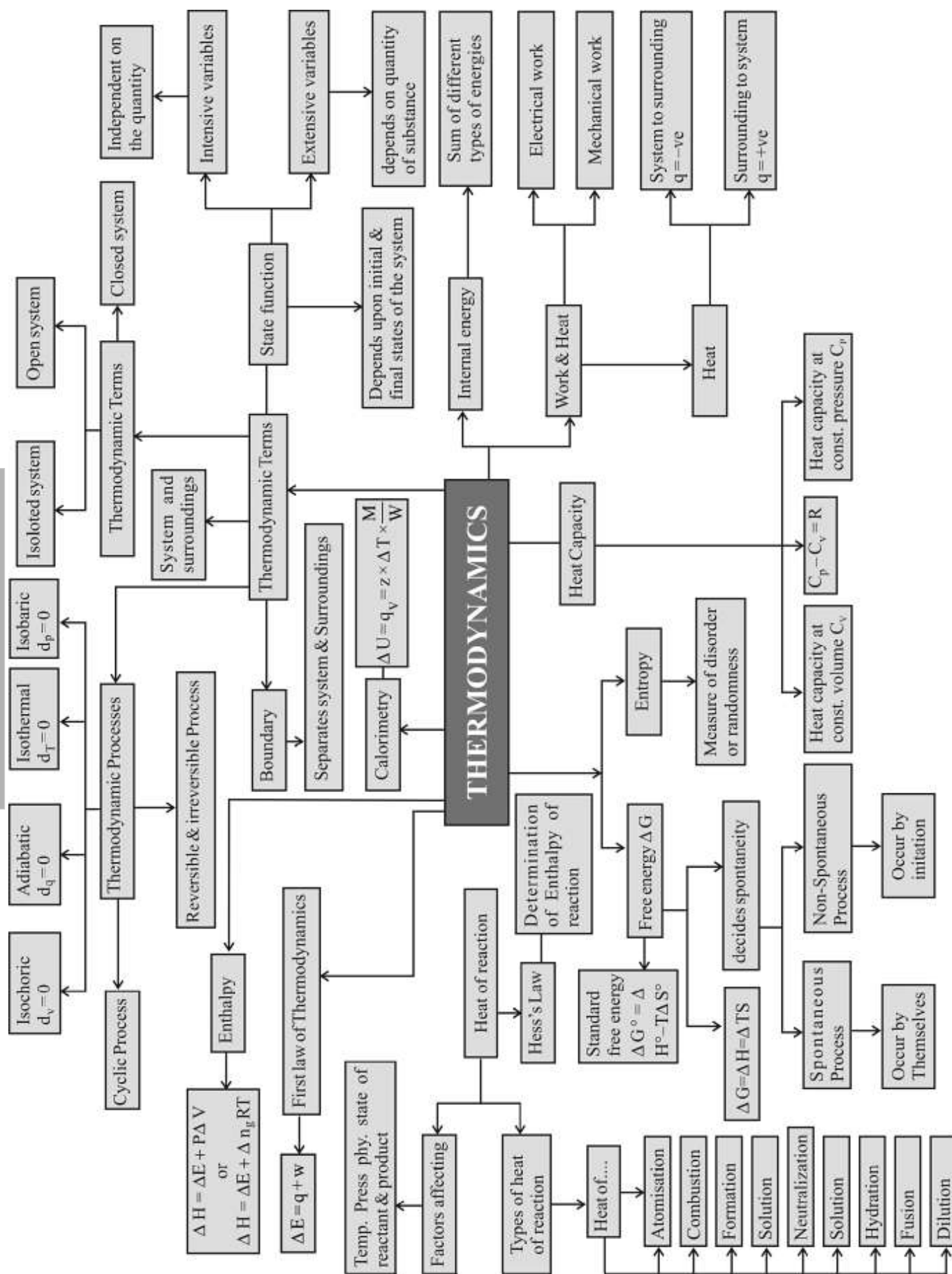
Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	Description of reaction
-	+	-	Spontaneous at all T
-	-	-(low T)	spontaneous at low T
-	-	+(high T)	non-spontaneous at high T
+	+	+(low T)	spontaneous at low T
+	+	-(high T)	spontaneous at high T
+	-	+(at all T)	non-spontaneous at all T

THIRD LAW OF THERMODYNAMICS

At absolute zero temperature, the entropy of a perfectly crystalline substance is taken as zero. This law was formulated by Nernst in 1906.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- For precipitation reaction of Ag^+ ions with NaCl , which of the following statements is correct ?
 - ΔH for the reaction is zero
 - ΔG for the reaction is zero
 - ΔG for the reaction is negative
 - $|\Delta G| = |\Delta H|$
- Calorie is equivalent to :
 - 0.4184 Joule
 - 4.184 Joule
 - 41.84 Joule
 - 418.4 Joule
- In the isochoric process, ΔH for a system is equal to
 - $P \cdot \Delta V$
 - PV
 - $E + P \cdot \Delta V$
 - ΔE
- If ΔH is the change in enthalpy and ΔE is change in internal energy accompanying a gaseous reaction, then
 - ΔH is always greater than ΔE
 - $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of moles of the reactants
 - ΔH is always less than ΔE
 - $\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants.
- Which of the following is correct order ?
 - 1 erg > 1 Joule > 1 calorie
 - 1 erg > 1 calorie > 1 joule
 - 1 calorie > 1 Joule > 1 erg
 - 1 Joule > 1 calorie > 1 erg
- For the reaction

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}), \Delta H = ?$$
 - $\Delta E + 2RT$
 - $\Delta E - 2RT$
 - $\Delta E - RT$
 - None of these
- The following is an endothermic reaction :
 - decomposition of water
 - conversion of graphite to diamond
 - dehydrogenation of ethane to ethylene
 - All of these
- Which process takes place on chemical bond formation :
 - Decrease in energy
 - Increase in energy
 - No change in energy
 - Attractive and repulsive forces are equal
- Gibbs free energy, for the reaction at equilibrium, is
 - zero
 - ve
 - +ve
 - either (a) or (c)
- For which of the following changes, $\Delta H \neq \Delta U$
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
 - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
 - $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 - $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is ($R = 2 \text{ cal. mol}^{-1} \text{ K}^{-1}$)
 - 163.7 cal
 - zero
 - 1381.1 cal
 - 9 lit. atm
- In a closed insulated container, a liquid is stirred with a paddle to increase the temperature, which of the following is true?
 - $\Delta E = W \neq 0, q = 0$
 - $\Delta E = W = q \neq 0$
 - $\Delta E = 0, W = q \neq 0$
 - $W = 0, \Delta E = q \neq 0$
- The heat of combustion of methane at 298°K is expressed by

$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O} \text{ and } \Delta H = 890.2 \text{ kJ.}$$
 Magnitude of ΔE of reaction at this temperature is
 - infinity
 - equal to ΔH
 - less than ΔH
 - greater than ΔH
- For the reaction

$$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$$
 at constant temperature, $\Delta H - \Delta E$ is
 - $-RT$
 - $+RT$
 - $-3RT$
 - $+3RT$
- The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is ($1 \text{ L atm} = 101.32 \text{ J}$)
 - 6 J
 - 608 J
 - +304 J
 - 304 J
- The molar heat capacity of water at constant pressure is $75 \text{ JK}^{-1} \text{ mol}^{-1}$. When 1 kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is
 - 6.6 K
 - 1.2 K
 - 2.4 K
 - 4.8 K
- Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?
 - $\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
 - $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
 - $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g})$
- Which of the following is combustion reaction?
 - $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
 - $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
 - $\text{Mg} + \text{O}_2 \rightarrow \text{MgO}$
 - all of these.
- An ideal gas expands in volume from 1×10^{-3} to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work done is
 - 270 kJ
 - 900 kJ
 - 900 J
 - 900 kJ

20. Consider the reaction : $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ?
 (a) $\Delta H > \Delta U$ (b) $\Delta H < \Delta U$
 (c) $\Delta H = \Delta U$ (d) $\Delta H = 0$
21. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its elements at 298 K is ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
 (a) $-2477.57 \text{ J mol}^{-1}$ (b) $2477.57 \text{ J mol}^{-1}$
 (c) $-1238.78 \text{ J mol}^{-1}$ (d) $1238.78 \text{ J mol}^{-1}$
22. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is
 (a) 11.4 kJ (b) -11.4 kJ
 (c) 0 kJ (d) 4.8 kJ
23. For a reaction $\text{Ag}_2\text{O(s)} \rightarrow 2\text{Ag} + \text{O}$, the value of $\Delta H = 132.6 \text{ kJ}$, $\Delta S = 66 \text{ J K}^{-1} \text{ mol}^{-1}$
 The free energy change for the reaction will be zero at which of the temperature :
 (a) 2000 K (b) 2009 K
 (c) 2023 K (d) 2029 K
24. For the reaction
 $\text{A(g)} + 2\text{B(g)} \rightarrow 2\text{C(g)} + 3\text{D(g)}$
 the change of enthalpy at 27°C is 19 kcal. The value of ΔE is
 (a) 21.2 kcal (b) 17.8 kcal
 (c) 18.4 kcal (d) 20.6 kcal
25. For a chemical reaction the enthalpy and entropy change are $-2.5 \times 10^3 \text{ cal}$ and 7.4 cal deg^{-1} respectively. At 25°C the reaction is :
 (a) spontaneous (b) non-spontaneous
 (c) reversible (d) irreversible
26. A well stoppered thermos flask contains some ice cubes. This is an example of a
 (a) closed system
 (b) open system
 (c) isolated system
 (d) non-thermodynamic system
27. Given that $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 : \Delta H^\circ = -x \text{ kJ}$
 $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 : \Delta H^\circ = -y \text{ kJ}$
 the enthalpy of formation of carbon monoxide will be
 (a) $\frac{2x-y}{2}$ (b) $\frac{y-2x}{2}$
 (c) $2x-y$ (d) $y-2x$
28. The values of ΔH for the combustion of ethane and acetylene are -341.1 and -310.0 kcal , respectively. The better fuel is :
 (a) ethane (b) acetylene
 (c) both (d) none of these
29. The values of heat of formation of SO_2 and SO_3 are -298.2 kJ and -98.2 kJ . The heat of formation of the reaction $\text{SO}_2 + (1/2)\text{O}_2 \rightarrow \text{SO}_3$ will be
 (a) -200 kJ (b) -356.2 kJ
 (c) $+200 \text{ kJ}$ (d) -396.2 kJ
30. What is the enthalpy change for,
 $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ if heat of formation of $\text{H}_2\text{O}_2(l)$ and $\text{H}_2\text{O}(l)$ are -188 and -286 kJ/mol respectively?
 (a) -196 kJ/mol (b) $+948 \text{ kJ/mol}$
 (c) $+196 \text{ kJ/mol}$ (d) -948 kJ/mol
31. $\text{C}_{(\text{dia})} + \text{O}_2 \rightarrow \text{CO}_2 ; \Delta H = -395.4 \text{ kJ/mole}$
 $\text{C}_{(\text{gr})} + \text{O}_2 \rightarrow \text{CO}_2 ; \Delta H = -393.5 \text{ kJ/mole}$
 $\text{C}_{(\text{gr})} \rightarrow \text{C}_{(\text{dia})} ; \Delta H = ?$
 (a) -3.8 (b) -1.9
 (c) $+3.8$ (d) $+1.9$
32. The $\Delta_f H^\circ$ of O_3 , CO_2 , NH_3 and HI are 142.2 , -393.3 , -46.2 and $+25.9 \text{ kJ per mol}$ respectively. The order of their increasing stabilities will be
 (a) $\text{O}_3, \text{CO}_2, \text{NH}_3, \text{HI}$ (b) $\text{CO}_2, \text{NH}_3, \text{HI}, \text{O}_3$
 (c) $\text{O}_3, \text{HI}, \text{NH}_3, \text{CO}_2$ (d) $\text{NH}_3, \text{HI}, \text{CO}_2, \text{O}_3$
33. If the bond energies of $\text{H}-\text{H}$, $\text{Br}-\text{Br}$, and $\text{H}-\text{Br}$ are 433 , 192 and 364 kJ mol^{-1} respectively, the ΔH° for the reaction
 $\text{H}_2(g) + \text{Br}_2(g) \rightarrow 2\text{HBr}(g)$ is
 (a) -261 kJ (b) $+103 \text{ kJ}$
 (c) $+261 \text{ kJ}$ (d) -103 kJ
34. The absolute enthalpy of neutralisation of the reaction:
 $\text{MgO(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O(l)}$ will be:
 (a) $-57.33 \text{ kJ mol}^{-1}$
 (b) greater than $-57.33 \text{ kJ mol}^{-1}$
 (c) less than $-57.33 \text{ kJ mol}^{-1}$
 (d) $57.33 \text{ kJ mol}^{-1}$
35. $\text{A}_{2(g)} + \text{B}_{2(g)} \rightleftharpoons 2\text{AB}_{(g)} ; \Delta H = +ve$, It :
 (a) increases by pressure
 (b) it occurs at 1000 atm pressure
 (c) it occurs at high temperature
 (d) it occurs at high pressure and temperature
36. The enthalpy of hydrogenation of cyclohexene is $-119.5 \text{ kJ mol}^{-1}$. If resonance energy of benzene is $-150.4 \text{ kJ mol}^{-1}$, its enthalpy of hydrogenation would be
 (a) $-208.1 \text{ kJ mol}^{-1}$ (b) $-269.9 \text{ kJ mol}^{-1}$
 (c) $-358.5 \text{ kJ mol}^{-1}$ (d) $-508.9 \text{ kJ mol}^{-1}$
37. Which of the following equations correctly represents the standard heat of formation ($\Delta_f H^\circ$) of methane ?
 (a) $\text{C(diamond)} + 4\text{H(g)} \rightarrow \text{CH}_4(g)$
 (b) $\text{C(diamond)} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g)$
 (c) $\text{C(graphite)} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g)$
 (d) $\text{C(graphite)} + 4\text{H(g)} \rightarrow \text{CH}_4(g)$
38. Enthalpy of solution of NaOH (solid) in water is $-41.6 \text{ kJ mol}^{-1}$. When NaOH is dissolved in water, the temperature of water :
 (a) increases (b) decreases
 (c) does not change (d) fluctuates indefinitely
39. For a Carnot engine, the source is at 500 K and the sink at 300 K . What is efficiency of this engine :
 (a) 0.2 (b) 0.4
 (c) 0.6 (d) 0.3

40. The $\Delta_f H^\circ$ for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -393.5 , -110.5 and -241.8 kJ/mol respectively, the standard enthalpy change (in kJ) for the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ is :
 (a) 524.1 (b) 41.2
 (c) -262.5 (d) -41.2
41. If enthalpies of formation of $\text{C}_2\text{H}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at 25°C and 1 atm pressure are 52, -394 and -286 kJ/mol respectively, the change in enthalpy is equal to
 (a) -141.2 kJ/mol (b) -1412 kJ/mol
 (c) $+14.2$ kJ/mol (d) $+1412$ kJ/mol
42. How many joules of heat are absorbed when 70.0 grams of water is completely vaporised at its boiling point?
 (a) 23,352 (b) 7,000
 (c) 15,813 (d) 158,200
43. Heat of neutralization of strong acid against strong base is constant and is equal to
 (a) 13.7 kcal (b) 57.3 kJ
 (c) 5.73×10^4 J (d) All of the above
44. Work done during isothermal expansion of one mole of an ideal gas from 10 atm. to 1 atm. at 300 K is :
 (a) 4938.8 joule (b) 4138.8 joule
 (c) 5744.1 joule (d) 6257.2 joule
45. Given the bond energies N $\equiv$ N, H – H and N – H bonds are 945, 436 and 391 kJ mole^{-1} respectively, the enthalpy of the following reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ is
 (a) -93 kJ (b) 102 kJ
 (c) 90 kJ (d) 105 kJ
46. The $\text{H}_2\text{O}(\text{g})$ molecule dissociates as
 (i) $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{OH}(\text{g}); \Delta H = 490$ kJ
 (ii) $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g}); \Delta H = 424$ kJ
 The average bond energy (in kJ) for water is
 (a) 490 (b) 424
 (c) 914 (d) 914/2
47. ΔS° will be highest for the reaction
 (a) $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CaO}(\text{s})$
 (b) $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 (c) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
 (d) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$
48. The maximum work which a system can perform at constant temperature and pressure equals
 (a) $\Delta H - \Delta E$ (b) $(-\Delta G)$
 (c) $q - \Delta E$ (d) $P\Delta V - \Delta G$
49. For which of the following process, ΔS is negative?
 (a) $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$
 (b) $2\text{SO}_3(\text{g}) \longrightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$
 (c) $\text{N}_2(4\ell) \xrightarrow{\text{compressed}} \text{N}_2(2\ell)$
 (d) $\text{C}_{(\text{diamond})} \longrightarrow \text{C}_{(\text{graphite})}$
50. Which one of the following is correct ?
 (a) $\Delta H = \Delta G - T\Delta S$ (b) $\Delta S = \frac{1}{T} [\Delta G - \Delta H]$
 (c) $\Delta S = \frac{1}{T} [\Delta H - \Delta G]$ (d) $-\Delta G = \Delta H - T\Delta S$
51. The latent heat of vaporisation of water at 100°C is 540 cal g^{-1} . Calculate the entropy increase when one mole of water at 100°C is evaporated?
 (a) 1.82 cal $\text{K}^{-1} \text{mol}^{-1}$ (b) 540×18 cal $\text{K}^{-1} \text{mol}^{-1}$
 (c) 26 cal $\text{K}^{-1} \text{mol}^{-1}$ (d) 367 cal $\text{K}^{-1} \text{mol}^{-1}$
52. The entropy change in the fusion of one mole of a solid melting at 27°C (Latent heat of fusion, 2930 J mol^{-1}) is :
 (a) 9.77 J $\text{K}^{-1} \text{mol}^{-1}$ (b) 10.73 J $\text{K}^{-1} \text{mol}^{-1}$
 (c) 2930 J $\text{K}^{-1} \text{mol}^{-1}$ (d) 108.5 J $\text{K}^{-1} \text{mol}^{-1}$
53. 2 mole of an ideal gas at 27°C temperature is expanded reversibly from 2 lit to 20 lit. Find the entropy change ($R = 2$ cal/mol K)
 (a) 92.1 (b) 0
 (c) 4 (d) 9.2
54. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is
 (a) $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
 (b) $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$
 (c) $\Delta S_{\text{system}} > 0$ only
 (d) $\Delta S_{\text{surroundings}} > 0$ only
55. Entropy of vaporisation of water at 100°C , if molar heat of vaporisation is 9710 cal mol^{-1} , will be
 (a) 28 cal $\text{mol}^{-1} \text{K}^{-1}$ (b) 26 cal $\text{mol}^{-1} \text{K}^{-1}$
 (c) 24 cal $\text{mol}^{-1} \text{K}^{-1}$ (d) 20 cal $\text{mol}^{-1} \text{K}^{-1}$
56. For conversion C (graphite) $\rightarrow$ C (diamond) the ΔS is
 (a) zero (b) positive
 (c) negative (d) cannot be predicted
57. The following thermochemical reactions are given :

$$\text{M} + \frac{1}{2}\text{O}_2 \rightarrow \text{MO} + 351.4 \text{ kJ}$$

$$\text{X} + \frac{1}{2}\text{O}_2 \rightarrow \text{XO} + 90.8 \text{ kJ}$$
 It follows that the heat of reaction for the following process

$$\text{M} + \text{XO} \rightarrow \text{MO} + \text{X}$$
 is given by :
 (a) 442.2 kJ (b) 260.7 kJ
 (c) -442.2 kJ (d) 260.6 kJ
58. According to second law of thermodynamics heat is partly converted into useful work and part of it :
 (a) becomes electrical energy
 (b) always wasted
 (c) increases the weight of the body
 (d) becomes K.E.
59. If $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \Delta H = R$ and

$$\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \Delta H = S,$$
 then heat of formation of CO is:
 (a) $R + S$ (b) $R - S$
 (c) $R \times S$ (d) $S - R$
60. Which of the following pairs of processes is certain to occur in a spontaneous chemical reaction?
 (a) Exothermic and increasing disorder
 (b) Exothermic and decreasing disorder
 (c) Endothermic and increasing disorder
 (d) Endothermic and decreasing disorder

61. The H–H bond energy is 430 kJ mol^{-1} and Cl–Cl bond energy is 240 kJ mol^{-1} . ΔH for HCl is -90 kJ/mol . The H–Cl bond energy is about :
 (a) 180 kJ mol^{-1} (b) 360 kJ mol^{-1}
 (c) 213 kJ mol^{-1} (d) 425 kJ mol^{-1}
62. A chemical reaction will be spontaneous if it is accompanied by a decrease of
 (a) entropy of the system
 (b) enthalpy of the system
 (c) internal energy of the system
 (d) free energy of the system
63. For a reaction in which all reactants and products are liquids, which one of the following equations is most applicable ?
 (a) $\Delta H < \Delta E$ (b) $\Delta H = \Delta S$
 (c) $\Delta H = \Delta E$ (d) $\Delta H = \Delta G$
64. Highest entropy is in :
 (a) hydrogen (b) water
 (c) graphite (d) mercury
65. If the value of C_p for nitrogen gas is $7 \text{ JK}^{-1} \text{ mol}^{-1}$, then the value of ΔH on heating 28 g of nitrogen gas from 0°C to 100°C at constant pressure will be :
 (a) 1200 J (b) 1300 J
 (c) 1400 J (d) 1500 J
66. The enthalpy and entropy change for the reaction $\text{Br}_2(l) + \text{Cl}_2(g) \rightarrow 2 \text{ BrCl}(g)$ are 30 kJ mol^{-1} and $105 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. The temperature at which the reaction will be in equilibrium is
 (a) 273 K (b) 450 K
 (c) 300 K (d) 285.7 K
67. Given the value of $\Delta H = 177.9 \text{ kJ}$ and $\Delta S = 160.4 \text{ JK}^{-1} \text{ mol}^{-1}$. For the reaction
 $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
 at 298 K, the free energy change per mole would be :
 (a) $+130.1 \text{ kJ}$ (b) -130.1 kJ
 (c) -4.90 kJ (d) $+4.90 \text{ kJ}$
68. For spontaneous cooling of a hot metal rod (system) in air :
 (a) $\Delta S_{\text{system}} > 0, \Delta S_{\text{universe}} < 0$
 (b) $\Delta S_{\text{system}} > 0, \Delta S_{\text{universe}} > 0$
 (c) $\Delta S_{\text{system}} < 0, \Delta S_{\text{universe}} > 0$
 (d) $\Delta S_{\text{system}} < 0, \Delta S_{\text{universe}} < 0$
69. Following reaction occurs in an automobile
 $2\text{C}_8\text{H}_{18}(g) + 25\text{O}_2(g) \rightarrow 16\text{CO}_2(g) + 18\text{H}_2\text{O}(g)$. The sign of $\Delta H, \Delta S$ and ΔG would be
 (a) $+, -, +$ (b) $-, +, -$
 (c) $-, +, +$ (d) $+, +, -$
70. Consider the following reactions at 1000°C
 (A) $\text{Zn}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{ZnO}(s); \Delta G^\circ = -360 \text{ kJ mol}^{-1}$.
 (B) $\text{C}(gr) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}(g); \Delta G^\circ = -460 \text{ kJ mol}^{-1}$.
 Choose the correct statement at 1000°C
 (a) Zinc can be oxidized by carbon monoxide
 (b) Zinc oxide can be reduced by graphite
 (c) Both statements (A) and (B) are true
 (d) Both statements (A) and (B) are false
71. ΔE of combustion of isobutylene is $-X \text{ kJ mol}^{-1}$. The value of ΔH is :
 (a) $= \Delta E$ (b) $> \Delta E$
 (c) $= 0$ (d) $< \Delta E$
72. For the reaction $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$, ΔH , and ΔS are -283 kJ and -87 JK^{-1} , respectively. It was intended to carry out this reaction at 1000, 1500, 3000 and 3500 K. At which of these temperatures would this reaction be thermodynamically spontaneous?
 (a) 1500 and 3500 K (b) 3000 and 3500 K
 (c) 1500, 1500 and 3000 K (d) 1500, 3000 and 3500 K
 (d) Energy due to gravitational pull
73. The enthalpy of combustion of C_6H_6 is -3250 kJ , when 0.39 gm of C_6H_6 is burnt in excess of oxygen in an open vessel, the amount of heat evolved is
 (a) 8.32 kJ (b) 12.36 kJ
 (c) 16.25 kJ (d) 20.74 kJ
74. The free energy change for the following reactions are given below,
 $\text{C}_2\text{H}_2(g) + \frac{5}{2}\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(l); \Delta G^\circ = -1234 \text{ kJ}$
 $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g); \Delta G^\circ = -394 \text{ kJ}$
 $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l); \Delta G^\circ = -237 \text{ kJ}$
 What is the standard free energy change for the reaction
 $\text{H}_2(g) + 2\text{C}(s) \longrightarrow \text{C}_2\text{H}_2(g)$
 (a) -209 kJ (b) -2259 kJ
 (c) $+2259 \text{ kJ}$ (d) 209 kJ
75. One mole of an ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C . If the work done during the process is 3 kJ, then final temperature of the gas is ($C_v = 20 \text{ J/K}$):
 (a) 100 K (b) 150 K
 (c) 195 K (d) 255 K
76. The heat of atomization of $\text{PH}_3(g)$ is $228 \text{ kcal mol}^{-1}$ and that of $\text{P}_2\text{H}_4(g)$ is $335 \text{ kcal mol}^{-1}$. The energy of the P–P bond is
 (a) $102 \text{ kcal mol}^{-1}$ (b) 51 kcal mol^{-1}
 (c) 26 kcal mol^{-1} (d) $204 \text{ kcal mol}^{-1}$
77. The value $\Delta H - \Delta E$ for the following reaction at 27°C will be
 $2\text{NH}_3(g) \longrightarrow \text{N}_2 + 3\text{H}_2(g)$
 (a) $8.314 \times 273 \times (-2)$ (b) $8.314 \times 300 \times (-2)$
 (c) $8.314 \times 27 \times (-2)$ (d) $8.314 \times 300 \times (2)$
78. Given that bond energies of H – H and Cl – Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and $\Delta_f H$ for HCl is -90 kJ mol^{-1} , bond enthalpy of HCl is
 (a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}
 (c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1}

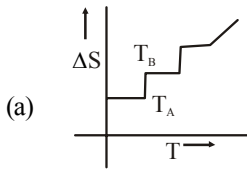
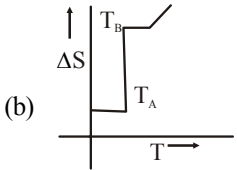
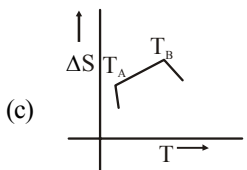
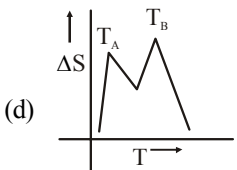
79. Which of the following are *not* state functions ?
 (I) $q + w$ (II) q
 (III) w (IV) $H - TS$
 (a) (I) and (IV) (b) (II), (III) and (IV)
 (c) (I), (II) and (III) (d) (II) and (III)
80. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively. The temperature when Gibbs energy change (ΔG) for this transformation will be zero, is:
 (a) 293.4 K (b) 273.4 K
 (c) 393.4 K (d) 373.4 K
81. The following two reactions are known :
 $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \longrightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g}); \Delta H = -26.8 \text{ kJ}$
 $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \longrightarrow \text{Fe}(\text{s}) + \text{CO}_2(\text{g}); \Delta H = -16.5 \text{ kJ}$
 The value of ΔH for the following reaction
 $\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \longrightarrow 2\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$ is;
 (a) +6.2 kJ (b) +10.3 kJ
 (c) -43.3 kJ (d) -10.3 kJ
82. Three moles of an ideal gas expanded spontaneously into vacuum. The work done will be :
 (a) Zero (b) Infinite
 (c) 3 Joules (d) 9 Joules
83. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C , the entropy change for the process would be :
 (a) $10 \text{ J mol}^{-1} \text{ K}^{-1}$ (b) $1.0 \text{ J mol}^{-1} \text{ K}^{-1}$
 (c) $0.1 \text{ J mol}^{-1} \text{ K}^{-1}$ (d) $100 \text{ J mol}^{-1} \text{ K}^{-1}$
84. Enthalpy change for the reaction,
 $4\text{H}(\text{g}) \longrightarrow 2\text{H}_2(\text{g})$ is -869.6 kJ .
 The dissociation energy of H-H bond is :
 (a) -434.8 kJ (b) -869.6 kJ
 (c) $+434.8 \text{ kJ}$ (d) $+217.4 \text{ kJ}$
85. The enthalpy of fusion of water is 1.435 kcal/mol . The molar entropy change for the melting of ice at 0°C is :
 (a) $10.52 \text{ cal / (mol K)}$ (b) $21.04 \text{ cal / (mol K)}$
 (c) $5.260 \text{ cal / (mol K)}$ (d) $0.526 \text{ cal / (mol K)}$
86. Equal volumes of two monoatomic gases, A and B, at same temperature and pressure are mixed. The ratio of specific heats (C_p/C_v) of the mixture will be :
 (a) 0.83 (b) 1.50
 (c) 3.3 (d) 1.67
87. Identify the correct statement regarding a spontaneous process
 (a) Lowering of energy in the process is the only criterion for spontaneity.
 (b) For a spontaneous process in an isolated system, the change in entropy is positive.
 (c) Endothermic processes are never spontaneous.
 (d) Exothermic processes are always spontaneous.
88. The standard enthalpy of formation of NH_3 is $-46.0 \text{ kJ mol}^{-1}$. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of N-H bond in NH_3 is
 (a) -964 kJ mol^{-1} (b) $+352 \text{ kJ mol}^{-1}$
 (c) $+1056 \text{ kJ mol}^{-1}$ (d) $-1102 \text{ kJ mol}^{-1}$
89. The value of enthalpy change (ΔH) for the reaction
 $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$
 at 27°C is $-1366.5 \text{ kJ mol}^{-1}$. The value of internal energy change for the above reaction at this temperature will be :
 (a) -1369.0 kJ (b) -1364.0 kJ
 (c) -1361.5 kJ (d) -1371.5 kJ
90. The heats of atomization of $\text{PH}_3(\text{g})$ and $\text{P}_2\text{H}_4(\text{g})$ are 954 kJ mol^{-1} and 1485 kJ mol^{-1} respectively. The P-P bond energy in kJ mol^{-1} is
 (a) 213 (b) 426
 (c) 318 (d) 1272
91. Pick out the wrong statement
 (a) The standard free energy of formation of all elements is zero
 (b) A process accompanied by decrease in entropy is spontaneous under certain conditions
 (c) The entropy of a perfectly crystalline substance at absolute zero is zero
 (d) A process that leads to increase in free energy will be spontaneous
92. Which one of the following demonstrates a decrease in entropy?
 (a) Dissolving a solid into solution
 (b) An expanding universe
 (c) Burning a log in a fireplace
 (d) Raking up leaves into a trash bag
93. A certain reaction is at equilibrium at 82°C and the enthalpy change for this reaction is 21.3 kJ . The value of ΔS (in JK mol^{-1}) for the reaction is
 (a) 55.0 (b) 60.0
 (c) 68.5 (d) 120.0
94. The bond enthalpy is the highest for
 (a) F_2 (b) Cl_2
 (c) Br_2 (d) H_2
95. At the sublimation temperature, for the process
 $\text{CO}_{2(\text{s})} \rightleftharpoons \text{CO}_{2(\text{g})}$
 (a) ΔH , ΔS and ΔG are all positive
 (b) $\Delta H > 0$, $\Delta S > 0$ and $\Delta G < 0$
 (c) $\Delta H < 0$, $\Delta S > 0$ and $\Delta G < 0$
 (d) $\Delta H > 0$, $\Delta S > 0$ and $\Delta G = 0$
96. The enthalpy of solution of sodium chloride is 4 kJ mol^{-1} and its enthalpy of hydration of ions is -784 kJ mol^{-1} . Then the lattice enthalpy of NaCl (in kJ mol^{-1}) is
 (a) +788 (b) +4
 (c) +398 (d) +780

97. Calculate the work done (in Joules) when 0.2 mole of an ideal gas at 300 K expands isothermally and reversibly from an initial volume of 2.5 litres to the final volume of 25 litres.
- (a) 996 (b) 1148
(c) 11.48 (d) 897
98. Choose the reaction with negative ΔS value.
- (a) $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
(b) $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$
(c) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
(d) $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$
99. A chemical reaction is spontaneous at 298 K but non-spontaneous at 350 K. Which one of the following is true for the reaction?
- | | ΔG | ΔH | ΔS |
|-----|------------|------------|------------|
| (a) | – | – | + |
| (b) | + | + | + |
| (c) | – | + | – |
| (d) | – | – | – |
100. A reaction cannot take place spontaneously at any temperature when
- (a) both ΔH and ΔS are positive
(b) both ΔH and ΔS are negative
(c) ΔH is negative and ΔS is positive
(d) ΔH is positive and ΔS is negative

EXERCISE - 2

Applied Questions

1. In which of the following equations, the enthalpy change will represent ΔH_f° of $\text{N}_2\text{H}_{4(\ell)}$ with sign reversed?
- (a) $\text{N}_{2(\text{g})} + 2\text{H}_{2(\text{g})} \rightarrow \text{N}_2\text{H}_{4(\text{g})}$
(b) $2\text{N}_{(\text{g})} + 4\text{H}_{(\text{g})} \rightarrow \text{N}_2\text{H}_{4(\ell)}$
(c) $\text{N}_2\text{H}_{4(\ell)} \rightarrow 2\text{N}_{(\text{g})} + 4\text{H}_{(\text{g})}$
(d) $\text{N}_2\text{H}_{4(\ell)} \rightarrow \text{N}_{2(\text{g})} + 2\text{H}_{2(\text{g})}$
2. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true?
- (a) $x = y$ (b) $x = \frac{1}{2}y$
(c) $x = 2y$ (d) None of these
3. Hydrogen has an ionisation energy of 1311 kJ mol^{-1} and for chlorine it is 1256 kJ mol^{-1} . Hydrogen forms $\text{H}^+(\text{aq})$ ions but chlorine does not form $\text{Cl}^+(\text{aq})$ ions because
- (a) H^+ has lower hydration enthalpy
(b) Cl^+ has lower hydration enthalpy
(c) Cl has high electron affinity
(d) Cl has high electronegativity
4. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as :
- $\text{S}_2(\text{s}) + 2\text{O}_2(\text{g}) \longrightarrow 2\text{SO}_2(\text{g}) ; \Delta G = -544 \text{ kJ}$
 $2\text{Zn}(\text{s}) + \text{S}_2(\text{s}) \longrightarrow 2\text{ZnS}(\text{s}) ; \Delta G = -293 \text{ kJ}$
 $2\text{Zn}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{ZnO}(\text{s}) ; \Delta G = -480 \text{ kJ}$
Then ΔG for the reaction :
- $2\text{ZnS}(\text{s}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{ZnO}(\text{s}) + 2\text{SO}_2(\text{g})$
will be :
- (a) -357 kJ (b) -731 kJ (c) -773 kJ (d) -229 kJ
5. For the reaction $A \rightarrow B$; $\Delta H = +24 \text{ kJ/mol}$ and $B \rightarrow C$; $\Delta H = -18 \text{ kJ/mol}$, the decreasing order of enthalpy of A , B and C follows the order
- (a) A, B, C (b) B, C, A
(c) C, B, A (d) C, A, B
6. For the reactions,
- $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 ; \Delta H = -393 \text{ J}$
 $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO} ; \Delta H = -412 \text{ J}$
- (a) carbon can oxidise Zn
(b) oxidation of carbon is not feasible
(c) oxidation of Zn is not feasible
(d) Zn can reduce carbon dioxide.
7. The internal energy change when a system goes from state A to B is 40 kJ/mole . If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy?
- (a) $> 40 \text{ kJ}$ (b) $< 40 \text{ kJ}$ (c) Zero (d) 40 kJ
8. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria
- (a) $(dS)_{V,E} > 0, (dG)_{T,P} < 0$ (b) $(dS)_{V,E} = 0, (dG)_{T,P} = 0$
(c) $(dS)_{V,E} = 0, (dG)_{T,P} > 0$ (d) $(dS)_{V,E} < 0, (dG)_{T,P} < 0$
9. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of $1 : 1 : 0.5$ and $\Delta_f H$ for the formation of XY is $-200 \text{ kJ mole}^{-1}$. The bond dissociation energy of X_2 will be
- (a) 400 kJ mol^{-1} (b) 300 kJ mol^{-1}
(c) 200 kJ mol^{-1} (d) 800 kJ mol^{-1}
10. The standard enthalpy of formation ($\Delta_f H^\circ$) at 298 K for methane, $\text{CH}_4(\text{g})$ is $-74.8 \text{ kJ mol}^{-1}$. The additional information required to determine the average energy for C–H bond formation would be
- (a) the first four ionization energies of carbon and electron gain enthalpy of hydrogen
(b) the dissociation energy of hydrogen molecule, H_2
(c) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(d) latent heat of vapourization of methane

11. The enthalpy changes for the following processes are listed below :
- $$\begin{array}{ll} \text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g}), & 242.3 \text{ kJ mol}^{-1} \\ \text{I}_2(\text{g}) \rightarrow 2\text{I}(\text{g}), & 151.0 \text{ kJ mol}^{-1} \\ \text{ICl}(\text{g}) \rightarrow \text{I}(\text{g}) + \text{Cl}(\text{g}), & 211.3 \text{ kJ mol}^{-1} \\ \text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g}), & 62.76 \text{ kJ mol}^{-1} \end{array}$$
- Given that the standard states for iodine and chlorine are $\text{I}_2(\text{s})$ and $\text{Cl}_2(\text{g})$, the standard enthalpy of formation for $\text{ICl}(\text{g})$ is :
- (a) $+16.8 \text{ kJ mol}^{-1}$ (b) $+244.8 \text{ kJ mol}^{-1}$
(c) $-14.6 \text{ kJ mol}^{-1}$ (d) $-16.8 \text{ kJ mol}^{-1}$
12. The heat of neutralisation of strong base and strong acid is 57.0 kJ . The heat released when 0.5 mole of HNO_3 is added to 0.20 mole of NaOH solution is :
- (a) 34.9 kJ (b) 57.0 kJ (c) 11.4 kJ (d) 28.5 kJ
13. Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atoms is 208 kcal at 25°C . The bond energy of H-H will be :
- (a) 104 kcal (b) 52 kcal (c) 10.4 kcal (d) 1040 kcal
14. Given that heat of neutralisation of strong acid and strong base is -57.1 kJ . The heat produced when 0.25 mole of HCl is neutralised with 0.25 mole of NaOH in aqueous solution is :
- (a) 14.275 kJ (b) 57.1 kJ (c) 22.5 kJ (d) 28.6 kJ
15. The heat of neutralisation of HCl by NaOH is -55.9 kJ/mole . The energy of dissociation of HCN is : ($\text{HCN} + \text{OH}^- \rightarrow \text{CN}^- + \text{H}_2\text{O}$; $\Delta H = -12.1 \text{ kJ}$)
- (a) 43.8 kJ (b) -43.8 kJ (c) -68 kJ (d) 68 kJ
16. Calculate enthalpy change for the change $8\text{S}(\text{g}) \rightarrow \text{S}_8(\text{g})$, given that
- $$\text{H}_2\text{S}_2(\text{g}) \rightarrow 2\text{H}(\text{g}) + 2\text{S}(\text{g}), \Delta H = 239.0 \text{ kcal mol}^{-1} ;$$
- $$\text{H}_2\text{S}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{S}(\text{g}), \Delta H = 175.0 \text{ kcal mol}^{-1}$$
- (a) $+512.0 \text{ kcal}$ (b) -512.0 kcal
(c) 508.0 kcal (d) -508.0 kcal
17. If x_1, x_2 and x_3 are enthalpies of H-H , O=O and O-H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen:
- (a) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$ (b) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$
(c) $x_1 + \frac{x_2}{2} - x_3 + x_4$ (d) $2x_3 - x_1 - \frac{x_2}{2} - x_4$
18. If for a given substance melting point is T_B and freezing point is T_A , then correct variation shown by, graph between entropy change and temperature is
- (a)  (b) 
(c)  (d) 
19. If ΔH and ΔE are the change in enthalpy and change in internal energy respectively for a gaseous reaction, then
- (a) $\Delta H > \Delta E$, always
(b) $\Delta H < \Delta E$, only if $n_{\text{product}} > n_{\text{reactants}}$
(c) $\Delta H < \Delta E$, always
(d) $\Delta H < \Delta E$, only if $n_{\text{product}} < n_{\text{reactants}}$
20. Consider the following reactions:
- (i) $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}), \Delta H = -X_1 \text{ kJ mol}^{-1}$
(ii) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}), \Delta H = -X_2 \text{ kJ mol}^{-1}$
(iii) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}, \Delta H = -X_3 \text{ kJ mol}^{-1}$
(iv) $\text{C}_2\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}), \Delta H = +4X_4 \text{ kJ mol}^{-1}$
- Enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ is
- (a) $+X_3 \text{ kJ mol}^{-1}$ (b) $-X_4 \text{ kJ mol}^{-1}$
(c) $+X_1 \text{ kJ mol}^{-1}$ (d) $-X_2 \text{ kJ mol}^{-1}$
21. For the gas phase reaction, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ which of the following conditions are correct ?
- (a) $\Delta H = 0$ and $\Delta S < 0$ (b) $\Delta H > 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$ (d) $\Delta H > 0$ and $\Delta S < 0$
22. Bond dissociation enthalpy of H_2, Cl_2 and HCl are $434, 242$ and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is :
- (a) 93 kJ mol^{-1} (b) -245 kJ mol^{-1}
(c) -93 kJ mol^{-1} (d) 245 kJ mol^{-1}
23. The values of ΔH and ΔS for the reaction, $\text{C}(\text{graphite}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ are 170 kJ and 170 JK^{-1} , respectively. This reaction will be spontaneous at
- (a) 910 K (b) 1110 K (c) 510 K (d) 710 K
24. From the following bond energies:
- H-H bond energy: $431.37 \text{ kJ mol}^{-1}$
 C=C bond energy: $606.10 \text{ kJ mol}^{-1}$
 C-C bond energy: $336.49 \text{ kJ mol}^{-1}$
 C-H bond energy: $410.50 \text{ kJ mol}^{-1}$
- Enthalpy for the reaction,
- $$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C} = \text{C} + \text{H} - \text{H} \longrightarrow \text{H} - \text{C} - \text{C} - \text{H} \\ | \quad | \quad \quad \quad | \quad | \\ \text{H} \quad \text{H} \quad \quad \quad \text{H} \quad \text{H} \end{array}$$
- will be:
- (a) $-243.6 \text{ kJ mol}^{-1}$ (b) $-120.0 \text{ kJ mol}^{-1}$
(c) $553.0 \text{ kJ mol}^{-1}$ (d) $1523.6 \text{ kJ mol}^{-1}$
25. Standard entropies of X_2, Y_2 and XY_3 are $60, 40$ and $50 \text{ JK}^{-1}\text{mol}^{-1}$ respectively. For the reaction
- $$\frac{1}{2}\text{X}_2 + \frac{3}{2}\text{Y}_2 \rightleftharpoons \text{XY}_3, \Delta H = -30 \text{ kJ}$$
- to be at equilibrium, the temperature should be:
- (a) 750 K (b) 1000 K (c) 1250 K (d) 500 K

26. Match List-I (Equations) with List-II (Type of processes) and select the correct option.

List I**Equations**

- (1) $K_p > Q$
 (2) $\Delta G^\circ < RT \ln Q$
 (3) $K_p = Q$

(4) $T > \frac{\Delta H}{\Delta S}$

List II**Type of processes**

- (i) Non spontaneous
 (ii) Equilibrium
 (iii) Spontaneous and endothermic

(iv) Spontaneous

Options:

(1)	(2)	(3)	(4)
(a) (ii)	(i)	(iv)	(iii)
(b) (i)	(ii)	(iii)	(iv)
(c) (iii)	(iv)	(ii)	(i)
(d) (iv)	(i)	(ii)	(iii)

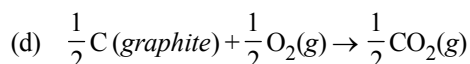
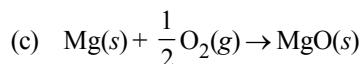
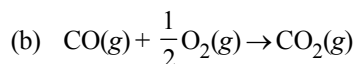
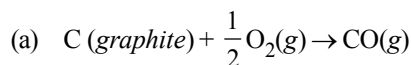
27. Consider the following processes :

	ΔH (kJ/mol)
$1/2 A \rightarrow B$	+150
$3B \rightarrow 2C + D$	-125
$E + A \rightarrow 2D$	+350

For $B + D \rightarrow E + 2C$, ΔH will be :

- (a) 525 kJ/mol (b) -175 kJ/mol
 (c) -325 kJ/mol (d) 325 kJ/mol

28. In which of the following reactions, standard entropy change (ΔS°) is positive and standard Gibbs's energy change (ΔG°) decreases sharply with increase in temperature ?



29. Standard enthalpy of vapourisation $\Delta_{\text{vap}} H^\circ$ for water at 100°C is $40.66 \text{ kJ mol}^{-1}$. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is :

- (a) +37.56 (b) -43.76
 (c) +43.76 (d) +40.66

(Assume water vapour to behave like an ideal gas).

30. In conversion of lime-stone to lime,

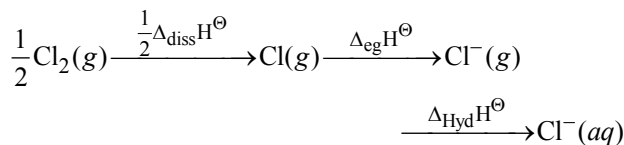
$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$ the values of ΔH° and ΔS° are $+179.1 \text{ kJ mol}^{-1}$ and 160.2 J/K respectively at 298 K and 1 bar . Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

- (a) 1118 K (b) 1008 K
 (c) 1200 K (d) 845 K

31. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C , (given : molar enthalpy of vapourisation of water at 1 bar and $373 \text{ K} = 41 \text{ kJ mol}^{-1}$ and $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$) will be

- (a) $41.00 \text{ kJ mol}^{-1}$ (b) $4.100 \text{ kJ mol}^{-1}$
 (c) $3.7904 \text{ kJ mol}^{-1}$ (d) $37.904 \text{ kJ mol}^{-1}$

32. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:



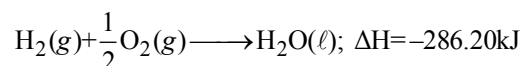
(using the data, $\Delta_{\text{diss}} H^\ominus_{\text{Cl}_2} = 240 \text{ kJ mol}^{-1}$,

$\Delta_{\text{eg}} H^\ominus_{\text{Cl}} = -349 \text{ kJ mol}^{-1}$, $\Delta_{\text{hyd}} H^\ominus_{\text{Cl}^-} = -381 \text{ kJ mol}^{-1}$), will be

- (a) $+152 \text{ kJ mol}^{-1}$ (b) -610 kJ mol^{-1}
 (c) -850 kJ mol^{-1} (d) $+120 \text{ kJ mol}^{-1}$

33. On the basis of the following thermochemical data :

$$[\Delta_f H^\ominus(\text{H}^+_{\text{(aq)}}) = 0]$$



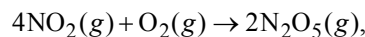
The value of enthalpy of formation of OH^- ion at 25°C is:

- (a) -228.88 kJ (b) $+228.88 \text{ kJ}$
 (c) -343.52 kJ (d) -22.88 kJ

34. For a particular reversible reaction at temperature T , ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when

- (a) $T_e > T$ (b) $T > T_e$
 (c) T_e is 5 times T (d) $T = T_e$

35. Consider the reaction



$$\Delta_r H = -111 \text{ kJ}.$$

If $\text{N}_2\text{O}_5(s)$ is formed instead of $\text{N}_2\text{O}_5(g)$ in the above reaction, the $\Delta_r H$ value will be :

(given, ΔH of sublimation for N_2O_5 is -54 kJ mol^{-1})

- (a) $+54 \text{ kJ}$ (b) $+219 \text{ kJ}$
 (c) -219 J (d) -165 kJ

36. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

(Given : $\Delta_r H^\ominus_{298\text{K}} = -54.07 \text{ kJ mol}^{-1}$,

$$\Delta_r S^\ominus_{298\text{K}} = 10 \text{ JK}^{-1} \text{ mol}^{-1} \text{ and } R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1};$$

$$2.303 \times 8.314 \times 298 = 5705)$$

- (a) 5 (b) 10
 (c) 95 (d) 100

37. For the process $\text{H}_2\text{O}(l) (1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g) (1 \text{ bar}, 373 \text{ K})$, the correct set of thermodynamic parameters is

- (a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$
 (c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

38. The species which by definition has **ZERO** standard molar enthalpy of formation at 298 K is

- (a) $\text{Br}_2(g)$ (b) $\text{Cl}_2(g)$
 (c) $\text{H}_2\text{O}(g)$ (d) $\text{CH}_4(g)$

39. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $\text{C} \equiv \text{C}$ bond in C_2H_2 . That energy is (take the bond energy of a $\text{C}-\text{H}$ bond as 350 kJ mol^{-1})
 $2\text{C}(s) + \text{H}_2(g) \longrightarrow \text{HC} \equiv \text{CH}(g); \Delta H = 225 \text{ kJ mol}^{-1}$
 $2\text{C}(s) \longrightarrow 2\text{C}(g); \Delta H = 1410 \text{ kJ mol}^{-1}$
 $\text{H}_2(g) \longrightarrow 2\text{H}(g); \Delta H = 330 \text{ kJ mol}^{-1}$
 (a) 1165 (b) 837
 (c) 865 (d) 815
40. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C . As it does so, it absorbs 208 J of heat. The values of q and w for the process will be:
 $(R = 8.314 \text{ J/mol K}) (\ln 7.5 = 2.01)$
 (a) $q = +208 \text{ J}, w = -208 \text{ J}$ (b) $q = -208 \text{ J}, w = -208 \text{ J}$
 (c) $q = -208 \text{ J}, w = +208 \text{ J}$ (d) $q = +208 \text{ J}, w = +208 \text{ J}$
41. Four grams of graphite is burnt in a bomb calorimeter of heat capacity 30 kJ K^{-1} in excess of oxygen at 1 atmospheric pressure. The temperature rises from 300 to 304 K. What is the enthalpy of combustion of graphite (in kJ mol^{-1})?
 (a) 360 (b) 1440 [Kerala PMT 2011]
 (c) -360 (d) -1440
42. The enthalpy change for reaction
 $\frac{1}{2}\text{X}_2(g) + \frac{3}{2}\text{Y}_2(g) \rightarrow \text{XY}_3(g)$ is -50 kJ mol^{-1} . If the bond enthalpies of $\text{X}-\text{X}$ and $\text{X}-\text{Y}$ are respectively 380 and 150 kJ mol^{-1} the bond enthalpy of $\text{Y}-\text{Y}$ in kJ mol^{-1} is
 (a) 35 (b) 210 [Kerala PMT 2013]
 (c) 280 (d) 140
43. Consider the following spontaneous reaction
 $2\text{C}_8\text{H}_{18}(g) + 25\text{O}_2(g) \rightarrow 16\text{CO}_2(g) + 18\text{H}_2\text{O}(g)$
 The sign of ΔH , ΔS , ΔG would be respectively
 (a) $+, -, +$ (b) $-, +, -$ [Kerala PMT 2013]
 (c) $+, +, -$ (d) $-, -, -$
44. One mole of solid iron was vaporized in an oven at its boiling point of 3433 K and enthalpy of vaporization of iron is $344.3 \text{ kJ mol}^{-1}$. The value of entropy vaporization (in J mol^{-1}) of iron is [Kerala PMT 2013]
 (a) 100 (b) 10
 (c) -100 (d) 110
45. The enthalpies of the following reactions are shown below. [AFMC 2011]
 $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{OH}(g); \Delta H = 42.09 \text{ kJ mol}^{-1}$
 $\text{H}_2(g) \rightarrow 2\text{H}(g); \Delta H = 435.89 \text{ kJ mol}^{-1}$
 $\text{O}_2(g) \rightarrow 2\text{O}(g); \Delta H = 495.05 \text{ kJ mol}^{-1}$
 Calculate the $\text{O}-\text{H}$ bond energy for the hydroxyl radical.
 (a) $223.18 \text{ kJ mol}^{-1}$ (b) $423.38 \text{ kJ mol}^{-1}$
 (c) $513.28 \text{ kJ mol}^{-1}$ (d) $113.38 \text{ kJ mol}^{-1}$
- DIRECTIONS for Qs. 46 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement - 1 is True, Statement-2 is False
 (d) Statement -1 is False, Statement-2 is True
46. **Statement 1 :** Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
Statement 2 : Entropy of the system increases with increase in temperature. [AIIMS 2013]
47. **Statement 1 :** For an isothermal reversible process $Q = -W$ i.e. work done by the system equals the heat absorbed by the system.
Statement 2 : Enthalpy change (ΔH) is zero for isothermal process. [AIIMS 2013]
48. **Statement 1 :** The mass and volume of a substance are the extensive properties and are proportional to each other.
Statement 2 : The ratio of mass of a sample to its volume is an intensive property.
49. **Statement 1 :** Internal energy is an extensive property.
Statement 2 : Internal energy depends upon the amount of the system.
50. **Statement 1 :** Absolute value of internal energy of a substance cannot be determined.
Statement 2 : It is impossible to determine exact values of constituent energies of the substances.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Thermodynamics is not concerned about
 - energy changes involved in a chemical reaction
 - the extent to which a chemical reaction proceeds
 - the rate at which a reaction proceeds
 - the feasibility of a chemical reaction
- Which of the following statement is correct?
 - The presence of reacting species in a covered beaker is an example of open system.
 - There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
 - The presence of reactants in a closed vessel made up of copper is an example of a closed system.
 - The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

3. The state of a gas can be described by quoting the relationship between
 (a) pressure, volume, temperature
 (b) temperature, amount, pressure
 (c) amount, volume, temperature
 (d) pressure, volume, temperature, amount
4. The volume of gas is reduced to half from its original volume. The specific heat will be
 (a) reduce to half (b) be doubled
 (c) remain constant (d) increase four times
5. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is
 (a) $2\text{C}_4\text{H}_{10}(\text{g}) + 13\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 10\text{H}_2\text{O}(\text{l}); \Delta_c H = -2658.0 \text{ kJ mol}^{-1}$
 (b) $\text{C}_4\text{H}_{10}(\text{g}) + \frac{13}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}); \Delta_c H = -1329.0 \text{ kJ mol}^{-1}$
 (c) $\text{C}_4\text{H}_{10}(\text{g}) + \frac{13}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}); \Delta_c H = -2658.0 \text{ kJ mol}^{-1}$
 (d) $\text{C}_4\text{H}_{10}(\text{g}) + \frac{13}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}); \Delta_c H = +2658.0 \text{ kJ mol}^{-1}$
6. $\Delta_f H^\circ$ of formation of $\text{CH}_4(\text{g})$ at certain temperature is -393 kJ mol^{-1} . The value of $\Delta_f H^\circ$ is
 (a) zero (b) $< \Delta_f H^\circ$
 (c) $> \Delta_f H^\circ$ (d) equal to $\Delta_f H^\circ$
7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.
 (a) $q = 0, \Delta T \neq 0, W = 0$ (b) $q \neq 0, \Delta T = 0, W = 0$
 (c) $q = 0, \Delta T = 0, W = 0$ (d) $q = 0, \Delta T < 0, W \neq 0$
8. The pressure-volume work for an ideal gas can be calculated

by using the expression $W = - \int_{V_i}^{V_f} p_{\text{ex}} dV$. The work can also

be calculated from the pV-plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f . Choose the correct option.

- (a) $W(\text{reversible}) = W(\text{irreversible})$
 (b) $W(\text{reversible}) < W(\text{irreversible})$
 (c) $W(\text{reversible}) > W(\text{irreversible})$
 (d) $W(\text{reversible}) = W(\text{irreversible}) + p_{\text{ex}} \cdot \Delta V$
9. The entropy change can be calculated by using the expression $\Delta S = \frac{q_{\text{rev}}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following.

- (a) $\Delta S(\text{system})$ decreases but $\Delta S(\text{surroundings})$ remains the same
 (b) $\Delta S(\text{system})$ increases but $\Delta S(\text{surroundings})$ decreases
 (c) $\Delta S(\text{system})$ decreases but $\Delta S(\text{surroundings})$ increases
 (d) $\Delta S(\text{system})$ decreases but $\Delta S(\text{surroundings})$ also decreases
10. On the basis of thermochemical equations (1), (2) and (3), find out which of the algebraic relationships given in options (a) to (d) is correct
 1. $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_f H = x \text{ kJ mol}^{-1}$
 2. $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}); \Delta_f H = y \text{ kJ mol}^{-1}$
 3. $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_f H = z \text{ kJ mol}^{-1}$
 (a) $z = x + y$ (b) $x = y - z$
 (c) $x = y + z$ (d) $y = 2z - x$
11. Consider the reactions given below. On the basis of these reactions find out which of the algebraic relationship given in options (a) to (d) is correct?
 1. $\text{C}(\text{g}) + 4\text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g}); \Delta_f H = x \text{ kJ mol}^{-1}$
 2. $\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}); \Delta_f H = y \text{ kJ mol}^{-1}$
 (a) $x = y$ (b) $x = 2y$
 (c) $x > y$ (d) $x < y$
12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound
 (a) is always negative
 (b) is always positive
 (c) may be positive or negative
 (d) is never negative
13. Enthalpy of sublimation of a substance is equal to
 (a) enthalpy of fusion + enthalpy of vaporisation
 (b) enthalpy of fusion
 (c) enthalpy of vaporisation
 (d) twice the enthalpy of vaporisation
14. Which of the following is not correct?
 (a) ΔG is zero for a reversible reaction.
 (b) ΔG is positive for a spontaneous reaction.
 (c) ΔG is negative for a spontaneous reaction.
 (d) ΔG is positive for a non-spontaneous reaction.

NEET/AIPMT (2013-2017) Questions

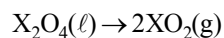
15. When 5 litres of a gas mixture of methane and propane is perfectly combusted at 0°C and 1 atmosphere, 16 litre of oxygen at the same temperature and pressure is consumed. The amount of heat released from this combustion in kJ ($\Delta H_{\text{comb}}(\text{CH}_4) = 890 \text{ kJ mol}^{-1}$, $\Delta H_{\text{comb}}(\text{C}_3\text{H}_8) = 2220 \text{ kJ mol}^{-1}$) is
 (a) 32 (b) 38
 (c) 317 (d) 477
16. Three thermochemical equations are given below:
 (i) $\text{C}_{(\text{graphite})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_f H^\circ = x \text{ kJ mol}^{-1}$
 (ii) $\text{C}_{(\text{graphite})} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}); \Delta_f H^\circ = y \text{ kJ mol}^{-1}$
 (iii) $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_f H^\circ = z \text{ kJ mol}^{-1}$

[NEET Kar. 2013]

Based on the above equations, find out which of the relationship given below is correct? [NEET Kar. 2013]

- (a) $x = y - z$ (b) $z = x + y$
(c) $x = y + z$ (d) $y = 2z - x$

17. For the reaction :



$$\Delta U = 2.1 \text{ k cal}, \Delta S = 20 \text{ cal K}^{-1} \text{ at } 300 \text{ K}$$

Hence ΔG is:-

- (a) 2.7 k cal (b) -2.7 k cal
(c) 9.3 k cal (d) -9.3 k cal

18. The heat of combustion of carbon to CO_2 is -393.5 kJ/mol . The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is [2015 RS]

- (a) -315 kJ (b) $+315 \text{ kJ}$
(c) -630 kJ (d) -3.15 kJ

19. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is [2016]

- (a) $\Delta H < 0$ and $\Delta S = 0$ (b) $\Delta H > 0$ and $\Delta S < 0$
(c) $\Delta H < 0$ and $\Delta S > 0$ (d) $\Delta H < 0$ and $\Delta S < 0$

20. For a given reaction, $\Delta H = 35.5 \text{ kJ mol}^{-1}$ and $\Delta S = 83.6 \text{ JK}^{-1} \text{ mol}^{-1}$. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with temperature) [2017]

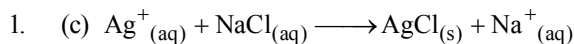
- (a) $T > 425 \text{ K}$ (b) All temperatures
(c) $T > 298 \text{ K}$ (d) $T < 425 \text{ K}$

21. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be:- [2017]

- (a) -500 J (b) -505 J
(c) $+505 \text{ J}$ (d) 1136.25 J

Hints & Solutions

EXERCISE - 1



The precipitation reaction is spontaneous and hence

$$\Delta G_{\text{P,T}} < 0.$$

2. (b) 1 calorie = 4.184 joule

3. (d) $\Delta H = \Delta E + P\Delta V$

For isochoric process, $\Delta V = 0$

$$\therefore \Delta H = \Delta E$$

4. (d) As $\Delta H = \Delta E + \Delta n_g RT$

$$\text{if } n_p < n_r; \Delta n_g = n_p - n_r = -ve$$

$$\text{Hence } \Delta H < \Delta E$$

5. (c) $10^7 \text{ erg} = 1 \text{ Joule}$, $1 \text{ cal} = 4.183 \text{ J}$

Hence calorie is the largest amount of energy.

6. (b) $\Delta n_g = 2 - 4 = -2$, $\Delta H = \Delta E - 2RT$.

7. (d) Heat energy is absorbed during endothermic reaction. In all the given reactions, heat is absorbed during reaction. $\therefore$ All of them are endothermic reactions.

8. (b) When a chemical bond is formed between the two free atoms in a gaseous state to form a molecular product in a gaseous state, some heat is always evolved which is known as bond energy. Hence, there is increase in energy.

9. (a) The Gibb's free energy is zero at equilibrium because the rate of backward reaction is equal to the rate of forward reaction.

Hence, option (a) is correct.

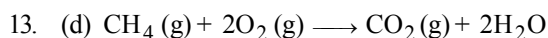
10. (d) $\Delta H = \Delta U + \Delta n_g RT$; $\Delta n_g = 1$ in (d); $\Delta n_g = 0$ in other cases.

11. (b) For an isothermal process $\Delta E = 0$

12. (a) Internal energy is dependent upon temperature and according to first law of thermodynamics total energy of an isolated system remains same, i.e., in a system of constant mass, energy can neither be created nor destroyed by any physical or chemical change but can be transformed from one form to another

$$\Delta E = q + W$$

For closed insulated container, $q = 0$, so, $\Delta E = +W$, as work is done by the system



$$(1) \qquad (2) \qquad (1)$$

$$\Delta H = 890 \text{ kJ (given)}$$

By 1st law of thermodynamics

$$\Delta H = \Delta E + \Delta nRT$$

Where,

ΔH = change in enthalpy of reaction

ΔE = change in internal energy of reaction

Δn = change in number of gaseous moles.

$$= (n_p - n_r)$$

According to question,

$$\Rightarrow \Delta E = \Delta H - \Delta nRT$$

$$= \Delta H - (1 - 3)RT$$

$$= \Delta H + 2RT = 890 + 2RT$$

$$\text{Hence } \Delta E > \Delta H$$

Option (d) is correct.

14. (c) $\Delta H = \Delta E + nRT$

$$\Delta n = 3 - (1 + 5) = 3 - 6 = -3$$

$$\Delta H - \Delta E = (-3RT)$$

15. (b) $W = -p\Delta V = -3(6 - 4) = -6 \text{ litre atmosphere}$

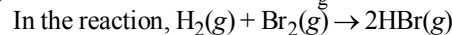
$$= -6 \times 101.32 = -608 \text{ J}$$

16. (c) Given $C_p = 75 \text{ JK}^{-1} \text{ mol}^{-1}$.

$$n = \frac{100}{18} \text{ mole} \cdot Q = 1000 \text{ J} \quad \Delta T = ?$$

$$Q = nC_p\Delta T \Rightarrow \Delta T = \frac{1000 \times 18}{100 \times 75} = 2.4 \text{ K}$$

17. (d) We know that $\Delta H = \Delta E + \Delta n_g RT$



$$\Delta n = n_p - n_r = 2 - 2 = 0$$

$$\text{So, } \Delta H = \Delta E \text{ for this reaction}$$

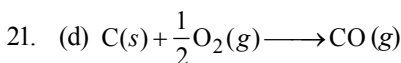
18. (d) Combustion is heating of substance in excess of oxygen so as to form carbon dioxide and water. Sometimes water is not formed during combustion.

19. (c) $W = -P\Delta V = -10^5 (1 \times 10^{-2} - 1 \times 10^{-3}) = -900 \text{ J}$

20. (b) $\Delta H = \Delta U + \Delta nRT$ for $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

$$\Delta n_g = 2 - 4 = -2$$

$$\therefore \Delta H = \Delta U - 2RT \text{ or } \Delta U = \Delta H + 2RT \therefore \Delta U > \Delta H$$



$$[\Delta n = 1 - \frac{1}{2} = \frac{1}{2}]$$

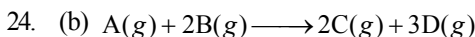
$$\Delta H - \Delta U = \Delta nRT = \frac{1}{2} \times 8.314 \times 298 = 1238.78 \text{ J mol}^{-1}$$

22. (c) $\Delta H = nC_p \Delta T$ solution; since $\Delta T = 0$ so, $\Delta H = 0$

23. (a) $\Delta G = \Delta H - T\Delta S$

$$0 = 132.6 \times 1000 - T \times 66$$

$$T = \frac{132.6 \times 1000}{66} = 2000 \text{ K}$$



$$\Delta n = 5 - 3 = 2$$

$$\Delta H = \Delta E + nRT \text{ or } \Delta E = \Delta H - nRT$$

$$= 19 - 2 \times 2 \times 10^{-3} \times 300 = 17.8 \text{ kcal}$$

25. (a) $\Delta H = -2.5 \times 10^3 \text{ Cals}$; $\Delta S = 7.4 \text{ Cals deg}^{-1}$

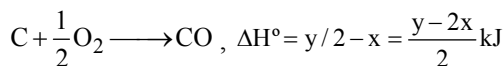
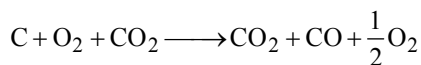
$$\text{Now, } \Delta G = \Delta H - T\Delta S$$

$$= -2.5 \times 10^{-3} - 298 \times 7.4 = -4705.2 = -ve$$

As, ΔG is negative so, reaction is spontaneous.

26. (c) In isolated system neither exchange of matter nor exchange of energy is possible with surroundings.

27. (b) Given $C + O_2 \rightarrow CO_2$, $\Delta H^\circ = -x$ kJ(i)
 $2CO_2 \rightarrow 2CO + O_2$, $\Delta H^\circ = +y$ kJ ... (ii)
 or $CO_2 \rightarrow CO + 1/2 O_2$, $\Delta H^\circ = +y/2$ kJ ... (iii)
 By adding no. (i) and (iii) eq.



28. (b) M.W. of ethane (C_2H_6) = 30 gm.
 M.W. of acetylene (C_2H_2) = 26 gm.
 Heat evolved per gm of ethane

$$= \frac{341}{30} = 11.36 \text{ cal/gm.}$$

Heat evolved per gm of acetylene

$$= \frac{310}{26} = 11.92 \text{ cal/gm}$$

So, acetylene is better fuel.

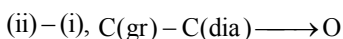
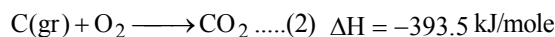
29. (c) $SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3$

$$\Delta H = \Delta H_f^\circ(SO_3) - \Delta H_f^\circ(SO_2) \\ = -98.2 + 298.2 = 200 \text{ kJ/mole}$$

30. (a) $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$ $\Delta H = ?$

$$\Delta H = [2 \times \Delta H_f^\circ \text{ of } H_2O(l) + (\Delta H_f^\circ \text{ of } O_2) \\ - (2 \times \Delta H_f^\circ \text{ of } H_2O_2(l))] \\ = [(2 \times -286) + (0) - (2 \times -188)] \\ = [-572 + 376] = -196 \text{ kJ/mole}$$

31. (d) $C(\text{dia}) + O_2 \longrightarrow CO_2$ (i) $\Delta H = -395.4$ kJ/mole



$$\Delta H = -393.5 + 395.4 \text{ kJ/mole} = +1.9 \text{ kJ/mole.}$$

32. (c) Energy absorbed $\propto \frac{1}{\text{stability of compound}}$

Energy released $\propto$ stability of compound

Thus, the order of stability is

$$142.2 > 25.9 > -46.2 > -393.2$$

i.e., $O_3 > HI > NH_3 > CO_2$

33. (d) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

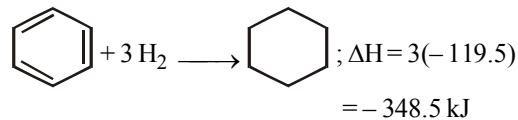
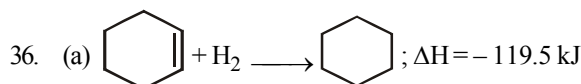
$$\Delta H^\circ = (BE)_{\text{reactant}} - (BE)_{\text{product}}$$

$$= (433 + 192) - (2 \times 364) = 625 - 728 = -103 \text{ kJ}$$

34. (c) As MgO is a weak base hence some energy got consumed to break MgO (s). Hence enthalpy is less than $-57.33 \text{ kJ mol}^{-1}$.

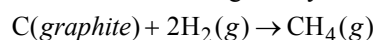
35. (c) $A_2 + B_2 \rightleftharpoons 2AB$

There is no change in volume so pressure will have no effect on it. As the reaction is endothermic (ΔH is positive), high temperature favours the forward reaction.



The resonance energy provides extra stability to the benzene molecule so it has to be overcome for hydrogenation to take place. So $\Delta H = -358.5 - (-150.4) = -208.1 \text{ kJ}$

37. (c) Standard heat of formation of a substance is amount of heat evolved or absorbed when one mole of substance is formed from its elements in their standard states. Since standard state of carbon and hydrogen are graphite and gaseous H_2 respectively. Hence standard heat of formation of methane is given by



38. (a) Dissolution of NaOH in water is an exothermic reaction as indicated by negative value of enthalpy leading to increase in temperature.

39. (b) Efficiency of engine $= \frac{T_1 - T_2}{T_1} = \frac{200}{500} = 0.4$

40. (b) $\Delta H = \Sigma [\Delta H_f^\circ \text{ products}] - \Sigma [\Delta H_f^\circ \text{ reactants}]$

$$\Delta H^\circ = [\Delta H_f^\circ(CO)(g) + \Delta H_f^\circ(H_2O)(g)] - \\ [\Delta H_f^\circ(CO_2)(g) + \Delta H_f^\circ(H_2)(g)] \\ = [-110.5 + (-241.8)] - [-393.5 + 0] = 41.2$$

41. (b) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$.

Change in enthalpy,

$$\Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

$$= 2 \times (-394) + 2 \times (-286) - (52 + 0) = -1412 \text{ kJ/mol.}$$

42. (d) $Q = mL$

where L = latent heat of vapourisation of water

$$= 2260 \text{ kJ/kg}$$

$$= 2260 \times 10^3 \text{ J/kg}$$

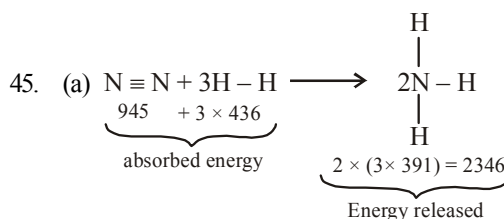
$$Q = 70 \times 10^{-3} \times 2260 \times 10^3 = 158155 \text{ Joule}$$

43. (d) $13.7 \text{ kcal} = 57 \text{ kJ} = 5.7 \times 10^4 \text{ J.}$

44. (c) Work done by a gas $= 2.303RT \log \frac{p_1}{p_2}$

$$= 2.303 \times 8.314 \times 300 \times \log \frac{10}{1}$$

$$= 2.303 \times 8.314 \times 300 = 5744.1 \text{ Joule}$$



$$\Delta H = 2253 - 2346 = -93 \text{ kJ}$$

46. (d) eq. (i) + eq. (ii) find the required result and divide by 2.
 47. (b) Eq. (b) shows largest phase change i.e., gas $\longrightarrow$ solid
 48. (b) Maximum work done by a system at constant pressure and constant temperature is $-\Delta G$. It can be derived as follows :

From first law of thermodynamics,

$$q = \Delta E + w_{\text{exp.}} + w_{\text{non exp.}}$$

At constant pressure, $w_{\text{exp}} = P\Delta V$

$$q = \Delta E + P\Delta V + w_{\text{non-exp.}}$$

$$q = \Delta H + w_{\text{non exp.}} \quad \dots\dots (1)$$

For the reversible change at const temp.,

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ or } q_{\text{rev}} = T\Delta S$$

so from equ. (1), $T\Delta S = \Delta H + w_{\text{non exp.}}$

$$\Rightarrow \Delta H - T\Delta S = -w_{\text{non exp.}} \quad \dots\dots (2)$$

For a change taking place under constant pressure and constant temperature,

$$\Delta H - T\Delta S = \Delta G$$

so from equ (2)

$$\Delta G = -w_{\text{non exp.}}$$

(it means $w_{\text{non exp.}}$ or w_{useful})

$$\text{or } w_{\text{max}} = -\Delta G$$

49. (c) When gas is compressed its entropy decreases so, ΔS is negative.

50. (c) According to Gibb's – Helmholtz equation

$$\Delta G = \Delta H - T\Delta S$$

$$\Rightarrow T\Delta S = \Delta H - \Delta G$$

$$\Rightarrow \Delta S = \frac{1}{T} [\Delta H - \Delta G]$$

51. (c) Latent heat of vaporisation of water

$$= 540 \text{ cal g}^{-1}$$

$\therefore$ latent heat of vaporisation for 1 mol of water = $540 \times 18 \text{ cal} = 9720 \text{ cal}$

$$\text{Thus } \Delta H_{\text{vap.}} = 9720 \text{ cal mol}^{-1}$$

and $T = 100^\circ\text{C} = 373 \text{ K}$

$$\text{and } \Delta S = \frac{\Delta H_{\text{vap.}}}{T} = \frac{9720}{373} \text{ cal mol}^{-1} \text{ K}^{-1} \\ \approx 26.6 \text{ cal mol}^{-1} \text{ K}^{-1}$$

52. (a) $\Delta S = \frac{\text{Latent heat of fusion}}{\text{Melting point}} = \frac{\Delta H}{T}$

$$= \frac{2930}{300} \text{ J K}^{-1} \text{ mol}^{-1} = 9.77 \text{ J K}^{-1} \text{ mol}^{-1}$$

53. (d) For isothermal reversible expansion

$$w = q = nRT \times 2.303 \log \frac{V_2}{V_1}$$

$$= 2RT \times 2.303 \log \frac{20}{2}$$

$$= 2 \times 2 \times T \times 2.303 \times 1 = 9.2 T$$

$$\text{Entropy change, } \Delta S = \frac{q}{T} = \frac{9.2T}{T} = 9.2 \text{ cal.}$$

54. (a) For a spontaneous process, ΔS_{total} is always positive

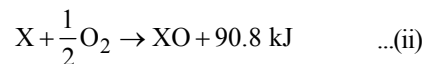
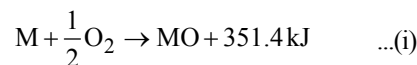
55. (b) Given $\Delta H_v = 9710 \text{ cal mol}^{-1}$

$$T = 100^\circ\text{C} = 373 \text{ K}$$

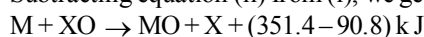
$$\text{Using } \Delta S = \frac{\Delta H_v}{T} = \frac{9710}{373} \text{ cal mol}^{-1} \text{ K}^{-1} \\ = 26.032 \text{ cal mol}^{-1} \text{ K}^{-1}$$

56. (c) Conversion of graphite into diamond is an endothermic reaction. But ΔS would be negative for the conversion of graphite into diamond. Diamond has more compact structure so the volume is smaller. However, the atoms in graphite are able to move with in their lattice so the entropy is higher.

57. (d) Given reactions are



Subtracting equation (ii) from (i), we get

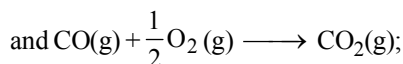


$$\text{or } \Delta H = (351.4 - 90.8) \text{ kJ}$$

$$= 260.6 \text{ kJ}$$

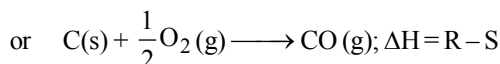
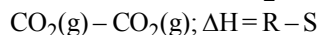
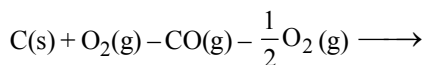
58. (b) Follow II law of thermodynamics.

59. (b) Let, $\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g});$
 $\Delta H = R \quad \dots\dots (i)$



$$\Delta H = S \quad \dots\dots (ii)$$

Subtracting equ. (i) from equ (ii), we get



Hence, heat of formation of CO = $R - S$

60. (a) Measure of disorder of a system is nothing but entropy. For a spontaneous reaction, $\Delta G < 0$. As per Gibbs Helmholtz equation,

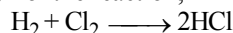
$$\Delta G = \Delta H - T\Delta S$$

Thus ΔG is -ve only

When $\Delta H = -\text{ve}$ (exothermic)

and $\Delta S = +\text{ve}$ (increasing disorder)

61. (d) For the reaction,



$$\Delta H \text{ for HCl} = -90 \text{ kJ}$$

$$\text{for } 2 \text{ HCl} = -180 \text{ kJ}$$

$$\Delta H = \Sigma(\text{bond energies of reactants})$$

$$- \Sigma(\text{bond energies of product})$$

$$\Rightarrow -180 \text{ kJ} = (\text{B.E.}_{\text{H-H}} + \text{B.E.}_{\text{Cl-Cl}}) - 2\text{B.E.}_{\text{H-Cl}}$$

$$\Rightarrow -180 \text{ kJ} = (430 \text{ kJ} + 240 \text{ kJ}) - 2 \text{ B.E.}_{\text{HCl}}$$

$$\Rightarrow 2 \text{ B.E.}_{\text{HCl}} = 670 \text{ kJ} + 180 \text{ kJ} = 850 \text{ kJ}$$

$$\Rightarrow \text{B.E.}_{\text{H-Cl}} = \frac{850}{2} \text{ kJ} = 425 \text{ kJ}$$

So, the H – Cl bond energy is 425 kJ mol^{-1}

62. (d) ΔG is negative for a spontaneous process.

63. (c) As all reactants and products are liquid $\Delta n_{(\text{g})} = 0$

$$\Delta H = \Delta E - \Delta n_{\text{RT}}$$

$$\Delta H = \Delta E \quad (\because \Delta n = 0)$$

64. (a) Entropy is a measure of randomness of the system which is highest in gases. So, entropy of hydrogen is highest among the given options.

65. (c) As we know that,
 $\Delta H = nC_p \Delta T$ (where n is no. of moles)

$$= \frac{28}{14} \times 7 \times (373\text{K} - 273\text{K})$$

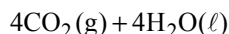
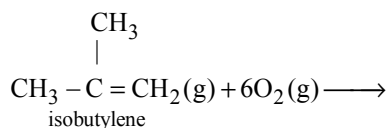
$$= 2 \times 7 \times 100\text{J} = 1400\text{J}$$

66. (d) We know that, $\Delta G = \Delta H - T\Delta S$
 When the reaction is in equilibrium, $\Delta G = 0$

$$0 = \Delta H - T\Delta S \Rightarrow T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{30 \times 1000}{105} = 285.7\text{K}$$

67. (a) $\Delta G = \Delta H - T\Delta S$
 $= 177.9 - (298 \times 160.4/1000) = 177.9 - 47.79 = +130.1\text{kJ}$
 68. (c) For spontaneous cooling of hot metal rod in air ΔS_{system} decreases (as metal rod cools down) and ΔS_{air} increases (as surrounding air becomes hot). So, $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{universe}} > 0$.
 69. (b) For combustion reaction, ΔH is negative,
 $\Delta n = (16 + 18) - (25 + 2) = +7$, so ΔS is +ve, reaction is spontaneous, hence ΔG is -ve.
 70. (b)
 71. (d) Isobutylene on combustion gives CO_2 and H_2O as shown below:



Here $\Delta n_g = 4 - 7 = -3 < 0$

Using IInd law of thermodynamics,

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta H = (\Delta E) + (-\text{ve term})$$

$$\Rightarrow \Delta H < \Delta E$$

72. (c) $\therefore \Delta G = \Delta H - T \cdot \Delta S$
 For a spontaneous reaction ΔG should be negative
 $\Delta H = -238\text{kJ}$, $\Delta S = -87\text{JK}^{-1}$
 Hence, reaction will be spontaneous when $\Delta H > T \cdot \Delta S$.
 Therefore, at 1000, 1500 and 3000 K the reaction would be spontaneous.

73. (c) $\text{C}_6\text{H}_6 + \frac{15}{2}\text{O}_2 \longrightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$

$$1\text{ mole} \equiv 3250\text{KJ}$$

$$\frac{0.39}{78}\text{mole} \equiv 3250 \times \frac{0.39}{78} = 16.25\text{kJ}$$

74. (d) By $2 \times (\text{ii}) - (\text{i}) + (\text{iii})$
 $\text{H}_2(\text{g}) + 2\text{C}(\text{s}) \rightarrow \text{C}_2\text{H}_2(\text{g})$, $\Delta G^\circ = 209\text{kJ}$
 75. (b) Since the gas expands adiabatically (*i.e.*, no change in enthalpy) so the heat is totally converted into work.
 For the gas $C_V = 20\text{J/K}$. Thus, 20 J of heat is required for 1° change in temperature of the gas.
 Heat change involved during the process (*i.e.*, work done)
 $= 3\text{kJ} = 3000\text{J}$

$$\text{Change in temperature} = \frac{3000}{20}\text{K} = 150\text{K}$$

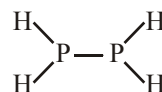
$$\text{Initial temperature} = 300\text{K}$$

Since the gas expands so the temperature decreases and thus, final temperature is

$$150\text{K} (300 - 150 = 150)$$

76. (b) Bond dissociation energy of $\text{PH}_3(\text{g})$
 $= 228\text{kcal mol}^{-1}$

$$\text{P} - \text{H bond energy} = \frac{228}{3} = 76\text{kcal mol}^{-1}$$



$$\text{Bond energy of } 4(\text{P} - \text{H}) + (\text{P} - \text{P}) = 355\text{kcal mol}^{-1}$$

$$\text{or } 4 \times 76 + (\text{P} - \text{P}) = 355\text{kcal mol}^{-1}$$

$$\text{P} - \text{P bond energy} = 51\text{kcal mol}^{-1}$$

77. (d) $\Delta n = \Delta E + P\Delta V$
 Now $PV = nRT$
 where n = no of gaseous moles.
 From this we derive

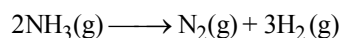
$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta n_g = n_2 - n_1$$

where n_1 = no of moles of gaseous reactant

n_2 - no of moles of gaseous moles product

For the reaction,



$$\Delta n_g = 4 - 2 = 2.$$

Hence,

$$\Delta H - \Delta E = \Delta n_g RT = 2 \times 8.314 \times (273 + 27) = 2 \times 8.314 \times 300$$

78. (b) $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \longrightarrow \text{HCl}$

$$\Delta_f H_{\text{HCl}} = \sum \text{B.E. of reactants} - \sum \text{B.E. of products}$$

$$-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - \text{B.E. of HCl}$$

$$\therefore \text{B.E. of HCl} = 215 + 120 + 90 = 425\text{kJ mol}^{-1}$$

79. (d) We know that heat (q) and work (w) are not state functions but (q + w) is a state function. $H - TS$ (*i.e.* G) is also a state function. Thus II and III are not state functions so the correct answer is option (d).

80. (d) $\text{H}_2\text{O}(\ell) \xrightleftharpoons{1\text{atm}} \text{H}_2\text{O}(\text{g})$

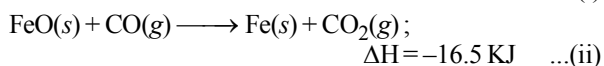
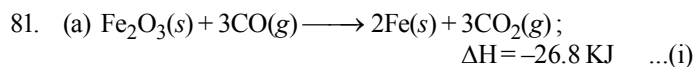
$$\Delta H = 40630\text{J mol}^{-1}$$

$$\Delta S = 108.8\text{JK}^{-1}\text{mol}^{-1}$$

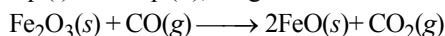
$$\Delta G = \Delta H - T\Delta S \quad \text{When } \Delta G = 0, \Delta H - T\Delta S = 0$$

$$T = \frac{\Delta H}{\Delta S} = \frac{40630\text{J mol}^{-1}}{108.8\text{J K}^{-1}\text{mol}^{-1}} = 373.4\text{K}$$

$\therefore$ Correct choice : (d)



eq. (i) $- 2 \times$ eq. (ii), we get



$\Delta H = -26.8 + 33.0 = +6.2 \text{ kJ}$

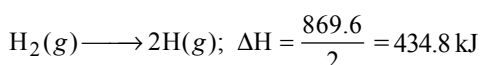
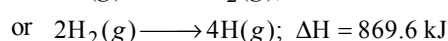
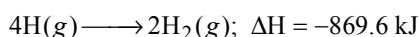
82. (a) Ideal gas during spontaneous expansion into vacuum does not do any external work.

83. (d) Given $\Delta H = 30 \text{ kJ mol}^{-1}$ $T = 273 + 27 = 300 \text{ K}$

$$\Delta S_T = \frac{\Delta H_T}{T} = \frac{3 \times 10^4}{300} \text{ J mol}^{-1}$$

$$= 100 \text{ J mol}^{-1} \text{ K}^{-1}$$

84. (c) Given



85. (c) $\Delta S = \frac{\Delta H}{T} = \frac{1.435 \times 10^3}{273} = 5.260 \text{ cal/molK}$

86. (d) $\frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$

87. (b) Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.



Let x be the bond enthalpy of N – H bond then

[Note : Enthalpy of formation or bond formation enthalpy is given which is negative but the given reaction involves bond breaking hence values should be taken as positive.]

$\Delta H = \sum \text{Bond energies of reactants} - \sum \text{Bond energies of products}$

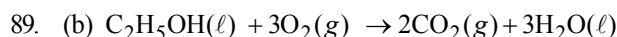
$2 \times -46 = 712 + 3 \times (436) - 6x$

$-92 = 2020 - 6x$

$6x = 2020 + 92$

$6x = 2112$

$x = +352 \text{ kJ/mol}$



$\Delta n_g = 2 - 3 = -1$

$\Delta U = \Delta H - \Delta n_g RT$

$= -1366.5 - (-1) \times \frac{8.314}{10^3} \times 300$

$= -1366.5 + (1) \times \frac{8.314}{10^3} \times 300$

$= -1366.5 + 0.8314 \times 3 = -1364.006 \text{ kJ}$

90. (a) In $\text{PH}_3(\text{g})$, energy required to break 3 P–H bonds = 954 kJ mol^{-1}

$\therefore$ Energy required to break 1 P – H bond

$= \frac{954}{3} = 318 \text{ kJ mol}^{-1}$

In $\text{P}_2\text{H}_4(\text{g})$, energy of 1 P – P bond + 4 P – H bonds = 1485 kJ mol^{-1}

$\therefore$ Energy of 1 P – H bond = 318 kJ mol^{-1}

$\therefore$ Energy of 4 P – H bond = 318×4
 $= 1272 \text{ kJ mol}^{-1}$

Thus, the P – P bond energy = $1485 - 1272$
 $= 213 \text{ kJ mol}^{-1}$

91. (d) A process is spontaneous only when there is decrease in the value of free energy, i.e., ΔG is $-ve$.

92. (d) Raking up leaves into a thrash bag results in decrease in randomness i.e. decrease in entropy.

93. (b) According to Gibb's equation,

$\Delta G = \Delta H - T\Delta S$

Since reaction is at equilibrium

$\therefore \Delta G = 0, \therefore \Delta H = T\Delta S$

$\Delta H = 21.3 \text{ kJ} = 21300 \text{ J}$

$T = 82^\circ\text{C} = (82 + 273) \text{ K} = 355 \text{ K}$

On substituting these values,

$\Delta S = \frac{\Delta H}{T} = \frac{21300}{355} = 60.0 \text{ JK}^{-1} \text{ mol}^{-1}$

94. (d) Lesser the bond length higher is the bond energy. H–H bond energy is the highest.

Bond	Bond length	Bond energy (kJ) mol^{-1}
H–H	0.74	435.1
F–F	1.42	154.8
Cl–Cl	1.99	242.7
Br–Br	2.28	192.5
I–I	2.26	149.0

95. (d) Since the process is at equilibrium $\Delta G = 0$ for $\Delta G = 0$, they should be $\Delta H > 0$, $\Delta S > 0$.

96. (a) $\Delta H_{\text{sol}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$

$\Delta H_{\text{lattice}} = \Delta H_{\text{sol}} - \Delta H_{\text{hydration}}$

$4 - (-784) = \Delta H_{\text{lattice}} \Rightarrow \Delta H_{\text{lattice}} = +788$

97. (b) Work done in reversible isothermal expansion

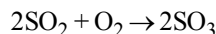
$W = -2.303nRT \log \frac{V_2}{V_1}$

$= -2.303 \times 0.2 \times 8.314 \times 300 \log \frac{25}{2.5}$

$= -2.303 \times 0.2 \times 8.314 \times 300 = -1148$

98. (c) ΔS has negative value if number of gaseous moles decreases during a reaction, $\Delta n_g = -ve$

For the reaction



$\Delta n_g = 2 - 3 = -1$

99. (d) $\Delta G = \Delta H - T\Delta S$

For a reaction to be spontaneous,

$\Delta H = -ve, \Delta S = +ve$

at all temperatures.

but at high temperature, $\Delta G = \frac{\Delta H}{-ve} - \frac{T\Delta S}{+ve}$

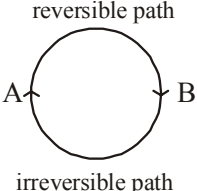
Thus the second term will have high positive value and reaction will be non-spontaneous.

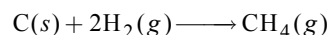
100. (d) Gibb's-Helmholtz equation is

$\Delta G = \Delta H - T\Delta S$

For a reaction to be non-spontaneous at all temperatures, ΔH should be +ve and ΔS should be -ve
 $\therefore \Delta G = +ve - T \times (-ve)$; the value of ΔG is always positive for such a reaction and hence it will be non-spontaneous at all temperatures.

EXERCISE - 2

- (d)
- (b) $1 \text{ M H}_2\text{SO}_4 = 2 \text{ g eq. of H}_2\text{SO}_4$.
 Hence $y = 2x$ or $x = \frac{1}{2}y$.
- (b) Hydration energy of Cl^+ is very less than H^+ hence it doesn't form $\text{Cl}^+(aq)$ ion.
- (b) For the reaction
 $2 \text{ ZnS} \rightarrow 2 \text{ Zn} + \text{S}_2$; $\Delta G_1^\circ = 293 \text{ kJ}$ (1)
 $2 \text{ Zn} + \text{O}_2 \rightarrow 2 \text{ ZnO}$; $\Delta G_2^\circ = -480 \text{ kJ}$ (2)
 $\text{S}_2 + 2 \text{ O}_2 \rightarrow 2 \text{ SO}_2$; $\Delta G_3^\circ = -544 \text{ kJ}$ (3)
 ΔG° for the reaction
 $2 \text{ ZnS} + 3 \text{ O}_2 \rightarrow 2 \text{ ZnO} + 2 \text{ SO}_2$
 can be obtained by adding eqn. (1), (2) and (3)
 $\Rightarrow \Delta G^\circ = 293 - 480 - 544 = -731 \text{ kJ}$
- (b) $A \rightarrow B$, $\Delta H = +24 \text{ kJ/mol}$
 $\Rightarrow H_B - H_A = +24$ (i)
 $B \rightarrow C$, $\Delta H = -18 \text{ kJ/mol}$
 $\Rightarrow H_C - H_B = -18$
 or $H_B - H_C = +18$
 From Eqs. (i) and (ii), we have
 $H_C - H_A = 6$ (ii)
 $\therefore H_B > H_C > H_A$
- (d) $\text{CO}_2 \rightarrow \text{C} + \text{O}_2$, $\Delta H = 393 \text{ J}$ (i)
 $2 \text{ Zn} + \text{O}_2 \rightarrow 2 \text{ ZnO}$, $\Delta H = -412 \text{ J}$ (ii)
 By adding eq. (i) and (ii) we get
 $2 \text{ Zn} + \text{CO}_2 \rightarrow 2 \text{ ZnO} + \text{C}$, $\Delta H = -19 \text{ J}$
- (c)

 For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.
- (a) For spontaneous reaction, $dS > 0$ and dG should be negative i.e., < 0 .
- (d) $\text{X}_2 + \text{Y}_2 \rightarrow 2 \text{ XY}$, $\Delta H = 2(-200) \text{ kJ mol}^{-1}$
 Let x be the bond dissociation energy of X_2 . Then
 $\Delta H = -400 = \Sigma_{x-x} + \Sigma_{y-y} - 2\Sigma_{x-y}$
 $= x + 0.5x - 2x = -0.5x$
 or $x = \frac{400}{0.5} = 800 \text{ kJ mol}^{-1}$
- (c) The standard enthalpy of formation of CH_4 is given by the equation :



Hence, dissociation energy of hydrogen and enthalpy of sublimation of carbon is required.

- (a) $\text{I}_2(s) + \text{Cl}_2(g) \rightarrow 2 \text{ ICl}(g)$
 $\Delta_r H = [\Delta H(\text{I}_2(s) \rightarrow \text{I}_2(g)) + \Delta H_{\text{I-I}} + \Delta H_{\text{Cl-Cl}}] - [\Delta H_{\text{I-Cl}}]$
 $= 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46$
 $\Delta_f H^\circ(\text{ICl}) = \frac{33.46}{2} = 16.73 \text{ kJ/mol}$
- (c) Given $\text{NaOH} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$
 $\frac{1 \text{ mol}}{0.2 \text{ mol}} \quad \frac{1 \text{ mol}}{0.5 \text{ mol}} \quad \Delta H = 57.0 \text{ kJ}$
 $\Delta H = ?$
 Given heat of neutralisation of strong acid by strong base = 57.0 kJ
 $\therefore 0.2 \text{ mole NaOH}$ is limiting reagent.
 $\therefore$ Heat of neutralization = $0.2 \times 57 = 11.4 \text{ kJ}$
- (a) No. of moles of hydrogen
 $= \frac{\text{Mass}}{\text{Molecular mass}} = \frac{4}{2} = 2 \text{ moles}$
 Given $2 \text{ H}_2(g) \rightarrow 4 \text{ H}(g)$, $\Delta H = 208 \text{ kcal}$
 $\therefore \text{H}_2(g) \rightarrow 2 \text{ H}(g)$, $\Delta H = 104 \text{ kcal}$
 $\therefore$ Bond energy of H-H bond is $104 \text{ kcal mol}^{-1}$
- (a) Conc. of $\text{HCl} = 0.25 \text{ mole}$
 Conc. of $\text{NaOH} = 0.25 \text{ mole}$
 Heat of neutralization of strong acid by strong base = -57.1 kJ
 $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} - 57.1 \text{ kJ}$
 1 mole of HCl neutralise 1 mole of NaOH , heat evolved = 57.1 kJ
 $\therefore 0.25 \text{ mole of HCl}$ neutralise $0.25 \text{ mole of NaOH}$
 $\therefore$ Heat evolved = $57.1 \times 0.25 = 14.275 \text{ kJ}$
- (a) $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$, $\Delta H = -55.9 \text{ kJ}$
 Actually, heat of neutralisation of a strong acid by a strong base means heat of formation of water.
 Thus,
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$; $\Delta H = -55.9 \text{ kJ}$
 or $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$; $\Delta H = 55.9 \text{ kJ}$ (i)
 Given, $\text{HCN} + \text{OH}^- \rightarrow \text{CN}^- + \text{H}_2\text{O}$; $\Delta H = -12.1 \text{ kJ}$ (ii)
 Adding equations (i) and (ii), we get
 $\text{HCN} \rightarrow \text{H}^+ + \text{CN}^-$; $\Delta H = 55.9 - 12.1 \text{ kJ} = 43.8 \text{ kJ}$
- (b) $\Delta H_{\text{S-S}} + 2\Delta H_{\text{H-S}} = 239$ $2\Delta H_{\text{H-S}} = 175$
 Hence, $\Delta H_{\text{S-S}} = 239 - 175 = 64 \text{ kcal mol}^{-1}$
 Then, ΔH for $8 \text{ S}(g) \rightarrow \text{S}_8(g)$ is $8 \times (-64) = -512 \text{ kcal}$
- (b)
- (a) For a pure substance T_A and T_B represent the same temperature. Hence A is a correct choice.

19. (d) If $n_p < n_r$ then $\Delta n_{(g)} = n_p - n_r = \text{'-'} \text{'ve}$
 Since $\Delta H = \Delta E + \Delta nRT$
 $\therefore \Delta H = \Delta E - \text{some quantity} [\because \Delta n \text{ is } - \text{tive}]$
 or $\Delta H < \Delta E$
20. (d) This reaction shows the formation of H_2O , and the $-X_2$ represents the enthalpy of formation of H_2O because as the definition suggests that the enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constituent elements.
21. (b) For the reaction
 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
 The reaction given is an example of decomposition reaction and we know that decomposition reactions are endothermic in nature, i.e., $\Delta H > 0$.
 Further
 $\Delta n = (1+1) - 1 = +1$
 Hence more number of gaseous molecules are present in products which shows more randomness i.e., $\Delta S > 0$ (ΔS is positive)
22. (c) The reaction for formation of HCl can be written as
 $H_2 + Cl_2 \rightarrow 2HCl$
 $H-H + Cl-Cl \rightarrow 2(H-Cl)$
 Substituting the given values, we get enthalpy of formation of
 $2HCl = (676 - 862) = -186 \text{ kJ}$
 $\therefore$ Enthalpy of formation of $HCl = \frac{-186}{2} \text{ kJ} = -93 \text{ kJ}$
23. (b) $\Delta G = \Delta H - T \Delta S$
 At equilibrium, $\Delta G = 0$
 $\Rightarrow 0 = (170 \times 10^3 \text{ J}) - T(170 \text{ JK}^{-1})$
 $\Rightarrow T = 1000 \text{ K}$
 For spontaneity, ΔG is $-ve$, which is possible only if $T > 1000 \text{ K}$.
24. (b) Enthalpy of reaction
 $= B.E_{(\text{Reactant})} - B.E_{(\text{Product})}$
 $= [B.E_{(C=C)} + 4B.E_{(C-H)} + B.E_{(H-H)}]$
 $- [B.E_{(C-C)} + 6B.E_{(C-H)}]$
 $= [606.1 + (4 \times 410.5) + 431.37] - [336.49 + (6 \times 410.5)]$
 $= -120.0 \text{ kJ mol}^{-1}$
25. (a) ΔS for the reaction $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$
 $\Delta S = 50 - (30 + 60) = -40 \text{ J}$
 For equilibrium $\Delta G = 0 = \Delta H - T \Delta S$
 $T = \frac{\Delta H}{\Delta S} = \frac{-30000}{-40} = 750 \text{ K}$
26. (d)
 (1) $K_p > 0$ (iv) Spontaneous
 (2) $\Delta G < RT \ln Q$ (i) Non spontaneous
 (3) $K_p = 0$ (ii) Equilibrium
 (4) $T > \frac{\Delta H}{\Delta S}$ (iii) Spontaneous
 and endothermic
27. (b) Given ΔH
 $\frac{1}{2}A \longrightarrow B \quad +150 \quad \dots(1)$
 $3B \longrightarrow 2C + D \quad -125 \quad \dots(2)$
 $E + A \longrightarrow 2D \quad +350 \quad \dots(3)$
 To calculate ΔH operate
 $2 \times \text{eq. (1)} + \text{eq. (2)} - \text{eq. (3)}$
 $\Delta H = 300 - 125 - 350 = -175$
28. (a) Since, in the first reaction value of Δn is positive.
 $\Delta n = 1 - \frac{1}{2} = \frac{1}{2}$ hence entropy will increase i.e., $\Delta S = +ve$.
 $C(\text{gr.}) + \frac{1}{2}O_2(g) \rightarrow CO(g); \Delta S^\circ = +ve$
 Since, $\Delta G^\circ = \Delta H^\circ - T \Delta S$ hence the value of ΔG decreases on increasing temperature.
29. (d) $H_2O(\ell) \rightleftharpoons H_2O(g) \quad \Delta H = 40.66 \text{ kJ mol}^{-1}$
 $T = 373 \text{ K}$
 $\Delta E = \Delta H - \Delta nRT$
 $= 40.66 \times 10^3 \text{ J mol}^{-1} - 1 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 373 \text{ K}$
 $\Delta E = 37558 \text{ J/mol}$
 $\Delta E = 37.56 \text{ kJ mol}^{-1}$
30. (a) $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$
 For a spontaneous reaction $\Delta G^\circ < 0$
 or $\Delta H^\circ - T \Delta S^\circ < 0 \Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$
 $\Rightarrow T > \frac{179.1 \times 10^3}{160.2} > 1117.9 \text{ K} \approx 1118 \text{ K}$
31. (d) Given $\Delta H = 41 \text{ kJ mol}^{-1} = 41000 \text{ J mol}^{-1}$
 $T = 100^\circ\text{C} = 273 + 100 = 373 \text{ K}$
 $n = 1$
 $\Delta U = \Delta H - \Delta nRT = 41000 - (1 \times 8.314 \times 373)$
 $= 37898.88 \text{ J mol}^{-1} \approx 37.9 \text{ kJ mol}^{-1}$
32. (b)
33. (a) Given, for reaction
 (i) $H_2O(\ell) \longrightarrow H^+(aq.) + OH^-(aq.);$
 $\Delta H_f = 57.32 \text{ kJ}$
 (ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell);$
 $\Delta H_f = -286.20 \text{ kJ}$
 For reaction (i)
 $\Delta H_f = \Delta H^\circ_f(H^+, aq.) + \Delta H^\circ_f(OH^-, aq.) - \Delta H^\circ_f(H_2O, \ell)$
 $57.32 = 0 + \Delta H^\circ_f(OH^-, aq.) - \Delta H^\circ_f(H_2O, \ell) \dots(iii)$
 For reaction (ii)
 $\Delta H_f = \Delta H^\circ_f(H_2O, \ell) - \Delta H^\circ_f(H_2, g) - \frac{1}{2}\Delta H^\circ_f(O_2, g)$
 $-286.20 = \Delta H^\circ_f(H_2O, \ell)$
 On replacing this value in eq. (iii) we have
 $57.32 = \Delta H^\circ_f(OH^-, aq.) - (-286.20)$

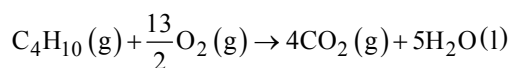
- $\Delta H_f^\circ(\text{OH}^-, \text{aq}) = -286.20 + 57.32 = -228.88 \text{ kJ}$
34. (b) At equilibrium $\Delta G = 0$
Hence, $\Delta G = \Delta H - T_e \Delta S = 0$
 $\therefore \Delta H = T_e \Delta S$ or $T_e = \frac{\Delta H}{\Delta S}$
For a spontaneous reaction
 ΔG must be negative which is possible only if $\Delta H - T \Delta S < 0$
 $\therefore \Delta H < T \Delta S$
or $T > \frac{\Delta H}{\Delta S}$; $T_e < T$
35. (d) $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g}), \Delta_r H = -111 \text{ kJ}$
 $\Delta H'$ $\downarrow -54 \text{ kJ}$
 $2\text{N}_2\text{O}_5(\text{s})$
 $-111 - 54 = \Delta H'$
 $\Delta H' = -165 \text{ kJ}$
36. (b) $\text{A} \rightleftharpoons \text{B}$
 $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$
 $\Delta G^\circ = -2.303 RT \log_{10} K$
 $-2.303 RT \log_{10} K = \Delta H^\circ - T \Delta S^\circ$
 $2.303 RT \log_{10} K = T \Delta S^\circ - \Delta H^\circ$
 $\log_{10} K = \frac{T \Delta S^\circ - \Delta H^\circ}{2.303 RT} = \frac{298 \times 10 + 54.07 \times 1000}{2.303 \times 8.314 \times 298}$
 $= 9.998 \approx 10$
37. (a) Since, liquid is passing into gaseous phase so entropy will increase and at 373 K during the phase transformation it remains at equilibrium. So, $\Delta G = 0$.
38. (b) The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298 K, Cl_2 is gas while Br_2 is liquid.
39. (d) (i) $2\text{C}(\text{s}) + \text{H}_2(\text{g}) \longrightarrow \text{H}-\text{C} \equiv \text{C}-\text{H}(\text{g})$
 $\Delta H = 225 \text{ kJ mol}^{-1}$
(ii) $2\text{C}(\text{s}) \longrightarrow 2\text{C}(\text{g})$ $\Delta H = 1410 \text{ kJ mol}^{-1}$
 $\text{C}(\text{s}) \longrightarrow \text{C}(\text{g}) \Delta H = \frac{1410}{2} = 705 \text{ kJ mol}^{-1}$
(iii) $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$ $\Delta H = 330 \text{ kJ mol}^{-1}$
From equation (i):
 $225 = [2 \times \Delta H_{\text{C}(\text{s}) \longrightarrow \text{C}(\text{g})} + 1 \times \text{BE}_{\text{H}-\text{H}}] - [2 \times \text{BE}_{\text{C}-\text{H}} + 1 \times \text{BE}_{\text{C} \equiv \text{C}}]$
 $225 = [1410 + 1 \times 330] - [2 \times 350 + 1 \times \text{BE}_{\text{C} \equiv \text{C}}]$
 $225 = [1410 + 330] - [700 + \text{BE}_{\text{C} \equiv \text{C}}]$
 $225 = 1740 - 700 - \text{BE}_{\text{C} \equiv \text{C}}$
 $\text{BE}_{\text{C} \equiv \text{C}} = 815 \text{ kJ mol}^{-1}$
40. (a) Process is isothermal reversible expansion, hence $\Delta U = 0$, therefore $q = -W$.
Since $q = +208 \text{ J}$, $W = -208 \text{ J}$
41. (c) $\Delta E = C \times \Delta t \times \frac{M}{m} = 30 \times 4 \times \frac{12}{4} = 360$
 $\Delta E = -360 \text{ kJ mol}^{-1}$
42. (d) The bond enthalpy of reaction =
[Sum of bond enthalpies of reactants] -
[Sum of bond enthalpies of products]
 $-50 = \left[\frac{1}{2} \times 380 + \frac{3}{2} \times Y - Y \right] - 3 \times 150 = \frac{3}{2}(Y - Y) - 260$
 $Y - Y = \frac{210 \times 2}{3} = 140$
43. (b) $2\text{C}_8\text{H}_{18}(\text{g}) + 25\text{O}_2(\text{g}) \longrightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{g})$
The given reaction is a combustion reaction. Hence this will be an exothermic reaction.
i.e. $\Delta H = -ve$
Further $\Delta n = +ve$ i.e. $\Delta S = +ve$
 $\Delta G = \Delta H - T \Delta S = -\Delta H - T \Delta S = -ve$
44. (c) $\Delta S = \frac{\Delta H}{T} = \frac{344.3 \times 10^3}{3443} = 100 \text{ J mol}^{-1}$
45. (b) We have to calculate the enthalpy of the reaction
 $\text{OH}(\text{g}) \rightarrow \text{O}(\text{g}) + \text{H}(\text{g})$
From the given reactions, this can be obtained as follows.
 $-\left[\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{OH}(\text{g}) \right]; \Delta H = -42.09 \text{ kJ mol}^{-1}$
 $+\frac{1}{2} [\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})]; \Delta H = \frac{1}{2} \times 435.89 \text{ kJ mol}^{-1}$
 $+\frac{1}{2} [\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})]; \Delta H = \frac{1}{2} \times 495.05 \text{ kJ mol}^{-1}$
Add
 $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g}); \Delta H = 423.38 \text{ kJ mol}^{-1}$
46. (b) The factor $T \Delta S$ increases with increase in temperature.
47. (b) In an isothermal process change in internal energy (ΔE) is zero (as it is a function of temperature).
 $\therefore$ According to first law of thermodynamics
 $\therefore Q + W = \Delta E$. Hence $Q = -W$ (if $\Delta E = 0$)
If a system undergoes a change in which internal energy of the system remains constant (i.e. $\Delta E = 0$) then $-W = Q$. This means that work done by the system equals the heat absorbed by the system.
48. (b) The mass and volume depend upon the quantity of matter so these are extensive properties while ratio of mass to its volume does not depend upon the quantity of matter so this ratio is an extensive property.
49. (a) The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties eg, internal energy.
50. (a) It is fact that absolute values of internal energy of substances cannot be determined. It is also true that it is not possible to determine exact values of constituent energies of a substance.

EXERCISE - 3

Exemplar Questions

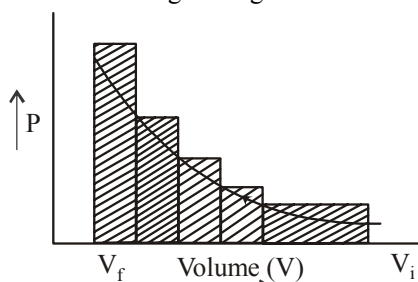
1. (c) Thermodynamics deals with the energy change, feasibility and extent of a reaction, but not with the rate and mechanism of a process.
2. (c) For a closed vessel made of copper, there will be no exchange of matter between the system and the surroundings but energy exchange can occur through its walls.

3. (d) The state of a gas can be described by quoting the relationship between pressure, volume, temperature and amount. The ideal gas equation is
 $PV = nRT$
4. (c) Specific heat is an intensive property which depends only on the nature of the gas. Hence, if the volume of gas is reduced to half from its original volume the specific heat will remain constant.
5. (c) The complete combustion of one mole of butane is represented by

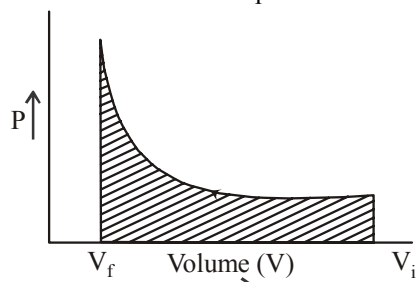


$\Delta_c H$ should be negative and have a value of 2658 kJ mol⁻¹.

6. (b) $\Delta_f H^\circ = \Delta_f U^\circ + \Delta n_g RT$
 For the reaction, $\Delta_f H^\circ$
 $C(s) + 2H_2(g) \rightarrow CH_4(g)$
 $\Delta_f H^\circ = 1 - 2 = -1$
 $\therefore \Delta_f H^\circ = \Delta U - 1 \times RT$
 $\therefore \Delta_f H^\circ < \Delta_f U^\circ$
7. (c) For free expansion, $W = 0$; and
 For Adiabatic process, $q = 0$
 According to first law of thermodynamics,
 $\Delta U = q + W = 0$
 Since there is no change in ΔU hence, temperature change will be zero i.e., $\Delta T = 0$
8. (b) Area under the curve is always greater in irreversible compression than that in reversible compression which can be seen from given figure.



Irreversible compression



Reversible compression

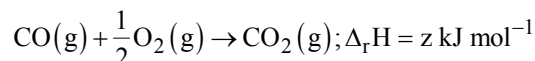
9. (c) During the process of freezing, energy is released which is absorbed by the surroundings.

$$\therefore \Delta S_{sys} = \frac{-q_{rev}}{T}$$

$\Delta S_{surr} = \frac{q_{rev}}{T}$ i.e., on freezing, entropy of the system decreases and of surrounding increases.

10. (c)
 (a) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g); \Delta_r H = x \text{ kJ mol}^{-1} \dots$
 (i)
 (b) $C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g); \Delta_r H = y \text{ kJ mol}^{-1} \dots$
 (ii)

On subtracting eqn (i) & (ii) we get



Hence, $x - y = z$ or $x = y + z$

11. (c) $x > y$ because same bonds are formed in reaction (1) and (2) but no bonds are broken in reaction (1) whereas in reaction (2) bonds in the reactant molecules are broken. As energy is absorbed when bonds are broken, energy released in reaction (1) is greater than that in reaction (2).
12. (c) Enthalpy of formation can be positive or negative.
 For example :
 $C + O_2 \rightarrow CO_2$ is exothermic whereas, $C + 2S \rightarrow CS_2$ is endothermic.
13. (a) Enthalpy of sublimation of a substance is equal to enthalpy of fusion + enthalpy of vaporisation.
 Sublimation is, direct conversion of solid to vapour.
 Writing in two steps, we have solid $\rightarrow$ liquid $\rightarrow$ vapour
 solid $\rightarrow$ liquid requires enthalpy of fusion
 liquid $\rightarrow$ vapour requires enthalpy of vaporisation
14. (b) ΔG gives a criterion for spontaneity at constant pressure and temperature.
 (i) If ΔG is negative (< 0), the process is spontaneous.
 (ii) If ΔG is positive (> 0), the process is non-spontaneous.
 (iii) If ΔG is zero then reaction is at equilibrium.

NEET/AIPMT (2013-2017) Questions

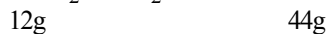
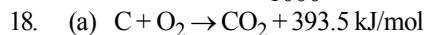
15. (c) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
 $\quad \quad \quad x \quad \quad \quad 2x$
 $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$
 $\quad (5-x) \quad 5(5-x)$
 $2x + 5(5-x) = 16$
 $\Rightarrow x = 3L$
 $\therefore$ Heat released
 $= \frac{3}{22.4} \times 890 + \frac{2}{22.4} \times 2220 = 317$
16. (c) Applying Hess's law, equation (i) can be obtained by adding equations (ii) and (iii).
 $\therefore x = y + z$
17. (b) Given $\Delta U = 2.1 \text{ k cal.}$, $\Delta S = 20 \text{ cal. K}^{-1}$
 $T = 300 \text{ K}$
 $\therefore \Delta H = \Delta U + \Delta n_g RT$
 Putting the values given in the equation

$$\Delta H = 2.1 + 2 \times \frac{2}{1000} \times 300$$

$$= 2.1 + 1.2 = 3.3 \text{ k cal.}$$

$$\text{Now, } \Delta G = \Delta H - T\Delta S$$

$$= 3.3 - 300 \times \frac{20}{1000} = -2.7 \text{ k cal}$$



44g is formed from 12g of carbon

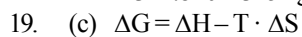
$$35.2\text{g is formed from } \frac{12 \times 35.2}{44} \text{ g of C}$$

$$= 9.6 \text{ g of C} = 9.6/12 = 0.8 \text{ mole}$$

$$1 \text{ mole release heat } 393.5 \text{ kJ}$$

$$0.8 \text{ mole release heat} = 393.5 \times 0.8$$

$$= 314.8 \text{ kJ} \approx 315 \text{ kJ}$$

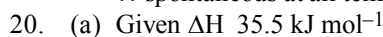


For a spontaneous reaction $\Delta G = -\text{ve}$ (always)

which is possible only if

$$\Delta H < 0 \text{ and } \Delta S > 0$$

$\therefore$ spontaneous at all temperatures.



$$\Delta S = 83.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

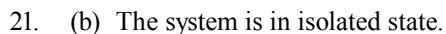
$$\therefore \Delta G = \Delta H - T\Delta S$$

For a reaction to be spontaneous, $\Delta G = -\text{ve}$

$$\text{i.e., } \Delta H < T\Delta S$$

$$\therefore T > \frac{\Delta H}{\Delta S} = \frac{35.5 \times 10^3 \text{ Jmol}^{-1}}{83.6 \text{ JK}^{-1}}$$

So, the given reaction will be spontaneous at $T > 425 \text{ K}$



$\therefore$ For an adiabatic process, $q = 0$

$$\Delta U = q + w$$

$$\therefore \Delta U = w$$

$$= -p\Delta V$$

$$= -2.5 \text{ atm} \times (4.5 - 2.5) \text{ L}$$

$$= -2.5 \times 2 \text{ L-atm}$$

$$= -5 \times 101.3 \text{ J}$$

$$= -506.5 \text{ J} \approx -505 \text{ J}$$

Chapter

7

Equilibrium

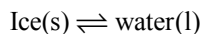
Equilibrium state arises when the rate of forward reaction becomes equal to the rate of backward reaction

EQUILIBRIUM IN PHYSICAL PROCESSES

The most familiar examples are phase transformation processes, eg : solid - liquid; liquid - gas and gas - solid

(i) Solid-Liquid Equilibrium

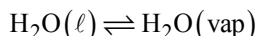
Ice and water in an isolated thermos flask. The equilibrium that exists is:



For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called normal melting point or normal freezing point of the substance.

(ii) Liquid - Vapour Equilibrium

At equilibrium, rate of evaporation = rate of condensation and,



At equilibrium, the pressure exerted by water molecules at a given temperature remains constant and is called equilibrium vapour pressure of water. Vapour pressure of a liquid increases with temperature.

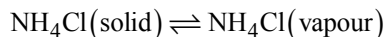
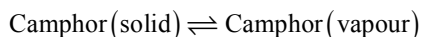
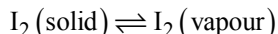
For any liquid at 1 atm pressure, the temperature at which liquid and vapours are at equilibrium is called normal boiling point of the liquid.

Boiling point depends on atmospheric pressure and on altitude of a place. At high altitude boiling point decreases.

(iii) Solid - Vapour Equilibrium

At equilibrium,

Rate of sublimation = Rate of condensation



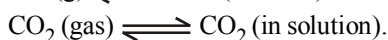
(iv) Equilibrium Involving Dissolution of Solids or Gases in Liquids

- (a) **Solids in Liquids** : Example : Dissolution of sugar in water. At equilibrium, in saturated solution.

Sugar (solution) $\rightleftharpoons$ Sugar (solid) and, rate of dissolution of sugar = rate of crystallization of sugar.

- (b) **Gases in liquids** : The concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. There is equilibrium between molecules in gaseous state and molecules dissolved in liquid under pressure

Example: Soda water bottle in which CO_2 is dissolved in solution.
 $\text{Gas(g)} \rightleftharpoons \text{Gas(solution)}$.



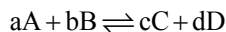
This equilibrium is governed by Henry's law which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

Chemical reactions also attain a state of equilibrium. These reactions occur both in forward and backward directions. When the rates of forward and reverse reactions become equal, concentrations of reactants and products remain constant. This is the stage of chemical equilibrium. It is dynamic in nature i.e., at equilibrium stage, the reaction does not stop. Instead, the reactants give product(s) in forward reaction and product(s) give the original reactants in backward reaction; the rates of the forward and backward reaction become equal and there is no net change in composition.

Law of Chemical Equilibrium and Equilibrium Constant

According to equilibrium law or law of chemical equilibrium, at a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in balanced chemical equation divided by product of concentrations of the reactants raised to their individual stoichiometric coefficients in a balanced chemical equation has a constant value. For a general reversible reaction,



The concentrations in an equilibrium mixture are related by the equilibrium equation:

$$K_C(\text{constant}) = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where K_C is the equilibrium constant. The subscript 'C' indicates that K_C is expressed in concentrations of mol L^{-1} .

According to law of mass action,

$$R_f = K_f [A]^a [B]^b$$

$$R_b = K_b [C]^c [D]^d$$

At equilibrium,

$$R_f = R_b$$

$$K_f [A]^a [B]^b = K_b [C]^c [D]^d$$

$$\frac{K_f}{K_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\therefore K_c = \frac{K_f}{K_b}$$

Relations Between Equilibrium Constants for a General Reaction and its Multiples

Chemical Equation	Equilibrium Constant
$aA + bB \rightleftharpoons cC + dD$	K_C
$cC + dD \rightleftharpoons aA + bB$	$K'_C = 1/K_C$
$n aA + n bB \rightleftharpoons n cC + n dD$	$K''_C = (K_C)^n$

Equilibrium Constant in Gaseous Systems

In gaseous system, equilibrium constant is denoted by K_p and it is related to K_C by the expression :

$$K_p = K_C (RT)^{\Delta n}$$

Where $\Delta n = (\text{no. of moles of products}) - (\text{no. of moles of reactants})$
 K_p = equilibrium constant when conc. of gaseous reactants and products are expressed in terms of pressure.

Unit of Equilibrium Constant :

Unit of K_C = (Concentration) $^{\Delta n}$

Unit of K_p = (atm) $^{\Delta n}$

Significance of Equilibrium Constant

(i) High value of K_C :

$$K_C \gg 1$$

Concentration of product > concentration of reactant

(ii) Low value of K_C :

$$K_C \ll 1$$

Concentration of product < concentration of reactant

(iii) K_C or K_p is the measurement of the tendency of the reaction to proceed forward direction

Relation Between K_p and K_C

$$K_p = K_C (RT)^{\Delta n}$$

When $\Delta n = 0$

$$K_p = K_C (RT)^0 \therefore K_p = K_C$$

When $\Delta n = +ve$ i.e., $\Delta n > 0$

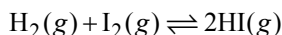
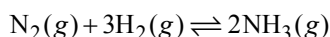
$$K_p > K_C$$

When $\Delta n = -ve$ i.e., $\Delta n < 0$

$$K_p < K_C$$

Types of Chemical Equilibrium

Homogeneous Equilibrium : In a homogeneous system, all the reactants and products are in the same phase. For example:



Heterogeneous Equilibrium : Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium expression for the heterogeneous equilibria involving a pure liquid or a pure solid can be simplified, as the molar concentration of a pure solid or liquid is constant. In other words,

if a substance 'X' is involved, then $[X(s)]$ and $[X(l)]$ are constant. However,

$[X(g)]$ and $[X(aq)]$ will vary.



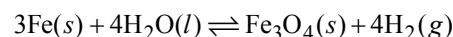
$$K_C = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

As, $[CaO(s)]$ and $[CaCO_3(s)]$ are constant therefore

$$K'_C = [CO_2(g)]$$

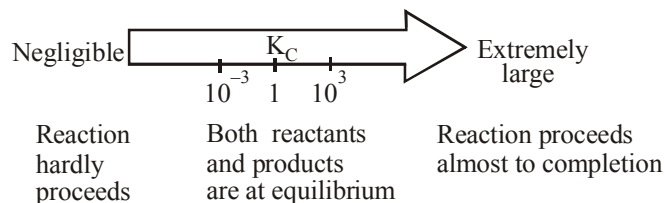
$$\text{or } K_p = P_{CO_2}$$

Some other examples are,



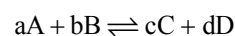
Predicting the Extent and Direction of Reaction

Extent of a Reaction : The numerical value of K_C for a reaction indicates the extent of reaction. The magnitude of K_C or K_p is directly proportional to conc. of products and inversely proportional to conc. of reactants. This implies that high value of K_C is suggestive of high conc. of products. Dependence of extent of reaction on K_C is shown as :



Direction of reaction

For a general reaction :



$$\text{The reaction quotient, } Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Then,

- if $Q_c > K_C$, reaction will proceed in the backward direction, i.e. in direction of reactants
- if $Q_c < K_C$, reaction will proceed in the forward direction, i.e. in direction of products.
- if $Q_c = K_C$, the reaction mixture is at equilibrium.

Standard Free Energy Change of a Reaction and Its Equilibrium Constant

$$\Delta G^\circ = -2.303 RT \log K_C$$

$$\text{and } \Delta G^\circ = -2.303 RT \log K_p$$

where ΔG° = free energy change.

K_C and K_p = equilibrium constant.

$$\text{If } \Delta G < 0, \log K_C > 1$$

$\therefore$ Spontaneous reaction proceeds in forward direction

$$\text{If } \Delta G > 0, \log K_C < 1$$

$\therefore$ Non-spontaneous reaction proceeds in backward direction

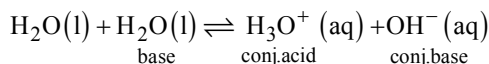
• If $\Delta G^\circ = 0, K_C = 1$

Reaction will be at equilibrium.

WWW.JEEBOOKS.IN

Ionic Product of Water

In pure water, the following equilibrium exists :



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K[\text{H}_2\text{O}] = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

($K_w \rightarrow$ ionic product of water)

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M (For pure water)}$$

$$\therefore K_w = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2.$$

Value of K_w depends on temperature. Value of K_w increases with increase in temperature and decreases with decrease in temperature.

if $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, aqueous solution is acidic

if $[\text{H}_3\text{O}^+] < [\text{OH}^-]$, aqueous solution is basic

if $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, aqueous solution is neutral

The pH Scale

The term pH was given by **Sorenson**. pH is defined as the negative logarithm to the base 10 of the hydrogen ion concentration i.e.,

$$\text{pH} = -\log [\text{H}^+]$$

Acidic solution has $\text{pH} < 7$

Basic solution has $\text{pH} > 7$

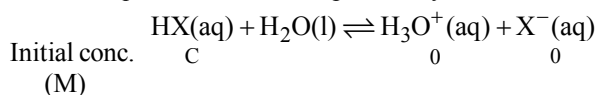
Neutral solution has $\text{pH} = 7$

pH value decreases on heating the solution.

Ionisation of Weak Acids and Bases

Ionization constants of weak acids

Consider a weak acid HX that is partially ionized in aqueous solution. The equilibrium can be expressed by:



If α is the extent of ionization, then

At, equilibrium

conc. (M) $C - C\alpha$ $C\alpha$ $C\alpha$

$$\therefore K_a = \frac{C\alpha \cdot C\alpha}{C - C\alpha} = \frac{C^2\alpha^2}{C(1-\alpha)}$$

$$\Rightarrow K_a = \frac{C\alpha^2}{1-\alpha} \text{ and } (\text{p}K_a = -\log K_a)$$

$\therefore$ Larger the value of K_a , stronger is the acid.

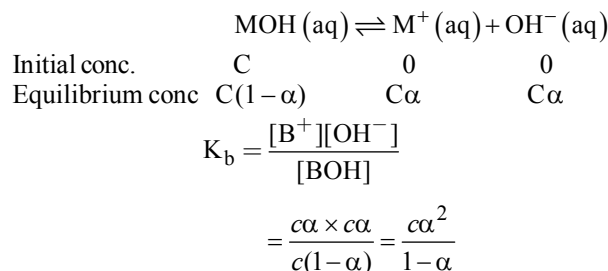
In case of weak acids, the degree of dissociation (α) is very small, therefore $(1-\alpha)$ may be taken as 1.

$$\therefore K_a = C\alpha^2$$

$$\text{or } \alpha = \sqrt{\frac{K_a}{C}}$$

Ionization of weak bases :

The equation for ionization of weak base is:



In the case of weak base, $(1-\alpha)$ is equal to 1.

$$\therefore K_b = C\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_b}{C}}$$

$$\text{p}K_b = -\log (K_b)$$

Relation Between K_a and K_b

$$K_a \times K_b = K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14 \text{ (at 298 K)}$$

Polybasic Acids and Polyacidic Bases

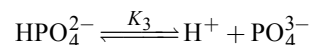
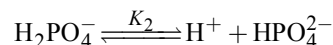
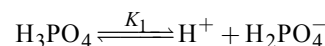
The acids which have more than one ionizable proton per molecule of the acid are called polybasic or polyprotic acids.

The bases which have more than one ionizable OH^- ion per molecule of the base are called polyacidic bases.

Polybasic acids :

These acids undergo complete ionisation in several steps; the number of steps is equal to the number of replaceable hydrogen atoms in the molecule of the acid

For example, orthophosphoric acid (H_3PO_4) is completely ionised in three steps :



The relative value of these constants is as below :

$$K_1 > K_2 > K_3$$

The overall dissociation constant (K) is given by the following relation.

$$K = K_1 \times K_2 \times K_3$$

The higher order ionization constants are smaller than lower order ionization constants. This is because it is difficult to remove positively charged proton from a negative ion due to electrostatic forces.

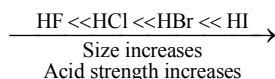
Factors affecting Acid Strength

The extent of dissociation depends on the strength and polarity of H-A bond.

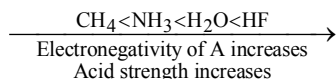
In general, when strength of H-A bond decreases, i.e., energy required to break the bond also decreases, HA becomes a stronger acid. On the other hand, when H-A bond becomes more polar, i.e. electronegativity difference between atoms H and A increases, charge separation occurs, cleavage of the bond becomes easier thereby increasing the acidity.

While comparing elements of the same group of the periodic table, H-A strength is more important factor in determining acidity than

its polar nature. As the size of A increases down the group, H-A bond strength decreases and so acid strength increases. For ex:



While comparing the elements of the same period, bond polarity dominates. As the electronegativity of A increases, acid strength increases.



Note :

- Strength of all strong acids in water is same and become equal to the strength of H_3O^+ . This is called **levelling effect**.
- Relative strength of acids in glacial acetic acid is in the following order :
 $\text{HClO}_4 > \text{HI} > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{H}_3\text{O}^+$
 $\text{H}_3\text{PO}_4 > \text{HF} > \text{CH}_3\text{COOH} > \text{H}_2\text{CO}_3 > \text{H}_2\text{S} > \text{HCN}$

Relative Strength of Some Acids

- Oxy acid (Non-metal + O-H)
Case I : When non metals are different
 Acidic character $\propto$ electronegativity of non-metal
Case-II : When non metals are similar
 Acidic character $\propto$ Oxidation Number
- In hydride : EN increase, Acidic character increase

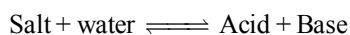
- In carbonic acid : $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$
 Acidic character $\propto -\text{I effect} \propto \frac{1}{+\text{I effect}}$
- Mathematical explanation of acids :
 Acidic character $\propto [\text{H}^+] \propto \sqrt{K_a}$

Relative Strength of Some Bases

- Hydroxide (metal + O-H)**
 Basic character $\propto \frac{1}{\text{Electronegativity of metal}}$
- Basic strength of amine :**
 Basic strength $\propto +\text{I effect} \propto \frac{1}{-\text{I effect}}$
 e.g. : $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
 $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > (\text{C}_2\text{H}_5)_3\text{N}$
- Explanation of mathematical bases :**
 Basic character $\propto [\text{OH}^-] \propto \sqrt{K_b}$

Hydrolysis of Salts and pH of Their Solutions

Hydrolysis may be defined as a process involving the action of water on a salt to form a mixture of acid and alkali. Thus hydrolysis is the reverse of neutralization.



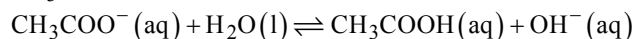
The pH of the solution changes as a result of hydrolysis.

- The cations of strong bases and anions of strong acids simply get hydrated and are not hydrolysed. As a result, pH of the solution of the salt of strong acid and strong base is 7 i.e. neutral solution.

- For the salt of weak acid and strong base, Example : CH_3COONa ,



CH_3COO^- ions undergo hydrolysis to give :



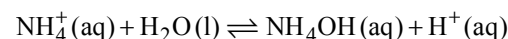
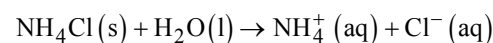
Thus, the solution is alkaline with $\text{pH} > 7$.

$$K_h = \frac{K_w}{K_a}$$

$$\Rightarrow K_h = Ch^2 \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

$$[\text{H}^+] = \sqrt{\frac{K_a \cdot K_w}{c}}, \text{pH} = [7 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C]$$

- For a salt of strong acid and weak base, Example : NH_4Cl , we have



Thus, the solution is acidic with $\text{pH} < 7$

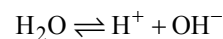
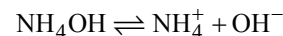
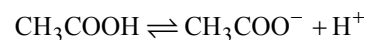
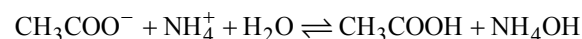
$$K_h = \frac{K_w}{K_b}$$

$$K_h = ch^2 \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

$$[\text{H}^+] = ch = c \sqrt{\frac{K_w}{K_b \times c}} = \sqrt{\frac{K_w \times c}{K_b}}$$

$$\text{pH} = \left[7 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \right] < 7$$

- For a salt of weak acid and weak base, example : $\text{CH}_3\text{COONH}_4$ we have



$$K_h = \frac{K_w}{K_a \cdot K_b}$$

$$h = \sqrt{K_h}$$

$$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

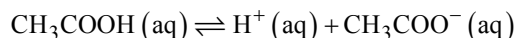
$$\text{pH} = 7 + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b$$

$\text{pH} > 7$ if difference is positive and $\text{pH} < 7$ if difference is negative

Common - Ion Effect

It states that *if to the solution of a weak electrolyte, a solution of strong electrolyte is added which furnishes an ion common to that furnished by the weak electrolyte, the ionization of the weak electrolyte is suppressed.*

For example : Dissociation of acetic acid



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Addition of acetate ions results in decrease in the concentration of H^+ ions. Also, if H^+ ions are added, equilibrium moves in the direction of undissociated acetic acid, i.e., in a direction of reducing the conc. of H^+ ions.

Buffer Solutions

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called buffer solutions.

Types of Buffer Solution

(i) Simple buffers :

- (a) A salt of weak acid and weak base in water.

Example $\text{CH}_3\text{COONH}_4, \text{NH}_4\text{CN}$

- (b) A mixture of an acid salt & normal salt of a poly basic acid.

Example $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$

(ii) Mixed buffers : These are of two types

- (a) **Acidic buffer mixtures** : Solution of a weak acid and its salt with strong base is acid buffer.

e.g. : $\text{NaHCO}_3 + \text{H}_2\text{CO}_3, \text{CH}_3\text{COOH} + \text{CH}_3\text{COONa},$

pH of an acidic buffer :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

This equation is called **Henderson equation**

- (b) **Basic buffer mixture** : A weak base with its salt with strong acid.

e.g. : $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}, \text{glycine} + \text{Glycine Hydrochloride}$

pOH and pH values of basic buffers can be determined from the following Henderson's equation.

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Change in concentration or number of moles of acid or base added to litre of Buffer

$$\text{Buffer Capacity} = \frac{\text{Change in pH}}{\text{Change in concentration or number of moles of acid or base added to litre of Buffer}}$$

Solubility Equilibria of Sparingly Soluble Salts

For a salt to be soluble in a solvent, the solvation energy (or hydration energy) should be greater than lattice energy.

Each salt has characteristic solubility which depends on temperature.

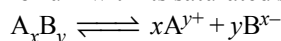
On the basis of solubility, salts are classified as:

1. Soluble : Solubility $> 0.1 \text{ M}$
2. Slightly soluble : $0.01 \text{ M} < \text{Solubility} < 0.1 \text{ M}$
3. Sparingly soluble : Solubility $< 0.01 \text{ M}$

Solubility Product (K_{sp}) : Solubility product of a sparingly soluble electrolyte is equal to the product of ionic concentrations in a saturated solution at a given temperature.

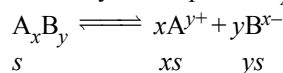
Solubility product constant

A solid salt of general formula A_xB_y with molecular solubility S in equilibrium with its saturated solution may be represented as:



$$K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

Let solubility of compound A_xB_y is $s \text{ mol lit}^{-1}$, then



$$K_{sp} = (xs)^x (ys)^y$$

$$K_{sp} = x^x y^y s^{x+y}$$

$$S^{(x+y)} = K_{sp} / x^x \cdot y^y$$

$$S = (K_{sp} / x^x \cdot y^y)^{1/(x+y)}$$

EXERCISE - 1

Conceptual Questions

- The solubility of PbCl_2 is given by
 - $\left[\frac{K_{sp}}{4}\right]^{1/3}$
 - $[8K_{sp}]^{1/2}$
 - $[K_{sp}]^{1/2}$
 - $\sqrt{K_{sp}}$
- For the following reaction in gaseous phase

$$\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g), K_p / K_c \text{ is}$$
 - $(RT)^{1/2}$
 - $(RT)^{-1/2}$
 - (RT)
 - $(RT)^{-1}$
- The solubility of $\text{Ca}_3(\text{PO}_4)_2$ is 's' moles per litre. Its solubility product is
 - $72s^5$
 - $108s^5$
 - $9s^2$
 - $8s^3$
- Which of the following is correct for the reaction?

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$
 - $K_p = K_c$
 - $K_p < K_c$
 - $K_p > K_c$
 - Pressure is required to predict the correlation
- The equilibrium constant for a reaction $\text{A} + 2\text{B} \rightleftharpoons 2\text{C}$ is 40. The equilibrium constant for reaction

$$\text{C} \rightleftharpoons \text{B} + \frac{1}{2}\text{A} \text{ is}$$
 - 40
 - $\left(\frac{1}{40}\right)^2$
 - $\frac{1}{40}$
 - $\frac{1}{(40)^{1/2}}$
- For which one of the following reactions $K_p = K_c$?
 - $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$
 - $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$
 - $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
 - $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$
- K_1 and K_2 are equilibrium constant for reactions (i) and (ii)

$$\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \dots(i)$$

$$\text{NO}(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \dots(ii)$$
 Then,
 - $K_1 = \left(\frac{1}{K_2}\right)^2$
 - $K_1 = K_2^2$
 - $K_1 = \frac{1}{K_2}$
 - $K_1 = (K_2)^0$
- Some chemists at ISRO wished to prepare a saturated solution of a silver compound and they wanted it to have the highest concentration of silver ion possible. Which of the following compounds, would they use?

$$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$$

$$K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}$$

$$K_{sp}(\text{Ag}_2\text{CrO}_4) = 2.4 \times 10^{-12}$$
 - AgCl
 - AgBr
 - Ag_2CrO_4
 - Any of these
- The K_p/K_c ratio will be highest in case of
 - $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{CO}_2(g)$
 - $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$
 - $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
 - $7\text{H}_2(g) + 2\text{NO}_2(g) \rightleftharpoons 2\text{NH}_3(g) + 4\text{H}_2\text{O}(g)$
- A solution of FeCl_3 in water acts as acidic solution due to :
 - hydrolysis of Fe^{3+}
 - acidic impurities
 - dissociation
 - ionisation
- Pure ammonia is placed in a vessel at a temperature where its dissociation constant (a) is appreciable. At equilibrium :
 - K_p does not change significantly with pressure.
 - does not change with pressure.
 - concentration of NH_3 does not change with pressure.
 - concentration of hydrogen is less than that of nitrogen.
- The value of K_p for the reaction:

$$2\text{H}_2\text{S}(g) \rightleftharpoons 2\text{H}_2(g) + \text{S}_2(g) \text{ is } 1.2 \times 10^{-2} \text{ at } 1065^\circ\text{C}.$$
 The value for K_c is:
 - $< 1.2 \times 10^{-2}$
 - $> 1.2 \times 10^{-2}$
 - 1.2×10^{-2}
 - 0.12×10^{-2}
- For a chemical reaction;

$$\text{A}(g) + \text{B}(l) \rightleftharpoons \text{D}(g) + \text{E}(g)$$
 Hypothetically at what temperature, $K_p = K_c$ (when, $R = 0.08 \text{ l-atm/mole-K}$)
 - $T = 0 \text{ K}$
 - $T = 1 \text{ K}$
 - $T = 12.5 \text{ K}$
 - $T = 273 \text{ K}$
- PCl_5 is dissociating 50% at 250°C at a total pressure of P atm. If equilibrium constant is K_p , then which of the following relation is numerically correct—
 - $K_p = 3P$
 - $P = 3K_p$
 - $P = \frac{2K_p}{3}$
 - $K_p = \frac{2P}{3}$
- One mole of CH_3COOH and one mole of $\text{C}_2\text{H}_5\text{OH}$ reacts to produce $\frac{2}{3}$ mol of $\text{CH}_3\text{COOC}_2\text{H}_5$. The equilibrium constant is :
 - 2
 - +2
 - 4
 - +4
- 5 mole of $\text{NH}_4\text{HS}(s)$ start to decompose at a particular temperature in a closed vessel. If pressure of $\text{NH}_3(g)$ in the vessel is 2 atm, then K_p for the reaction,

$$\text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g), \text{ will be -}$$
 - 2
 - 4
 - 0.4
 - 0.8

17. For homogeneous gaseous reaction,
 $4\text{NH}_3 + 5\text{O}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}$
 The units of equilibrium constant K_c will be –
 (a) mol lit^{-1} (b) $\text{mol}^{-1} \text{lit}^{-1}$
 (c) $\text{mol}^2 \text{lit}^{-2}$ (d) K_c is unitless
18. If α is the fraction of HI dissociated at equilibrium in the reaction, $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, starting with 2 moles of HI, the total number of moles of reactants and products at equilibrium are
 (a) $2 + 2\alpha$ (b) 2 (c) $1 + \alpha$ (d) $2 - \alpha$
19. A solution having hydrogen ion concentration is 0.0005 g eqvt./litre, its pOH is :
 (a) 8.2798 (b) 10.6990
 (c) 12.7854 (d) 13.3344
20. Vapour density of the equilibrium mixture of the reaction $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is 50.0. Percent dissociation of SO_2Cl_2 is :
 (a) 33.33 (b) 35.0 (c) 30.0 (d) 66.67
21. In a gaseous reversible reaction
 $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} + \text{heat}$
 If pressure is increased then the equilibrium constant would be :
 (a) unchanged
 (b) increased
 (c) decreased
 (d) sometimes increased, sometimes decreased
22. In which of the following reactions, the concentration of the product is higher than the concentration of reactant at equilibrium?
 (K = equilibrium constant)
 (a) $\text{A} \rightleftharpoons \text{B}; K = 0.001$
 (b) $\text{M} \rightleftharpoons \text{N}; K = 10$
 (c) $\text{X} \rightleftharpoons \text{Y}; K = 0.005$
 (d) $\text{R} \rightleftharpoons \text{P}; K = 0.01$
23. For the gaseous reaction
 $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$, $\Delta H = -130 \text{ kJ mol}^{-1}$ carried in a closed vessel, the equilibrium concentration of C_2H_6 can definitely be increased by :
 (a) increasing temperature and decreasing pressure
 (b) decreasing temperature and increasing pressure
 (c) increasing temperature and pressure both
 (d) decreasing temperature and pressure both
24. On adding 0.1 M solution each of $[\text{Ag}^+]$, $[\text{Ba}^{2+}]$, $[\text{Ca}^{2+}]$ in a Na_2SO_4 solution, species first precipitated is
 $[K_{\text{sp}} \text{BaSO}_4 = 10^{-11}, K_{\text{sp}} \text{CaSO}_4 = 10^{-6}, K_{\text{sp}} \text{Ag}_2\text{SO}_4 = 10^{-5}]$
 (a) Ag_2SO_4 (b) BaSO_4
 (c) CaSO_4 (d) All of these
25. Which reaction is not affected by change in pressure?
 (a) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ (b) $2\text{C} + \text{O}_2 \rightleftharpoons 2\text{CO}$
 (c) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ (d) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$
26. According to Le-chatelier's principle, adding heat to a solid $\rightleftharpoons$ liquid equilibrium will cause the
 (a) temperature to increase
 (b) temperature to decrease
 (c) amount of liquid to decrease
 (d) amount of solid to decrease.
27. The reaction quotient (Q) for the reaction
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 is given by $Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$. The reaction will proceed from right to left if
 (a) $Q = 0$ (b) $Q = K_c$ (c) $Q < K_c$ (d) $Q > K_c$
 where K_c is the equilibrium constant
28. A weak acid, HA is found to be 10% ionized in 0.01 M aqueous solution. Calculate the pH of a solution which is 0.1 M in HA and 0.05 M in NaA.
 (a) 5.365 (b) 6.355
 (c) 3.653 (d) 6.593
29. The equilibrium constant for a reaction, $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ is 4×10^{-4} at 2000 K. In the presence of catalyst, the equilibrium is attained 10 times faster. The equilibrium constant in presence of catalyst at 2000 K is :
 (a) 10×10^{-4} (b) 4×10^{-2}
 (c) 4×10^{-4} (d) 40×10^{-4}
30. The solubility of PbF_2 in water at 25°C is $\sim 10^{-3}$ M. What is its solubility in 0.05 M NaF solution? Assume the latter to be fully ionised.
 (a) 1.6×10^{-6} M (b) 1.2×10^{-6} M
 (c) 1.2×10^{-5} M (d) 1.6×10^{-4} M
31. The reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} + \text{heat}$, has reached equilibrium. The reaction may be made to proceed forward by
 (a) adding more C
 (b) adding more D
 (c) decreasing the temperature
 (d) increasing the temperature
32. Which of the following equilibria will shift to right side on increasing the temperature
 (a) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$
 (b) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
 (c) $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2}(\text{O}_2)(\text{g})$
 (d) $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + 2\text{Cl}_2(\text{g})$
33. Solubility product of a salt AB is 1×10^{-8} in a solution in which the concentration of A^+ ions is 10^{-3} M. The salt will precipitate when the concentration of B^- ions is kept
 (a) between 10^{-8} M to 10^{-7} M
 (b) between 10^{-7} M to 10^{-8} M
 (c) $> 10^{-5}$ M
 (d) $< 10^{-8}$ M

34. Le-Chatelier principle is not applicable to
 (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 (b) $\text{Fe}(\text{s}) + \text{S}(\text{s}) \rightleftharpoons \text{FeS}(\text{s})$
 (c) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (d) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
35. A base when dissolved in water yields a solution with a hydroxyl ion concentration of $0.05 \text{ mol litre}^{-1}$. The solution is
 (a) basic (b) acidic
 (c) neutral (d) either (b) or (c)
36. Solution of $0.1 \text{ N NH}_4\text{OH}$ and $0.1 \text{ N NH}_4\text{Cl}$ has pH 9.25. Then find out pK_b of NH_4OH
 (a) 9.25 (b) 4.75 (c) 3.75 (d) 8.25
37. Which one of the following compounds is **not** a protonic acid?
 (a) $\text{SO}_2(\text{OH})_2$ (b) $\text{B}(\text{OH})_3$
 (c) $\text{PO}(\text{OH})_3$ (d) $\text{SO}(\text{OH})_2$
38. In which of the following cases, pH is greater than 7?
 (a) 50 ml of 0.1 M HCl + 50 ml of 0.1 M NaCl
 (b) 50 ml of $0.1 \text{ M H}_2\text{SO}_4$ + 50 ml of 0.2 M NaOH
 (c) 50 ml of $0.1 \text{ M CH}_3\text{COOH}$ + 50 ml of 0.1 M KOH
 (d) 50 ml of 0.1 M HNO_3 + 50 ml of 0.1 M NH_3
39. Species acting as both Bronsted acid and base, is
 (a) $(\text{HSO}_4)^-$ (b) Na_2CO_3 (c) NH_3 (d) OH^-
40. In the equation $\text{I}_2 + \text{I}^- \longrightarrow \text{I}_3^-$, Lewis base is
 (a) I_2 (b) I^- (c) I_3^- (d) None
41. The pH of 10^{-10} M NaOH solution is nearest to:
 (a) 6 (b) -10 (c) 4 (d) 7
42. The strongest Bronsted base is :
 (a) ClO_3^- (b) ClO_2^- (c) ClO_4^- (d) ClO^-
43. The pH value for $1/1000 \text{ N-KOH}$ solution is :
 (a) 3 (b) 10^{-11} (c) 1 (d) 11
44. The pH of 0.1 M solution of the following salts increases in the order :
 (a) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
 (b) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
 (c) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
 (d) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
45. The pH of 0.005 molar solution of H_2SO_4 is approximately:
 (a) 0.010 (b) 1 (c) 2 (d) 0.005
46. Which of the following has highest pH ?
 (a) $\frac{\text{M}}{4} \text{ KOH}$ (b) $\frac{\text{M}}{4} \text{ NaOH}$
 (c) $\frac{\text{M}}{4} \text{ NH}_4\text{OH}$ (d) $\frac{\text{M}}{4} \text{ Ca}(\text{OH})_2$
47. pH of 0.1 M NH_3 aqueous solution is : ($K_b = 1.8 \times 10^{-5}$)
 (a) 11.13 (b) 12.5 (c) 13.42 (d) 11.55
48. 100 mL of 0.04 N HCl aqueous solution is mixed with 100 mL of 0.02 N NaOH solution. The pH of the resulting solution is:
 (a) 1.0 (b) 1.7 (c) 2.0 (d) 2.3
49. Among BMe_3 , BCl_3 , BF_3 and B_2H_6 , which one will be the best Lewis acid ?
 (a) BCl_3 (b) BMe_3 (c) B_2H_6 (d) BF_3
50. The value of the ionic product of water
 (a) depends on volume of water
 (b) depends on temperature
 (c) changes by adding acid or alkali
 (d) always remains constant
51. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.

$$\text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$$

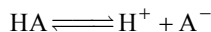
 The set that characterises the conjugate acid-base pairs is
 (a) $(\text{HCl}, \text{CH}_3\text{COOH})$ and $(\text{CH}_3\text{COOH}_2^+, \text{Cl}^-)$
 (b) $(\text{HCl}, \text{CH}_3\text{COOH}_2^+)$ and $(\text{CH}_3\text{COOH}, \text{Cl}^-)$
 (c) $(\text{CH}_3\text{COOH}_2^+, \text{HCl})$ and $(\text{Cl}^-, \text{CH}_3\text{COOH})$
 (d) $(\text{HCl}, \text{Cl}^-)$ and $(\text{CH}_3\text{COOH}_2^+, \text{CH}_3\text{COOH})$
52. Diacidic base is
 (a) $\text{CH}_2(\text{OH})_2$ (b) $\text{Ca}(\text{OH})_2$
 (c) $\text{CH}_3\text{CH}(\text{OH})_2$ (d) All of these
53. Which of the following behaves as Lewis acid and not as Bronsted acid
 (a) HCl (b) H_2SO_4 (c) HSO_3^- (d) SO_3
54. Water is well known amphoprotic solvent. In which chemical reaction water is behaving as a base?
 (a) $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^-$
 (b) $\text{H}_2\text{O} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$
 (c) $\text{H}_2\text{O} + \text{NH}_2^- \longrightarrow \text{NH}_3 + \text{OH}^-$
 (d) $\text{H}_2\text{O} + \text{NH}_3 \longrightarrow \text{NH}_4^+ + \text{OH}^-$
55. The pH of a 10^{-3} M HCl solution at 25°C if it is diluted 1000 times, will be –
 (a) 3 (b) zero (c) 5.98 (d) 6.02
56. What will be the pH of a solution formed by mixing 50ml of 0.5 M HCl solution and 150ml of 0.5 M NaOH solution and 300 ml H_2O ?
 (a) 13 (b) 12.7 (c) 7 (d) 11
57. The pH of a weak mono acidic base, neutralized upto 80% with a strong acid in a dilute solution, is 7.40. The ionization constant of the base is –
 (a) 1.0×10^{-5} (b) 1.6×10^{-7}
 (c) 1.0×10^{-6} (d) None of these

58. For the system : $A(g) + 2B(g) \rightarrow C(g)$
the equilibrium concentration is
 $A = 0.06$ moles/l, $B = 0.12$ moles/l
 $C = 0.216$ moles/l
The K_{eq} for the reaction is
(a) 250 (b) 416
(c) 4×10^{-3} (d) 125
59. At 25°C , the dissociation constant of a base, BOH, is 1.0×10^{-12} . The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be
(a) 1.0×10^{-5} mol L^{-1} (b) 1.0×10^{-6} mol L^{-1}
(c) 2.0×10^{-6} mol L^{-1} (d) 1.0×10^{-7} mol L^{-1}
60. Which of the following pK_a value represents the strongest acid ?
(a) 10^{-4} (b) 10^{-8} (c) 10^{-5} (d) 10^{-2}
61. The product of ionic concentration in a saturated solution of an electrolyte at a given temperature is constant and is known as
(a) Ionic product of the electrolyte
(b) Solubility product
(c) Ionization constant
(d) Dissociation constant
62. If degree of dissociation of pure water at 100°C is 1.8×10^{-8} , then the dissociation constant of water will be (density of $\text{H}_2\text{O} = 1$ gm/cc)
(a) 1×10^{-12} (b) 1×10^{-14}
(c) 1.8×10^{-12} (d) 1.8×10^{-14}
63. The dissociation constant of two acids HA_1 and HA_2 are 3.14×10^{-4} and 1.96×10^{-5} respectively. The relative strength of the acids will be approximately
(a) 1 : 4 (b) 4 : 1
(c) 1 : 16 (d) 16 : 1
64. Ionisation of weak acid can be calculated by the formula
(a) $100\sqrt{\frac{K_a}{c}}$ (b) $\frac{100}{1+10^{(pK_a - pH)}}$
(c) Both (a) and (b) (d) None of these
65. $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$
In the above reaction one mole each of acetic acid and alcohol are heated in the presence of little conc. H_2SO_4 . On equilibrium being attained
(a) 1 mole of ethyl acetate is formed
(b) 2 moles of ethyl acetate are formed
(c) $\frac{1}{3}$ mole of ethyl acetate is formed
(d) $\frac{2}{3}$ mole of ethyl acetate is formed
66. Given
 $\text{HF} + \text{H}_2\text{O} \xrightarrow{K_a} \text{H}_3\text{O}^+ + \text{F}^-$
 $\text{F}^- + \text{H}_2\text{O} \xrightarrow{K_b} \text{HF} + \text{OH}^-$
Which of the following reaction is correct
(a) $K_b = K_w$ (b) $K_b = \frac{1}{K_w}$
(c) $K_a \times K_b = K_w$ (d) $\frac{K_a}{K_b} = K_w$
67. At 298K a 0.1 M CH_3COOH solution is 1.34% ionized. The ionization constant K_a for acetic acid will be
(a) 1.82×10^{-5} (b) 18.2×10^{-5}
(c) 0.182×10^{-5} (d) None of these
68. If the solubility of PbCl_2 at 25°C is 6.3×10^{-3} mole/litre, its solubility product at that temperature is
(a) $(6.3 \times 10^{-3}) \times (12.6 \times 10^{-3})^2$
(b) $(6.3 \times 10^{-3})^2 \times (12.6 \times 10^{-3})$
(c) $(6.3 \times 10^{-3}) \times (12.6 \times 10^{-3})$
(d) $(12.6 \times 10^{-3}) \times (12.6 \times 10^{-3})$
69. Which of the following is most soluble ?
(a) Bi_2S_3 ($K_{sp} = 1 \times 10^{-17}$) (b) MnS ($K_{sp} = 7 \times 10^{-16}$)
(c) CuS ($K_{sp} = 8 \times 10^{-37}$) (d) Ag_2S ($K_{sp} = 6 \times 10^{-51}$).
70. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be
(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach
71. Which of the following solution cannot act as a buffer?
(a) $\text{NaH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$
(b) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
(c) $\text{HCl} + \text{NH}_4\text{Cl}$
(d) $\text{H}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$
72. Which one has maximum solubility in liquid CCl_4 ?
(a) NaCl (b) Cl_2 (c) I_2 (d) Br_2
73. The solubility of AgCl in 0.2 M NaCl solution is : (K_{sp} of $\text{AgCl} = 1.20 \times 10^{-10}$)
(a) 6.0×10^{-10} M (b) 0.2 M
(c) 1.2×10^{-10} M (d) 0.2×10^{-10} M
74. If s and S are respectively solubility and solubility product of a sparingly soluble binary electrolyte then :
(a) $s = S$ (b) $s = S^2$
(c) $s = S^{1/2}$ (d) $s = \frac{1}{2}S$

75. A buffer solution is prepared by mixing 10 ml of 1.0 M CH_3COOH and 20 ml of 0.5 M CH_3COONa and then diluted to 100 ml with distilled water. If $\text{p}K_a$ of CH_3COOH is 4.76, what is the pH of the buffer solution ?
 (a) 5.8 (b) 4.34 (c) 5.21 (d) 4.76
76. Solubility product of BaCl_2 is 4×10^{-9} moles/litre. Its solubility would be :
 (a) 1×10^{-27} (b) 1×10^{-3}
 (c) 1×10^{-7} (d) 1×10^{-2}
77. 100 ml solution of an acid of $\text{pH} = 1$, is mixed with 100 ml solution of the same acid of $\text{pH} = 2$. The hydrogen ion concentration of the mixture will be :
 (a) 5.5×10^{-2} (b) 10^{-2}
 (c) 10^{-3} (d) 10^{-4}
78. The degree of hydrolysis in hydrolytic equilibrium
 $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$
 at salt concentration of 0.001 M is : ($K_a = 1 \times 10^{-5}$)
 (a) 1×10^{-3} (b) 1×10^{-4}
 (c) 5×10^{-4} (d) 1×10^{-6}
79. A litre of solution is saturated with AgCl . To this solution if 1.0×10^{-4} mole of solid NaCl is added, what will be the $[\text{Ag}^+]$, assuming no volume change?
 (a) More (b) Less (c) Equal (d) Zero
80. The value of K_c for the reaction
 $2\text{NO}_{(g)} \rightarrow \text{N}_{2(g)} + \text{O}_{2(g)}$ is 1.8×10^{-2} . Calculate the value of K_c for the reaction
 $\frac{1}{2}\text{N}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \longrightarrow \text{NO}_{(g)}$
 (a) 7.6 (b) 8.5 (c) 6.5 (d) 2
81. The solubility of CaF_2 in pure water is 2.3×10^{-4} mol dm^{-3} . Its solubility product will be :
 (a) 4.6×10^{-4} (b) 4.6×10^{-8}
 (c) 6.9×10^{-12} (d) 4.9×10^{-11}
82. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is :
 (a) $\text{Mg}(\text{OH})_2$ (b) $\text{Ca}(\text{OH})_2$
 (c) $\text{Ba}(\text{OH})_2$ (d) $\text{Be}(\text{OH})_2$
83. In qualitative analysis, in III group NH_4Cl is added before NH_4OH because
 (a) to increase the concentration of NH_4^+ ions
 (b) to increase concentration of Cl^- ions
 (c) to reduce the concentration of OH^- ions
 (d) to increase concentration of OH^- ions
84. The buffering action of an acidic buffer is maximum when its pH is equal
 (a) 5 (b) 7 (c) 1 (d) $\text{p}K_a$
85. If the equilibrium constant of the reaction of weak acid HA with strong base is 10^7 , then pOH of the aqueous solution of 0.1 M NaA is
 (a) 8 (b) 10 (c) 4 (d) 5
86. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 3 \times 10^{-10}$) will occur with –
 (a) 10^{-4} M AgNO_3 and 10^{-5} M KCl
 (b) 10^{-5} M AgNO_3 and 10^{-5} M KCl
 (c) 10^{-4} M AgNO_3 and 10^{-4} M KCl
 (d) Both (a) and (c)
87. Solubility of BaF_2 in a solution of $\text{Ba}(\text{NO}_3)_2$ will be represented by
 (a) $[\text{Ba}^{2+}]$ (b) $[\text{NO}_3]^{-2}$
 (c) $\frac{1}{2} [\text{F}^-]$ (d) $[\text{Ba}]^2$
88. A buffer solution is prepared by mixing 0.1 M ammonia and 1.0 M ammonium chloride. At 298 K, the $\text{p}K_b$ of NH_4OH is 5.0. The pH of the buffer is
 (a) 10.0 (b) 9.0 (c) 6.0 (d) 8.0
89. Which of the following is conjugate base of $[\text{C}_2\text{H}_5\text{NH}_3]^+$
 (a) $\text{C}_2\text{H}_5\text{NH}_2$ (b) $\text{C}_2\text{N}^+\text{H}_4(\text{OH})^-$
 (c) $[\text{C}_2\text{H}_2\text{NH}]^-$ (d) None of these
90. A weak acid, HA, has a K_a of 1.0×10^{-5} . If 0.1 mole of this acid dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to
 (a) 1.0% (b) 99.9% (c) 0.1% (d) 99.0%
91. Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, i.e. H_3O^+ .
 (a) 4.0 (b) 9.0 (c) 1.0 (d) 7.0
92. If the concentration of OH^- ions in the reaction
 $\text{Fe}(\text{OH})_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq)$ is decreased by $\frac{1}{4}$ times, then equilibrium concentration of Fe^{3+} will increase by :
 (a) 8 times (b) 16 times (c) 64 times (d) 4 times
93. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH ?
 (a) SrCl_2 (b) BaCl_2
 (c) MgCl_2 (d) CaCl_2
94. The value of equilibrium constant of the reaction
 $\text{HI}(g) \rightleftharpoons \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{I}_2$ is 8.0
 The equilibrium constant of the reaction
 $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$ will be:
 (a) $\frac{1}{16}$ (b) $\frac{1}{64}$ (c) 16 (d) $\frac{1}{8}$

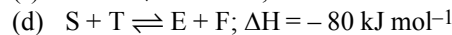
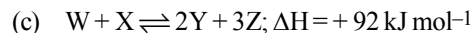
95. Which of the following molecules acts as a Lewis acid ?
 (a) $(\text{CH}_3)_2\text{O}$ (b) $(\text{CH}_3)_3\text{P}$
 (c) $(\text{CH}_3)_3\text{N}$ (d) $(\text{CH}_3)_3\text{B}$
96. The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is:
 (a) 6.50×10^{-12} (b) 5.65×10^{-13}
 (c) 5.65×10^{-12} (d) 5.65×10^{-10}
97. In which of the following equilibrium K_c and K_p are not equal?
 (a) $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$
 (b) $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$
 (c) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 (d) $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$
98. In a buffer solution containing equal concentration of B^- and HB , the K_b for B^- is 10^{-10} . The pH of buffer solution is :
 (a) 10 (b) 7 (c) 6 (d) 4
99. Which one of the following molecular hydrides acts as a Lewis acid?
 (a) NH_3 (b) H_2O (c) B_2H_6 (d) CH_4
100. Which of the following is least likely to behave as Lewis base ?
 (a) H_2O (b) NH_3 (c) BF_3 (d) OH^-
101. pH of a saturated solution of $\text{Ba}(\text{OH})_2$ is 12. The value of solubility product (K_{sp}) of $\text{Ba}(\text{OH})_2$ is :
 (a) 3.3×10^{-7} (b) 5.0×10^{-7}
 (c) 4.0×10^{-6} (d) 5.0×10^{-6}
102. For the following three reactions a, b and c, equilibrium constants are given:
 (i) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}); K_1$
 (ii) $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}); K_2$
 (iii) $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}); K_3$
 (a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$
 (c) $K_3 = K_1K_2$ (d) $K_3.K_2^3 = K_1^2$
103. Three reactions involving H_2PO_4^- are given below :
 (i) $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$
 (ii) $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$
 (iii) $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_3\text{PO}_4 + \text{O}^{2-}$
 In which of the above does H_2PO_4^- act as an acid ?
 (a) (ii) only (b) (i) and (ii) (c) (iii) only (d) (i) only
104. The K_{sp} for $\text{Cr}(\text{OH})_3$ is 1.6×10^{-30} . The solubility of this compound in water is :
 (a) $\sqrt[4]{1.6 \times 10^{-30}}$ (b) $\sqrt[4]{1.6 \times 10^{-30} / 27}$
 (c) $1.6 \times 10^{-30/27}$ (d) $\sqrt[4]{1.6 \times 10^{-30}}$
105. The equilibrium constant (K_c) for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$ at temperature T is 4×10^{-4} . The value of K_c for the reaction $\text{NO}(\text{g}) \rightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ at the same temperature is:
 (a) 0.02 (b) 2.5×10^2 (c) 4×10^{-4} (d) 50.0
106. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of the acid is :
 (a) 3×10^{-1} (b) 1×10^{-3} (c) 1×10^{-5} (d) 1×10^{-7}
107. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffer solution of HA in which 50% of the acid is ionized is
 (a) 7.0 (b) 4.5 (c) 2.5 (d) 9.5
108. In a saturated solution of the sparingly soluble strong electrolyte AgIO_3 (molecular mass = 283) the equilibrium which sets is $\text{AgIO}_3(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{IO}_3^-(\text{aq})$. If the solubility product constant K_{sp} of AgIO_3 at a given temperature is 1.0×10^{-8} , what is the mass of AgIO_3 contained in 100 ml of its saturated solution?
 (a) 1.0×10^{-4} g (b) 28.3×10^{-2} g
 (c) 2.83×10^{-3} g (d) 1.0×10^{-7} g.
109. Four species are listed below :
 i. HCO_3^- ii. H_3O^+ iii. HSO_4^- iv. HSO_3F
 Which one of the following is the correct sequence of their acid strength?
 (a) $\text{iv} < \text{ii} < \text{iii} < \text{i}$ (b) $\text{ii} < \text{iii} < \text{i} < \text{iv}$
 (c) $\text{i} < \text{iii} < \text{ii} < \text{iv}$ (d) $\text{iii} < \text{i} < \text{iv} < \text{ii}$
110. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be
 (a) 9.58 (b) 4.79 (c) 7.01 (d) 9.22
111. Solid $\text{Ba}(\text{NO}_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $\text{BaCO}_3 = 5.1 \times 10^{-9}$)
 (a) 5.1×10^{-5} M (b) 8.1×10^{-8} M
 (c) 8.1×10^{-7} M (d) 4.1×10^{-5} M
112. In aqueous solution the ionization constants for carbonic acid are $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$. Select the correct statement for a saturated 0.034 M solution of the carbonic acid.
 (a) The concentration of CO_3^{2-} is 0.034 M.
 (b) The concentration of CO_3^{2-} is greater than that of HCO_3^- .
 (c) The concentrations of H^+ and HCO_3^- are approximately equal.
 (d) The concentration of H^+ is double that of CO_3^{2-} .
113. Solubility product of silver bromide is 5.0×10^{-13} . The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is
 (a) 1.2×10^{-10} g (b) 1.2×10^{-9} g
 (c) 6.2×10^{-5} g (d) 5.0×10^{-8} g
114. At 25°C , the solubility product of $\text{Mg}(\text{OH})_2$ is 1.0×10^{-11} . At which pH, will Mg^{2+} ions start precipitating in the form of $\text{Mg}(\text{OH})_2$ from a solution of 0.001 M Mg^{2+} ions?
 (a) 9 (b) 10 (c) 11 (d) 8

115. An acid HA ionises as



The pH of 1.0 M solution is 5. Its dissociation constant would be :

- (a) 5 (b) 5×10^{-8} (c) 1×10^{-5} (d) 1×10^{-10}
116. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :
- (a) 1.8 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm
117. 2.5 ml of (2/5) M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with (2/15) M HCl in water at 25°C . The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)
- (a) 3.7×10^{-14} M (b) 3.2×10^{-7} M
(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M
118. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order –
- (a) $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$ (b) $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$
(c) $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$ (d) $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$
119. How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ?
- (a) 0.1 L (b) 0.9 L (c) 2.0 L (d) 9.0 L
120. Five gaseous homogenous equilibrium reactions are given below. Choose the reaction in which both increase in pressure and increase in temperature favour the formation of products.
- (a) $2\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$; $\Delta H = -78 \text{ kJ mol}^{-1}$
(b) $2\text{M} + 3\text{N} \rightleftharpoons \text{P} + 2\text{Q}$; $\Delta H = +105 \text{ kJ mol}^{-1}$



121. In the decomposition reaction

$\text{AB}_5(\text{g}) \rightleftharpoons \text{AB}_3(\text{g}) + \text{B}_2(\text{g})$, at equilibrium in a 10 litre closed vessel at 227°C , 2 moles of AB_3 , 5 moles of B_2 and 4 moles of AB_5 , are present. The equilibrium constant K_c for the formation of $\text{AB}_5(\text{g})$ is

- (a) 0.25 (b) 4.0
(c) 0.04 (d) 2.5
122. Which one of the following will decrease the pH of 50 mL of 0.01 M hydrochloric acid?
- (a) Addition of 50 mL of 0.01 M HCl
(b) Addition of 50 mL of 0.002 M HCl
(c) Addition of 150 mL of 0.002 M HCl
(d) Addition of 5 mL of 1 M HCl
123. The equilibrium constant for the reaction $\text{A}_2 \rightleftharpoons 2\text{A}$ at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The given reaction is [1996]
- (a) exothermic (b) slow
(c) endothermic (d) fast
124. What is the H^+ ion concentration of a solution prepared by dissolving 4 g of NaOH (Atomic weight of Na = 23 amu) in 1000 ml? [1999]
- (a) 10^{-10} M (b) 10^{-4} M
(c) 10^{-1} M (d) 10^{-13} M
125. A physician wishes to prepare a buffer solution of pH = 3.58 that efficiently resists a change in pH yet contains only small concentrations of the buffering agents. Which one of the following weak acids together with its sodium salt would be the best to use ? [1997]
- (a) m-chlorobenzoic acid ($\text{pK}_a = 3.98$)
(b) p-chlorocinnamic acid ($\text{pK}_a = 4.41$)
(c) 2, 5-dihydroxy benzoic acid ($\text{pK}_a = 2.97$)
(d) Acetoacetic acid ($\text{pK}_a = 3.58$)

EXERCISE - 2

Applied Questions

1. In a closed system : $\text{A}_{(\text{s})} \rightleftharpoons 2\text{B}_{(\text{g})} + 3 \text{C}_{(\text{g})}$, if the partial pressure of C is doubled, then partial pressure of B will be:
- (a) two times the original value
(b) one-half of its original value
(c) $\frac{1}{2\sqrt{2}}$ times the original value
(d) $2\sqrt{2}$ times its original value
2. The dissociation constants of two weak acids are K_1 and K_2 . The relative strength of two acids is given by :
- (a) $\left[\frac{K_1}{K_2}\right]^{-3/2}$ (b) $\left[\frac{K_1}{K_2}\right]^{+1/2}$
(c) $\frac{K_1 + \sqrt{K_2}}{K_2 + \sqrt{K_1}}$ (d) $\frac{K_1}{K_2}$
3. Solubilities of three sparingly soluble salts XY (K_{sp}), XY_2 (K'_{sp}) and X_2Y_3 (K''_{sp}) are equal in water. What will be the correct order of their solubility products –
- (a) $K_{sp} < K'_{sp} < K''_{sp}$ (b) $K_{sp} < K''_{sp} < K'_{sp}$
(c) $K''_{sp} < K'_{sp} < K_{sp}$ (d) $K''_{sp} < K_{sp} < K'_{sp}$
4. Three sparingly soluble salts A_2B , AB and AB_3 have the same values of solubility products (K_{sp}). In a saturated solution the correct order of their solubilities is
- (a) $\text{AB}_2 > \text{AB} > \text{A}_2\text{B}$ (b) $\text{AB}_3 > \text{A}_2\text{B} > \text{AB}$
(c) $\text{AB} > \text{AB}_3 > \text{A}_2\text{B}$ (d) $\text{AB} > \text{A}_2\text{B} > \text{AB}_3$
5. Solid AgNO_3 is slowly added to a solution containing each of 0.01 M NaCl and 0.001 M NaBr. What will be the concentration of Cl^- ions in solution when AgBr will just start to precipitate ?
- $K_{sp}(\text{AgBr}) = 3.6 \times 10^{-13}$, $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$.
- (a) 1.8×10^{-7} (b) 3.6×10^{-10}
(c) 0.01 (d) 2×10^{-4}

6. If the K_p for the equilibrium,
 $M.5H_2O(s) \rightleftharpoons M.3H_2O(s) + 2H_2O(g)$
 is 1×10^{-4} . Then $M.5H_2O(s)$ will show efflorescence when it is exposed to an atmosphere where vapour pressure of water is –
 (a) more than 10^{-2} atm (b) below 10^{-2} atm
 (c) more than 10^{-4} atm (d) below 10^{-4} atm
7. pH of a solution containing 0.3 M HX and 0.1 M X^- (K_b for $X^- = 1.0 \times 10^{-5}$) is –
 (a) $5 + \log 3$ (b) $5 - \log 3$ (c) $9 - \log 3$ (d) $9 + \log 3$
8. For which one of the following systems at equilibrium, at constant temperature will the doubling of the volume cause a shift to the right?
 (a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
 (b) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$
 (c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 (d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
9. If K_1 and K_2 are the respective equilibrium constants for the two reactions
 $XeF_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2HF(g)$
 $XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g)$
 the equilibrium constant of the reaction
 $XeO_4(g) + 2HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$ will be
 (a) $K_1/(K_2)^2$ (b) $K_1 \cdot K_2$
 (c) K_1/K_2 (d) K_2/K_1
10. For the reaction : $2BaO_2(s) \rightleftharpoons 2BaO(s) + O_2(g)$;
 $\Delta H = +ve$. In equilibrium condition, pressure of O_2 is dependent on
 (a) mass of BaO_2
 (b) mass of BaO
 (c) temperature of equilibrium
 (d) mass of BaO_2 and BaO both
11. For the reaction : $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$,
 $(K_c = 1.8 \times 10^{-6}$ at $184^\circ C$ and $R = 0.0831$ kJ/mol. K)
 When K_p and K_c are compared at $184^\circ C$, it is found that
 (a) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
 (b) $K_p = K_c$
 (c) K_p is less than K_c
 (d) K_p is greater than K_c
12. For the reactions
 $A \rightleftharpoons B \quad K_c = 2$
 $B \rightleftharpoons C \quad K_c = 4$
 $C \rightleftharpoons D \quad K_c = 6$
 K_c for the reaction $A \rightleftharpoons D$ is
 (a) $2 \times 4 \times 6$ (b) $\frac{2 \times 4}{6}$
 (c) $2 + 4 + 6$ (d) $\frac{4 \times 6}{2}$
13. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm? The equilibrium constant for NH_4HS decomposition at this temperature is
 (a) 0.11 (b) 0.17 (c) 0.18 (d) 0.30
14. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at $500^\circ C$, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c , with concentration in mole litre $^{-1}$, is
 (a) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (b) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
 (c) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$ (d) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$
15. Highest pH (14) is given by
 (a) 0.1 M H_2SO_4 (b) 0.1 M NaOH
 (c) 1 N NaOH (d) 1 N HCl
16. A physician wishes to prepare a buffer solution of pH = 3.58 that efficiently resists a change in pH yet contains only small concentrations of the buffering agents. Which one of the following weak acids together with its sodium salt would be the best to use ?
 (a) *m*-chlorobenzoic acid ($pK_a = 3.98$)
 (b) *p*-chlorocinnamic acid ($pK_a = 4.41$)
 (c) 2,5-dihydroxybenzoic acid ($pK_a = 2.97$)
 (d) Acetoacetic acid ($pK_a = 3.58$)
17. The dissociation constant of monobasic acids A, B and C are 10^{-4} , 10^{-6} and 10^{-10} respectively. The concentration of each is 0.1 M. Which of the following has been arranged in order of increasing pH?
 (a) $A < B < C$ (b) $C < A < B$
 (c) $B < C < A$ (d) $B < A < C$
18. In HS^- , I^- , RNH_2 and NH_3 , order of proton accepting tendency will be
 (a) $I^- > NH_3 > RNH_2 > HS^-$ (b) $HS^- > RNH_2 > NH_3 > I^-$
 (c) $RNH_2 > NH_3 > HS^- > I^-$ (d) $NH_3 > RNH_2 > HS^- > I^-$
19. Which one of the following orders of acid strength is correct?
 (a) $RCOOH > HC \equiv CH > HOH > ROH$
 (b) $RCOOH > ROH > HOH > HC \equiv CH$
 (c) $RCOOH > HOH > ROH > HC \equiv CH$
 (d) $RCOOH > HOH > HC \equiv CH > ROH$
20. The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression
 (a) $\log \frac{[In^-]}{[HIn]} = pK_{In} - pH$
 (b) $\log \frac{[HIn]}{[In^-]} = pK_{In} - pH$

- (c) $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pH} - \text{pK}_{\text{In}}$
- (d) $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} - \text{pK}_{\text{In}}$
21. What is the correct relationship between the pHs of isomolar solutions of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4)?
- (a) $\text{pH}_1 > \text{pH}_2 > \text{pH}_3 > \text{pH}_4$
 (b) $\text{pH}_1 > \text{pH}_2 \approx \text{pH}_3 > \text{pH}_4$
 (c) $\text{pH}_1 < \text{pH}_2 < \text{pH}_3 < \text{pH}_4$
 (d) $\text{pH}_1 < \text{pH}_2 < \text{pH}_3 \approx \text{pH}_4$
22. A solution of NH_4Cl and NH_3 has $\text{pH} = 8.0$. Which of the following hydroxides may be precipitated when this solution is mixed with equal volume of 0.2 M of metal ion.
- (a) $\text{Ba}(\text{OH})_2$ ($K_{\text{sp}} = 1.1 \times 10^{-4}$)
 (b) $\text{Mg}(\text{OH})_2$ ($K_{\text{sp}} = 3.5 \times 10^{-4}$)
 (c) $\text{Fe}(\text{OH})_2$ ($K_{\text{sp}} = 8.1 \times 10^{-16}$)
 (d) $\text{Ca}(\text{OH})_2$ ($K_{\text{sp}} = 2.1 \times 10^{-5}$).
23. For a concentrated solution of a weak electrolyte A_xB_y of concentration 'c', the degree of dissociation ' α ' is given as
- (a) $\alpha = \sqrt{K_{\text{eq}} / c(x+y)}$
 (b) $\alpha = \sqrt{K_{\text{eq}} c / (xy)}$
 (c) $\alpha = (K_{\text{eq}} / c^{x+y-1} x^x y^y)^{1/(x+y)}$
 (d) $\alpha = (K_{\text{eq}} / cxy)$
24. The pH of a solution containing equimolar amounts of CH_3COOH ($\text{pK}_a = 4.74$ at 25°C) and sodium acetate at 50°C is:
- (a) 4.74 (b) < 4.74
 (c) > 4.74 (d) none of these
25. Two samples of CH_3COOH each of 10gm were taken separately in two vessels containing water of 6 litre and 12 litre respectively at 27°C . The degree of dissociation of CH_3COOH will be—
- (a) More in 12 litre vessel
 (b) More in 6 litre vessel
 (c) Equal in both vessels
 (d) Half in 6 litre vessel than in 12 litre vessel
26. Consider the following equilibrium at 25°C ,
 $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$; $K_1 = 4 \times 10^{30} \text{ mol litre}^{-1}$ and
 $\text{NO}(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g})$; $K_2 = 1.4 \text{ mol}^{-1/2} \text{ litre}^{1/2}$
 The value of K_c for the reaction (at the same temperature)
 $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g})$ is
- (a) 3.5×10^{-31} (b) 2.8×10^{15}
 (c) 7.0×10^{-16} (d) 5.6×10^{30}
27. At 25°C the pH of 0.01 M KOH is 12. If the temperature of this solution is raised to 50°C without changing the volume, which of the following is correct?
- (a) Both pH and pOH will remain constant
 (b) pH will decrease while pOH will remain constant
 (c) pH will increase while pOH will remain constant
 (d) pH will increase while pOH will decrease.
28. Equilibrium constant for the reaction,
 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, follows the equation
 $\ln K_p = 7 - \frac{8400}{T}$, where T = absolute temperature. Find the equilibrium temperature if decomposition of CaCO_3 produces CO_2 gas having partial pressure equal to atmospheric pressure.
- (a) 1200°C (b) 927 K (c) 927°C (d) None
29. For a certain reaction, $\text{rate} = k \times [\text{H}^+]^n$. If pH of reaction changes from two to one, the rate becomes 100 times of its value at $\text{pH} = 2$, the order of reaction is —
- (a) 1 (b) 2 (c) 0 (d) 3
30. Which of the following solutions will have pH close to 1.0?
- (a) 100 ml of 0.1 M HCl + 100 ml of 0.1 M NaOH
 (b) 55 ml of 0.1 M HCl + 45 ml of 0.1 M NaOH
 (c) 75 ml of 0.2 M HCl + 25 ml of 0.2 M NaOH
 (d) 10 ml of 0.1 M HCl + 90 ml of 0.1 M NaOH
31. At certain temperature K_w for water 4.0×10^{-14} . Which of the following is wrong for pure water at this temperature?
- (a) $\text{pH} = 6.699$; water is acidic
 (b) $\text{pH} = 6.699$; water is neutral
 (c) $\text{pOH} = 6.699$; water is neutral
 (d) $\text{pH} + \text{pOH} = 13.398$; water is neutral
32. K_{sp} of $\text{Ca}(\text{OH})_2$ is 4.0×10^{-6} . At what minimum pH, Ca^{2+} ions start precipitating in 0.01 M CaCl_2 ?
- (a) $12 - \log 2$ (b) $12 + \log 2$
 (c) $2 - \log 2$ (d) $2 + \log 2$
33. The following equilibrium constants are given:
- $$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3; K_1$$
- $$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}; K_2$$
- $$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}; K_3$$
- The equilibrium constant for the oxidation of NH_3 by oxygen to give NO is
- (a) $\frac{K_2 K_3^2}{K_1}$ (b) $\frac{K_2^2 K_3}{K_1}$
 (c) $\frac{K_1 K_2}{K_3}$ (d) $\frac{K_2 K_3^3}{K_1}$
34. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?
- (a) $1.11 \times 10^{-4} \text{ M}$ (b) $3.7 \times 10^{-4} \text{ M}$
 (c) $3.7 \times 10^{-3} \text{ M}$ (d) $1.11 \times 10^{-3} \text{ M}$
35. The dissociation equilibrium of a gas AB_2 can be represented as:
- $$2\text{AB}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g}) + \text{B}_2(\text{g})$$

The degree of dissociation is 'x' and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure P is :

- (a) $(2K_p/P)$ (b) $(2K_p/P)^{1/3}$
(c) $(2K_p/P)^{1/2}$ (d) (K_p/P)

36. The values of K_{p1} and K_{p2} for the reactions



are in the ratio of 9 : 1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (1) and (2) are in the ratio :

- (a) 3 : 1 (b) 1 : 9 (c) 36 : 1 (d) 1 : 1

37. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium



- (a) 3.0×10^{-5} (b) 3.0×10^{-4}
(c) 3.0×10^4 (d) 3.0×10^5

38. If pH of a saturated solution of $\text{Ba}(\text{OH})_2$ is 12, the value of its K_{sp} is :

- (a) $4.00 \times 10^{-6} \text{ M}^3$ (b) $4.00 \times 10^{-7} \text{ M}^3$
(c) $5.00 \times 10^{-6} \text{ M}^3$ (d) $5.00 \times 10^{-7} \text{ M}^3$

39. What is $[\text{H}^+]$ in mol/L of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH ? K_a for $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$.

- (a) 3.5×10^{-4} (b) 1.1×10^{-5}
(c) 1.8×10^{-5} (d) 9.0×10^{-6}

40. The reaction $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$ is began with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression

- (a) $[(0.75)^3(0.25)] \div [(0.75)^2(0.25)]$
(b) $[(0.75)^3(0.25)] \div [(1.00)^2(1.00)]$
(c) $[(0.75)^3(0.25)] \div [(0.50)^2(0.75)]$
(d) $[(0.75)^3(0.25)] \div [(0.50)^2(0.25)]$

41. A buffer solution is prepared in which the concentration of NH_3 is 0.30M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, K_b for NH_3 equals 1.8×10^{-5} , what is the pH of this solution ? ($\log 2.7 = 0.433$).

- (a) 9.08 (b) 9.43 (c) 11.72 (d) 8.73

42. In qualitative analysis, the metals of Group I can be separated from other ions by precipitating them as chloride salts. A solution initially contains Ag^+ and Pb^{2+} at a concentration of 0.10 M. Aqueous HCl is added to this solution until the Cl^- concentration is 0.10 M. What will the concentrations of Ag^+ and Pb^{2+} be at equilibrium?

(K_{sp} for $\text{AgCl} = 1.8 \times 10^{-10}$, K_{sp} for $\text{PbCl}_2 = 1.7 \times 10^{-5}$)

- (a) $[\text{Ag}^+] = 1.8 \times 10^{-7} \text{ M}$; $[\text{Pb}^{2+}] = 1.7 \times 10^{-6} \text{ M}$
(b) $[\text{Ag}^+] = 1.8 \times 10^{-11} \text{ M}$; $[\text{Pb}^{2+}] = 8.5 \times 10^{-5} \text{ M}$
(c) $[\text{Ag}^+] = 1.8 \times 10^{-9} \text{ M}$; $[\text{Pb}^{2+}] = 1.7 \times 10^{-3} \text{ M}$
(d) $[\text{Ag}^+] = 1.8 \times 10^{-11} \text{ M}$; $[\text{Pb}^{2+}] = 8.5 \times 10^{-4} \text{ M}$

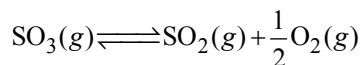
43. Buffer solutions have constant acidity and alkalinity because
(a) these give unionised acid or base on reaction with added acid or alkali.

(b) acids and alkalies in these solutions are shielded from attack by other ions.

(c) they have large excess of H^+ or OH^- ions

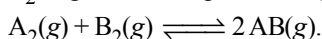
(d) they have fixed value of pH

44. Given that the equilibrium constant for the reaction $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ has a value of 278 at a particular temperature. What is the value of the equilibrium constant for the following reaction at the same temperature ?



- (a) 1.8×10^{-3} (b) 3.6×10^{-3}
(c) 6.0×10^{-2} (d) 1.3×10^{-5}

45. Given the reaction between 2 gases represented by A_2 and B_2 to give the compound $AB(g)$.



At equilibrium, the concentration

of $A_2 = 3.0 \times 10^{-3} \text{ M}$

of $B_2 = 4.2 \times 10^{-3} \text{ M}$

of $AB = 2.8 \times 10^{-3} \text{ M}$

If the reaction takes place in a sealed vessel at 527°C, then the value of K_c will be :

- (a) 2.0 (b) 1.9 (c) 0.62 (d) 4.5

46. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be

- (a) 0.2×10^5 (b) 5.0×10^{-5}
(c) 5.0×10^{15} (d) 5.0×10^{-15} .

DIRECTIONS for Qs. 47 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement- 1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1

- (b) Statement -1 is True, Statement -2 is True, Statement-2 is NOT a correct explanation for Statement - 1

- (c) Statement - 1 is True, Statement- 2 is False

- (d) Statement -1 is False, Statement -2 is True

47. **Statement-1 :** In a titration of weak acid and NaOH, the pH at half equivalence point is pK_a .

Statement-2 : At half equivalence point, it forms an acidic buffer and the buffer capacity is maximum where $[\text{acid}] = [\text{salt}]$

[2009]

48. **Statement-1 :** $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is a stronger acid than $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$.

Statement-2 : Size of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is smaller than $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and possesses more effective nuclear charge.

[2010]

49. **Statement-1 :** Reaction quotient is defined in the same way as equilibrium constant at any stage of the reaction.

Statement-2 : If Q_c (reaction quotient) $< K_c$ (equilibrium constant) reaction moves in direction of reactants. [2011]

50. **Statement-1 :** KOH is more soluble in water than NaOH.

Statement-2 : NaOH is a stronger base than KOH. [2011]

EXERCISE - 3

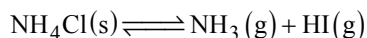
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

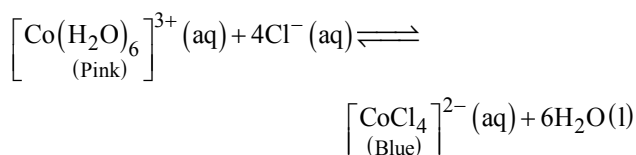
1. We know that the relationship between K_c and K_p is

$$K_p = K_c (RT)^{\Delta n}$$

What would be the value of Δn for the reaction?



- (a) 1 (b) 0.5
(c) 1.5 (d) 2
2. For the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, the standard free energy is $\Delta G^\ominus > 0$. The equilibrium constant (K) would be
(a) $K = 0$ (b) $K > 1$
(c) $K = 1$ (d) $K < 1$
3. Which of the following is not a general characteristic of equilibria involving physical processes?
(a) Equilibrium is possible only in a closed system at a given temperature.
(b) All measurable properties of the system remain constant.
(c) All the physical processes stop at equilibrium.
(d) The opposing processes occur at the same rate and there is dynamic but stable condition.
4. PCl_5 , PCl_3 , and Cl_2 are at equilibrium at 500 K in a closed container and their concentrations are $0.8 \times 10^{-3} \text{ mol L}^{-1}$, $1.2 \times 10^{-3} \text{ mol L}^{-1}$ and $1.2 \times 10^{-3} \text{ mol L}^{-1}$ respectively. The value of K_c for the reaction
 $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ will be
(a) $1.8 \times 10^3 \text{ mol L}^{-1}$ (b) 1.8×10^{-3}
(c) $1.8 \times 10^{-3} \text{ mol}^{-1} \text{ L}$ (d) 0.55×10^4
5. Which of the following statements is incorrect?
(a) In equilibrium mixture of ice and water kept in perfectly insulated flask, mass of ice and water does not change with time
(b) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate
(c) On addition of catalyst the equilibrium constant value is not affected
(d) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases.
6. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and thus the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.



- (a) $\Delta H > 0$ for the reaction
(b) $\Delta H < 0$ for the reaction
(c) $\Delta H = 0$ for the reaction
(d) The sign of ΔH cannot be predicted on the basis of this information
7. The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C ?
(a) Equal to 7.0 (b) Greater than 7.0
(c) Less than 7.0 (d) Equal to zero
8. The ionisation constant of an acid, K_a is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5} , 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of pH of 0.1 mol dm^{-3} solutions of these acids is correct?
(a) Acetic acid > hypochlorous acid > formic acid
(b) Hypochlorous acid > acetic acid > formic acid
(c) Formic acid > hypochlorous acid > acetic acid
(d) Formic acid > acetic acid > hypochlorous acid
9. K_{a1} , K_{a2} and K_{a3} are the respective ionisation constants for the following reactions.
$$\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$$
$$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$$
$$\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$$

The correct relationship between K_{a1} , K_{a2} and K_{a3} is
(a) $K_{a3} = K_{a1} \times K_{a2}$ (b) $K_{a3} = K_{a1} + K_{a2}$
(c) $K_{a3} = K_{a1} - K_{a2}$ (d) $K_{a3} = K_{a1} / K_{a2}$
10. Acidity of BF_3 can be explained on the basis of which of the following concepts?
(a) Arrhenius concept
(b) Bronsted Lowry concept
(c) Lewis concept
(d) Bronsted Lowry as well as Lewis concept
11. Which of the following will produce a buffer solution when mixed in equal volumes?
(a) $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{OH}$ and $0.1 \text{ mol dm}^{-3} \text{ HCl}$
(b) $0.05 \text{ mol dm}^{-3} \text{ NH}_4\text{OH}$ and $0.1 \text{ mol dm}^{-3} \text{ HCl}$
(c) $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{OH}$ and $0.05 \text{ mol dm}^{-3} \text{ HCl}$
(d) $0.1 \text{ mol dm}^{-3} \text{ CH}_3\text{COONa}$ and $0.1 \text{ mol dm}^{-3} \text{ NaOH}$
12. In which of the following solvent silver chloride is most soluble?
(a) $0.1 \text{ mol dm}^{-3} \text{ AgNO}_3$ solution
(b) $0.1 \text{ mol dm}^{-3} \text{ HCl}$ solution
(c) H_2O
(d) Aqueous ammonia

13. What will be the value of pH of $0.01 \text{ mol dm}^{-3} \text{CH}_3\text{COOH}$ ($K_a = 1.74 \times 10^{-5}$)?
 (a) 3.4 (b) 3.6
 (c) 3.9 (d) 3.0
14. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5} . The pH of ammonium acetate will be
 (a) 7.005 (b) 4.75
 (c) 7.0 (d) Between 6 and 7
15. Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$?
 (a) $\Delta G^\ominus = 0$ (b) $\Delta G^\ominus > 0$
 (c) $\Delta G^\ominus < 0$ (d) $\Delta G^\ominus = -RT \ln K$
16. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le-Chatelier's principle. Consider the reaction,

$$\text{N}_2(\text{g}) + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3(\text{g})$$

 Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?
 (a) K will remain same
 (b) K will decrease
 (c) K will increase
 (d) K will increase initially and decrease when pressure is very high
17. What will be the correct order of vapour pressure of water, acetone and ether at 30°C ? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?
 (a) Water < ether < acetone (b) Water < acetone < ether
 (c) Ether < acetone < water (d) Acetone < ether < water
18. At 500 K, equilibrium constant, K_c , for the following reaction is 5.

$$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{g}) \rightleftharpoons \text{HI}(\text{g})$$

 What would be the equilibrium constant K_c for the reaction?

$$2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$$

 (a) 0.04 (b) 0.4
 (c) 25 (d) 2.5
19. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?
 (a) $\text{H}_2(\text{g}) + \text{I}_2 \rightleftharpoons 2\text{HI}(\text{g})$
 (b) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (c) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (d) The equilibrium will remain unaffected in all the three cases
20. Identify the correct order of solubility in aqueous medium:
 (a) $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$ (b) $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$
 (c) $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$ (d) $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$
21. Which of these is least likely to act as Lewis base? [2013]
 (a) F^- (b) BF_3
 (c) PF_3 (d) CO
22. The values of K_{sp} of CaCO_3 and CaC_2O_4 are 4.7×10^{-9} and 1.3×10^{-9} respectively at 25°C . If the mixture of these two is washed with water, what is the concentration of Ca^{2+} ions in water? [NEET Kar. 2013]
 (a) $7.746 \times 10^{-5} \text{ M}$ (b) $5.831 \times 10^{-5} \text{ M}$
 (c) $6.856 \times 10^{-5} \text{ M}$ (d) $3.606 \times 10^{-5} \text{ M}$
23. At 100°C the K_w of water is 55 times its value at 25°C . What will be the pH of neutral solution? ($\log 55 = 1.74$) [NEET Kar. 2013]
 (a) 6.13 (b) 7.00
 (c) 7.87 (d) 5.13
24. The dissociation constant of a weak acid is 1×10^{-4} . In order to prepare a buffer solution with a pH = 5 the $[\text{Salt}]/[\text{Acid}]$ ratio should be [NEET Kar. 2013]
 (a) 1 : 10 (b) 4 : 5
 (c) 10 : 1 (d) 5 : 4
25. Accumulation of lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$), a monobasic acid in tissues leads to pain and a feeling of fatigue. In a 0.10 M aqueous solution, lactic acid is 3.7% dissociated. The value of dissociation constant, K_a , for this acid will be: [NEET Kar. 2013]
 (a) 2.8×10^{-4} (b) 1.4×10^{-5}
 (c) 1.4×10^{-4} (d) 3.7×10^{-4}
26. Which of the following salts will give highest pH in water?
 (a) KCl (b) NaCl [2014]
 (c) Na_2CO_3 (d) CuSO_4
27. Using the Gibbs energy change, $\Delta G^\ominus = + 63.3 \text{ kJ}$, for the following reaction,

$$\text{Ag}_2\text{CO}_3 \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$

 the K_{sp} of $\text{Ag}_2\text{CO}_3(\text{s})$ in water at 25°C is:-
 ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
 (a) 3.2×10^{-26} (b) 8.0×10^{-12}
 (c) 2.9×10^{-3} (d) 7.9×10^{-2}
28. For the reversible reaction,

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{heat}$$

 The equilibrium shifts in forward direction
 (a) By increasing the concentration of $\text{NH}_3(\text{g})$
 (b) By decreasing the pressure
 (c) By decreasing concentration of $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$
 (d) By increasing pressure and decreasing temperature.
29. For a given exothermic reaction, K_p and K_p' are the equilibrium constants at temperatures T_1 and T_2 , respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2 , it is readily observed that: [2014]
 (a) $K_p > K_p'$ (b) $K_p < K_p'$
 (c) $K_p = K_p'$ (d) $K_p = \frac{1}{K_p'}$

NEET/AIPMT (2013-2017) Questions

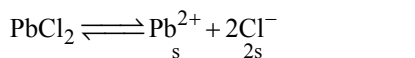
20. Identify the correct order of solubility in aqueous medium: [2013]
 (a) $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$ (b) $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$
 (c) $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$ (d) $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$

30. The K_{sp} of Ag_2CrO_4 , $AgCl$, $AgBr$ and AgI are respectively, 1.1×10^{-12} , 1.8×10^{-10} , 5.0×10^{-13} , 8.3×10^{-17} . Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of $NaCl$, $NaBr$, NaI and Na_2CrO_4 ? [2015]
- (a) $AgCl$ (b) $AgBr$
(c) Ag_2CrO_4 (d) AgI
31. If the value of an equilibrium constant for a particular reaction is 1.6×10^{12} , then at equilibrium the system will contain :- [2015]
- (a) mostly reactants
(b) mostly products
(c) similar amounts of reactants and products
(d) all reactants
32. Which of the following statements is correct for a reversible process in a state of equilibrium? [2015]
- (a) $\Delta G = 2.30 RT \log K$
(b) $\Delta G^\circ = -2.30 RT \log K$
(c) $\Delta G^\circ = 2.30 RT \log K$
(d) $\Delta G = -2.30 RT \log K$
33. Which one of the following pairs of solution is not an acidic buffer? [2015 RS]
- (a) $HClO_4$ and $NaClO_4$
(b) CH_3COOH and CH_3COONa
(c) H_2CO_3 and Na_2CO_3
(d) H_3PO_4 and Na_3PO_4
34. What is the pH of the resulting solution when equal volumes of 0.1 M $NaOH$ and 0.01 M HCl are mixed? [2015 RS]
- (a) 12.65 (b) 2.0
(c) 7.0 (d) 1.04
35. If the equilibrium constant for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K , the equilibrium constant for $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons NO(g)$ will be: [2015 RS]
- (a) $K^{\frac{1}{2}}$ (b) $\frac{1}{2} K$
(c) K (d) K^2
36. MY and NY_3 , two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3 ? [2016]
- (a) The molar solubilities of MY and NY_3 in water are identical.
(b) The molar solubility of MY in water is less than that of NY_3
(c) The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water.
(d) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities.
37. Consider the nitration of benzene using mixed conc of H_2SO_4 and HNO_3 . If a large amount of $KHSO_4$ is added to the mixture, the rate of nitration will be [2016]
- (a) faster (b) slower
(c) unchanged (d) doubled
38. Consider the following liquid - vapour equilibrium. [2016]
- Liquid $\rightleftharpoons$ Vapour
- Which of the following relations is correct?
- (a) $\frac{d \ln G}{dT^2} = \frac{\Delta H_v}{RT^2}$ (b) $\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT}$
(c) $\frac{d \ln P}{dT^2} = \frac{-\Delta H_v}{T^2}$ (d) $\frac{d \ln P}{dT} = \frac{-\Delta H_v}{RT^2}$
39. The equilibrium constant of the following are : [2017]
- $$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad K_1$$
- $$N_2 + O_2 \rightleftharpoons 2NO \quad K_2$$
- $$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad K_3$$
- The equilibrium constant (K) of the reaction :
- $$2NH_3 + \frac{5}{2} O_2 \xrightleftharpoons{K} 2NO + 3H_2O, \text{ will be;}$$
- (a) $K_2 K_3^3 / K_1$ (b) $K_2 K_3 / K_1$
(c) $K_2^3 K_3 / K_1$ (d) $K_1 K_3^3 / K_2$
40. Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is $2.2 \times 10^{-4} \text{ mol L}^{-1}$. Solubility product of $Ag_2C_2O_4$ is :- [2017]
- (a) 2.66×10^{-12} (b) 4.5×10^{-11}
(c) 5.3×10^{-12} (d) 2.42×10^{-8}
41. A 20 litre container at 400 K contains $CO_2(g)$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be :-
(Given that : $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$, $K_p = 1.6 \text{ atm}$) [2017]
- (a) 10 litre (b) 4 litre
(c) 2 litre (d) 5 litre

Hints & Solutions

EXERCISE - 1

1. (a) Let s be the solubility of PbCl_2 and K_{sp} be its solubility product
The solubility equilibrium of PbCl_2 is represented as



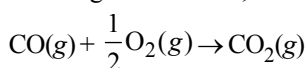
$$\therefore K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (s)(2s)^2 = 4s^3$$

$$\Rightarrow s = \left(\frac{K_{\text{sp}}}{4}\right)^{1/3}$$

2. (b) For a gaseous phase reaction K_p and K_c are related as

$$K_p = K_c (RT)^{\Delta n_g}$$

For the given reaction,

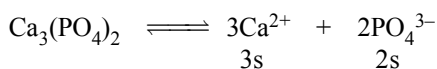


$$\Delta n_g = 1 - (1 + 0.5) = -0.5 \text{ or } -\frac{1}{2}$$

$$\therefore K_p = K_c (RT)^{-\frac{1}{2}}$$

$$\text{or } \frac{K_p}{K_c} = (RT)^{-\frac{1}{2}}$$

3. (b) The solubility equilibrium of $\text{Ca}_3(\text{PO}_4)_2$ is represented as,



$$\therefore K_{\text{sp}} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = [3s]^3 [2s]^2 = 108s^5$$

4. (b) $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

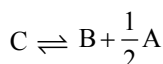
$$\Delta n = n_{\text{products}} - n_{\text{reactants}} = 2 - 4 = -2$$

$$\therefore K_p = K_c (RT)^{-2} \text{ or } K_p = \frac{K_c}{(RT)^2},$$

Thus $K_p < K_c$.

5. (d) Given $\text{A} + 2\text{B} \rightleftharpoons 2\text{C}$

$$K = \frac{[\text{C}]^2}{[\text{A}][\text{B}]^2} \quad (\text{i})$$



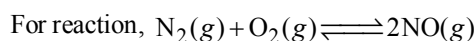
$$K' = \frac{[\text{B}][\text{A}]^{1/2}}{[\text{C}]} \quad (\text{ii})$$

Dividing (ii) by (i)

$$K' = \left[\frac{1}{K}\right]^{1/2} = \left[\frac{1}{40}\right]^{1/2}$$

6. (b) $K_p = K_c (RT)^{\Delta n_g}$

$$\therefore K_p = K_c \text{ only when } \Delta n_g = 0$$



$$\Delta n_{(g)} = 2 - 2 = 0$$

$$\therefore K_p = K_c (RT)^0 \text{ or } K_p = K_c$$

7. (a) For reaction (i)

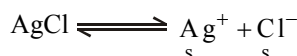
$$K_1 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

and for reaction (ii)

$$K_2 = \frac{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]}; \therefore K_1 = \frac{1}{K_2^2}$$

8. (c) To find which of the given compound among AgCl , AgBr and Ag_2CrO_4 would they use, first find which has highest conc. of Ag^+ ions. For this, we have to calculate the solubility of Ag^+ ions (let s be the solubility of Ag^+ ions)

For AgCl ,



$$\Rightarrow K_{\text{sp}} = (s)(s) = s^2$$

$$\Rightarrow s = \sqrt{K_{\text{sp}}} = \sqrt{(1.8 \times 10^{-10})^3}$$

For AgBr ,

$$s = \sqrt{K_{\text{sp}}} = \sqrt{(5.0 \times 10^{-13})^3}$$

For Ag_2CrO_4 ,

$$s = \sqrt[3]{K_{\text{sp}}} = \sqrt[3]{(2.4 \times 10^{-12})^2}$$

So, solution of silver compound can be made from Ag_2CrO_4 which has highest solubility among the given silver halides.

9. (c) Using the relation $K_p = K_c (RT)^{\Delta n}$, we get

$$\frac{K_p}{K_c} = (RT)^{\Delta n}$$

Thus $\frac{K_p}{K_c}$ will be highest for the reaction having highest value of Δn .

The Δn values for various reactions are

$$(a) \Delta n = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$$

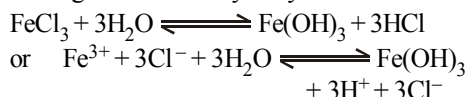
$$(b) \Delta n = 2 - (1 + 1) = 0$$

$$(c) \Delta n = (1 + 1) - 1 = 1$$

$$(d) \Delta n = (2 + 4) - (7 + 2) = -3$$

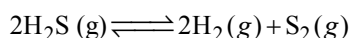
Thus maximum value of $\Delta n = 1$

10. (a) FeCl_3 which is a salt of strong acid and weak base, undergoes cationic hydrolysis in water as follows :



So, it produces H^+ ions due to which solution of FeCl_3 in water is acidic.

11. (a) Statement (a) is correct and the rest statements are wrong. K_p depends only on temperature hence at constant temp. K_p will not change.
12. (a) For the given reaction,



$$\Delta n = 3 - 2 = 1$$

$$K_c = \frac{K_p}{(RT)^n} = \frac{1.2 \times 10^{-2}}{(RT)^1}$$

$$\therefore K_c < K_p \text{ or } K_c < 1.2 \times 10^{-2}$$

13. (c) As $K_p = K_c \text{ RT}^{\Delta n_g}$

$$\text{Here } \Delta n_g = 1$$

$$\text{So, } K_p = K_c \text{ when } \text{RT} = 1$$

$$\text{Thus } T = 12.5 \text{ K}$$

14. (b) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

Moles at equilibrium

$$\frac{1}{2} \quad \quad \quad \frac{1}{2} \quad \quad \quad \frac{1}{2}$$

Mole fraction at equilibrium

$$\frac{1}{3} \quad \quad \quad \frac{1}{3} \quad \quad \quad \frac{1}{3}$$

Partial pressure at equilibrium

$$\frac{P}{3} \quad \quad \quad \frac{P}{3} \quad \quad \quad \frac{P}{3}$$

$$K_p = \frac{\frac{P}{3} \times \frac{P}{3}}{\frac{P}{3}} = \frac{P}{3}$$

15. (d) $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$

$$\text{At start} \quad \quad \quad 1 \text{ mole} \quad 1 \text{ mole} \quad 0 \quad \quad 0$$

$$\text{At equb.} \quad \quad \quad 1 - \frac{2}{3} \quad 1 - \frac{2}{3} \quad \frac{2}{3} \quad \quad \frac{2}{3}$$

Let the total volume = $V \text{ L}$

$$\therefore [\text{CH}_3\text{COOH}] = \frac{1}{3} V \text{ mol/L}$$

$$[\text{C}_2\text{H}_5\text{OH}] = \frac{1}{3} V \text{ mol/L}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = \frac{2}{3} V \text{ mol/L}$$

$$[\text{H}_2\text{O}] = \frac{2}{3} V \text{ mol/L}$$

$$\therefore K = \frac{\frac{2}{3} V \times \frac{2}{3} V}{\frac{1}{3} V \times \frac{1}{3} V} = 4$$

16. (b) $P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = 2 \text{ atm}$

$$\therefore K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = 4$$

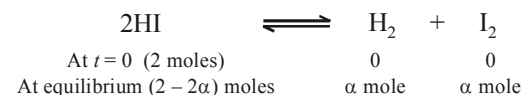
17. (a) Unit of $K_c \Rightarrow (\text{mol lit}^{-1})^{\Delta n}$

For given reaction,

$$\Delta n = (4 + 6) - (4 + 5) = 1,$$

$$K_c \rightarrow \text{mol lit}^{-1}$$

18. (b) According to equation



Total moles at equilibrium

$$= 2 - 2\alpha + \alpha + \alpha = 2 \text{ mole}$$

19. (b) $\text{pH} = -\log [\text{H}^+] = -\log [5 \times 10^{-4}]$

$$= 4 - \log 5 = 4 - [\log 10 - \log 2]$$

$$= 3 + \log 2 = 3.3010$$

$$\text{pOH} = 14 - \text{pH} = 14 - 3.3 = 10.7.$$

20. (b) $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

$$\alpha \% = \frac{D - d}{d(y - 1)} \times 100 \quad (y = 2)$$

$$D = \frac{\text{molar mass of } \text{SO}_2\text{Cl}_2}{2} = \frac{135}{2} = 67.5; d = 50.0 \quad (\text{given})$$

$$\therefore \alpha = \frac{67.5 - 50.0}{50.0(2 - 1)} \times 100 = 35\%$$

21. (a) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Heat}$

No. of moles of reactants = No. of moles of products.

The reaction in which number of moles of reactants are equal to number of moles of products are not affected by change in pressure (*Le-chatelier's principle*).

22. (b) $K = \frac{[\text{Product}]}{[\text{Reactant}]}$

$$\text{Hence, } [\text{Product}] = K[\text{Reactant}]$$

$$\therefore [\text{Product}] > \text{Reactant, when } K > 1$$

23. (b) $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6, \Delta H = -130 \text{ kJ mol}^{-1}$

$$\begin{array}{ccc} 2 \text{ moles} & & 1 \text{ mole} \end{array}$$

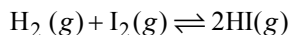
The reaction is exothermic and involves decrease in volume, so forward reaction will be favoured by decreasing temperature and increasing pressure (*Le Chatelier principle*).

24. (b) The species having minimum value of K_{sp} will get precipitated first of all because ionic product will exceed the solubility product of such a species.

The K_{sp} value is minimum for $\text{BaSO}_4 (10^{-11})$,

so, BaSO_4 will get precipitated first of all.

25. (a) Reactions in which number of moles of gaseous reactants and gaseous products is equal (i.e. $\Delta n = 0$) are not affected by change in pressure (**Le Chatelier principle**)



26. (d) Solid $\rightleftharpoons$ Liquid
It is an endothermic process. So when temperature is raised, more liquid is formed. Hence adding heat will shift the equilibrium in the forward direction.

27. (d) For reaction to proceed from right to left

$Q > K_c$ i.e. the reaction will be fast in backward direction
i.e. $r_b > r_f$

28. (c) $\alpha = 0.1$,

$$K_a = \frac{\alpha^2 C}{1 - \alpha} = \frac{(0.1)^2 \times (0.01)}{(1 - 0.1)} = 1.11 \times 10^{-4}$$

$$\text{Now } pK_a = -\log 1.11 \times 10^{-4} = 3.9542$$

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 3.9542 + \log \left[\frac{0.05}{0.10} \right] = 3.653$$

29. (c) Catalyst only changes time to achieve equilibrium, it does not affect the value of equilibrium constant.

30. (a) Solubility of $\text{PbF}_2 \approx 10^{-3} \text{ M}$

$$\therefore K_{sp} = 4S^3 = 4 \times 10^{-9}$$

In 0.05 M NaF we have 0.05 M of F^- ion contributed by NaF . If the solubility of PbF_2 in this solution is $S \text{ M}$, then

$$\text{total } [\text{F}^-] = [2S + 0.05] \text{ M.}$$

$$\therefore S[2S + 0.05]^2 = 4 \times 10^{-9}$$

$$\text{Assuming } 2S \ll 0.05,$$

$$S \times 25 \times 10^{-4} = 4 \times 10^{-9}$$

$$\therefore S = 0.16 \times 10^{-5} \text{ M} \Rightarrow 1.6 \times 10^{-6} \text{ M}$$

We observe that our approximation that $2S \ll 0.05$ is justified.

31. (c) Exothermic reaction is favoured by low temperature to proceed in forward direction.

32. (c) $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

In this reaction volume is increasing in the forward direction. So on increasing temperature reaction will proceed in forward direction.

33. (c) $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$

$$K_{sp} = [\text{A}^+][\text{B}^-]$$

Salt will precipitate if ionic conc. $> K_{sp}$

$$[\text{A}^+][\text{B}^-] > 1 \times 10^{-8}$$

$$(1 \times 10^{-3})[\text{B}^-] > 1 \times 10^{-8}$$

$$[\text{B}^-] > \frac{1 \times 10^{-8}}{1 \times 10^{-3}} \text{ or } 1 \times 10^{-5}$$

34. (b) Le Chatelier principle is not applicable to solid-solid equilibrium.

35. (a) **Given :** Hydroxyl ion concentration $[\text{OH}^-] = 0.05 \text{ mol L}^{-1}$. We know that

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\text{or } [\text{H}^+] = \frac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13} \text{ mol L}^{-1}$$

We also know that

$$\text{pH} = -\log[\text{H}^+] = -\log[2 \times 10^{-13}]$$

$$= -\log 2 - \log 10^{-13} = -\log 2 - (-13) \log 10$$

$$= -0.3010 + 13.0000 = 12.6990.$$

Since the value of $\text{pH} > 7$, therefore the solution is basic.

36. (b) $\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

$$\text{or } \text{pK}_b = \text{pOH} - \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{but } \text{pOH} + \text{pH} = 14 \text{ or } \text{pOH} = 14 - \text{pH}$$

$$\therefore 14 - \text{pH} - \log \frac{[\text{Salt}]}{[\text{Base}]} = \text{pK}_b$$

$$14 - 9.25 - \log \frac{0.1}{0.1} = \text{pK}_b$$

$$14 - 9.25 - 0 = \text{pK}_b \quad \text{pK}_b = 4.75$$

37. (b) $\text{B}(\text{OH})_3$ does not provide H^+ ions in water instead it accepts OH^- ion and hence it is Lewis acid.



38. (c) (a) $[\text{H}_3\text{O}^+] = \frac{0.1}{2} = 0.05$;

$$\text{pH} = -\log 0.05 = 1.301$$

- (b) Complete neutralization of strong acid and strong base, $\text{pH} = 7$.

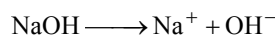
- (c) Hydrolysis of the salt CH_3COOK , $\text{pH} > 7$ (salt of weak acid with strong base)

- (d) Hydrolysis of the salt NH_4NO_3 , $\text{pH} < 7$ (salt of strong acid with weak base)

39. (a) $(\text{HSO}_4)^-$ can accept and donate a proton
 $(\text{HSO}_4)^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{SO}_4$ (acting as base)
 $(\text{HSO}_4)^- - \text{H}^+ \rightleftharpoons \text{SO}_4^{2-}$ (acting as acid)

40. (b) I^- is electron donor. Hence it is Lewis base.

41. (d) Given concentration of $\text{NaOH} = 10^{-10} \text{ M}$



$$10^{-10} \text{ M} \quad 10^{-10}$$

$$\therefore [\text{OH}^-] \text{ from NaOH} = 10^{-10}$$

We have to consider dissociation of H_2O

$$[\text{OH}^-] \text{ from } \text{H}_2\text{O} = 10^{-7}$$

$$\text{Total } [\text{OH}^-] = 10^{-7} + 10^{-10}$$

$$= 10^{-7} (0.001 + 1) = 10^{-7} \left(\frac{1001}{1000} \right) = 10^{-10} \times 1001$$

$$\therefore \text{pOH} = -\log [\text{OH}^-]$$

$$= -(\log 1001 \times 10^{-10}) = -3.004 + 10 = 6.9996$$

$$\text{pH} = 14 - \text{pOH} = 14 - 6.996 = 7.004$$

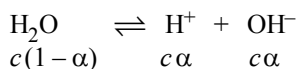
$$\therefore \text{pH of } 10^{-10} \text{ M NaOH solution is nearest to 7.}$$

42. (d) Strongest Bronsted base has weakest conjugate acid.
 $\therefore$ HOCl is weakest acid among HOCl, HClO₂, HClO₃ and HClO₄.
 $\therefore$ Conjugate base of HOCl (i.e. OCl⁻) is strongest Bronsted base.
43. (d) In N/1000 KOH, [OH⁻] = 10⁻³ M
 pOH = -log [OH⁻] = -log 10⁻³ = 3
 pH = 14 - pOH = 14 - 3 = 11
44. (b) (i) $\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$
 0.1 M 0.1 M
 $\therefore$ [H⁺] = 0.1 M
 pH = -log [H⁺] = -log 0.1 = 1
 (ii) NaCl is a salt of strong acid and strong base so it is not hydrolysed and hence its pH is 7.
 (iii) $\text{NH}_4\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{HCl}$
 $\therefore$ The solution is acidic and pH is less than that of 0.1 M HCl.
 (iv) $\text{NaCN} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{HCN}$
 $\therefore$ The solution is basic and pH is more than that of 0.1 M HCl.
 $\therefore$ Correct order for increase in pH is
 HCl < NH₄Cl < NaCl < NaCN.
45. (c) $\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$
 Given concentration of H₂SO₄ = 0.005 M
 $\therefore$ [H⁺] = 0.005 $\times$ 2 = 0.01 = 10⁻²
 pH = -log [H⁺] = -log 10⁻² = 2
46. (d) Among M/4 KOH, M/4 NaOH, M/4 NH₄OH and M/4 Ca(OH)₂, Ca(OH)₂ furnishes highest number of OH⁻ ions
 ($\therefore$ $\text{Ca(OH)}_2 \longrightarrow \text{Ca}^{2+} + 2\text{OH}^-$). So pH of M/4 Ca(OH)₂ is highest.
47. (a) $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
 $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x \times x}{0.1}$
 or $1.8 \times 10^{-5} = \frac{x^2}{0.1}$
 $x^2 = 1.8 \times 10^{-6}$
 $x = 1.35 \times 10^{-3}$
 Thus at equilibrium, [OH⁻] = 1.35 $\times$ 10⁻³
 pOH = -log (1.35 $\times$ 10⁻³) = 2.87
 $\therefore$ pH = 14.00 - 2.87 = 11.13
48. (c) Number of meq. of the acid = 0.04 $\times$ 100 = 4
 Number of meq. of the base = 0.02 $\times$ 100 = 2
 $\therefore$ Number of meq. of the acid left on mixing = 4 - 2 = 2
 Total volume of the solution = 200 mL
 $\therefore$ No. of meq of the acid present in 1000 mL of the solution = 10
 or No. of eq. of the acid in 1000 mL of the solution
 $= \frac{10}{1000} = 0.01$
 Since the acid is monobasic and completely ionises in solution
 0.01 N HCl = 0.01 M HCl
 Thus [H⁺] = 0.01
 $\therefore$ pH = -log (0.01) = -(-2) = 2
49. (a) In BCl₃ and BF₃ due to -I effect of F and Cl these are better Lewis acids than BMe₃ and B₂H₆. Among BCl₃ and BF₃, the former is better Lewis acid as in it p π -p π back bonding is lesser than in BF₃.
50. (b) The value of ionic product of water changes with the temperature.
51. (d) HCl is stronger acid than CH₃COOH and Cl⁻ is a stronger base than CH₃COOH₂⁺ and is the conjugate base of HCl.
 $\text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$
 acid₁ base₂ base₁ acid₂
52. (b) Diacidic base has two replaceable hydroxyl groups. -OH groups present in compounds (a) and (c) represent alcoholic group, not base.
53. (d) Lewis acids are electron pair acceptor whereas Bronsted acids are proton donor.
- $\text{SO}_3 + \text{:}\ddot{\text{O}}\text{:}^{2-} \longrightarrow \text{SO}_4^{2-}$
 Lewis acid
54. (a) Bronsted base is a substance which accepts proton. In option (a), H₂O is accepting proton, i.e., acting as a base.
55. (c) On dilution [H⁺] = 10⁻⁶ M = 10⁻⁶ mol
 Now dissociation of water cannot be neglected,
 Total [H⁺] = 10⁻⁶ + 10⁻⁷ = 11 $\times$ 10⁻⁷
 pH = -log [H⁺]
 $= -\log (11 \times 10^{-7}) = 5.98$
56. (a) Acid and base will neutralise each other. Since volume of NaOH is more (150 mL) in solution.
 $\therefore$ $[\text{OH}^-] = \frac{M_2V_2 - M_1V_1}{V_1 + V_2 + V_3} = \frac{150 \times 0.5 - 50 \times 0.5}{50 + 150 + 300} = \frac{1}{10}$
 Now [H⁺][OH⁻] = 10⁻¹⁴
 $\Rightarrow$ [H⁺] = 10⁻¹³
 pH = 13.
57. (c) At 80% neutralization, $\frac{[\text{Salt}]}{[\text{Base}]} = \frac{8}{2} = \frac{4}{1}$
 $\therefore$ pOH = pK_b + log $\frac{[\text{Salt}]}{[\text{Base}]}$
 14 - 7.4 = pK_b + log 4
 pK_b = 6.6 - 0.6 = 6
 K_b = 10⁻⁶
58. (a) $K = \frac{[\text{C}]}{[\text{A}][\text{B}]^2} = \frac{0.216}{0.06 \times 0.12 \times 0.12} = 250$
59. (d) Given K_b = 1.0 $\times$ 10⁻¹²
 [BOH] = 0.01 M [OH] = ?
 $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$
 $\begin{matrix} t=0 & c & 0 & 0 \\ t_{\text{eq}} & c(1-x) & cx & cx \end{matrix}$
 $K_b = \frac{c^2x^2}{c(1-x)} = \frac{cx^2}{(1-x)} \Rightarrow 1.0 \times 10^{-12} = \frac{0.01x^2}{(1-x)}$
 On calculation, we get, $x = 1.0 \times 10^{-5}$
 Now, [OH⁻] = $cx = 0.01 \times 10^{-5} = 1 \times 10^{-7}$ mol L⁻¹

60. (b) $pK_a = -\log K_a$
Smaller the value of pK_a , stronger will be acid
 $\therefore$ Acid having pK_a value of 10^{-8} is strongest acid.
61. (b) Solubility product is the product of ionic concentration in a saturated solution of an electrolyte at a given temperature.

62. (d) As, molarity, $= \frac{\text{wt. of solute per litre of solution}}{\text{Mol. wt. of solute}}$

$$\text{Molarity of H}_2\text{O} = \frac{1000}{18} \text{ mole/litre}$$



$$\text{Thus, } K_a = \frac{c\alpha^2}{1-\alpha} = c\alpha^2 = 1.8 \times 10^{-14}$$

63. (b) $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \sqrt{\frac{3.14 \times 10^{-4}}{1.96 \times 10^{-5}}} = 4:1$

64. (c) For weak acid dissociation equilibria, degree of dissociation α is given as :

$$\alpha = \sqrt{\frac{K_a}{c}} \quad \therefore \% \alpha = 100 \sqrt{\frac{K_a}{c}}$$

$$\text{Also, } K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+]c\alpha}{c(1-\alpha)} = \frac{[\text{H}^+]\alpha}{(1-\alpha)}$$

$$\log K_a = \log \text{H}^+ + \log \frac{\alpha}{1-\alpha}$$

$$\text{or } pK_a = \text{pH} + \log \frac{1-\alpha}{\alpha}$$

$$pK_a - \text{pH} = \log \frac{1-\alpha}{\alpha}$$

$$\frac{1-\alpha}{\alpha} = 10^{pK_a - \text{pH}}$$

$$\text{or, } \frac{1}{\alpha} = 10^{pK_a - \text{pH}} + 1$$

$$\therefore \alpha = \frac{1}{[1 + 10^{pK_a - \text{pH}}]}$$

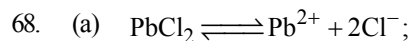
65. (d) In presence of little H_2SO_4 (as catalyst) about 2/3 mole of each of CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$ react to form 2/3 mole of the product at equilibrium.

66. (c) $K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \quad \dots(\text{i})$

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} \quad \dots(\text{ii})$$

From (i) and (ii), $K_a K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$
(ionic product of water)

67. (a) $K = c\alpha^2 = 0.1 \times \left(\frac{1.34}{100}\right)^2 = 1.8 \times 10^{-5}$



$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$[\text{Pb}^{2+}] = 6.3 \times 10^{-3}; [\text{Cl}^-] = (2 \times 6.3 \times 10^{-3})$$

$$= 12.6 \times 10^{-3}$$

$$K_{sp} = (6.3 \times 10^{-3})(12.6 \times 10^{-3})^2$$

69. (b) For Bi_2S_3
 $K_{sp} = (2s)^2(3s)^3 = 4s^2 \cdot 27s^3 = 108s^5$
where s = solubility

$$\therefore s = 5\sqrt[5]{\frac{K_{sp}}{108}}$$

$$\text{For MnS, } K_{sp} = s^2$$

$$\therefore s = \sqrt{K_{sp}} = \sqrt{7 \times 10^{-16}}$$

$$\text{For CuS, } K_{sp} = s^2$$

$$\therefore s = \sqrt{K_{sp}} = \sqrt{8 \times 10^{-37}}$$

$$\text{For Ag}_2\text{S, } K_{sp} = 4s^3$$

$$\therefore s = \sqrt[3]{\frac{K_{sp}}{4}}$$

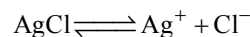
Thus MnS has maximum solubility.

70. (d) Aspirin is a weak acid. Due to common ion effect, it is unionised in acid medium but completely ionised in alkaline medium.
71. (c) $\text{HCl} + \text{NH}_4\text{Cl}$. HCl is strong acid hence not used in buffer.
72. (b) (i) NaCl is ionic compound and therefore it is least soluble in liquid CCl_4 .
(ii) Covalent compounds are soluble in liquid CCl_4 .
Solubility of covalent compounds

$$\propto \frac{1}{\text{Molecular mass}}$$

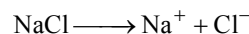
$\therefore \text{Cl}_2$ has highest solubility in liquid CCl_4 .

73. (a) Let solubility of $\text{AgCl} = x$ moles/L



$$\text{before dissociation} \quad x \quad 0 \quad 0$$

$$\text{after dissociation} \quad x \quad x$$



Connection of $\text{Cl}^- = 0.2$

$$\text{Total } [\text{Cl}^-] = x + 0.2$$

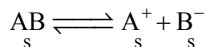
$$K_{sp}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-] = (x)(x + 0.2) = x^2 + 0.2x$$

$$\therefore K_{sp} \approx 0.2x \quad (\because x^2 \ll 0.2)$$

$$\therefore 1.2 \times 10^{-10} = 0.2x$$

$$\therefore x = 6 \times 10^{-10} \text{ M}$$

74. (c) Let binary electrolyte be AB



Hence, solubility product of AB

$$K_{sp} = [A^+][B^-]$$

$$S = [s.] [s] \Rightarrow s = S^{1/2}$$

75. (d) Total volume = 100 mL

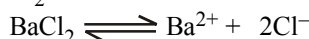
$$[\text{acid}] = 10 \text{ mL} \times \frac{1.0}{100} = 0.1$$

$$[\text{salt}] = 20 \text{ mL} \times \frac{0.5}{100} = 0.1$$

$$\text{pH of acidic buffer} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 4.76 + \log \frac{0.1}{0.1} = 4.76$$

76. (b) Let solubility of $\text{BaCl}_2 = x$ moles/L



No. of moles $x \quad x \quad 2x$

$$K_{sp} = [\text{Ba}^{2+}][\text{Cl}^-]^2$$

$$= (x) \times (2x)^2 = 4x^3$$

$$\therefore 4 \times 10^{-9} = 4x^3$$

$$\text{or, } x = \sqrt[3]{\frac{4 \times 10^{-9}}{4}} = 1 \times 10^{-3}$$

77. (a) $[\text{H}^+]$ of 100 ml solution which has $(\text{pH} = 1)$, $N_1 = 10^{-1}$

(From $C_{\text{H}^+} = 10^{-\text{pH}}$)

$[\text{H}^+]$ of 100 ml solution which has $(\text{pH} = 2)$ $N_2 = 10^{-2}$

$$N_1 V_1 + N_2 V_2 = N_s V_s$$

$$10^{-1} \times 100 + 10^{-2} \times 100$$

$$= N_s \times (100 + 100)$$

$$10 + 1 = 200 N_s \text{ or } \frac{11}{200} = N_s$$

$$\text{or } N_s = 5.5 \times 10^{-2}$$

Hence, the hydrogen ion concentration of the mixture solution is 5.5×10^{-2} .

78. (a) $A^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$

$$\begin{array}{cccc} 0.001 \text{ M} & 0 & 0 & (\text{At start}) \\ (0.001 - h) & (0.001 \times h) & (0.001 \times h) & (\text{At eq.}) \end{array}$$

$$K_h = \frac{(0.001 \times h)(0.001 \times h)}{(0.001 - h)}$$

$$\text{or, } K_h = 0.001 \times h^2 \text{ (as, } 0.001 - h \approx 0.001)$$

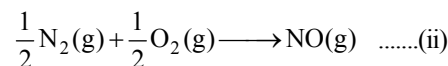
$$10^{-9} = 0.001 \times h^2 \quad \left(K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-5}} = 10^{-9} \right)$$

$$h^2 = 10^{-6} \quad \therefore h = 10^{-3}$$

79. (b) The dissociation of a weak electrolyte (AgCl) is suppressed on adding the strong electrolyte having a common ion (Cl^-), hence concentration of Ag^+ ion will be less.

80. (a) $2\text{NO}(\text{g}) \longrightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \quad \dots\dots(i)$

$$\text{Where, } K_c = 1.8 \times 10^2$$



For equation (i),

By Equilibrium's Law

$$\frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = K_c \quad \dots\dots(iii)$$

For equation (ii)

By Equilibrium's law

$$K'_c = \frac{[\text{NO}(\text{g})]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}}$$

On squaring,

$$(K'_c)^2 = \frac{[\text{NO}(\text{g})]^2}{[\text{N}_2][\text{O}_2]} \quad \dots\dots(iv)$$

From equation (iii) and (iv),

$$K_c \times (K'_c)^2 = 1$$

$$K'_c = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{1.8 \times 10^2}} = 7.6$$

81. (d) $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$

$$K_{sp} = s \times (2s)^2 = 4s^3$$

$$K_{sp} = 4 \times (2.3 \times 10^{-4})^3$$

$$= 4.9 \times 10^{-11} (\text{mol dm}^{-3})^3$$

82. (d) In case of alkaline earth hydroxides solubility increases on moving down the group.

$\text{Be}(\text{OH})_2$ has lowest solubility and hence lowest K_{sp} .

83. (c) Due to common ion effect addition of NH_4Cl in group (III) suppresses the ionisation of NH_4OH with the result concentration of OH^- decreases.

84. (d) Buffering action is maximum when

$$[\text{Salt}] = [\text{Acid}]$$

$$\text{i.e., } \text{pH} = \text{p}K_a$$

85. (c) Hydrolysis of a salt is reverse reaction of acid base neutralization reaction.

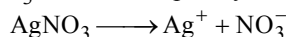
$$\therefore K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-7}} = 10^{-7}$$

$$[\text{OH}^-] = ch = c \times \sqrt{\frac{K_h}{c}} = \sqrt{c \times K_h} = \sqrt{10^{-8}} = 10^{-4}$$

$$\Rightarrow \text{pOH}^- = -\log [\text{OH}^-] \\ = -\log [10^{-4}] = 4$$

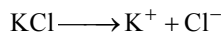
86. (c) Precipitation will occur when, ionic product $> K_{sp}$.
Among the given choices, the ionic product of 10^{-4} M AgNO_3 and 10^{-4} M KCl is 25×10^{-10} which exceeds the K_{sp} of AgCl which is shown below:

AgNO_3 ionizes completely in the solution as



$$[\text{Ag}^+] = [\text{AgNO}_3] = 10^{-4} \text{ M}$$

KCl ionizes completely in the solution of



$$\therefore [\text{Cl}^-] = [\text{KCl}] = 10^{-4} \text{ M}$$

Since equal volumes of two solutions are mixed together, therefore, the concentration of Ag^+ ions and Cl^- ions after mixing will be

$$[\text{Ag}^+] = \frac{10^{-4}}{2} \text{ M}$$

$$\text{and } [\text{Cl}^-] = \frac{10^{-4}}{2} \text{ M}$$

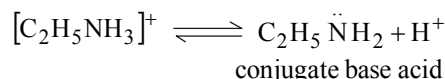
$$\therefore \text{Ionic product of AgCl} = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = 25 \times 10^{-10}$$

87. (c) Ba^{++} is common ion in the both solution. The solubility will depend on more reactive element.
Option (c) is correct.

88. (a) The pOH of a buffer consisting of NH_3 (i.e. NH_4OH) and salt NH_4Cl (salt) is given by the equation

$$\begin{aligned} \text{pOH} &= \text{p}K_b + \log \frac{[\text{ammonia}]}{[\text{salt}]} = 5.0 + \log \frac{[0.1]}{[1.0]} \\ &= 5.0 - \log 10 = 5 - 1 = 4.0 \\ \therefore \text{pH} &= 14 - \text{pOH} = 14 - 4.0 = 10 \end{aligned}$$

89. (a) $\text{C}_2\text{H}_5\ddot{\text{N}}\text{H}_2$ is conjugate base of $[\text{C}_2\text{H}_5\text{NH}_3]^+$
[Conjugate base - acid differ by one proton]



90. (a) Given $K_a = 1.00 \times 10^{-5}$, $c = 0.100$ mol
for a weak electrolyte,
degree of dissociation

$$(\alpha) = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1 \times 10^{-5}}{0.100}} = 10^{-2} = 1\%$$

91. (a) Given $[\text{H}_3\text{O}^+] = 1 \times 10^{-10}$ M
at 25° $[\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{10^{-10}} = 10^{-4}$$

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ &= -\log [10^{-4}] \\ &= 4 \end{aligned}$$

$$\therefore \text{pOH} = 4$$

92. (c) For this reaction K_{eq} is given by

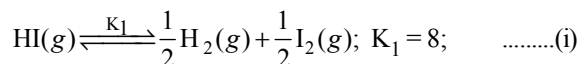
$$K = \frac{[\text{Fe}^{3+}][\text{OH}^-]^3}{[\text{Fe}(\text{OH})_3]}$$

$$= [\text{Fe}^{3+}][\text{OH}^-]^3 \quad [\therefore [\text{solid}] = 1]$$

If $[\text{OH}^-]$ is decreased by $\frac{1}{4}$ times then for reaction equilibrium constant to remain constant, we have to increase the concentration of $[\text{Fe}^{3+}]$ by a factor of 4^3 i.e. $4 \times 4 \times 4 = 64$. Thus option (c) is correct answer.

93. (b) The highest pH will be recorded by the most basic solution. The basic nature of hydroxides of alkaline earth metals increase as we move from Mg to Ba and thus the solution of BaCl_2 in water will be most basic and so it will have highest pH.

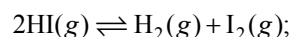
94. (b) Given: Equilibrium constant (K_1) for the reaction



To find equilibrium constant for the following reaction



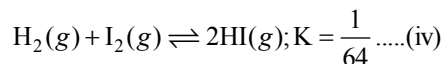
For this multiply (i) by 2, we get



$$K_1 = 8^2 = 64. \quad \text{.....(iii)}$$

[Note: When the equation for an equilibrium is multiplied by a factor, the equilibrium constant must be raised to the power equal to the factor]

Now reverse equation (iii), we get



[Note: For a reversible reaction, the equilibrium constant of the backward reaction is inverse of the equilibrium constant for the forward reaction.]

Equation (iv) is the same as the required equation (ii),

thus K_2 for equation (ii) is $\frac{1}{64}$ i.e. option (b) is correct.

95. (d) $(\text{CH}_3)_3\text{B}$ - is an electron deficient, thus behave as a Lewis acid.

96. (d) Ammonium chloride is a salt of weak base and strong acid. In this case hydrolysis constant K_h can be calculated as

$$K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.77 \times 10^{-5}} = 5.65 \times 10^{-10}$$

97. (d) $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$

$$\Delta n = 2 - 1 = +1$$

$\therefore K_c$ and K_p are not equal.

98. (d) $K_b = 10^{-10}$; $K_a = 10^{-4}$ or $\text{p}K_a = 4$

For the buffer solution containing equal concentration of B^- and HB

$$\text{pH} = \text{p}K_a + \log 1$$

$$\text{pH} = \text{p}K_a = 4$$

99. (c) Boron in B_2H_6 is electron deficient

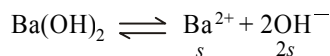
100. (c) BF_3 behaves as Lewis acid.

101. (b) Given $\text{pH} = 12$

$$\text{or } [\text{H}^+] = 10^{-12}$$

$$\text{Since, } [\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$



$$[\text{OH}^-] = 10^{-2}$$

$$2s = 10^{-2}$$

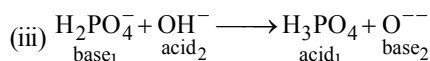
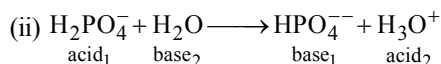
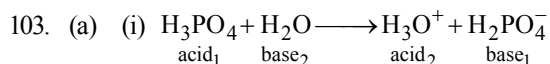
$$s = \frac{10^{-2}}{2}$$

$$K_{sp} = 4s^3$$

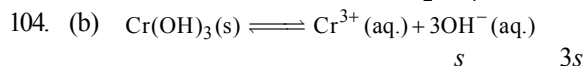
$$= 4 \times \left(\frac{10^{-2}}{2} \right)^3$$

$$= 5 \times 10^{-7}$$

102. (c) Reaction (c) can be obtained by adding reactions (a) and (b) therefore $K_3 = K_1 \cdot K_2$
Hence (c) is the correct answer.



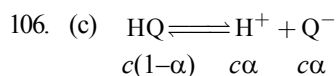
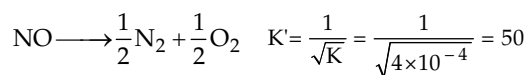
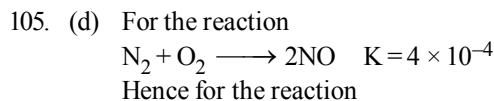
Hence only in (ii) reaction H_2PO_4^- is acting as an acid.



$$(s)(3s)^3 = K_{sp}$$

$$27s^4 = K_{sp}$$

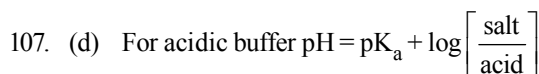
$$s = \left(\frac{K_{sp}}{27} \right)^{1/4} = \left(\frac{1.6 \times 10^{-30}}{27} \right)^{1/4}$$



$$[\text{H}^+] = c\alpha; \alpha = \frac{[\text{H}^+]}{c}$$

$$\text{or } \alpha = \frac{10^{-3}}{0.1} = 10^{-2}$$

$$K_a = c\alpha^2 = 0.1 \times 10^{-2} \times 10^{-2} = 10^{-5}$$



$$\text{or } \text{pH} = \text{pK}_a + \log \left[\frac{[\text{A}^-]}{[\text{HA}]} \right]$$

Given $\text{pK}_a = 4.5$ and acid is 50% ionised.

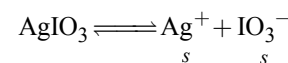
$[\text{HA}] = [\text{A}^-]$ (when acid is 50% ionised)

$$\therefore \text{pH} = \text{pK}_a + \log 1$$

$$\therefore \text{pH} = \text{pK}_a = 4.5$$

$$\text{pOH} = 14 - \text{pH} = 14 - 4.5 = 9.5$$

108. (c) Let s = solubility



$$K_{sp} = [\text{Ag}^+][\text{IO}_3^-] = s \times s = s^2$$

$$\text{Given } K_{sp} = 1 \times 10^{-8}$$

$$\therefore s = \sqrt{K_{sp}} = \sqrt{1 \times 10^{-8}}$$

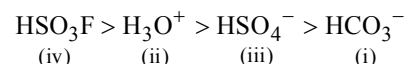
$$= 1.0 \times 10^{-4} \text{ mol/lit} = 1.0 \times 10^{-4} \times 283 \text{ g/lit}$$

($\because$ Molecular mass of $\text{AgIO}_3 = 283$)

$$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000} \text{ gm/100ml}$$

$$= 2.83 \times 10^{-3} \text{ gm/100 ml}$$

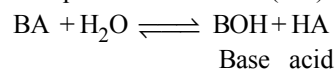
109. (c) The correct order of acidic strength of the given species



or (i) < (iii) < (ii) < (iv)

It corresponds to choice (c) which is correct answer.

110. (c) In aqueous solution BA (salt) hydrolyses to give

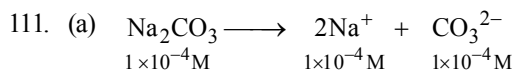


Now pH is given by

$$\text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$$

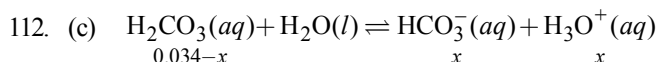
substituting given values, we get

$$\text{pH} = \frac{1}{2} (14 + 4.80 - 4.78) = 7.01$$



$$K_{sp}(\text{BaCO}_3) = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

$$[\text{Ba}^{2+}] = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}} = 5.1 \times 10^{-5} \text{ M}$$

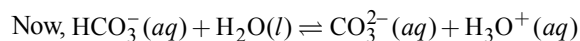


$$K_1 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = \frac{x \times x}{0.034 - x}$$

$$\Rightarrow 4.2 \times 10^{-7} \simeq \frac{x^2}{0.034} \Rightarrow x = 1.195 \times 10^{-4}$$

As H_2CO_3 is a weak acid so the concentration of H_2CO_3 will remain 0.034 as $0.034 \gg x$.

$$x = [\text{H}^+] = [\text{HCO}_3^-] = 1.195 \times 10^{-4}$$



As HCO_3^- is again a weak acid (weaker than H_2CO_3) with $x \gg y$.

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = \frac{y \times (x+y)}{(x-y)}$$

Note : $[\text{H}_3\text{O}^+] = \text{H}^+$ from first step (x) and from second step (y) $= (x+y)$

[As $x \gg y$ so $x+y \approx x$ and $x-y \approx x$]

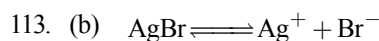
$$\text{So, } K_2 = \frac{y \times x}{x} = y$$

$$\Rightarrow K_2 = 4.8 \times 10^{-11} = y = [\text{CO}_3^{2-}]$$

So the concentration of $[\text{H}^+] \approx [\text{HCO}_3^-] =$ concentrations obtained from the first step. As the dissociation will be very low in second step so there will be no change in these concentrations.

Thus the final concentrations are

$$[\text{H}^+] = [\text{HCO}_3^-] = 1.195 \times 10^{-4} \text{ \& } [\text{CO}_3^{2-}] = 4.8 \times 10^{-11}$$



$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$

For precipitation to occur

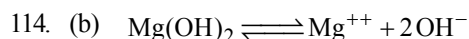
Ionic product > Solubility product

$$[\text{Br}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1 l AgNO_3 solution

$\therefore$ Number of moles of Br^- needed from KBr = 10^{-11}

$\therefore$ Mass of KBr = $10^{-11} \times 120 = 1.2 \times 10^{-9}$ g



$$K_{sp} = [\text{Mg}^{++}][\text{OH}^-]^2$$

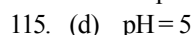
$$1.0 \times 10^{-11} = 10^{-3} \times [\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4}$$

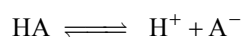
$$\therefore \text{pOH} = 4$$

$$\therefore \text{pH} + \text{pOH} = 14$$

$$\therefore \text{pH} = 10$$



$$\therefore [\text{H}^+] = 10^{-5}$$



$$t=0 \quad c \quad 0 \quad 0$$

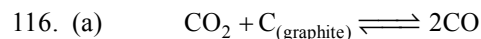
$$t_{\text{eq}} \quad c(1-\alpha) \quad c\alpha \quad c\alpha$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{[\text{H}^+]^2}{c - [\text{H}^+]}$$

$$(\text{As } [\text{H}^+]) = [\text{A}^-] = c\alpha$$

But, $[\text{H}^+] \ll c$

$$\therefore K_a = (10^{-5})^2 = 10^{-10}$$



$$P_{\text{initial}} \quad 0.5 \text{ atm} \quad 0$$

$$P_{\text{final}} \quad (0.5 - x) \text{ atm} \quad 2x \text{ atm}$$

$$\text{Total P at equilibrium} = 0.5 - x + 2x = 0.5 + x \text{ atm}$$

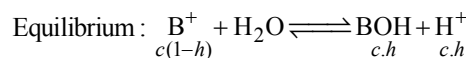
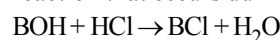
$$0.8 = 0.5 + x$$

$$\therefore x = 0.8 - 0.5 = 0.3 \text{ atm}$$

$$\text{Now } K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}}$$

$$= \frac{(2 \times 0.3)^2}{(0.5 - 0.3)} = \frac{(0.6)^2}{(0.2)} = 1.8 \text{ atm}$$

117. (d) Let the weak monoacidic base be BOH, then the reaction that occurs during titration is



Using the normality equation, $N_1 V_1 = N_2 V_2$
(acid) (base)

Substituting various given values, we get

$$\frac{2}{15} \times V_1 = 2.5 \times \frac{2}{5}$$

$$\text{or } V_1 = 2.5 \times \frac{2}{5} \times \frac{15}{2} = 2.5 \times 3 = 7.5 \text{ ml}$$

Then the concentration of BCl in resulting solution is given by

$$[\text{BCl}] = \frac{\frac{2}{5} \times 2.5}{10} = \frac{1}{10} \text{ or } 0.1 \text{ M}$$

$$[\text{Total volume} = 2.5 + 7.5 = 10 \text{ ml}]$$

$$\text{Since } K_h = \frac{K_w}{K_b}$$

$$\therefore K_h = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 10^{-2}$$

$$\text{Thus } K_h = \frac{0.1h^2}{(1-h)} \text{ or } 10^{-2} = \frac{0.1h^2}{(1-h)}$$

$$\text{or } 10^{-2} - 10^{-2}h = 0.1h^2$$

$$\text{or } 0.1h^2 + 10^{-2}h - 10^{-2} = 0$$

(Solving this quadratic equation for h, we get)

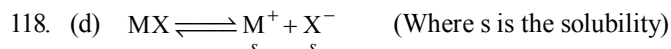
$$\text{Using } \left[x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \right]$$

$$h = \frac{-10^{-2} \pm \sqrt{(10^{-2})^2 + 4 \times 10^{-1} \times 10^{-2}}}{2 \times 0.1}$$

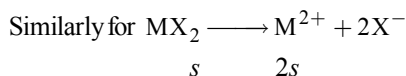
$$\begin{aligned}
 &= \frac{-10^{-2} \pm \sqrt{10^{-4} + 4 \times 10^{-3}}}{2 \times 0.1} \\
 &= \frac{-0.01 \pm \sqrt{0.001 + 0.004}}{0.2} \\
 &= \frac{-0.01 \pm \sqrt{0.0041}}{0.2} \\
 &= \frac{-0.01 \pm 0.064}{0.2} \\
 &= \frac{0.54}{0.2} \quad [\text{Neglecting the negative term}] \\
 &= 0.27
 \end{aligned}$$

$$\therefore [H^+] = c.h = 0.1 \times 0.27 = 2.7 \times 10^{-2} \text{ M}$$

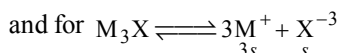
Thus the correct answer is [d].



$$\text{Then } K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$



$$K_{sp} = s \times (2s)^2 = 4s^3 \quad \text{or} \quad s = \left[\frac{K_{sp}}{4} \right]^{\frac{1}{3}}$$



$$K_{sp} = (3s)^3 \times s = 27s^4 \quad \text{or} \quad s = \left[\frac{K_{sp}}{27} \right]^{\frac{1}{4}}$$

From the given values of K_{sp} for MX , MX_2 and M_3X , we can find the solubilities of those salts at temperature, T.

$$\text{Solubility of } MX = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$$

$$\begin{aligned}
 \text{Solubility of } MX_2 &= \left[\frac{3.2 \times 10^{-14}}{4} \right]^{\frac{1}{3}} \quad \text{or} \quad \left[\frac{32}{4} \times 10^{-15} \right]^{\frac{1}{3}} \\
 &= \left[8 \times 10^{-15} \right]^{\frac{1}{3}} \quad \text{or} \quad 2 \times 10^{-5}
 \end{aligned}$$

$$\begin{aligned}
 \text{Solubility of } M_3X &= \left[\frac{2.7 \times 10^{-15}}{27} \right]^{\frac{1}{4}} \\
 &= \left[10^{-16} \right]^{\frac{1}{4}} \quad \text{or} \quad 10^{-4}
 \end{aligned}$$

Thus the solubilities are in the order $MX > M_3X > MX_2$ i.e. the correct answer is (d).

119. (d) $\therefore \text{pH} = 1$; $H^+ = 10^{-1} = 0.1 \text{ M}$
 $\text{pH} = 2$; $H^+ = 10^{-2} = 0.01 \text{ M}$
 $\therefore M_1 = 0.1 \quad V_1 = 1$
 $M_2 = 0.01 \quad V_2 = ?$

From

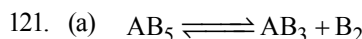
$$M_1 V_1 = M_2 V_2$$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10 \text{ litres}$$

$$\therefore \text{Volume of water added} = 10 - 1 = 9 \text{ litres}$$

120. (a) The reaction (b) is an endothermic reaction hence increase in temperature will favour the forward reaction i.e. formation of products. Further Reaction is occurring by decrease in volume, hence increase in pressure will favour the formation of product.



$$K_c = \frac{[AB_3][B_2]}{[AB_5]} = \frac{\frac{2}{10} \times \frac{5}{10}}{\frac{4}{10}} = \frac{10}{100} \times \frac{10}{4} = 0.25$$



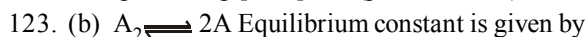
Using formula, $N_1 V_1 + N_2 V_2 = NV$

where $V = (V_1 + V_2)$

$$50 \times 0.01 + 5 \times 1 = N \times 55$$

$$N = \frac{0.5 + 5}{55} = 0.1$$

$$\text{pH} = -\log[10^{-1}] = 1 \quad (\text{pH decreased})$$



$$K_c = \frac{[A]^2}{[A_2]}$$

Since the value given is very small, hence conc. of products is less. It means the reaction is slow.

124. (d) No. of moles of NaOH = $\frac{4}{40} = 0.1$

[Molecular weight of NaOH = 40]

$$\text{No. of moles of } OH^- = 0.1$$

$$\text{Concentration of } OH^- = \frac{0.1}{1 \text{ litre}} = 0.1 \text{ Mole/L}$$

$$\text{As we know that, } [H^+][OH^-] = 10^{-14}$$

$$\therefore [H^+] = 10^{-13} \quad (\because OH^- = 10^{-1})$$

125. (d) $\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$

For small concentration of buffering agent and for maximum

$$\text{buffer capacity } \frac{[\text{salt}]}{[\text{acid}]} \cong 1$$

$$\therefore \text{pH} = \text{pK}_a$$

EXERCISE - 2

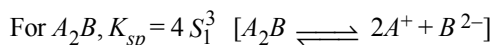
1. (c) $K_p = P_{B(1)}^2 P_{C(1)}^3 = P_{B(2)}^2 P_{C(2)}^3 = P_{B(2)}^2 (2P_{C(1)})^3$;

$$\text{hence } \frac{P_{B(2)}^2}{P_{B(1)}^2} = \frac{1}{8}, \text{ Br } \frac{P_{B(2)}}{P_{B(1)}} = \frac{1}{2\sqrt{2}}$$

2. (b) For weak acids, $K_a = \alpha^2$ or $\alpha = [K_a]^{1/2}$
 $\therefore$ ratio of relative strengths of two acids is

$$\frac{\alpha_1}{\alpha_2} = \left(\frac{K_1}{K_2} \right)^{1/2}$$

3. (c) Since for sparingly soluble salts, solubility (s) will be less than one. Therefore as the powers of s increases in K_{sp} expression, magnitude of K_{sp} will become smaller.
 4. (b) If the solubilities are S_1, S_2, S_3 respectively, then the K_{sp} values for them are.



Since the value of K_{sp} is same
 $\therefore$ The correct order of solubilities

is $AB > A_2B > AB_3$.

5. (c) $K_{sp}(\text{AgBr}) < K_{sp}(\text{AgCl})$
 Therefore, AgBr will precipitate first and at that time all Cl^- will be present.

6. (b) $K_p = (P_{\text{H}_2\text{O}})^2$

$$P_{\text{H}_2\text{O}} (\text{at equilibrium}) = \sqrt{K_p} = 10^{-2}$$

Forward reaction will occur if value of $P_{\text{H}_2\text{O}}$ is less than 10^{-2} .

7. (c) $K_a \times K_b = K_w$

$$\therefore K_a \text{ for HX} = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

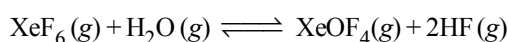
$$\text{p}K_a = 9$$

$$\text{pH} = \text{p}K_a + \log \frac{[X^-]}{[\text{HX}]}$$

$$\text{pH} = 9 + \log \frac{0.1}{0.3} = 9 - \log 3$$

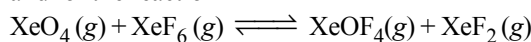
8. (d) When volume is increased the conc. decreases & the equilibrium shifts in the direction where more moles are formed.

9. (d) For the reaction



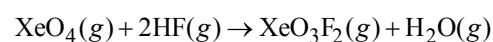
$$K_1 = \frac{[\text{XeOF}_4][\text{HF}]^2}{[\text{XeF}_6][\text{H}_2\text{O}]} \quad \dots(i)$$

and for the reaction



$$K_2 = \frac{[\text{XeOF}_4][\text{XeO}_3\text{F}_2]}{[\text{XeO}_4][\text{XeF}_6]} \quad \dots(ii)$$

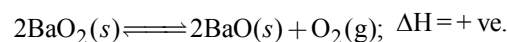
For reaction :



$$K = \frac{[\text{XeO}_3\text{F}_2][\text{H}_2\text{O}]}{[\text{XeO}_4][\text{HF}]^2}$$

$\therefore$ From eq. no. (i) and (ii) $K = K_2 / K_1$

10. (c) For the reaction



In equilibrium $k_p = P_{\text{O}_2}$

Hence, the value of equilibrium constant depends only upon partial pressure of O_2 . Further on increasing temperature formation of O_2 increases as this is an endothermic reaction. Hence, pressure of O_2 is dependent on temperature.

11. (d) For the reaction:- $2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$

Given $K_c = 1.8 \times 10^{-6}$ at 184°C

$$R = 0.0831 \text{ kJ/mol.k}$$

$$K_p = K_c (RT)^{\Delta n_g}$$

$$K_p = 1.8 \times 10^{-6} \times 0.0831 \times 457 = 6.836 \times 10^{-5}$$

$$[\because 184^\circ\text{C} = (273 + 184) = 457 \text{ K}, \Delta n = (2 + 1, -1) = 1]$$

Hence it is clear that $K_p > K_c$

12. (a) $\frac{[B]}{[A]} = 2, \frac{[C]}{[B]} = 4$ and $\left[\frac{D}{C} \right] = 6$

Multiply the three equations,

$$2 \times 4 \times 6 = \frac{[D]}{[A]} = K_c$$

13. (a) $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
 start 0.5 atm 0 atm
 At equilib. 0.5 + x atm x atm

Then $0.5 + x + x = 2x + 0.5 = 0.84$ (given)

$$\Rightarrow x = 0.17 \text{ atm.}$$

$$P_{\text{NH}_3} = 0.5 + 0.17 = 0.67 \text{ atm}; \quad P_{\text{H}_2\text{S}} = 0.17 \text{ atm}$$

$$K = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = 0.67 \times 0.17 \text{ atm}^2 = 0.1139 = 0.11$$

14. (d) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

$$\Delta n = 2 - 4 = -2 \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}},$$

(R in L.atm.K⁻¹ mole⁻¹).

15. (c) 1 N NaOH = 1 M NaOH.

$$\therefore [\text{OH}^-] = 10^0; [\text{H}^+] = 10^{-14}; \text{pH} = 14.66. \text{ (c)}$$

1 N NaOH = 1 M NaOH.

$$\therefore [\text{OH}^-] = 10^0; [\text{H}^+] = 10^{-14}; \text{pH} = 14.$$

16. (d) $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

For small concentration of buffering agent and for

$$\text{maximum buffer capacity } \frac{[\text{salt}]}{[\text{acid}]} \cong 1$$

$$\therefore \text{pH} = \text{pK}_a$$

$$\therefore \text{pK}_a = 3.58, \text{ thus at this state } \text{pH} = 3.58$$

17. (a) A B C

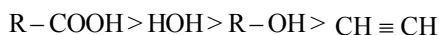
$$\text{K}_a \quad 10^{-4} \quad 10^{-6} \quad 10^{-10}$$

The higher the value of K_a , the stronger the acid and the lower is pH. Hence order of $\text{pH} \text{ A} < \text{B} < \text{C}$.

18. (c) Strong base has higher tendency to accept the proton. Increasing order of base and hence the order of

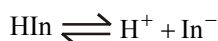
accepting tendency is $\text{I}^- < \text{HS}^- < \text{NH}_3 < \text{RNH}_2$

19. (c) The higher is the tendency to donate proton, stronger is the acid. Thus the correct order is



depending upon the rate of donation of proton.

20. (d) For an acid-base indicator



$$\therefore \text{K}_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \text{ or } [\text{H}^+] = \text{K}_{\text{In}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\text{or } \log \text{H}^+ = \log \text{K}_{\text{In}} + \log \frac{[\text{HIn}]}{[\text{In}^-]}$$

Taking negative on both sides

$$-\log[\text{H}^+] = -\log \text{K}_{\text{In}} - \log \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\text{or we can write } \text{pH} = \text{pK}_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\text{or } \log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} - \text{pK}_{\text{In}}$$

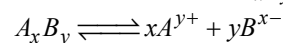
21. (a) The solution formed from isomolar solutions of sodium oxide, sodium sulphide, sodium selenide are H_2O , H_2S , H_2Se & H_2Te respectively. As the acidic strength increases from H_2O to H_2Te thus pH decreases and hence the correct order of pHs is

$$\text{pH}_1 > \text{pH}_2 > \text{pH}_3 > \text{pH}_4$$

22. (c) $\text{pH} = 8$, $\text{pOH} = 6$; $[\text{OH}^-] = 10^{-6} \text{ M}$;

$$\begin{aligned} \text{Ionic product of } \text{Fe}(\text{OH})_2 &= 0.2 \times (1 \times 10^{-6})^2 \\ &= 2 \times 10^{-13} > \text{K}_{\text{sp}} (= 8.1 \times 10^{-16}) \end{aligned}$$

23. (c) The weak electrolyte A_xB_y dissociates as follows



c	0	0	initially
$c(1-\alpha)$	$x\alpha$	$y\alpha$	at equilibrium

where, a = degree of dissociation
 c = concentration

$$\text{K}_{\text{eq}} = \frac{[\text{A}^{y+}]^x [\text{B}^{x-}]^y}{[\text{A}_x\text{B}_y]} = \frac{[x\alpha c]^x [y\alpha c]^y}{c(1-\alpha)}$$

$$= \frac{x^x \cdot c^x \cdot \alpha^x \cdot y^y \cdot c^y \cdot \alpha^y}{c} \quad [\because 1-\alpha \approx 1]$$

$$= x^x \cdot y^y \cdot \alpha^{x+y} \cdot c^{x+y-1}$$

$$\alpha^{x+y} = \frac{\text{K}_{\text{eq}}}{x^x \cdot y^y \cdot c^{x+y-1}}$$

$$\alpha = \left(\frac{\text{K}_{\text{eq}}}{x^x \cdot y^y \cdot c^{x+y-1}} \right)^{\left(\frac{1}{x+y} \right)}$$

24. (b) $\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pK}_a$;

$$\Rightarrow \text{at } 50^\circ\text{C } \text{pK}_a < 4.74$$

25. (a) $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$\text{K}_c = \frac{c\alpha^2}{(1-\alpha)}$$

α will increase with dilution

26. (c) $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$; $\text{K}_1 = 4 \times 10^{30}$... (Given)

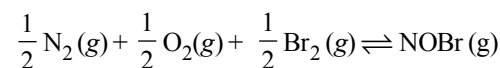
$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}); \text{K}' = \frac{1}{\text{K}_1} = \frac{1}{4 \times 10^{30}} \quad \dots (i)$$

Divide (i) by 2, we get

$$(ii) \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}); \text{K}'' = \sqrt{\text{K}'} = \frac{1}{2 \times 10^{15}}$$

$$(iii) \text{NO}(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g}); \text{K}_2 = 1.4 \text{ mol}^{-1/2} \text{ L}^{1/2} \quad \dots (\text{Given})$$

On adding (ii) and (iii)



$$\text{K} = \text{K}'' \times \text{K}_2 = \frac{1.4}{2 \times 10^{15}} = 7.0 \times 10^{-16}$$

27. (b) KOH , being strong electrolyte, ionizes completely.

$$\text{Hence } [\text{OH}^-] = 0.01 \text{ M}$$

which remains constant, even at 50°C (volume of solution is supposed to be constant). Hence, $\text{pOH} (= -\log 0.01 = 2)$ remains constant. At 50°C $\text{pK}_w < 14$. Hence pH at $50^\circ\text{C} = (\text{pK}_w - 2) < 12$.

28. (c) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$\text{K} = \text{P}_{\text{CO}_2} = 1 \text{ atm (given)}$$

$$\therefore \text{By } \ln \text{K}_p = 7 - \frac{8400}{\text{T}} \Rightarrow 0 = 7 - \frac{8400}{\text{T}} \quad [\ln 1 = 0]$$

$$\Rightarrow \text{T} = \frac{8400}{7} = 1200 \text{ K} = (1200 - 273) = 927^\circ\text{C}$$

29. (b) $\text{pH} = 2$; $r_1 = k \times (10^{-2})^n$ { $[\text{H}^+] = 10^{-\text{pH}}$ }
 $\text{pH} = 1$; $r_2 = k \times (10^{-1})^n$

$$\text{Given : } r_2 = 100 r_1 \Rightarrow \left(\frac{10^{-1}}{10^{-2}} \right)^n = 100 ; 10^n = 100$$

$$\therefore n = 2$$

30. (c) Milli moles of HCl = $75 \times 0.2 = 15$;
 Milli moles of NaOH = $25 \times 0.2 = 5$
 Milli moles of HCl left un-neutralized = $15 - 5 = 10$;

$$[\text{H}_3\text{O}^+] = \frac{10}{75 + 25} = 0.1 \text{ M} ; \text{pH} = 1$$

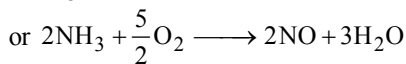
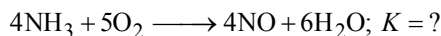
31. (a) $[\text{H}^+] = [\text{OH}^-] = \sqrt{40 \times 10^{-14}} = 2.0 \times 10^{-7}$

$$\text{pH} = \text{pOH} = -\log 2 \times 10^{-7} = 6.699$$

32. (b) $K_{sp}[\text{Ca}(\text{OH})_2] = 4.0 \times 10^{-6} = [\text{Ca}^{2+}][\text{OH}^-]^2$
 $= 0.01 \times [\text{OH}^-]^2 \Rightarrow [\text{OH}^-] = 2 \times 10^{-2}$;
 $\text{pOH} = -\log 2 \times 10^{-2} = 2 - \log 2$; $\text{pH} = 14 - (2 - \log 2)$
 $= 12 + 2 \log 2$

33. (d) Given,
 $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$; K_1 (i)
 $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$; K_2 (ii)
 $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$; K_3 (iii)

We have to calculate



$$\text{For this equation, } K = \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}}$$

$$\text{but } K_1 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}, K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$\& K_3 = \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]^{1/2}} \text{ or } K_3^3 = \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3 [\text{O}_2]^{3/2}}$$

$$\begin{aligned} \text{Now operate, } & \frac{K_2 \cdot K_3^3}{K_1} \\ &= \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3 [\text{O}_2]^{3/2}} \cdot \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} \\ &= \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}} = K \end{aligned}$$

$$\therefore K = \frac{K_2 \cdot K_3^3}{K_1}$$

34. (b) $[\text{H}_3\text{O}^+]$ for a solution having $\text{pH} = 3$ is given by
 $[\text{H}_3\text{O}^+] = 1 \times 10^{-3}$ moles/litre
 $[\therefore [\text{H}_3\text{O}^+] = 10^{-\text{pH}}]$
 Similarly for solution having $\text{pH} = 4$,
 $[\text{H}_3\text{O}^+] = 1 \times 10^{-4}$ moles/litre and for $\text{pH} = 5$
 $[\text{H}_3\text{O}^+] = 1 \times 10^{-5}$ moles/litre
 Let the volume of each solution in mixture be 1L , then
 total volume of mixture solution $L = (1 + 1 + 1) \text{ L}$
 $= 3\text{L}$

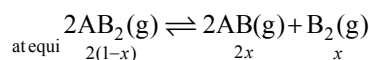
Total $[\text{H}_3\text{O}^+]$ ion present in mixture solution
 $= (10^{-3} + 10^{-4} + 10^{-5})$ moles

Then $[\text{H}_3\text{O}^+]$ ion concentration of mixture solution

$$= \frac{10^{-3} + 10^{-4} + 10^{-5}}{3} \text{ M} = \frac{0.00111}{3} \text{ M}$$

$$= 0.00037 \text{ M} = 3.7 \times 10^{-4} \text{ M}.$$

35. (b) For the reaction



$$K_c = \frac{[\text{AB}]^2 [\text{B}_2]}{[\text{AB}_2]^2} \text{ or } K_c = \frac{(2x)^2 \times x}{\{2(1-x)\}^2}$$

$$= x^3 [(1-x) \text{ can be neglected in denominator } (1-x) \approx 1]$$

The partial pressure at equilibrium are calculated on the basis of total number of moles at equilibrium.

$$\text{Total number of moles} = 2(1-x) + 2x + x = (2+x)$$

$$\therefore P_{\text{AB}_2} = \frac{2(1-x)}{(2+x)} \times P, \text{ where } P \text{ is the total pressure.}$$

$$P_{\text{AB}} = \frac{2x}{(2+x)} \times P, P_{\text{B}_2} = \frac{x}{(2+x)} \times P$$

Since x is very small so can be neglected in denominator

Thus, we get

$$P_{\text{AB}_2} = (1-x) \times P$$

$$P_{\text{AB}} = x \times P$$

$$P_{\text{B}_2} = \frac{x}{2} \times P$$

$$\text{Now, } K_p = \frac{(P_{\text{AB}})^2 (P_{\text{B}_2})}{(P_{\text{AB}_2})^2} = \frac{(x)^2 \times P^2 \cdot P \times \frac{x}{2}}{(1-x)^2 \times P^2}$$

$$= \frac{x^3 \cdot P^3}{2 \times 1 \times P^2} \quad [\therefore 1-x \approx 1]$$

$$= \frac{x^3 \cdot P}{2} \text{ or } x^3 = \frac{2 \cdot K_p}{P} \text{ or } x = \left(\frac{2K_p}{P} \right)^{\frac{1}{3}}$$

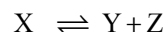
36. (c) Given reactions are



Let the total pressure for reaction (i) and (ii) be P_1 and P_2 respectively, then

$$\frac{K_{P_1}}{K_{P_2}} = \frac{9}{1} \quad (\text{given})$$

After dissociation,



At equilibrium $(1-\alpha) \quad \alpha \quad \alpha$

[Let 1 mole of X dissociate with α as degree of dissociation]

$$\begin{aligned} \text{Total number of moles} &= 1 - \alpha + \alpha + \alpha \\ &= (1 + \alpha) \end{aligned}$$

$$\text{Thus } P_X = \left(\frac{1-\alpha}{1+\alpha} \right) \cdot P_1; P_Y = \left(\frac{\alpha}{1+\alpha} \right) P_1;$$

$$P_Z = \left(\frac{\alpha}{1+\alpha} \right) P_1$$

$$\therefore K_{P_1} = \left(\frac{\alpha}{1+\alpha} \right) P_1 \times \frac{\alpha}{(1+\alpha)}$$

$$P_1 / \left(\frac{1-\alpha}{1+\alpha} \right) P_1 \dots\dots (i)$$

Similarly for $A \rightleftharpoons 2B$

At equilibrium $(1-\alpha) \quad 2\alpha$

We have,

$$K_{P_2} = \left(\frac{2\alpha P_2}{1+\alpha} \right)^2 / \left(\frac{1-\alpha}{1+\alpha} \right) P_2 \dots\dots (ii)$$

Dividing (i) by (ii), we get

$$\frac{K_{P_1}}{K_{P_2}} = \frac{\alpha^2 P_1}{4\alpha^2 P_2} \text{ or } \frac{K_{P_1}}{K_{P_2}} = \frac{1}{4} \cdot \frac{P_1}{P_2}$$

$$\text{or } 9 = \frac{1}{4} \cdot \frac{P_1}{P_2} \left[\therefore \frac{K_{P_1}}{K_{P_2}} = \frac{9}{1} \right]$$

$$\text{or } \frac{P_1}{P_2} = \frac{36}{1} \text{ or } P_1 : P_2 = 36 : 1$$

i.e. option (c) is correct answer.

37. (c) Given, $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$;

$$K_{a_1} = 1.5 \times 10^{-5} \dots\dots (i)$$

$$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-; K_{a_2} = 4.5 \times 10^{-10}$$

or $\text{H}^+ + \text{CN}^- \rightleftharpoons \text{HCN}$;

$$K'_{a_2} = \frac{1}{K_{a_2}} = \frac{1}{4.5 \times 10^{-10}} \dots\dots (ii)$$

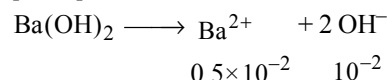
$\therefore$ From (i) and (ii), we find that the equilibrium constant (K_a) for the reaction,

$\text{CN}^- + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{HCN}$, is

$$K_a = K_{a_1} \times K'_{a_2} \\ = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} = \frac{1}{3} \times 10^5 = 3.33 \times 10^4$$

38. (d) $\text{Ba}(\text{OH})_2(\text{s}) \longrightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
pH = 12 or pOH = 2

$$[\text{OH}^-] = 10^{-2} \text{ M}$$



[$\therefore$ Concentration of Ba^{2+} is half of OH^-]

$$K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2 \\ = [0.5 \times 10^{-2}][1 \times 10^{-2}]^2 \\ = 0.5 \times 10^{-6} = 5 \times 10^{-7} \text{ M}^3$$

$$39. (d) \text{ pH} = pK_a + \log \left[\frac{\text{Salt}}{\text{Acid}} \right]$$

$$\log [\text{H}^+] = \log K_a - \log \left[\frac{\text{Salt}}{\text{Acid}} \right]$$

$$\log [\text{H}^+] = \log K_a + \log \left[\frac{\text{Acid}}{\text{Salt}} \right]$$

$$[\text{H}^+] = K_a \left[\frac{\text{Acid}}{\text{Salt}} \right]$$

$$= 1.8 \times 10^{-5} \times \frac{0.1}{0.2} = 9 \times 10^{-6} \text{ M}$$

$$40. (c) \quad 2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 3\text{C}(\text{g}) + \text{D}(\text{g})$$

$$\text{Mole ratio} \quad 2 \quad 1 \quad 3 \quad 1$$

$$\text{Molar concentration at } t = 0 \quad 1 \quad 1 \quad 0 \quad 0$$

$$\text{Equilibrium molar concentration} \quad 1-0.5 \quad 1-0.25 \quad 0.75 \quad 0.25 \\ = 0.50 \quad = 0.75$$

$$K_c = \frac{[\text{C}]^3[\text{D}]}{[\text{A}]^2[\text{B}]} = \frac{(0.75)^3(0.25)}{(0.50)^2(0.75)}$$

41. (b) Given $[\text{NH}_3] = 0.3 \text{ M}$, $[\text{NH}_4^+] = 0.2 \text{ M}$, $K_b = 1.8 \times 10^{-5}$.

$$\text{pOH} = \text{p}K_b + \log \left[\frac{[\text{salt}]}{[\text{base}]} \right] \quad [\text{p}K_b = -\log K_b;$$

$$\text{p}K_b = -\log 1.8 \times 10^{-5}]$$

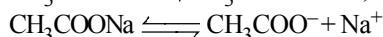
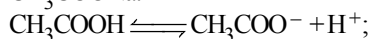
$$\therefore \text{p}K_b = 4.74$$

$$= 4.74 + \log \frac{0.2}{0.3} = 4.74 + 0.3010 - 0.4771 = 4.56$$

$$\text{pH} = 14 - 4.56 = 9.436$$

42. (c) $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$
 $1.8 \times 10^{-10} = [\text{Ag}^+][0.1]$
 $[\text{Ag}^+] = 1.8 \times 10^{-9} \text{ M}$
 $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$
 $1.7 \times 10^{-5} = [\text{Pb}^{2+}][0.1]^2$
 $[\text{Pb}^{2+}] = 1.7 \times 10^{-3} \text{ M}$

43. (a) Lets take an example of an acidic buffer CH_3COOH and CH_3COONa .

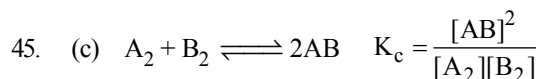


when few drops of HCl are added to this buffer, the H^+ of HCl immediately combine with CH_3COO^- ions to form undissociated acetic acid molecules. Thus there will be no appreciable change in its pH value. Like wise if few drops of NaOH are added, the OH^- ions will combine with H^+ ions to form unionised water molecule. Thus pH of solution will remain constant.

44. (c) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 \quad K = 278 \text{ (given)}$

$$\text{SO}_3 \rightleftharpoons \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad K' = \left(\sqrt{\frac{1}{K}} \right)$$

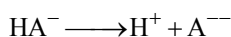
$$= \sqrt{\frac{1}{278}} = \sqrt{35.97 \times 10^{-4}} = 6 \times 10^{-2}$$



$$K_c = \frac{(2.8 \times 10^{-3})^2}{3 \times 10^{-3} \times 4.2 \times 10^{-3}} = \frac{(2.8)^2}{3 \times 4.2} = 0.62$$



$$\therefore K_1 = 1.0 \times 10^{-5} = \frac{[H^+][HA^-]}{[H_2A]} \text{ (Given)}$$



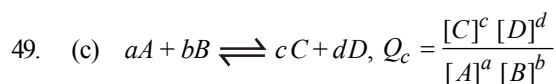
$$\therefore K_2 = 5.0 \times 10^{-10} = \frac{[H^+][A^{2-}]}{[HA^-]} \text{ (Given)}$$

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2$$

$$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$$

47. (a) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

48. (a) The size of $[Al(H_2O)_6]^{3+}$ is smaller than $[Mg(H_2O)_6]^{2+}$. Also, the former possesses more effective nuclear charge and thus, attracts electron pair from donor more effectively. This gives rise to relatively strong acidic nature of $[Al(H_2O)_6]^{3+}$.



If $Q_c > K_c$, reaction will proceed in the direction of reactants

If $Q_c < K_c$, reaction will move in direction of products.

If $Q_c = K_c$, the reaction mixture is already at equilibrium.

50. (c) NaOH is a weaker base than KOH.

EXERCISE - 3

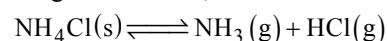
Exemplar Questions

1. (d) Relationship between K_c and K_p is given as :

$$K_p = K_c (RT)^{\Delta n}$$

where, $\Delta n = (\text{number of moles of gaseous products}) - (\text{number of moles of gaseous reactants})$

For given reaction,



$$\Delta n = 2 - 0 = 2$$

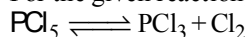
2. (d) The relationship between $\Delta G^\ominus$ and K is :

$$\Delta G^\ominus = -RT \ln K$$

When $G^\ominus > 0$ it implies $\Delta G^\ominus$ must be positive, which will be possible when K_c is negative i.e., $K_c < 1$.

3. (c) At the stage of equilibria physical processes does not stop but forward and reverse process occur at the same rate.

4. (b) For the given reaction,



At 500 K in a closed container,

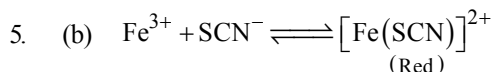
$$[PCl_5] = 0.8 \times 10^{-3} \text{ mol L}^{-1}$$

$$[PCl_3] = 1.2 \times 10^{-3} \text{ mol L}^{-1}$$

$$[Cl_2] = 1.2 \times 10^{-3} \text{ mol L}^{-1}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.2 \times 10^{-3}) \times (1.2 \times 10^{-3})}{(0.8 \times 10^{-3})}$$

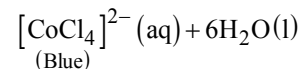
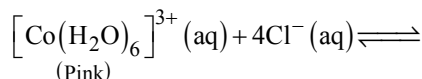
$$= 1.8 \times 10^{-3}$$



When oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate then, equilibrium shifts towards backward direction and intensity of red colour decreases.

Oxalic acid reacts with Fe^{3+} ions to form a stable complex ion $[Fe(C_2O_4)_3]^{3-}$. Thus, decreasing the concentration of Fe^{3+} ions.

6. (a) For the given reaction,



Equilibrium shifts to backward direction on cooling where as on heating, it shifts to forward direction. Thus, reaction is endothermic i.e., $\Delta H > 0$.

7. (c) pH of neutral water at $25^\circ C = 7.0$

At $25^\circ C$, $[H^+] = [OH^-] = 10^{-7}$ and

$$K_w = [H^+] = [OH^-] = 10^{-14}$$

On heating, K_w increases, i.e., $[H^+][OH^-] > 10^{-14}$

$$\text{As } [H^+] = [OH^-]$$

$$\therefore [H^+]^2 > 10^{-14}$$

$$\text{or, } [H^+] > 10^{-7} \text{ M}$$

$$\therefore \text{pH} < 7$$

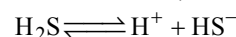
As temperature increases, pH of pure water decreases hence, it will become less than 7 at $60^\circ C$.

8. (d) With the increase in acidity or K_a value of the given acids pH decreases, hence the order of pH value of the acids will be :

hypochlorous acid < acetic acid < formic acid

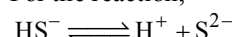
$$(3.8 \times 10^{-8}) \quad (1.74 \times 10^{-5}) \quad (1.8 \times 10^{-4})$$

9. (a) For the reaction,



$$K_{a1} = \frac{[H^+][HS^-]}{[H_2S]} \quad \dots (i)$$

For the reaction,

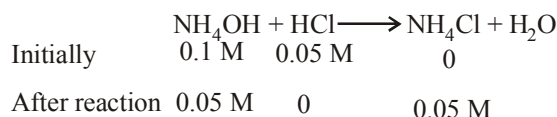


$$K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]} \quad \dots (ii)$$

$$K_{a_3} = \frac{[H^+]^2 [S^{2-}]}{[H_2S]} \quad \dots \text{ (iii)}$$

$$\text{Hence, } K_{a_3} = K_{a_1} \times K_{a_2}$$

10. (c) According to GN Lewis an acid is a species which accepts an electron pair and base which donates an electron pair. Since BF_3 is an electron deficient species, hence, it is a Lewis acid.
11. (c) When the concentration of weak base (NH_4OH) is higher than the strong acid (HCl) a mixture of weak base and its conjugate acid is obtained, which acts as basic buffer.



12. (d) $AgCl$, react with aqueous ammonia to form a complex, $[Ag(NH_3)_2]^+ Cl^-$.

13. (a) Given, $K_a = 1.74 \times 10^{-5}$
Concentration $CH_3COOH (C) = 0.01 \text{ mol dm}^{-3}$

$$\begin{aligned} [H^+] &= \sqrt{K_a \cdot C} \\ &= \sqrt{1.74 \times 10^{-5} \times 0.01} = 4.17 \times 10^{-4} \\ pH &= -\log [H^+] \\ &= -\log (4.17 \times 10^{-4}) = 3.4 \end{aligned}$$

14. (c) Given K_a for $CH_3COOH = 1.8 \times 10^{-5}$
 K_b for $NH_4OH = 1.8 \times 10^{-5}$.

Ammonium acetate is a salt of weak acid and weak base. For such salts

$$\begin{aligned} pH &= 7 + \frac{1}{2}(pK_a - pK_b) \\ &= 7 + \frac{[-\log 1.8 \times 10^{-5}] - [-\log 1.8 \times 10^{-5}]}{2} \\ &= 7 + \frac{4.74 - 4.74}{2} = 7.00 \end{aligned}$$

15. (a) $\Delta G^\ominus = -RT \ln K$
At the stage of half completion of the reaction,

$$[A] = [B]$$

$$\text{Therefore, } K = 1$$

As we know that

$$\begin{aligned} \Delta G^\ominus &= -RT \ln K \\ \therefore \Delta G^\ominus &= 0 \end{aligned}$$

16. (a) In the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
If the total pressure at which the equilibrium is established, is increased without changing the temperature, K will remain same but the equilibrium concentration will change.

17. (b) The order of boiling point of compounds given is

Water > acetone > ether

Lower the boiling point, higher is the vapour pressure of the solvent. Hence, the correct order of vapour pressure will be

Water < acetone < ether

18. For the reaction, $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g)$

$$K_c = \frac{[HI]}{[H_2]^{1/2} [I_2]^{1/2}} = 5$$

Thus, for the reaction,
 $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

$$K'_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K'_c = \left(\frac{1}{K_c}\right)^2 = \left(\frac{1}{5}\right)^2 = \frac{1}{25} = 0.04$$

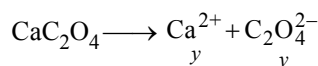
19. (d) Addition of inert gas at constant volume does not affect any equilibrium.

NEET/AIPMT (2013-2017) Questions

20. (c) Solubility of alkali metal is maximum among the following. Among $ZnS (1.7 \times 10^{-5})$ & $CuS (8 \times 10^{-37})$ ZnS has higher value of K_{sp} .

21. (b) BF_3 acts as Lewis acid.

22. (a) $CaCO_3 \longrightarrow Ca_x^{2+} + CO_3^{2-}_x$



$$\therefore [Ca^{2+}] = x + y$$

$$\text{Now, } K_{sp}(CaCO_3) = [Ca^{2+}][CO_3^{2-}]$$

$$\text{or } 4.7 \times 10^{-9} = (x + y)x$$

$$\text{similarly, } K_{sp}(CaC_2O_4) = [Ca^{2+}][C_2O_4^{2-}]$$

$$\text{or } 1.3 \times 10^{-9} = (x + y)y$$

On solving, we get

$$[Ca^{2+}] = 7.746 \times 10^{-5} \text{ M}$$

23. (a) K_w at $25^\circ\text{C} = 1 \times 10^{-14}$

At 25°C

$$K_w = [H^+][OH^-] = 10^{-14}$$

At 100°C (given)

$$K_w = [H^+][OH^-] = 55 \times 10^{-14}$$

$\therefore$ for a neutral solution

$$[H^+] = [OH^-]$$

$$\therefore [H^+]^2 = 55 \times 10^{-14}$$

$$\text{or } [H^+] = (55 \times 10^{-14})^{1/2}$$

$$\therefore pH = -\log [H^+]$$

On taking log on both side

$$-\log [H^+] = -\log (55 \times 10^{-14})^{1/2}$$

$$pH = \frac{1}{2} - \log 55 + 14 \log 10$$

$$pH = 6.13$$

24. (c) $pH = pK_a + \log \frac{[Salt]}{[Acid]}$

$$5 = 4 + \log \frac{[Salt]}{[Acid]} \quad [\because pK_a = -\log K_a]$$

$$\text{Given, } K_a = 1 \times 10^{-4}$$

$$\therefore pK_a = -\log (1 \times 10^{-4}) = 4$$

Now from Handerson equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Putting the values

$$5 = 4 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = 5 - 4 = 1$$

Taking antilog

$$[\text{Salt}]/[\text{Acid}] = 10 = 10 : 1$$

$$25. \quad (c) \quad \alpha = \sqrt{\frac{K_a}{c}} = 0.037 = \sqrt{\frac{K_a}{0.10}};$$

$$K_a = (0.037)^2 \times 0.10 = 1.37 \times 10^{-4} \\ \approx 1.4 \times 10^{-4}$$

26. (c) Na_2CO_3 is a salt of strong base (NaOH) and weak acid (H_2CO_3). On hydrolysis this salt will produce strongly basic solution. i.e. pH will be highest (pH > 7) for this solution. Others are combination of

KCl = Strong acid + Strong base

→ neutral solution (pH ≈ 7)

NaCl = Strong acid + Strong base

→ neutral solution (pH ≈ 7)

CuSO_4 = Strong acid + weak base

→ Acidic solution (pH < 7)

27. (b) $\Delta G = -2.303 \log K$

here $K = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = K_{sp}$

$$\therefore 63.3 \times 10^{-3} = -2.303 \times 8.314$$

$$\times 298 \log K_{sp}$$

$$\therefore \log K_{sp} = -\frac{63.3 \times 10^{-3}}{5705.8} = -11.09$$

$$\therefore K_{sp} = \text{Antilog}(-11.09) = 8 \times 10^{-12}$$

28. (d) Given reaction is exothermic reaction. Hence according to Le-Chatelier's principle low temperature favours the forward reaction and on increasing pressure equilibrium will shift, towards lesser number of moles i.e. forward direction.

29. (a) In exothermic reactions on increasing temperature value of K_p decreases

$$\therefore K_p > K_p' \quad (\text{Assuming } T_1 < T_2)$$

30. (c) Ag_2CrO_4

$$K_{sp} = [\text{Ag}^+]^2 [\text{Cr}_2\text{O}_4^{2-}] = 1.1 \times 10^{-12}$$

$$[\text{Ag}^+] = \sqrt{\frac{1.1 \times 10^{-12}}{[\text{Cr}_2\text{O}_4^{2-}]}}$$

AgCl

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{[\text{Cl}^-]}$$

AgBr

$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = 5.0 \times 10^{-13}$$

$$[\text{Ag}^+] = \frac{5.3 \times 10^{-13}}{[\text{Br}^-]}$$

AgI

$$K_{sp} = [\text{Ag}^+][\text{I}^-] = 8.3 \times 10^{-17}$$

$$[\text{Ag}^+] = \frac{8.3 \times 10^{-17}}{[\text{I}^-]}$$

If we take $[\text{Cr}_2\text{O}_4^{2-}] = [\text{Cl}^-] = [\text{Br}^-] = [\text{I}^-] = 1$

than maximum $[\text{Ag}^+]$ will be required in case of Ag_2CrO_4 .

31. (b) Equilibrium constant for reaction:

$$K = 1.6 \times 10^{12} = \frac{[\text{Product}]}{[\text{Reactant}]}$$

The value of K is very high so the system will contain mostly products at equilibrium.

32. (b) $\Delta G^\circ = -2.303RT \log K$

because at equilibrium $\Delta G = 0$

33. (a) Among the given acids, HClO_4 is a very strong acid, completely dissociates

$\therefore [\text{HA}] \rightarrow 0$ in this case, hence cannot be used for acidic buffer.

34. (a) gm eq of NaOH = $0.1 \times V = 0.1V$

$$\text{gm eq of HCl} = 0.01 \times V = 0.01V$$

$$\text{gm eq of NaOH} > \text{gm eq. HCl}$$

hence resultant solution should be basic, hence from the eqn

$$M_1V_1 - M_2V_2 = MV$$

$$0.1V - 0.01V = MV$$

$$M = \frac{0.09}{2} = 0.045 = 4.5 \times 10^{-2}$$

$$\text{Now pOH} = -\log [\text{OH}^-]$$

$$= -\log 4.5 \times 10^{-2} = 1.34$$

$$\therefore \text{pH} + \text{pOH} = 14$$

$$\therefore \text{pH} = 14 - 1.34 = 12.65$$

35. (a) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}$$

$$K' = \frac{[\text{NO}]}{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}} = K^{1/2}$$

36. (b) $\text{MY} \rightleftharpoons \text{M}^+ + \text{Y}^-$

$$K_{sp} = s^2 = 6.2 \times 10^{-13}$$

$$s = \sqrt{6.2 \times 10^{-13}}$$

$$s = 7.87 \times 10^{-7} \text{ mol L}^{-1}$$

$$\text{NY}_3 \rightleftharpoons \text{N}^{3+} + 3\text{Y}^-$$

$$K_{sp} = s \times (3s)^3 = 27s^4 = 6.2 \times 10^{-13}$$

$$s = \left(\frac{6.2 \times 10^{-13}}{27} \right)^{1/4}$$

$$s = 3.89 \times 10^{-4} \text{ mol L}^{-1}$$

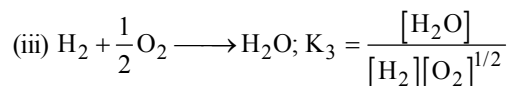
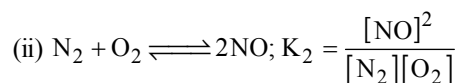
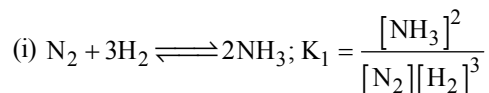
∴ molar solubility of NY_3 is more than MY in water.

37. (b) The presence of large amount of KHSO_4 will decrease ionisation of H_2SO_4 that result in lesser ionisation of nitric acid and lesser formation of nitronium ion $[\text{NO}_2^+]$. Hence the rate of nitration will be slower.

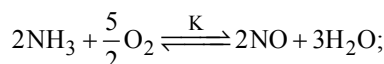
38. (d) Clausius – Clapeyron's equation

$$\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2}$$

39. (a)

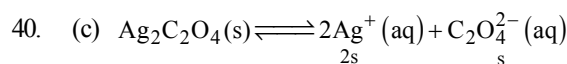


Applying $(\text{II} + 3 \times \text{III} - \text{I})$ we will get



$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3 \times [\text{O}_2]^{3/2}} \bigg/ \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$\therefore K = K_2 \times K_3^3 / K_1$$



$$K_{\text{SP}} = [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}]$$

$$[\text{Ag}^+] = 2.2 \times 10^{-4} \text{ M}$$

Given that:

∴ Concentration of $\text{C}_2\text{O}_4^{2-}$ ions,

$$[\text{C}_2\text{O}_4^{2-}] = \frac{2.2 \times 10^{-4}}{2} \text{ M}$$

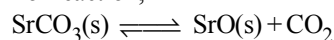
$$= 1.1 \times 10^{-4} \text{ M}$$

$$\therefore K_{\text{SP}} = (2.2 \times 10^{-4})^2 (1.1 \times 10^{-4})$$

$$= 5.324 \times 10^{-12}$$

41. (d) Max. pressure of CO_2 = Pressure of CO_2 at equilibrium

For reaction,



$$K_p = P_{\text{CO}_2} = 1.6 \text{ atm} = \text{maximum pressure of } \text{CO}_2$$

volume of container at this stage.

$$V = \frac{nRT}{P} \quad \dots(i)$$

Since container is sealed and reaction was not earlier at equilibrium.

∴ n = constant.

$$n = \frac{PV}{RT} = \frac{0.4 \times 20}{RT} \quad \dots(ii)$$

Put equation (ii) in equation (i)

$$V = \left[\frac{0.4 \times 20}{RT} \right] \frac{RT}{1.6} = 5 \text{ L}$$

Chapter

8

Redox Reactions

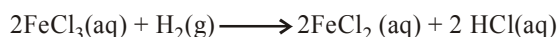
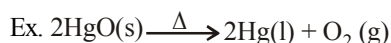
Many chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as oxidation-reduction or Redox reactions.

REDUCTION AND OXIDATION

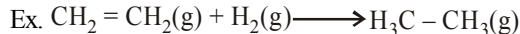
Reduction

Reduction is a process which involves

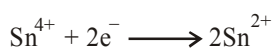
- (i) removal of O/electronegative element



- (ii) addition of H/electropositive element



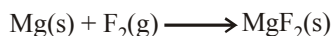
- (iii) involves gain of electrons by a species



Oxidation

Oxidation is a process which involve

- (i) addition of O/electronegative element



- (ii) removal of H/electropositive element



- (iii) involves loss of electrons by a species



OXIDANT AND REDUCTANT

Oxidising Agent or Oxidant : Acceptor of Electron(s)

Fluorine is the strongest oxidising agent.

Reducing agent or reductant: Donor of Electron(s)

In aq. solution, Li is the strongest reducing agent while in non aq. solution, Cs is the strongest reducing agent.

OXIDATION NUMBER

It is defined as the charge which an atom of the element has in its ion or appears to have when present in the combined state with other atoms

Oxidation number is also called oxidation state.

Rules for Assigning Oxidation Number

- The oxidation number of all the atoms of different elements in their respective elementary states and allotropic forms is taken to be zero. For ex: in N_2 , Cl_2 , H_2 , He, P_4 , S_8 , O_2 , O_3 , Br_2 , Na, Fe, Ag, etc. the oxidation number of each atom is zero.
- The O.N. of a monoatomic ion is the same as the charge on it. For ex: ON's of Na^+ , Mg^{2+} and Al^{3+} ions are +1, +2 and +3 while those of Cl^- , S^{2-} and N^{3-} ions are -1, -2 and -3.
- The O.N. of hydrogen is +1 when combined with non-metals and is -1 when combined with active metals called metal hydrides such as LiH , KH , MgH_2 , CaH_2 , etc.
- The O.N. of O is -2 in most of its compounds except in peroxides like H_2O_2 , BaO_2 etc. where it is -1 and in OF_2 and O_2F_2 where it is +2 and +1.
- The O.N. of alkali metals (Li, Na, K, etc.) is always +1 and that of alkaline earth metals (Be, Mg, Ca, etc.) is +2.
- In all its compounds, fluorine has an O.N. of -1. Other halogens (Cl, Br, I) also show O.N. of -1 when they occur as halide ions in their compounds.
- The algebraic sum of the O.N. of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the O.N.'s of atoms of the ion must equal the charge on the ion.
- O.N. of an atom may be fractional negative, zero as well as positive.

Applications of Oxidation Number

- (i) To compare the strength of acid and base :

Strength of acid $\propto$ Oxidation Number

Strength of base $\propto \frac{1}{\text{Oxidation number}}$

- (ii) To determine the oxidising and reducing nature :

Oxidising strength $\propto$ Oxidation number

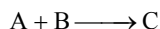
Reducing strength $\propto \frac{1}{\text{Oxidation number}}$

- (iii) To determine the molecular formula of compound

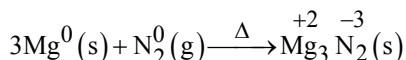
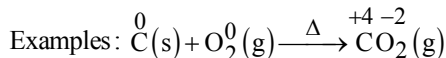
TYPES OF REDOX REACTIONS

Combination Reactions

It is denoted by

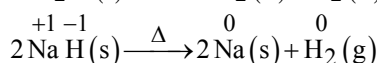
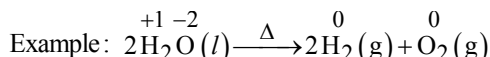


For such a reaction to be a redox reaction, either A or B or both A and B must be in the elemental form.



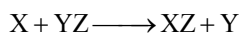
Decomposition Reactions

They are the opposite of combination reactions. It leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state.



Displacement Reactions

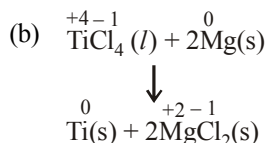
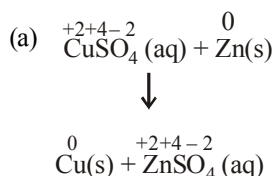
In these reactions an ion in a compound is replaced by an ion of another element, i.e.



Types of displacement reaction

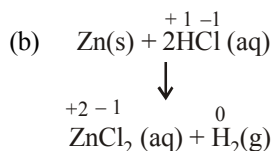
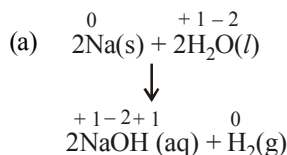
(i) Metal displacement

In these reactions, a metal in compound is displaced by some other metal in the elemental state. Examples :



(ii) Non-metal displacement

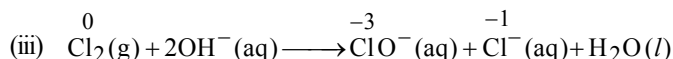
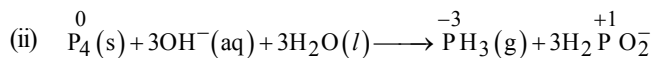
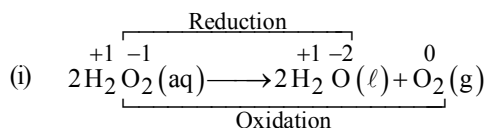
In these reactions, a metal or a non-metal displaces another non-metal from its compound.



Disproportionation Reactions

When reduction and oxidation takes place on same element of a compound, it is called disproportionation reaction.

Example :



BALANCING OF REDOX REACTIONS

There are two methods of balancing redox equations :

Oxidation Number Method

- Write the correct formula for each reactant and product.
- Identify atoms which undergo change in O.N. in the reaction by assigning O.N. to all elements in the reaction.
- Calculate the increase or decrease in O.N. per atom and for the entire molecule / ion in which it occurs. If these are not equal, then multiply by suitable coefficients so that these become equal.
- Add H^+ or OH^- ions on appropriate side of the reaction so that the total ionic charges of reactants and products are equal. In acidic solution, use H^+ ions and in basic solution, use OH^- ions.
- Make the number of H-atoms on the two sides equal by adding H_2O molecules to reactants or products.

Half Reaction Method

- Produce unbalanced equation for the reaction in ionic form.
- Separate the equation into two half reactions: oxidation half reaction and reduction half reaction.
- Balance the atoms other than O and H in each half reaction individually.
- For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms. For basic medium, OH^- ions equal in number of H^+ are added to both sides of balanced equation.
- Add e^- s to one side of half reaction to balance the charges.
- Add the two half reactions to achieve the overall reaction.
- Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation.

ELECTRODE POTENTIAL

The potential of any electrode is the potential difference between it and the electrolyte surrounding the electrode. When the ions are at unit activity and the temperature is 25°C (298K), the potential difference is called a standard electrode potential (E°)

Important Informations from Standard Reduction Potentials

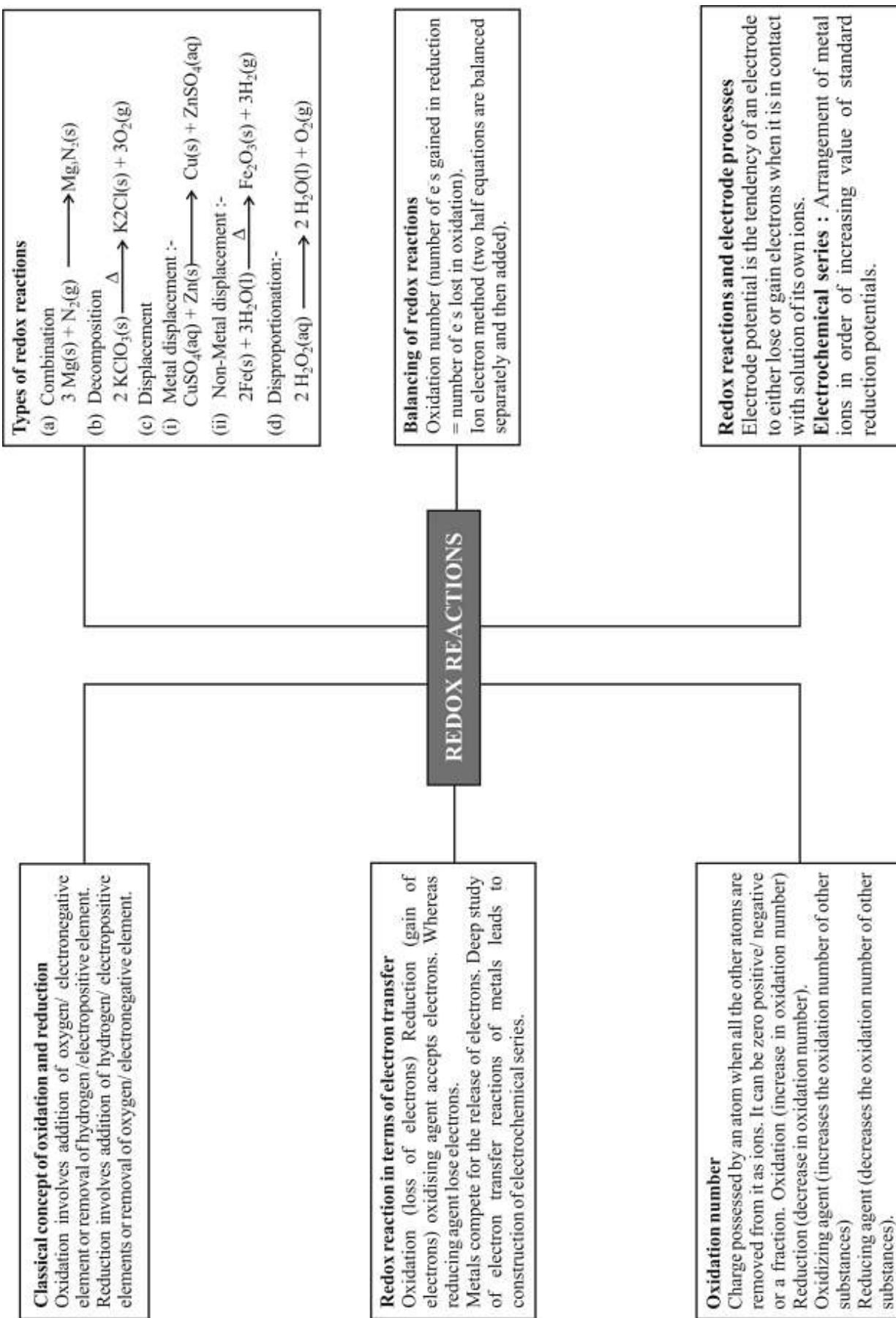
- It predicts relative reducing strength of reducing agents. Higher the standard reduction potential of a species, lesser will be its reducing strength.
- Lesser the standard reduction potential of an element (metal), greater will be its activity.
- Metal having positive value of E° oxide or negative value of E° red. (above H_2 in the activity series) will displace hydrogen from hydra acids and they themselves will be oxidised.
- An oxidising agent with a higher reduction potential will oxidise any reducing agent with a lower reduction potential.
- A reducing agent with a lower reduction potential will reduce any oxidising agent with a higher reduction potential

ELECTROCHEMICAL SERIES

The arrangement of various elements in order of increasing values of standard reduction potential is called electrochemical series. Standard reduction potentials at 298 K (Electrochemical Series)

TABLE		
Element	Electrode Reduction Reaction	Standard Reduction Potential E° (in Volt)
Li	$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	- 3.05
K	$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	- 2.93
Ba	$\text{Ba}^{2+} + 2\text{e}^- \longrightarrow \text{Ba}$	- 2.90
Ca	$\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$	- 2.87
Na	$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	- 2.71
Mg	$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	- 2.37
Al	$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	- 1.66
Mn	$\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$	- 1.18
Zn	$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	- 0.76
Cr	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	- 0.74
Fe	$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	- 0.44
Cd	$\text{Cd}^{2+} + 2\text{e}^- \longrightarrow \text{Cd}$	- 0.40
Ni	$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	- 0.25
Sn	$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	- 0.14
Pb	$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	- 0.13
H_2	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	0.34
I_2	$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	0.53
Hg	$\text{Hg}_2^{+2} + 2\text{e}^- \longrightarrow 2\text{Hg}$	0.79
Ag	$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	0.80
Hg	$\text{Hg}^{+2} + 2\text{e}^- \longrightarrow \text{Hg}$	0.85
Br_2	$\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$	1.08
Cl_2	$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	1.36
Au	$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	1.50
F_2	$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	2.87

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- Which of the following involves transfer of five electrons ?
 (a) $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ (b) $\text{CrO}_4^{2-} \rightarrow \text{Cr}^{3+}$
 (c) $\text{MnO}_4^{2-} \rightarrow \text{MnO}_2$ (d) $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$
- The standard reduction potential of Li^+/Li , Ba^{2+}/Ba , Na^+/Na and Mg^{2+}/Mg are -3.05 , -2.73 , -2.71 and -2.37 volts respectively. Which one of the following is strongest oxidising agent?
 (a) Li^+ (b) Na^+
 (c) Mg^{2+} (d) Ba^{2+}
- Which reaction involves neither oxidation nor reduction?
 (a) $\text{CrO}_4^{2-} \longrightarrow \text{Cr}_2\text{O}_7^{2-}$ (b) $\text{Cr} \longrightarrow \text{CrCl}_3$
 (c) $\text{Na} \longrightarrow \text{Na}^+$ (d) $2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-}$
- In the following reaction

$$4\text{P} + 3\text{KOH} + 3\text{H}_2\text{O} \longrightarrow 3\text{KH}_2\text{PO}_2 + \text{PH}_3$$
 (a) phosphorus is both oxidised and reduced.
 (b) only phosphorus is reduced.
 (c) phosphorus is not oxidised
 (d) None of these
- H_2S acts only as a reducing agent while SO_2 can act both as a reducing and oxidizing agent because
 (a) oxygen is more $-ve$ in SO_2
 (b) hydrogen in H_2S is more $+ve$ than oxygen
 (c) S in SO_2 has one oxidation state
 (d) S in H_2S has -2 oxidation state
- In the reaction

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2$$
 Which element is reduced
 (a) I (b) O
 (c) H (d) Cr
- Which one of the following reaction involves oxidation-reduction ?
 (a) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$
 (b) $\text{NaBr} + \text{HCl} \rightarrow \text{NaCl} + \text{HBr}$
 (c) $\text{HBr} + \text{AgNO}_3 \rightarrow \text{AgBr} + \text{HNO}_3$
 (d) $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
- The standard reduction potentials of some electrodes are $E^\circ(\text{K}^+, \text{K}) = -2.9 \text{ V}$; $E^\circ(\text{Zn}^{2+}, \text{Zn}) = -0.76 \text{ V}$

$$E^\circ\left(\text{H}^+, \frac{1}{2}\text{H}_2\right) = -0.0;$$

$$E^\circ(\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V}$$
 The electrode acting as strong reductant is
 (a) K (b) Cu
 (c) Zn (d) H_2
- In the reaction $\text{H}_2\text{S} + \text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{NO} + \text{S}$, H_2S is
 (a) oxidised (b) reduced
 (c) precipitated (d) None of these
- The oxidation number of C in CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 is respectively –
 (a) $+4, -2, 0, +2, +4$
 (b) $+2, 4, 0, -2, -4$
 (c) $4, 2, 0, -2, -4$
 (d) $0, 2, -2, 4, 4$
- In the reaction $3\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$
 (a) magnesium is reduced (b) magnesium is oxidized
 (c) nitrogen is oxidized (d) None of these
- The element that is easiest to be reduced:
 (a) Ag (b) Fe
 (c) Cu (d) Sn
- The conversion of sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow \text{CO}_2$ is
 (a) oxidation
 (b) reduction
 (c) Both oxidation and reduction
 (d) Neither oxidation nor reduction
- When Sn^{2+} changes to Sn^{4+} in a reaction
 (a) It loses two electrons (b) It gains two electrons
 (c) It loses two protons (d) It gains two protons
- Oxidation number of N in HNO_3 is :
 (a) -3.5 (b) $+3.5$
 (c) -5 (d) $+5$
- Which of the following cannot act as reducing agent?
 (a) NO_2 (b) SO_2
 (c) CO_2 (d) ClO_2
- Phosphorus has the oxidation state of $+3$ in
 (a) phosphorous acid (b) orthophosphoric acid
 (c) hypophosphorous acid (d) metaphosphoric acid.
- In which of the following reactions, there is no change in valency ?
 (a) $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
 (b) $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$
 (c) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
 (d) $3\text{BaO} + \text{O}_2 \longrightarrow 2\text{BaO}_2$
- Which will reduce zinc oxide to zinc ?
 (a) Mg (b) Pb
 (c) Cu (d) Fe
- The oxidation number of chromium in potassium dichromate is
 (a) $+6$ (b) -5
 (c) -2 (d) $+2$

21. The metal that does not displace hydrogen from an acid is :
 (a) Ca (b) Al
 (c) Zn (d) Hg
22. A compound contains atoms of three elements A, B and C. If the oxidation number of A is +2, B is +5, and that of C is -2, the possible formula of the compound is :
 (a) $A_2(BC_3)_2$ (b) $A_3(BC_4)_2$
 (c) $A_3(B_4C)_2$ (d) ABC_2
23. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)]SO_4$. The oxidation state of iron is :
 (a) 1 (b) 2
 (c) 3 (d) 0
24. The reaction
 $Ag_{(aq)}^{2+} + Ag_{(s)} \rightleftharpoons 2Ag_{(aq)}^+$
 is an example of :
 (a) reduction (b) oxidation
 (c) disproportionation (d) none of these
25. The oxidation number of sulphur in S_8 , S_2F_2 , H_2S respectively, are
 (a) 0, +1 and -2 (b) +2, +1 and -2
 (c) 0, +1 and +2 (d) -2, +1 and -2
26. What is the oxidation state of P in $Ba(H_2PO_2)_2$?
 (a) +1 (b) +2
 (c) +3 (d) -1
27. Oxidation number of nitrogen in $(NH_4)_2SO_4$ is
 (a) -1/3 (b) -1
 (c) +1 (d) -3
28. Oxidation numbers of chlorine atoms in $CaOCl_2$ are
 (a) 0, 0 (b) -1, -1
 (c) -1, +1 (d) None of these
29. The oxidation number of nitrogen in $(N_2H_5)^+$ is :
 (a) +2 (b) -2
 (c) +3 (d) -3
30. The oxidation number of sulphur in $Na_2S_4O_6$ is
 (a) 1.5 (b) 2.5
 (c) 3 (d) 2
31. $H_2C_2O_4 + KMnO_4$ in acidic medium reacts to have change in oxidation number of Mn from :
 (a) 7 to 5 (b) 2 to 7
 (c) 5 to 7 (d) 7 to 2
32. In which of the compounds does 'manganese' exhibit highest oxidation number ?
 (a) MnO_2 (b) Mn_3O_4
 (c) K_2MnO_4 (d) $MnSO_4$
33. On reduction of $KMnO_4$ by oxalic acid in acidic medium, the oxidation number of Mn changes. What is the magnitude of this change?
 (a) From 7 to 2 (b) From 6 to 2
 (c) From 5 to 2 (d) From 7 to 4
34. Among the following, identify the species with an atom in +6 oxidation state
 (a) MnO_4^- (b) $Cr(CN)_6^{3-}$
 (c) NiF_6^{2-} (d) CrO_2Cl_2
35. The values of standard oxidation potentials of following reactions are given below :
 (i) $Zn \longrightarrow Zn^{2+} + 2e^-$; $E^\circ = 0.762$ V
 (ii) $Fe \longrightarrow Fe^{2+} + 2e^-$; $E^\circ = 0.440$ V
 (iii) $Cu \longrightarrow Cu^{2+} + 2e^-$; $E^\circ = -0.345$ V
 (iv) $Ag \longrightarrow Ag^+ + e^-$; $E^\circ = -0.800$ V
 Which of the following is most easily reduced
 (a) Fe (b) Ag
 (c) Zn (d) Cu
36. In which of the following compounds the oxidation number of carbon is not zero?
 (a) HCHO (b) CH_3COOH
 (c) $C_{12}H_{22}O_{11}$ (d) CH_3CHO
37. When SO_2 is passed through acidified solution of potassium dichromate, then chromium sulphate is formed. The change in valency of chromium is
 (a) +4 to +2 (b) +5 to +3
 (c) +6 to +3 (d) +7 to +2
38. In which of the following transition metal complexes does the metal exhibit zero oxidation state ?
 (a) $[Co(NH_3)_6]Cl_3$ (b) $[Fe(H_2O)_6]SO_4$
 (c) $Ni(CO)_4$ (d) $[Fe(H_2O)_6]X_3$
39. In the reaction
 $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$, the H_2O_2 acts as :
 (a) reducing agent (b) oxidising agent
 (c) bleaching agent (d) none of the above
40. In which of the following compounds, the oxidation number of iodine is fractional ?
 (a) IF_7 (b) I_3^-
 (c) IF_5 (d) IF_3
41. A metal ion M^{3+} loses 3 electrons, its oxidation number will be
 (a) +3 (b) +6
 (c) 0 (d) -3
42. For the reaction : $NH_3 + OCl^- \longrightarrow N_2H_4 + Cl^-$ in basic medium, the coefficients of NH_3 , OCl^- and N_2H_4 for the balanced equation are respectively
 (a) 2, 2, 2 (b) 2, 2, 1
 (c) 2, 1, 1 (d) 4, 4, 2
43. $C_2H_6(g) + nO_2(g) \rightarrow CO_2(g) + H_2O(l)$
 In this equation, the ratio of the coefficients of CO_2 and H_2O is
 (a) 1 : 1 (b) 2 : 3
 (c) 3 : 2 (d) 1 : 3
44. Oxygen has an oxidation state of +2 in the compound :
 (a) H_2O_2 (b) CO_2
 (c) H_2O (d) F_2O

45. $2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Z} + 5\text{O}_2 + 8\text{H}_2\text{O}$. In this reaction Z is
 (a) Mn^{+2} (b) Mn^{+4}
 (c) MnO_2 (d) Mn
46. Which one of the following reactions involves disproportionation?
 (a) $2\text{H}_2\text{SO}_4 + \text{Cu} \rightarrow \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$
 (b) $\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$
 (c) $2\text{KOH} + \text{Cl}_2 \rightarrow \text{KCl} + \text{KOC} + \text{H}_2\text{O}$
 (d) $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
47. The following species will not exhibit disproportionation reaction
 (a) ClO^- (b) ClO_2^-
 (c) ClO_3^- (d) ClO_4^-
48. The standard electrode potentials of four elements A, B, C and D are -3.05 , -1.66 , -0.40 and $+0.80$. The highest chemical reactivity will be exhibited by:
 (a) A (b) B
 (c) C (d) D
49. What is 'A' in the following reaction
 $2\text{Fe}^{3+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{A}$
 (a) $\text{Sn}^{3+}(\text{aq})$ (b) $\text{Sn}^{4+}(\text{aq})$
 (c) $\text{Sn}^{2+}(\text{aq})$ (d) Sn
50. In a balance equation $\text{H}_2\text{SO}_4 + x\text{HI} \rightarrow \text{H}_2\text{S} + y\text{I}_2 + z\text{H}_2\text{O}$, the values of x , y , z are
 (a) $x=3, y=5, z=2$ (b) $x=4, y=8, z=5$
 (c) $x=8, y=4, z=4$ (d) $x=5, y=3, z=4$
51. $\text{CrO}_4^{2-} \text{ aq.} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} \text{ (aq.)} + \text{H}_2\text{O}$ Element oxidised is
 (a) Oxygen (b) H
 (c) Chromium (d) None
52. Which substance serves as reducing agent in the following reaction?
 $14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 3\text{Ni} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Ni}^{2+}$
 (a) H_2O (b) Ni
 (c) H^+ (d) $\text{Cr}_2\text{O}_7^{2-}$
53. Which of these substances is a good reducing agent?
 (a) HI (b) KBr
 (c) FeCl_3 (d) KClO
54. Which reaction is not feasible?
 (a) $2\text{KI} + \text{Br}_2 \rightarrow 2\text{KBr} + \text{I}_2$
 (b) $2\text{KBr} + \text{I}_2 \rightarrow 2\text{KI} + \text{Br}_2$
 (c) $2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2$
 (d) $2\text{H}_2\text{O} + 2\text{F}_2 \rightarrow 4\text{HF} + \text{O}_2$
55. $\text{Co(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Co}^{2+}(\text{aq}) + \text{Cu(s)}$
 The above reaction is :
 (a) Oxidation reaction
 (b) Reduction reaction
 (c) Redox reaction
 (d) None of these
56. In which of the following reactions, H_2O_2 acts as a reducing agent?
 (a) $2\text{KI} + \text{H}_2\text{O}_2 \rightarrow 2\text{KOH} + \text{I}_2$
 (b) $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$
 (c) $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$
 (d) $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$
57. Oxidation state of phosphorus in PO_4^{3-} , P_4O_{10} and $\text{P}_2\text{O}_7^{4-}$ is :
 (a) +3 (b) +2
 (c) -3 (d) +5
58. When KMnO_4 acts as an oxidising agent and ultimately forms MnO_4^{2-} , MnO_2 , Mn_2O_3 and Mn^{+2} , then the number of electrons transferred in each case respectively is
 (a) 4, 3, 1, 5 (b) 1, 5, 3, 7
 (c) 1, 3, 4, 5 (d) 3, 5, 7, 1
59. The compound that can work both as an oxidising as well as a reducing agent is
 (a) KMnO_4 (b) H_2SO_4
 (c) BaO_2 (d) H_2O_2
60. Which of the following is not oxidizing agent?
 (a) Na^+ (b) $[\text{CrO}_4]^{2-}$
 (c) $[\text{MnO}_4]^-$ (d) Ozone
61. Which of the following behaves as both oxidising and reducing agents ?
 (a) H_2SO_4 (b) SO_2
 (c) H_2O (d) HNO_3
62. Which of the following substances acts as an oxidising as well as a reducing agent?
 (a) Na_2O (b) SnCl_2
 (c) Na_2O_2 (d) NaNO_2
63. Which of the following reactions depict the oxidising behaviour of H_2SO_4 :
 (a) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
 (b) $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
 (c) $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$
 (d) $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
64. When NaCl is dissolved in water the sodium ion becomes
 (a) oxidised (b) reduced
 (c) hydrolysed (d) hydrated
65. In the reaction
 $\text{HAsO}_2 + \text{Sn}^{2+} \rightarrow \text{As} + \text{Sn}^{4+} + \text{H}_2\text{O}$ oxidising agent is
 (a) Sn^{2+} (b) Sn^{4+}
 (c) As (d) HAsO_2
66. A compound contains atoms X, Y, Z; the oxidation number of X is +2, Y is +5 and Z is -2, therefore a possible formula of the compound is :
 (a) XY_1Z_2 (b) $\text{X}_2(\text{YZ}_3)_2$
 (c) $\text{X}_3(\text{YZ}_4)_2$ (d) $\text{X}_3(\text{Y}_4\text{Z})_2$

67. Stronger is oxidising agent, more is :
 (a) standard reduction potential of that species
 (b) the tendency to get it self oxidised
 (c) the tendency to lose electrons by that species
 (d) standard oxidation potential of that species
68. Which of the following statements are correct concerning redox properties?
 (i) A metal M for which E° for the half life reaction $M^{n+} + ne^- \rightleftharpoons M$ is very negative will be a good reducing agent.
 (ii) The oxidizing power of the halogens decreases from chlorine to iodine.
 (iii) The reducing power of hydrogen halides increases from hydrogen chloride to hydrogen iodide
 (a) (i), (ii) and (iii) (b) (i) and (ii)
 (c) (i) only (d) (ii) and (iii)
69. In reaction of $KMnO_4$ and Mohr's salt, $FeSO_4$ is oxidised to
 (a) Fe^{2+} (b) Fe^{3+}
 (c) Fe (d) All of these
70. The violent reaction between sodium and water is an example of :
 (a) Reduction (b) Oxidation
 (c) Redox reaction (d) Neutralization reaction
71. The compound that can work both as an oxidizing and reducing agent is :
 (a) $KMnO_4$ (b) H_2O_2
 (c) BaO_2 (d) $K_2Cr_2O_7$
72. The oxidation number of phosphorus in pyrophosphoric acid is
 (a) +3 (b) +1
 (c) +4 (d) +5
73. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because
 (a) Zn acts as an oxidising agent when it reacts with HNO_3
 (b) HNO_3 is weaker acid than H_2SO_4 and HCl
 (c) in electrochemical series, Zn is above hydrogen
 (d) NO_3^- is reduced in preference to hydronium ion
74. The oxidation states of sulphur in the anions SO_3^{2-} , $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order
 (a) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$
 (b) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$
 (c) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$
 (d) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$
75. Oxidation numbers of P in PO_4^{3-} , of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively
 (a) +3, +6 and +5 (b) +5, +3 and +6
 (c) -3, +6 and +6 (d) +5, +6 and +6

EXERCISE - 2

Applied Questions

1. One mole of N_2H_4 loses 10 moles of electrons to form a new compound, y. Assuming that all nitrogen appear in the new compound, what is the oxidation state of nitrogen in y (There is no change in the oxidation state of hydrogen)
 (a) -1 (b) -3
 (c) +3 (d) +5
2. Which of the following reaction involves neither oxidation nor reduction
 (a) $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$ (b) $Cr \rightarrow CrCl_3$
 (c) $Na \rightarrow Na^+$ (d) $2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$
3. Among NH_3 , HNO_3 , NaN_3 and Mg_3N_2 the number of molecules having nitrogen in negative oxidation state is
 (a) 1 (b) 2
 (c) 3 (d) 4
4. The correct decreasing order of oxidation number of oxygen in compounds BaF_2 , O_3 , KO_2 and OF_2 is :
 (a) $BaO_2 > KO_2 > O_3 > OF_2$
 (b) $OF_2 > O_3 > KO_2 > BaO_2$
 (c) $KO_2 > OF_2 > O_3 > BaO_2$
 (d) $BaO_2 > O_3 > OF_2 > KO_2$
5. Standard electrode potentials of redox couples A^{2+}/A , B^{2+}/B , C/C^{2+} and D^{2+}/D are 0.3V, -0.5V, -0.75V and 0.9V respectively. Which of these is best oxidising agent and reducing agent respectively –
 (a) D^{2+}/D and B^{2+}/B (b) B^{2+}/B and D^{2+}/D
 (c) D^{2+}/D and C^{2+}/C (d) C^{2+}/C and D^{2+}/D
6. Oxidation state for nitrogen is incorrectly given for compound
 (a) $[Co(NH_3)_5Cl]Cl_2$ 0
 (b) NH_2OH -1
 (c) $(N_2H_5)_2SO_4$ -2
 (d) Mg_3N_2 -3
7. $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$
 In the above equation the number of electrons lost by one molecule of FeS_2 are –
 (a) 6 (b) 2
 (c) 1 (d) 11
8. The number of moles of $KMnO_4$ that will be completely reduced by one mole of ferrous oxalate in acidic medium –
 (a) 2/5 (b) 3/5
 (c) 4/5 (d) 1
9. The oxide, which cannot act as a reducing agent, is
 (a) NO_2 (b) SO_2
 (c) CO_2 (d) ClO_2

10. In which of the following reaction, oxidation number of N remains unchanged ?
 (a) $2\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HNO}_2$
 (b) $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$
 (c) $2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4$
 (d) $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
11. Which of the following statements is *not* correct?
 (a) CaOCl_2 is a mixed salt of two acids HCl and HOCl .
 (b) Oxidation number of chlorine in CaOCl_2 is zero since it exists as Cl_2
 (c) Oxidation number of chlorine is -1 since it exists as Cl^-
 (d) Oxidation number of chlorine is $+1$ since it exists as ClO^-
12. The following redox reaction is balanced by which set of coefficients ?

$$a\text{Zn} + b\text{NO}_3^- + c\text{H}^+ \rightarrow d\text{NH}_4^+ + e\text{H}_2\text{O} + f\text{Zn}^{2+}$$

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
(a)	1	1	10	1	3	1
(b)	2	2	10	2	3	2
(c)	4	2	10	1	3	4
(d)	4	1	10	1	3	4
13. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 is
 (a) 0 and -1 (b) -1 and -2
 (c) -2 and 0 (d) -2 and -1
14. In haemoglobin the iron is in the following oxidation state :
 (a) $+4$ (b) $+2$
 (c) $+3$ (d) $+1$
15. In which of the following reactions, H_2SO_4 acts as an acid as well as an oxidant?
 (a) $\text{C}_{12}\text{H}_{22}\text{O}_{11} \xrightarrow{\text{H}_2\text{SO}_4} 12\text{C} + 11\text{H}_2\text{O}$
 (b) $\text{S} + 2\text{H}_2\text{SO}_4 \longrightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$
 (c) $\text{Cu} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
 (d) $\text{NaHCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{H}_2\text{O} + \text{CO}_2$
16. Point out the correct statement of the following about $\text{Na}_2\text{S}_4\text{O}_6$.
 (a) Average oxidation number of S atom is $+2$
 (b) Oxidation number of two S atoms is zero each and that of other two is $+5$ each
 (c) Oxidation number of two S atoms is $+1$ each and that of other two is $+4$ each
 (d) None of these
17. The pair of compounds in which both the metals are in the highest possible oxidation state is
 (a) $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$
 (b) CrO_2Cl_2 , MnO_4^-
 (c) TiO_3 , MnO_2
 (d) $[\text{Co}(\text{CN})_6]^{3-}$, MnO_3
18. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from :
 (a) zero to $+1$ and zero to -5
 (b) zero to -1 and zero to $+5$
 (c) zero to -1 and zero to $+3$
 (d) zero to $+1$ and zero to -3
19. Standard reduction potentials of the half reactions are given below :
 $\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$; $E^\circ = +2.85 \text{ V}$
 $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$; $E^\circ = +1.36 \text{ V}$ $\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$; $E^\circ = +1.06 \text{ V}$ $\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$; $E^\circ = +0.53 \text{ V}$
 The strongest oxidising and reducing agents respectively are :
 (a) F_2 and I^- (b) Br_2 and Cl^-
 (c) Cl_2 and Br^- (d) Cl_2 and I_2
20. The compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ which shows superconductivity has copper in oxidation state Assume that the rare earth element Yttrium is in its usual $+3$ oxidation state
 (a) $3/7$ (b) $7/3$
 (c) 3 (d) 7
21. The standard reduction potential values of three metallic cations, X, Y and Z are 0.52 , -3.03 and -1.18 V respectively. The order of reducing power of the corresponding metals is
 (a) $\text{Y} > \text{Z} > \text{X}$ (b) $\text{X} > \text{Y} > \text{Z}$
 (c) $\text{Z} > \text{Y} > \text{X}$ (d) $\text{Z} > \text{X} > \text{Y}$
22. Consider the following reaction :

$$x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{H}^+ \rightarrow x\text{Mn}^{2+} + 2y\text{CO}_2 + \frac{z}{2}\text{H}_2\text{O}$$
 The value's of x , y and z in the reaction are, respectively :
 (a) 5, 2 and 16 (b) 2, 5 and 8
 (c) 2, 5 and 16 (d) 5, 2 and 8

DIRECTIONS for Qs. 23 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
 (b) Statement-1 is True, Statement -2 is True ; Statement-2 is NOT a correct explanation for Statement -1
 (c) Statement -1 is True, Statement-2 is False
 (d) Statement -1 is False, Statement -2 is True
23. **Statement-1** : Stannous chloride is a powerful oxidising agent which oxidises mercuric chloride to mercury.
Statement-2 : Stannous chloride gives grey precipitate with mercuric chloride, but stannic chloride does not do so.
24. **Statement-1** : HClO_4 is a stronger acid than HClO_3 .
Statement-2 : Oxidation state of Cl in HClO_4 is $+VII$ and in HClO_3 is $+V$.
25. **Statement-1** : In a reaction

$$\text{Zn}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu}(\text{s})$$
 Zn is a reductant but itself get oxidized.
Statement-2 : In a redox reaction, oxidant is reduced by accepting electrons and reductant is oxidized by losing electrons.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Which of the following is not an example of redox reaction?
 - $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$
 - $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
 - $2\text{K} + \text{F}_2 \longrightarrow 2\text{KF}$
 - $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{HCl}$

Redox reactions are those reactions which involve change in oxidation number of the reactants.

- The more positive the value of $E^\ominus$, the greater is the tendency of the species to get reduced. Using the standard electrode potential of redox couples given below find out which of the following is the strongest oxidising agent.

$E^\ominus$ values : $\text{Fe}^{3+}/\text{Fe}^{2+} = +0.77\text{V}$; $\text{I}_2(\text{s})/\text{I}^- = +0.54$;
 $\text{Cu}^{2+}/\text{Cu} = +0.34$; $\text{Ag}^+/\text{Ag} = 0.80\text{V}$

- Fe^{3+}
 - $\text{I}_2(\text{s})$
 - Cu^{2+}
 - Ag^+
- $E^\ominus$ values of some redox couples are given below. On the basis of these values choose the correct option.

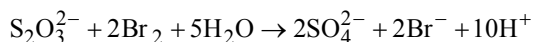
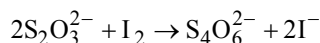
$E^\ominus$ values: $\text{Br}_2/\text{Br}^- = +1.09$
 $\text{Ag}^+/\text{Ag}(\text{s}) = +0.80$
 $\text{Cu}^{2+}/\text{Cu}(\text{s}) = +0.34$; $\text{I}_2(\text{s})/\text{I}^- = +0.54$

- Cu will reduce Br^-
 - Cu will reduce Ag
 - Cu will reduce I^-
 - Cu will reduce Br_2
- Using the standard electrode potential, find out the pair between which redox reaction is not feasible.

$E^\ominus$ values: $\text{Fe}^{3+}/\text{Fe}^{2+} = +0.77$; $\text{I}_2/\text{I}^- = +0.54$;
 $\text{Cu}^{2+}/\text{Cu} = +0.34$; $\text{Ag}^+/\text{Ag} = +0.80\text{V}$

- Fe^{3+} and I^-
 - Ag^+ and Cu
 - Fe^{3+} and Cu
 - Ag and Fe^{3+}
- Determine the $E^\ominus_{\text{cell}}$ of the four redox reactions. If the value of $E^\ominus_{\text{cell}}$ of a reaction is negative, that reaction will not take place.

- Thiosulphate reacts differently with iodine and bromine in the reactions given below.



Which of the following statements justifies the above dual behaviour of thiosulphate?

- Bromine is a stronger oxidant than iodine
 - Bromine is a weaker oxidant than iodine
 - Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reactions
 - Bromine undergoes oxidation and iodine undergoes reduction in these reactions
- The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following is incorrect in this respect?

- The oxidation number of hydrogen is always +1
- The algebraic sum of all the oxidation numbers in a compound is zero
- An element in the free or the uncombined state bears oxidation number zero
- In all its compounds, the oxidation number of fluorine is -1

- In which of the following compounds, an element exhibits two different oxidation states?

- NH_2OH
- NH_4NO_3
- N_2H_4
- N_3H

- Which of the following arrangements represent increasing oxidation number of the central atom?

- CrO_2^- , ClO_3^- , CrO_4^{2-} , MnO_4^-
- ClO_3^- , CrO_4^{2-} , MnO_4^- , CrO_2^-
- CrO_2^- , ClO_3^- , MnO_4^- , CrO_4^{2-}
- CrO_4^{2-} , MnO_4^- , CrO_2^- , ClO_3^-

- The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations the element will exhibit largest oxidation number?

- $3d^1 4s^2$
- $3d^2 4s^2$
- $3d^5 4s^1$
- $3d^5 4s^2$

- Identify disproportionation reaction

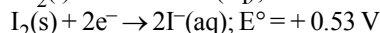
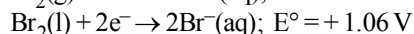
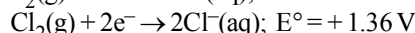
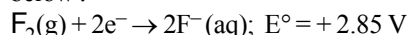
- $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
- $\text{CH}_4 + 4\text{Cl}_2 \longrightarrow \text{CCl}_4 + 4\text{HCl}$
- $2\text{F}_2 + 2\text{OH}^- \longrightarrow 2\text{F}^- + \text{OF}_2 + \text{H}_2\text{O}$
- $2\text{NO}_2 + 2\text{OH}^- \longrightarrow \text{NO}_2^- + \text{NO}_3^- + \text{H}_2\text{O}$

- Which of the following elements does not show disproportionation tendency?

- Cl
- Br
- F
- I

NEET/AIPMT (2013-2017) Questions

- Standard reduction potentials of the half reactions are given below :



The strongest oxidising and reducing agents respectively are :

[2012 M]

- F_2 and I^-
- Br_2 and Cl^-
- Cl_2 and Br^-
- Cl_2 and I_2

- A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. During the reaction which element undergoes maximum change in the oxidation number?

[2012]

- S
- H
- Cl
- C

14. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from : [2012]
 (a) zero to +1 and zero to -5
 (b) zero to -1 and zero to +5
 (c) zero to -1 and zero to +3
 (d) zero to +1 and zero to -3
15. Oxidation numbers of P in PO_4^{3-} , of S in SO_4^{2-} and that of Cr in $\text{Cr}_2\text{O}_7^{2-}$ are respectively [2009]
 (a) +3, +6 and +5 (b) +5, +3 and +6
 (c) -3, +6 and +6 (d) +5, +6 and +6
16. The oxidation states of sulphur in the anions SO_3^{2-} , $\text{S}_2\text{O}_4^{2-}$ and $\text{S}_2\text{O}_6^{2-}$ follow the order [2003]
 (a) $\text{S}_2\text{O}_6^{2-} < \text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-}$
 (b) $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-}$
 (c) $\text{SO}_3^{2-} < \text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-}$
 (d) $\text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_3^{2-}$
17. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because [2002]
 (a) Zn acts as an oxidising agent when it reacts with HNO_3
 (b) HNO_3 is weaker acid than H_2SO_4 and HCl
 (c) In electrochemical series, Zn is above hydrogen
 (d) NO_3^- is reduced in preference to hydronium ion
18. A compound contains atoms of three elements A, B and C. If the oxidation number of A is +2, B is +5, and that of C is -2, the possible formula of the compound is : [2000]
 (a) $\text{A}_2(\text{BC}_3)_2$ (b) $\text{A}_3(\text{BC}_4)_2$
 (c) $\text{A}_3(\text{B}_4\text{C})_2$ (d) ABC_2
19. The following redox reaction is balanced by which set of coefficients ? [1999]

$$a\text{Zn} + b\text{NO}_3^- + c\text{H}^+ \rightarrow d\text{NH}_4^+ + e\text{H}_2\text{O} + f\text{Zn}^{2+}$$

	a	b	c	d	e	f
(a)	1	1	10	1	3	1
(b)	2	2	10	2	3	2
(c)	4	2	10	1	3	4
(d)	4	1	10	1	3	4
20. The oxidation number of phosphorus in pyrophosphoric acid is [1999]
 (a) +3 (b) +1
 (c) +4 (d) +5
21. Which of the following involves a redox reaction? [1997]
 (a) Reaction of H_2SO_4 with NaOH
 (b) Production of ozone from oxygen in the atmosphere by lightning
 (c) Production of nitrogen oxides from nitrogen and oxygen in the atmosphere by lightning
 (d) Evaporation of water
22. The oxide, which cannot act as a reducing agent, is [1995]
 (a) NO_2 (b) SO_2
 (c) CO_2 (d) ClO_2
23. The loss of electron is termed as [1995]
 (a) oxidation (b) reduction
 (c) combustion (d) neutralization
24. The oxidation number of chromium in potassium dichromate is [1995]
 (a) +6 (b) -5
 (c) -2 (d) +2
25. In which of the following reactions, there is no change in valency ? [1994]
 (a) $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
 (b) $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$
 (c) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
 (d) $3\text{BaO} + \text{O}_2 \longrightarrow 2\text{BaO}_2$
26. Phosphorus has the oxidation state of +3 in [1994]
 (a) Phosphorus acid
 (b) Orthophosphoric acid
 (c) Hypophosphorus acid
 (d) Metaphosphoric acid.
27. Which substance serves as a reducing agent in the following reaction ? [1994]

$$14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 3\text{Ni} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Ni}^{2+}$$
 (a) H_2O (b) Ni
 (c) H^+ (d) $\text{Cr}_2\text{O}_7^{2-}$
28. The oxidation state of Cr in is [1988]
 (a) +5 (b) +3
 (c) +6 (d) +7

Hints & Solutions

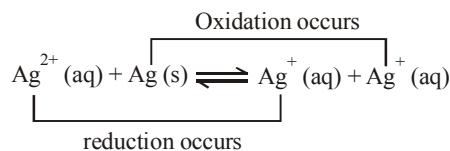
EXERCISE - 1

- (a) O.N. of Mn in MnO_4^- is +7 and in Mn^{2+} it is +2. The difference is of 5 electrons.
- (c) Higher values of reduction potential indicates the stronger oxidising agent. So, Mg^{2+} having reduction potential -2.37 V , is the strongest oxidising agent among the given choices.
- (a) Ox. no. of Cr on both side is + 6.
- (a) $4\text{P} + 3\text{KOH} + 3\text{H}_2\text{O} \rightarrow \text{KH}_2\text{PO}_2 + \text{PH}_3$
O.N. of P = 0, In KH_2PO_2 it is + 1, In PH_3 it is -3. Hence P is oxidised and reduced.
- (d) H_2S , the oxidation state of S is - 2. So it cannot accept more electrons because on accepting 2 electrons S acquires a noble gas configuration. So, it can act only as a reducing agent by losing electron. On the other hand, the oxidation state of S in SO_2 is + 4 which is an intermediate oxidation state of sulphur so it can reduce as well oxidise.
- (d) $2\text{I}^- \rightarrow \text{I}_2$ is oxidation (loss of electrons); Cr (+6) changes to Cr (+3) by gain of electrons. Hence Cr is reduced.
- (a) In a redox reaction, one molecule is oxidised and other molecule is reduced i.e. oxidation number of reactants are changed.

$$\begin{array}{ccccccc} 0 & 0 & & +1 & -1 & & \\ \text{H}_2 & + & \text{Br}_2 & \longrightarrow & 2 & \text{HBr} & \end{array}$$
 Here H_2 is oxidised and Br_2 is reduced, thus it is oxidation-reduction reaction.
- (a) The electrode for which the standard reduction potential values are more negative are strong reductants. So, K electrode ($E^\circ_{\text{red}} = -2.9\text{ V}$) acts as strong reductant among the given choices.
- (a) In this reaction H_2S is oxidised because the oxidation state of 'S' change from - 2 to 0.
- (a) Let x_1 be the oxidation state of C in CH_4
 $\therefore x_1 + 4(-1) = 0 \Rightarrow x_1 - 4 = 0$
 $\Rightarrow x_1 = 4$
 Similarly, let x_2 be oxidation state of C in CH_3Cl .
 $\therefore x_2 + 3(+1) + 1(-1) = 0$
 $\Rightarrow x_2 + 3 - 1 = 0 \Rightarrow x_2 + 2 = 0$
 $\Rightarrow x_2 = -2$
 Let x_3 be oxidation state of C in CH_2Cl_2
 $\therefore x_3 + 2(+1) + 2(-1) = 0 \Rightarrow x_3 = 0$
 Similarly, for CHCl_3 ,
 $\therefore x_4 + 1(+1) + 3(-1) = 0$
 $\Rightarrow x_4 + 1 - 3 = 0$
 $x_4 = 2$
 and for CCl_4
 $\therefore x_5 + 4(-1) = 0 \Rightarrow x_5 = 4$
 So, option (a) is correct choice.

- (b) In the given reaction oxidation state of Mg is changing from 0 to +2 while in nitrogen it is changing from 0 to -3. So oxidation of Mg and reduction of nitrogen takes place.
- (a) Ag is easiest to be reduced among the given choices because its reduction potential is highest among the given choices.
- (a) In this reaction oxidation occurs.
- (a) $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$. In this reaction Sn^{2+} change in Sn^{4+} it is called an oxidation reaction.
- (d) Let the oxidation no. of N in $\text{HNO}_3 = x$
 $\therefore 1 + x + (3 \times -2) = 0$
 $\therefore x = +5$
- (c) In all the given compounds oxidation number of non metal is + 4. As C belongs to group IV and it is in its maximum oxidation state. So, reduction in oxidation number of nonmetal is not possible only in CO_2 . As we know that reduction is always accompanied by an increase in oxidation number of reducing agent. So, CO_2 cannot act as reducing agent among the given choices.
- (a) O.N. of P in H_3PO_3 (phosphorous acid)
 $3 \times 1 + x + 3 \times (-2) = 0$ or $x = +3$
 In orthophosphoric acid (H_3PO_4) O.N. of P is + 5, in hypophosphorous acid (H_3PO_2) it is + 1 while in metaphosphoric acid (HPO_3), it is + 5,

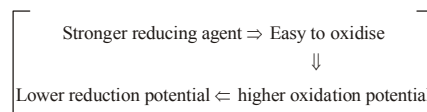
$$\begin{array}{ccccccc} +2 & -1 & +1 & +6 & -2 & +2 & +6 & -2 & +1 & -1 \\ \text{Ba} & \text{O}_2 & + & \text{H}_2 & \text{S} & \text{O}_4 & \longrightarrow & \text{Ba} & \text{S} & \text{O}_4 & + & \text{H}_2 & \text{O}_2 \end{array}$$
- (c) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
 In this reaction, none of the elements undergoes a change in oxidation number or valency.
- (a) Mg which is placed at higher position in electrochemical series will reduce zinc oxide to zinc.
- (a) Let x = oxidation no. of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$.
 $\therefore (2 \times 1) + (2 \times x) + 7(-2) = 0$
 or $2 + 2x - 14 = 0$ or $x = +6$.
- (d) Hg which lies below the hydrogen in electrochemical series cannot displace hydrogen from acid.
- (b) Oxidation number of a compound must be 0. Using the values for A, B and C in the four options, we find that $\text{A}_3(\text{BC}_4)_2$ is the answer.
 Check: $(+2)3 + [(+5)+4(-2)]2 = 6 + (5-8)2 = 0$
- (b) Sum of oxidation state of all atoms in neutral compound is zero.
 Let the oxidation state of iron in the complex ion $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+} \cdot \text{SO}_4^{2-}$ be x ; then $x + 5 \times 0 + 0 = +2$.
 $\therefore x = +2$
- (d) The given reaction can be written as



WWW.JEEBOOKS.IN

54. (b) $2\text{KBr} + \text{I}_2 \longrightarrow 2\text{KI} + \text{Br}_2$
reaction is not possible because Br^- ion is not oxidised in Br_2 with I_2 due to higher electrode (oxidation) potential of I_2 than bromine.
55. (c) $\text{Co(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Co}^{2+}(\text{aq}) + \text{Cu(s)}$
This reaction is a redox reaction as Co undergoes oxidation whereas Cu^{+2} undergoes reduction.
56. (d) In (a), (b) and (c) H_2O_2 acts as oxidising agent.
57. (d) In PO_4^{3-} : $x + 4(-2) = -3 \Rightarrow x = +5$
In P_4O_{10} : $4x + 10(-2) = 0 \Rightarrow x = +5$
 $4x - 20 = 0 \Rightarrow 4x = 20$
In $\text{P}_2\text{O}_7^{4-}$: $2x + 7(-2) = -4 \Rightarrow x = +5$
58. (c) In KMnO_4 the O.N. of Mn is +7, in MnO_4^{2-} +6, in MnO_2 +4 in Mn_2O_3 +3 and in Mn^{2+} is +2. The difference being 1, 3, 4 and 5 respectively.
59. (d) In H_2O_2 the O.N. of O is -1 which can be increased to 0 or decreased to -2 hence H_2O_2 can work as reducing and oxidising agent.
60. (a) Na^+ has a stable configuration of inert gas Ne, thus it can neither lose nor gain e. hence does not undergo oxidation or reduction.
61. (b) In SO_2 the O.N. of S can increase and decrease. Hence can behave as reducing and oxidising agent. Oxidation state of S varies from -2 to 6.
62. (d) In Na_2O , SnCl_2 and Na_2O_2 central atom is either in lowest or highest oxidation state, so it can function either as an oxidising or a reducing agent but not both. However, the oxidation state of N in NaNO_2 is +3 which lies between its highest (+5) and lowest (-3) values.
63. (d)
$$\begin{array}{ccccccc} -1 & & +6 & & 0 & & +4 \\ 2\text{HI} & + & \text{H}_2\text{SO}_4 & \rightarrow & \text{I}_2 & + & \text{SO}_2 + 2\text{H}_2\text{O} \\ \text{Oxidised} & & \text{Reduced} & & & & \\ \text{RA} & & \text{OA} & & & & \end{array}$$
64. (d) $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{HCl}$
Sodium ion hydrated in water.
65. (d) Oxidizing agent itself, undergoes reduction during a redox reaction
$$\begin{array}{ccccccc} +3 & & +2 & & 0 & & +4 \\ \text{HAsO}_2 & + & \text{Sn} & \rightarrow & \text{As} & + & \text{Sn} + \text{H}_2\text{O} \end{array}$$

Hence, here HAsO_2 is acting as oxidizing agent.
66. (c) On substituting the oxidation numbers of X, Y and Z in the formula, the sum is zero.
(a) $(+2 \times 3) + (+5 \times 2) + (-2 \times 8) = 6 + 10 - 16 = 0$, Hence, $\text{X}_3(\text{YZ}_4)_2$ is the correct formula of the compound.
67. (a) More is E°_{RP} , more is the tendency to get itself reduced or more is oxidising power.
68. (a) (i) $\text{Mn}^{n+} + n\text{e}^- \rightleftharpoons \text{M}$, for this reaction, high negative value of E° indicates lower reduction potential, that means M will be a good reducing agent.



(ii) Element	F	Cl	Br	I
Reduction potential	+2.87	+1.36	+1.06	+0.54
(E° volt)				

As reduction potential decreases from fluorine to iodine, oxidising nature also decreases from fluorine to iodine.
(iii) The size of halide ions increases from F^- to I^- . The bigger ion can loose electron easily. Hence the reducing nature increases from HF to HI.

69. (b) $2\text{MnO}_4^- + 10\text{Fe}^{2+} + 16\text{H}^+ \longrightarrow 10\text{Fe}^{3+} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$
70. (c) The violent reaction between sodium and water is an example of redox reaction :
$$\begin{array}{ccccccc} & & 2\text{Na} & + & 2\text{H}_2\text{O} & \longrightarrow & 2\text{NaOH} + \text{H}_2 \\ (\text{Oxd. state}) & & 0 & & +1 & & +1 & 0 \end{array}$$

In this reaction, sodium (Na) is oxidised to NaOH while H_2O is reduced to H_2 .
71. (b) H_2O_2 can act both as an oxidizing and reducing agent, as oxygen has intermediate oxd. state in it.
72. (d) Pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$
Let oxidation state of phosphorus is x
 $(4 \times 1 + (-2) \times 7 + 2x) = 0$
 $\therefore 2x = 10$ or $x = +5$
73. (d) Zinc gives H_2 gas with dil $\text{H}_2\text{SO}_4/\text{HCl}$ but not with HNO_3 because in HNO_3 , NO_3^- ion is reduced and give NH_4NO_3 , N_2O , NO and NO_2 (based upon the concentration of HNO_3)
$$4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$$

Zn is on the top position of hydrogen in electrochemical series. So Zn displaces H_2 from dilute H_2SO_4 and HCl with liberation of H_2 .
$$\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$$
74. (c) $\text{SO}_3^{2-} \rightarrow \text{S}$ is in +4 oxidation state
 $\text{S}_2\text{O}_4^{2-} \rightarrow \text{S}$ is in +3 oxidation state
 $\text{S}_2\text{O}_6^{2-} \rightarrow \text{S}$ is in +5 oxidation state
75. (d) $\text{PO}_4^{3-} = x + 4(-2) = -3; x - 8 = -3; x = +5$
 $\text{SO}_4^{2-} = x + 4(-2) = -2; x - 8 = -2; x = +6$
 $\text{Cr}_2\text{O}_7^{2-} = 2x + 7(-2) = -2; 2x - 14 = -2; 2x = 12; x = +6$

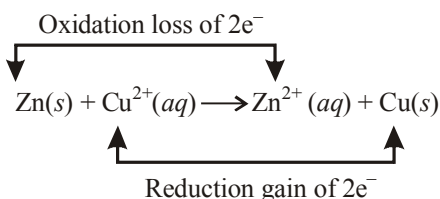
EXERCISE - 2

1. (c) $\text{N}_2^{4+}\text{H}_4^{+4} \xrightarrow[\text{N}]{\text{loss of } 10\text{e}^-} \text{N}_2^{+6}(\text{y});$
O.N. of N changes from -2 to +3
2. (a) $\text{CrO}_4^{2-} \rightarrow \text{Cr}_2\text{O}_7^{2-}$ O.N. of Cr does not change. It remains +6 on both sides. Hence there is no oxidation or reduction.

3. (c) Calculating the oxidation state of nitrogen in given molecules;
 Oxidation state of N in NH_3 is
 $x + 3 \times (+1) = 0$ or $x = -3$
 Oxidation state on N in NaNO_3 is
 $1 + x + 3 \times (-2) = 0$ or $x = +5$
 Oxidation state of N in NaN_3 is
 $+1 + 3x = 0$ or $x = -\frac{1}{3}$
 Oxidation state of N in Mg_3N_2 is
 $3 \times 2 + 2x = 0$ or $x = -3$
 Thus 3 molecules (i.e. NH_3 , NaN_3 and Mg_3N_2 have nitrogen in negative oxidation state.
4. (b) Oxidation no. of O are +2, 0, $-1/2$ and -1 respectively
5. (c) The redox couple with maximum reduction potential will be best oxidising agent and with minimum reduction potential will be best reducing agent.
6. (a) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $\begin{array}{c} +1 \\ \text{H} \\ -1 \\ \text{N} \\ +1 \end{array} \begin{array}{c} -1 \\ \text{O} \\ -2 \end{array} \begin{array}{c} +1 \\ \text{H} \end{array}$
 -3
 $\left(\begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \end{array} \text{N} \begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \end{array} \right)$, Mg_3N_2
 $-1, -2, -3$
7. (d) In FeS_2 , Fe^{2+} is converting into Fe^{3+} and sulphur is changing from -1 oxidation state to $+4$ oxidation state. There are two S^- and one Fe^{2+} in FeS_2 . Thus total no. of electrons lost in the given reaction are 11.
8. (b) $\text{KMnO}_4 + \text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{3+} + 2\text{CO}_2 + \text{Mn}^{2+}$
 So half reaction,
 $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$ (decrease in O.N. = 5)
 $\text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{3+} + 2\text{CO}_2$ (increase in O.N. = 1)
 Now equating the change in O.N. and then by adding both half reactions we get
 $5\text{FeC}_2\text{O}_4 + \text{MnO}_4^- \longrightarrow 5\text{Fe}^{3+} + 10\text{CO}_2 + \text{Mn}^{2+}$
 On balancing equation,
 $3\text{MnO}_4^- + 5\text{FeC}_2\text{O}_4 + 24\text{H}^+ \longrightarrow 5\text{Fe}^{3+} + 3\text{Mn}^{2+} + 10\text{CO}_2 + 12\text{H}_2\text{O}$
 $\therefore 3 \text{ moles of } \text{KMnO}_4 = 5 \text{ moles of } \text{FeC}_2\text{O}_4$
 $1 \text{ mole } \text{FeC}_2\text{O}_4 = \frac{3}{5} \text{ moles of } \text{KMnO}_4$
9. (c) Carbon has the maximum oxidation state of +4, therefore carbon dioxide (CO_2) cannot act as a reducing agent.
10. (c) The oxidation number of N in NO_2 is +4 and in N_2O_4 is also +4 (i.e. no change)
11. (b)
12. (d) $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^-$ (1)
 $8\text{e}^- + 10\text{H}^+ + \text{NO}_3^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$ (2)
 operate eq. (1) $\times 4$ + eq. (2) $\times 1$
 $4\text{Zn} + 10\text{H}^+ + \text{NO}_3^- \rightarrow 4\text{Zn}^{+2} + \text{NH}_4^+ + 3\text{H}_2\text{O}$
13. (b) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
 Oxygen is the most electronegative element in the reaction and has the oxidation states of -1 (in H_2O_2) and -2 (in BaSO_4). In H_2O_2 , peroxy ion is present.
14. (b) In haemoglobin, Fe is in +2 oxidation state.
15. (c) $\text{Cu} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2$ (as acid)
 $\text{H}_2 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{H}_2\text{O} + \text{SO}_2$ (as oxidant)
 In (a), H_2SO_4 acts just as dehydrating agent.
 In (b), it acts just as an oxidant.
 In (d), it neither acts as oxidant nor as acid.
16. (b) $\text{Na}_2\text{S}_4\text{O}_6$ has the structure : $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Na} - \text{S}^* - \text{S} - \text{S} - \text{S}^* - \text{Na} \\ \downarrow \qquad \qquad \downarrow \\ \text{O} \qquad \qquad \text{O} \end{array}$
 O.N. of two S^* atoms are +5 each and that of other two S atoms is zero each.
17. (b) CrO_2Cl_2 , MnO_4^- ; O.N. of Cr and Mn are +6 and +7 respectively.
18. (b) On reaction with hot and concentrated alkali a mixture of chloride and chlorate is formed
 $3\text{Cl}_2 + 3\text{NaOH}(\text{excess}) \xrightarrow{\text{Hot}}$
 $\begin{array}{c} -1 \qquad +5 \\ 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O} \end{array}$
19. (a) Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.
20. (b) $\text{YBa}_2\text{Cu}_3\text{O}_7$
 $3 + 2 \times 2 + 3x - (2 \times 7) = 0$
 $3 + 4 + 3x - 14 = 0$
 $3x = 7$
 $x = \frac{7}{3}$
21. (a) More negative or lower is the reduction potential, more is the reducing property. Thus the reducing power of the corresponding metal will follow the reverse order, i.e. $\text{Y} > \text{Z} > \text{X}$.
22. (c) On balancing the given equations, we get
 $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow 2\text{Mn}^{++} + 10\text{CO}_2 + 8\text{H}_2\text{O}$
 So, $x = 2, y = 5$ & $z = 16$
23. (d) Here, statement-1 is false, because stannous chloride is a strong reducing agent not strong oxidising agent. Stannous chlorides gives Grey precipitate with mercuric chloride. Hence statement-2 is true.
24. (b) Both statement-1 and statement-2 are true but reason is not the correct explanation of assertion. Greater the number of negative atoms present in the oxy-acid make the acid stronger. In general, the strengths of acids that have general formula $(\text{HO})_m\text{ZO}_n$ can be related to

the value of n . As the value of n increases, acidic character also increases. The negative atoms draw electrons away from the Z -atom and make it more positive. The Z -atom, therefore, becomes more effective in withdrawing electron density away from the oxygen atom that bonded to hydrogen. In turn, the electrons of $H-O$ bond are drawn more strongly away from the H -atom. The net effect makes it easier from the proton release and increases the acid strength.

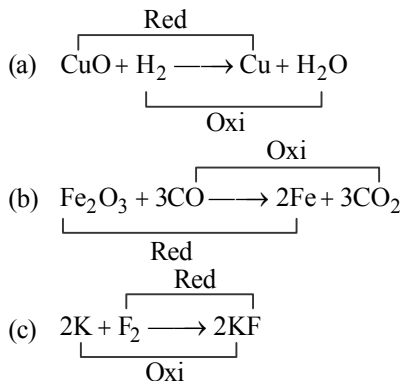
25. (a) Both statement-1 and statement-2 are true and statement-2 is the correct explanation of statement-1.



EXERCISE - 3

Exemplar Questions

1. (d) Following are the examples of redox reaction

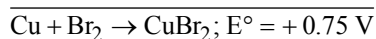
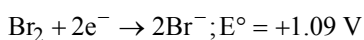
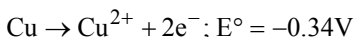


Option (d) is not an example of redox reaction as there is no change in oxidation number of any of the reactants.

2. (d) Since the redox couple Ag^+/Ag has the highest positive value of E° 0.80 V, therefore, Ag^+ is the strongest oxidising agent.
3. (d) Given that E° values of
 $\text{Br}_2/\text{Br}^- = +1.09 \text{ V}$
 $\text{Ag}^+/\text{Ag(s)} = 0.80 \text{ V}$
 $\text{Cu}^{2+}/\text{Cu(s)} = +0.34 \text{ V}$
 $\text{I}_2(\text{s})/\text{I}^- = +0.54 \text{ V}$
 $\text{Br}_2/\text{Br}^- = 1.09 \text{ V}$

The E° values show that copper will reduce Br_2 , if the E° of the following redox reaction is positive.

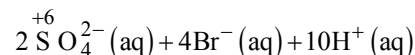
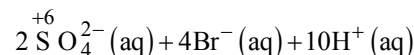
The electrode reactions will be



Since, E° of the overall reaction is positive, therefore, Cu can reduce Br_2 .

4. (d)
 (a) $2\text{Fe}^{3+} + 2e^- \rightarrow 2\text{Fe}^{2+}; E^\circ = +0.77 \text{ V}$
 $2\text{I}^- \rightarrow \text{I}_2 + 2e^-; E^\circ = -0.54 \text{ V}$
 $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2; E^\circ_{\text{cell}} = +0.23 \text{ V}$
 (b) $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-; E^\circ = -0.34 \text{ V}$
 $2\text{Ag}^+ + 2e^- \rightarrow 2\text{Ag}; E^\circ = +0.80 \text{ V}$
 $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}; E^\circ = +0.46 \text{ V}$
 (c) $2\text{Fe}^{3+} + 2e^- \rightarrow 2\text{Fe}^{2+}; E^\circ = +0.77 \text{ V}$
 $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-; E^\circ = -0.34 \text{ V}$
 $2\text{Fe}^{3+} + \text{Cu} \rightarrow 2\text{Fe}^{2+} + \text{Cu}^{2+}; E^\circ = +0.43 \text{ V}$
 (d) $\text{Ag} \rightarrow \text{Ag}^+ + e^-; E^\circ = -0.80 \text{ V}$
 $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}; E^\circ = +0.77 \text{ V}$
 $\text{Ag} + \text{Fe}^{3+} \rightarrow \text{Ag}^+ + \text{Fe}^{2+}; E^\circ = -0.03 \text{ V}$
 This reaction is not feasible since E°_{cell} is negative.

5. (a) $2 \overset{+2}{\text{S}} \overset{-2}{\text{O}_3}{}^{2-}(\text{aq}) + \overset{0}{\text{I}_2}(\text{s}) \rightarrow \overset{+2.5}{\text{S}_4} \overset{-2}{\text{O}_6}{}^{2-}(\text{aq}) + 2\text{I}^-(\text{aq})$



Hence, bromine is a stronger oxidising agent than I_2 , as it oxidises S of $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-} whereas I_2 oxidises it only into $\text{S}_4\text{O}_6^{2-}$ ion.

6. (a) Oxidation number of hydrogen is not always +1. It is +1 in hydrogen halides, -1 in hydrides and zero in H_2 molecule.
7. (b) Split NH_4NO_3 into two ions NH_4^+ and NO_3^- . Now calculate the oxidation number of nitrogen in the two species.

Let, oxidation number of N in NH_4^+ is x .

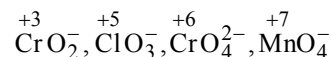
$$\Rightarrow x + (4 \times 1) = +1$$

$$\text{or } x + 4 = +1 \text{ or } x = -3$$

Let, oxidation number of N in NO_3^- is y

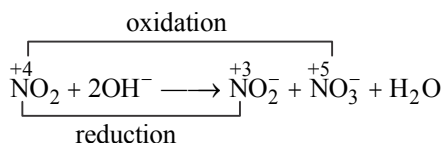
$$\Rightarrow y + (3 \times -2) = -1 \text{ or } y - 6 = -1 \text{ or } y = +5$$

8. (a) Calculating the oxidation number of central atom in the given species.



9. (d) Highest oxidation number of any transition element is the sum of $(n-1)$ d -electrons and ns electrons. Hence, large the number of electrons in the $3d$ -orbitals, higher is the maximum oxidation number.
10. (d) Reactions in which the same substance undergo oxidation as well as reduction are called disproportionation reactions. Writing the O.N. of each element above its symbol in the given reactions.
- In reaction (d), N is both oxidised as well as reduced

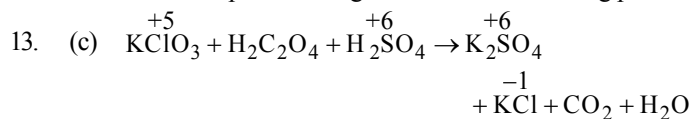
since the O. N. of N increases from +4 in NO_2 to +5 in NO_3^- and decreases from +4 in NO_2 to +3 in NO_2^- .



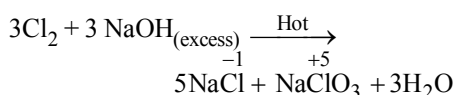
11. (c) Fluorine is the strongest oxidising agent. It does not show positive oxidation state hence it does not disproportionate.

NEET/AIPMT (2013-2017) Questions

12. (a) Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.



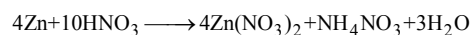
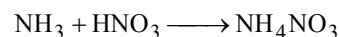
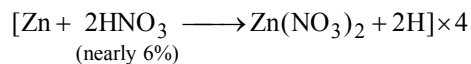
14. (b) On reaction with hot and concentrated alkali a mixture of chloride and chlorate is formed



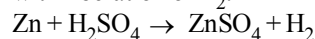
15. (d) $\text{PO}_4^{3-} = x + 4(-2) = -3$; $x - 8 = -3$; $x = +5$
 $\text{SO}_4^{2-} = x + 4(-2) = -2$; $x - 8 = -2$; $x = +6$
 $\text{Cr}_2\text{O}_7^{2-} = 2x + 7(-2) = -2$; $2x - 14 = -2$;
 $2x = 12$; $x = +6$

16. (c) $\text{SO}_3^{2-} \rightarrow \text{S}$ is in +4 oxidation state
 $\text{S}_2\text{O}_4^{2-} \rightarrow \text{S}$ is in +3 oxidation state
 $\text{S}_2\text{O}_6^{2-} \rightarrow \text{S}$ is in +5 oxidation state

17. (d) Zinc gives H_2 gas with dil $\text{H}_2\text{SO}_4/\text{HCl}$ but not with HNO_3 because in HNO_3 , NO_3^- ion is reduced and give NH_4NO_3 , N_2O , NO and NO_2 (based upon the concentration of HNO_3)



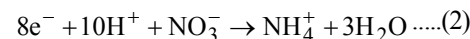
Zn is on the top position of hydrogen in electrochemical series. So Zn displaces H_2 from dilute H_2SO_4 and HCl with liberation of H_2 .



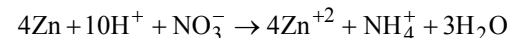
18. (b) Oxidation number of a compound must be 0. Using the values for A, B and C in the four options we find that $\text{A}_3(\text{BC}_4)_2$ is the answer.

$$\text{Check: } (+2)3 + [(+5)+4(-2)]2 = 6 + (5-8)2 = 0$$

19. (d) $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^- \quad \dots(1)$

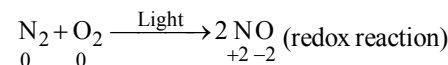
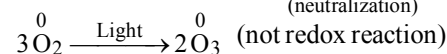


operate eq. (1) $\times 4$ + eq. (2) $\times 1$

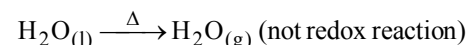


20. (d) Pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$
 Let oxidation state of phosphorus is x
 $(4 \times 1 + (-2) \times 7 + 2x) = 0$
 $\therefore 2x = 10$ or $x = +5$

21. (c) $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
 (neutralization)



here oxidation of N_2 & reduction of O_2 is taking place



22. (c) Carbon has the maximum oxidation state of +4, therefore carbon dioxide (CO_2) cannot act as a reducing agent.

23. (a) Losing of electron is called oxidation.

24. (a) Let x = oxidation no. of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$.
 $\therefore (2 \times 1) + (2 \times x) + 7(-2) = 0$
 or $2 + 2x - 14 = 0$ or $x = +6$.

25. (c) $\text{BaO}_2 + \text{H}_2\text{S} \longrightarrow \text{BaS} + \text{H}_2\text{O}_2$

In this reaction, none of the elements undergoes a change in oxidation number or valency.

26. (a) O.N. of P in H_3PO_3 (phosphorous acid)
 $3 \times 1 + x + 3 \times (-2) = 0$ or $x = +3$

In orthophosphoric acid (H_3PO_4) O.N. of P is +5, in hypophosphorous acid (H_3PO_2) it is +1 while in metaphosphoric acid (HPO_3), it is +5.

27. (b) The element undergo oxidation itself and reduces others is known as reducing agent. In this reaction O. N. of Ni Changes from 0 to +2 and hence Ni acts as a reducing agent.

28. (c) $= +2 + 2x - 14 = 0$ or $x = +6$

Chapter

9

Hydrogen

DIHYDROGEN, H₂

H₂ is the most abundant element in the universe and is the principal element in the solar atmosphere. In combined form it constitutes 15.4% of earth's crust and the oceans.

Isotopes of Hydrogen

Hydrogen has three isotopes: protium (${}^1_1\text{H}$), deuterium

(${}^2_1\text{H}$ or D) and tritium (${}^3_1\text{H}$ or T). Protium has no neutrons,

deuterium has one and tritium has 2 neutrons in the nucleus. Only tritium is radioactive and emits low energy β^- particles.

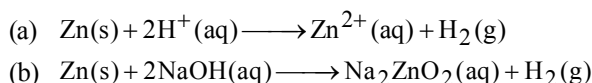
Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation. However, in physical properties these isotopes differ considerably due to their large mass differences.

Isotopes of hydrogen :

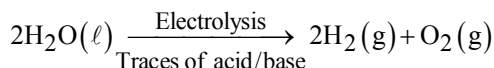
Protium	Deuterium	Tritium
(a) ${}^1_1\text{H}$	${}^2_1\text{H}$ or D	${}^3_1\text{H}$ or T
(b) p = 1, e = 1, n = 0	p = 1, e = 1, n = 1	p = 1, e = 1, n = 2
(c) Abundance 99%	0.0156%	10–15%
(d) Ordinary hydrogen	Heavy hydrogen	Radioactive used as tracer to study reaction mechanism.

Preparation of Dihydrogen

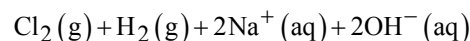
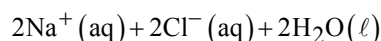
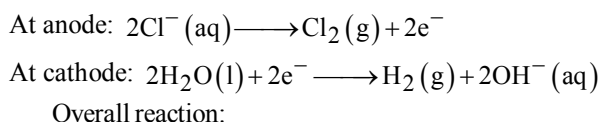
(i) Lab preparation:



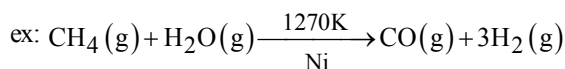
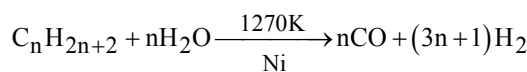
(ii) Commercial preparation:



(iii) By electrolysis of brine solution:



(iv) By reaction of steam on hydrocarbons or coke :



The mixture of CO and H₂ is called water gas and is also called syn gas or synthetic gas.

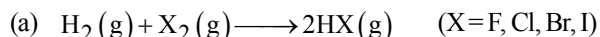
Properties of Dihydrogen

(i) **Physical properties:** It is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water.

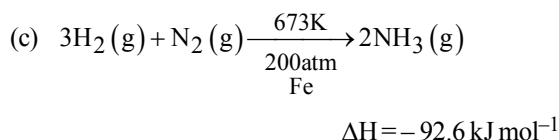
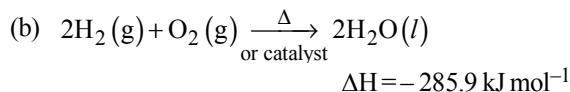
(ii) **Chemical properties:** (1) H₂ is inert at room temperature due to high H–H bond enthalpy.

(2) Due to incomplete orbital with 1s¹ configuration, H combines with almost all elements either by (a) loss of one e[−] to give H⁺ (b) gain of an e[−] to form H[−] (c) sharing e[−]s to form single covalent bond.

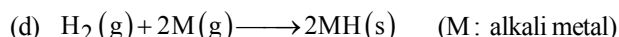
Reactions of dihydrogen :



Reaction with iodine requires a catalyst

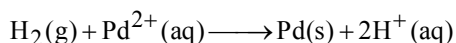


This is the Haber's process for the manufacture of ammonia.

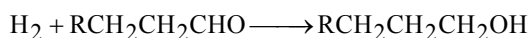
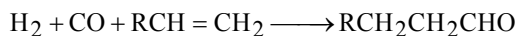


With many metals dihydrogen forms hydrides.

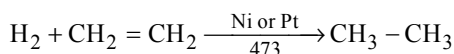
- (e) Reduction of metal ions (in aqueous solution) and oxides of metals into corresponding metals.



- (f) Hydroformylation of olefins.



- (g) Hydrogenation of unsaturated hydrocarbons



Uses

It is used,

- in the synthesis of ammonia.
- in the manufacture of vanaspati fat by hydrogenation of polyunsaturated vegetable oils.
- in the manufacture of bulk organic chemicals, for preparing metal hydrides, HCl and to reduce heavy metal oxides.
- as a rocket fuel in space research.
- in fuel cells for generating electrical energy.

HYDRIDES

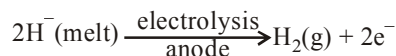
Dihydrogen combines with almost all elements to form binary compounds called hydrides, which can be represented as EH_x (ex. MgH_2) or E_mH_n (ex. B_2H_6) (E is the symbol of the element).

Classification of Hydrides

The hydrides are classified into three categories

(i) Ionic or saline hydrides

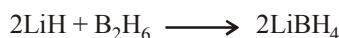
- They are formed with s-block elements (as they are electropositive in nature)
- They are crystalline, non-volatile and non-conducting in solid state
- Their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode.



- (d) Saline hydrides with water gives dihydrogen gas



- (e) Being unreactive at moderate temperature with O_2 or Cl_2 , LiH is used in synthesis of other hydrides.



(ii) Covalent or molecular hydrides

- They are formed with p-block elements and some s-block elements (Be and Mg)
ex: CH_4 , NH_3 , H_2O , HF

- (b) They are further classified as:

- Electron deficient:** which have few e^- s for writing Lewis structure
Ex: B_2H_6 . All elements of group 13 form e^- , deficient compounds. They act as Lewis acid.
- Electron precise:** They have the required no. of e^- to write Lewis structure. All elements of group 14 (ex: CH_4) form such compounds.

- Electron rich:** They have excess e^- s which are present as lone pairs. Elements of group 15-17 form such compounds.

They behave as Lewis bases, i.e., e^- donors.

Ex: NH_3 , H_2O , etc.

(iii) Metallic or interstitial hydrides

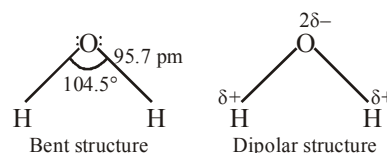
- They are formed by d- and f-block elements.
- They are non-stoichiometric, being deficient in hydrogen
ex: $\text{LaH}_{2.87}$, $\text{NiH}_{0.6-0.7}$
In such hydrides the law of constant composition does not hold good.
- Here, hydrogen occupies interstices in metal lattice producing distortion. Hence, the name interstitial hydrides.
- The property of absorption of hydrogen on transition metals is widely used in catalytic reduction or hydrogenation reactions for preparing large number of compounds.

WATER

Physical Properties

- It is colourless and tasteless liquid.
- Due to extensive H-bonding between water molecules, it has high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to H_2S , H_2Se , H_2Te etc.
- In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension and dipole moment.

Structure of water: In H_2O each oxygen forms four sp^3 -hybridized orbital. Two of these form sp^3 -s, O-H-bonds while other two contain a lone pair of electrons each. In gas phase, H_2O is a bent molecule with a bond angle of 104.5° and O-H bond length of 95.7 pm.



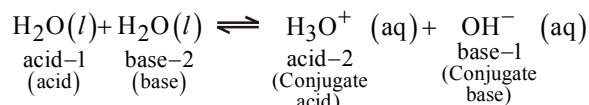
Structure of Ice: Ice has a highly ordered 3D H-bonded structure in which each O-atom is tetrahedrally surrounded by four other O-atoms at a distance of 276 pm. This gives ice an open cage like structure. Density of ice is less than that of water. Thus, ice floats on water.

Chemical Properties

- Amphoteric nature:** H_2O has the ability to act as an acid as well as a base.

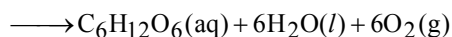


The auto-protolysis i.e. self ionization of water takes place as follows:

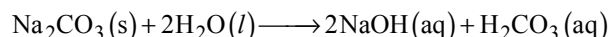
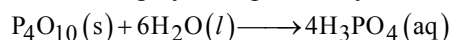


(ii) **Redox reactions involving water :**

- (a) $2\text{H}_2\text{O}(l) + 2\text{Na}(s) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$
i.e., highly electropositive metals reduce H_2O to H_2 .
- (b) It is oxidised to O_2 during photosynthesis:
 $6\text{CO}_2(g) + 12\text{H}_2\text{O}(l)$



- (c) $2\text{F}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4\text{H}^+(aq) + 4\text{F}^-(aq) + \text{O}_2(g)$

(iii) **Hydrolysis reaction:** Due to high dielectric constant, water shows strong hydrating tendency.(iv) **Hydrate formation :** Many ionic compounds crystallise from water with one or more molecules of water associated with them. These hydrates are classified as :

- (a) **Coordinated water :** ex., $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$
(b) **Interstitial water :** $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
(c) **H-bonded water :** $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} \text{SO}_4^{2-} \cdot \text{H}_2\text{O}$
in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

HARD AND SOFT WATER**Hard Water**

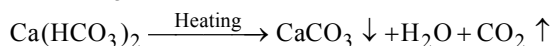
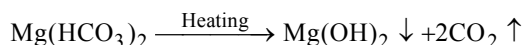
It does not give lather with soap. It contains salts of calcium and magnesium in the form of chloride, sulphate and hydrogen carbonate. Hard water forms scum with soap which is unsuitable for laundry and boilers.

Soft Water

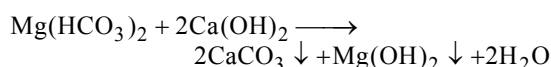
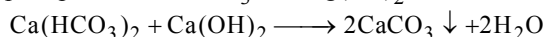
It gives lather with soap. It is free from soluble salts of calcium and magnesium.

Types of Hardness of Water**Hardness of water is of two types**(i) **Temporary :** It is due to presence of Mg and Ca hydrogen carbonates. It can be removed by

- (a) boiling

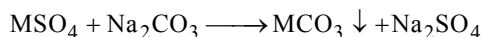


- (b) **Clark's method** (lime is added to hard water which precipitates out CaCO_3 and $\text{Mg}(\text{OH})_2$).

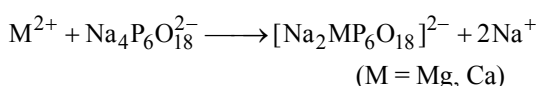
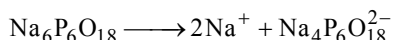
(ii) **Permanent :** It is due to presence of soluble salts of Mg and Ca as sulphates and chlorides.

It can be removed by

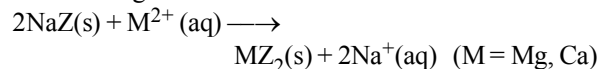
- (a) Treating with washing soda



- (b) Calgon's method



(c) Ion-exchange method



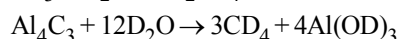
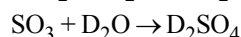
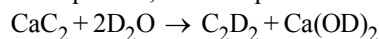
where, $\text{NaZ} \rightarrow \text{NaAlSiO}_4$ (zeolite)

(d) Synthetic resins method. Cation exchange resins exchange H^+ ions with cations such as Ca^{2+} and Mg^{2+} ions present in hard water.

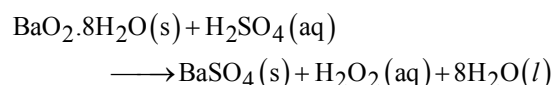
Anion exchange resins exchange OH^- ion with anions such as Cl^- and SO_4^{2-} .

HEAVY WATER (D_2O)

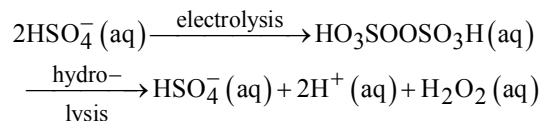
It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. It is used for the preparation of other deuterium compounds, for example:

**HYDROGEN PEROXIDE (H_2O_2)****Preparation**

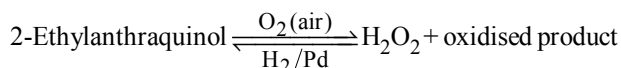
(i) By acidifying barium peroxide



(ii) By hydrolysis of peroxodisulphate



(iii) Industrial preparation

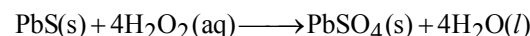
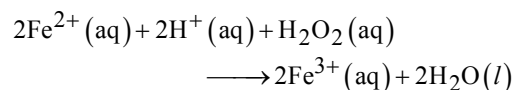
**Properties**

Physical properties : In the pure state, H_2O_2 is an almost colourless (very pale blue) liquid. H_2O_2 is miscible with water in all proportions and forms a hydrate $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ (mp 221 K).

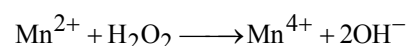
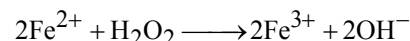
A 30% solution of H_2O_2 is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution will give 100 V of oxygen at STP.

Chemical properties

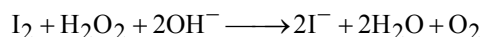
(i) Oxidising action in acidic medium



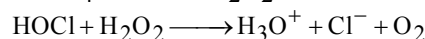
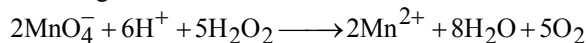
(ii) Oxidising action in basic medium



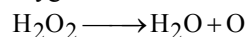
(iii) Reducing action in basic medium



(iv) Reducing action in acidic medium

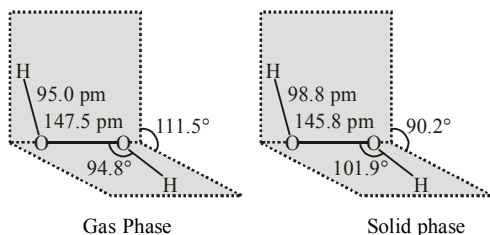


(iv) H_2O_2 acts as a bleaching agent due to the release of nascent oxygen



Structure

Hydrogen peroxide has a non-planar structure.

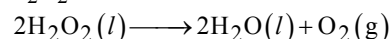


(i) H_2O_2 structure in gas phase, dihedral angle is 111.5° .

(ii) H_2O_2 structure in solid phase at 110 K, dihedral angle is 90.2° .

Storage

H_2O_2 decomposes on exposure to light



The reaction is catalysed in presence of metal surfaces or traces of alkali. Hence, it is stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

Uses of H_2O_2

- (i) In daily life it is used as a hair bleach and as a mild disinfectant.
- (ii) It is used to manufacture chemicals like sodium perborate and percarbonate, which are used in high quality detergents.
- (iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- (iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- (v) Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

Dihydrogen as a Fuel

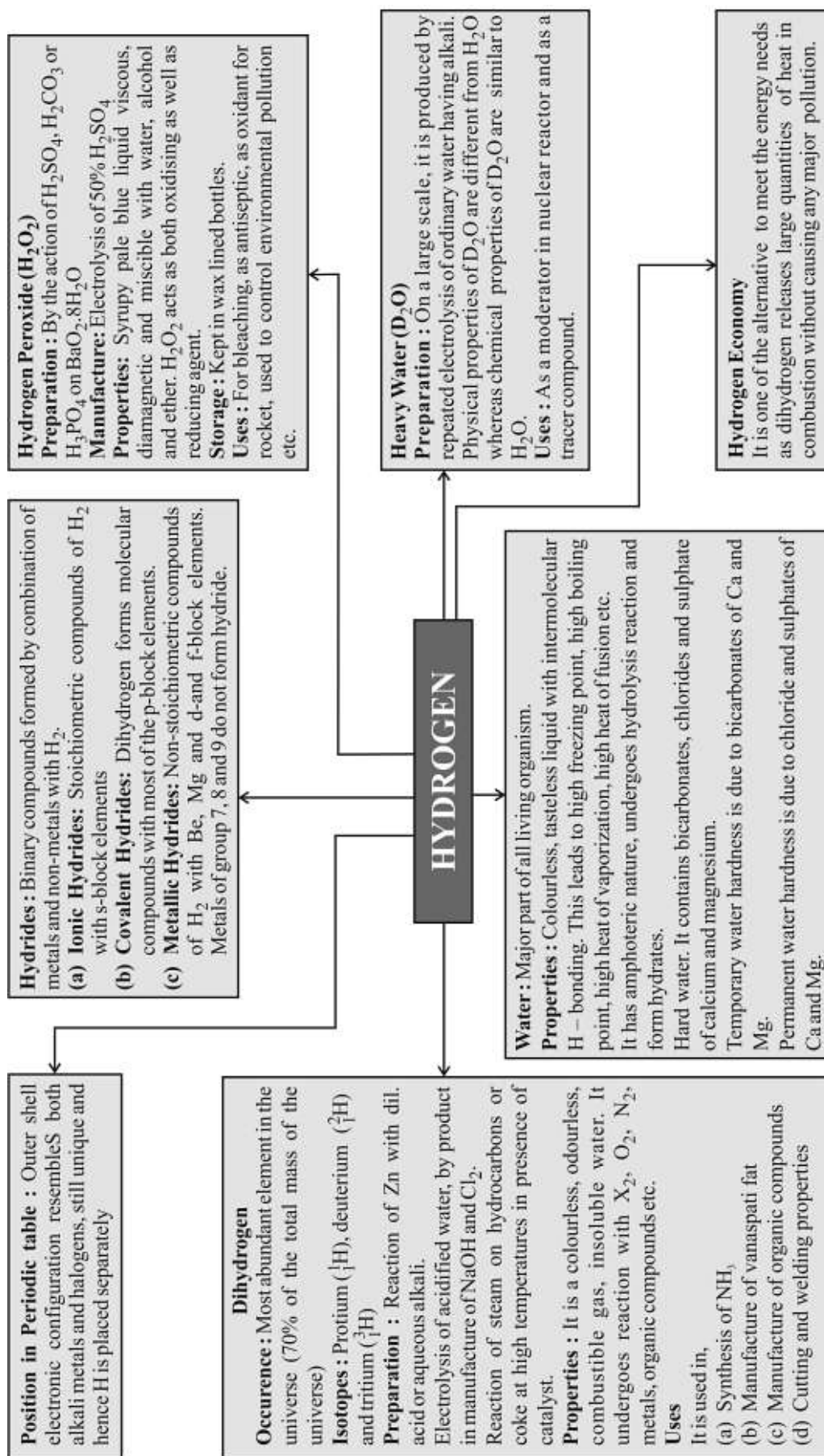
H_2 releases large amount of heat on combustion. On a mass basis, H_2 releases more energy than petrol. Moreover, it produces less pollution than petrol.

It has promising potential for use as a non-polluting fuel of near future. This is studied under 'Hydrogen Economy'. The basic principle of Hydrogen economy is transportation and storage of energy in form of liquid or gaseous dihydrogen.

Advantage of Hydrogen economy is that energy is transmitted in form of H_2 and not as electric power.

Now a days H_2 is also used in fuel cells for generation of electric power.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- Hydrogen is not more reactive at ordinary temperature, because at ordinary temperature it is in its:
(a) gaseous state (b) liquid state
(c) molecular state (d) atomic state
- Hydrogen has high ionization energy than alkali metals because it has :
(a) Ionic bond (b) Covalent bond
(c) Large size (d) Small size
- The number of moles of H_2 in 0.224 litre of hydrogen gas at STP (273 K, 1 atm) is :
(a) 0.1 (b) 0.01
(c) 0.001 (d) 1
- The ionization of hydrogen atom would give rise to
(a) hydride ion (b) hydronium ion
(c) proton (d) hydroxyl ion.
- Which of the following statement is not correct regarding hydrogen atom?
(a) It resembles with halogens in some properties
(b) It resembles with alkali metals in some properties.
(c) It cannot be placed in first group of periodic table.
(d) It is the lightest element
- Which one of the following pairs of substances on reaction will not evolve H_2 gas?
(a) Iron and H_2SO_4 (aqueous)
(b) Iron and steam
(c) Copper and HCl (aqueous)
(d) Sodium and ethyl alcohol
- When two ice cubes are pressed over each other, they unite to form one cube. Which of the following forces is responsible to hold them together ?
(a) Hydrogen bond formation
(b) van der Waals forces
(c) Covalent attraction
(d) Ionic interaction
- Which statement is correct for hydrogen ?
(a) It has a very high ionisation potential
(b) It is always collected at cathode
(c) It can form bonds in +1 as well as -1 oxidation state
(d) It has same electronegativity as halogens
- Hydrogen can be differentiated by other alkali metals due to its :
(a) nonmetallic character
(b) affinity for non-metals
(c) electropositive character
(d) reducing character
- Hydrogen molecules differs from chlorine molecule in the following respect
(a) Hydrogen molecule is non-polar but chlorine molecule is polar
(b) Hydrogen molecule is polar while chlorine molecule is non-polar
(c) Hydrogen molecule can form intermolecular hydrogen bonds but chlorine molecule does not
(d) Hydrogen molecule cannot participate in coordination bond formation but chlorine molecule can
- Hydrogen will not reduce
(a) heated cupric oxide (d) heated ferric oxide
(c) heated stannic oxide (d) heated aluminium oxide
- Hydrogen is evolved by the action of cold dil. HNO_3 on
(a) Fe (b) Mn
(c) Cu (d) Al
- On industrial scale, H_2O_2 is now generally prepared by
(a) The action of H_2SO_4 on barium
(b) The action of H_2SO_4 on sodium peroxide
(c) By the electrolysis of H_2SO_4
(d) By burning hydrogen in an excess of O_2 .
- Hydrogen can behave as a metal
(a) at very high temperature
(b) at very low temperature
(c) at very high pressure
(d) at very low pressure
- Which cannot be oxidised by H_2O_2 :
(a) Na_2SO_3 (b) PbS
(c) KI (d) O_3
- The property of hydrogen which distinguishes it from alkali metals is
(a) its electropositive character
(b) its affinity for non metal
(c) its reducing character
(d) its non-metallic character
- Hydrogen accepts an electron to form inert gas configuration. In this it resembles
(a) halogen (b) alkali metals
(c) chalcogens (d) alkaline earth metals
- In Bosch's process which gas is utilised for the production of hydrogen gas ?
(a) Producer gas (b) Water gas
(c) Coal gas (d) None of these
- The adsorption of hydrogen by metals is called
(a) Dehydrogenation (b) Hydrogenation
(c) Occlusion (d) Adsorption
- Which of the following ions can be replaced by H^+ ions when H_2 gas is bubbled through the solutions containing these ions ?
(a) Li^+ (b) Ba^{2+}
(c) Cu^{2+} (d) Be^{2+}
- Which of the following terms is not correct for hydrogen ?
(a) Its molecule is diatomic
(b) It exists both as H^+ and H^- in different chemical compounds
(c) It is the only species which has no neutrons in the nucleus
(d) Heavy water is unstable because hydrogen is substituted by its isotope deuterium

22. Water is :
 (a) more polar than H_2S
 (b) more or less identical in polarity with H_2S
 (c) less polar than H_2S
 (d) None of these
23. The reagent commonly used to determine hardness of water titrimetrically is
 (a) oxalic acid (b) sodium thiosulphate
 (c) sodium citrate (d) disodium salt of EDTA
24. Calgon used as a water softener is
 (a) $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ (b) $\text{Na}_4[\text{Na}_2(\text{PO}_3)_6]$
 (c) $\text{Na}_4[\text{Na}_4(\text{PO}_4)_5]$ (d) $\text{Na}_4[\text{Na}_2(\text{PO}_4)_6]$
25. Which of the following groups of ions makes the water hard?
 (a) Sodium and bicarbonate
 (b) Magnesium and chloride
 (c) Potassium and sulphate
 (d) Ammonium and chloride.
26. Consider the following statements :
 1. Atomic hydrogen is obtained by passing hydrogen through an electric arc.
 2. Hydrogen gas will not reduce heated aluminium oxide.
 3. Finely divided palladium adsorbs large volume of hydrogen gas
 4. Pure nascent hydrogen is best obtained by reacting Na with $\text{C}_2\text{H}_5\text{OH}$
 Which of the above statements is/are correct ?
 (a) 1 alone (b) 2 alone
 (c) 1, 2 and 3 (d) 2, 3 and 4
27. Pure water can be obtained from sea water by
 (a) centrifugation (b) plasmolysis
 (c) reverse osmosis (d) sedimentation
28. The $\text{H}-\text{O}-\text{H}$ angle in water molecule is about
 (a) 90° (b) 180°
 (c) 102.5° (d) 104.5°
29. D_2O is used in
 (a) motor vehicles (b) nuclear reactor
 (c) medicine (d) insecticide
30. The process used for the removal of hardness of water is
 (a) Calgon (b) Baeyer
 (c) Serpeck (d) Hoope
31. When zeolite (hydrated sodium aluminium silicate) is treated with hard water the sodium ions are exchanged with
 (a) H^+ ions (b) Ca^{2+} ions
 (c) SO_4^{2-} ions (d) OH^- ions
32. The percentage by weight of hydrogen in H_2O_2 is
 (a) 5.88 (b) 6.25
 (c) 25 (d) 50
33. The alum used for purifying water is
 (a) ferric alum (b) chrome alum
 (c) potash alum (d) ammonium alum
34. The boiling point of water is exceptionally high because
 (a) there is covalent bond between H and O
 (b) water molecule is linear
 (c) water molecules associate due to hydrogen bonding
 (d) water molecule is not linear
35. What is formed when calcium carbide reacts with heavy water?
 (a) C_2D_2 (b) CaD_2
 (c) $\text{Ca}_2\text{D}_2\text{O}$ (d) CD_2
36. Water possesses a high dielectric constant, therefore :
 (a) it always contains ions
 (b) it is a universal solvent
 (c) can dissolve covalent compounds
 (d) can conduct electricity
37. Chemical A is used for water softening to remove temporary hardness. A reacts with sodium carbonate to generate caustic soda. When CO_2 is bubbled through a solution of A, it turns cloudy. What is the chemical formula of A.
 (a) CaCO_3 (b) CaO
 (c) $\text{Ca}(\text{OH})_2$ (d) $\text{Ca}(\text{HCO}_3)_2$
38. Which of the following is not true?
 (a) D_2O freezes at lower temperature than H_2O
 (b) Reaction between H_2 and Cl_2 is much faster than D_2 and Cl_2
 (c) Ordinary water gets electrolysed more rapidly than D_2O
 (d) Bond dissociation energy of D_2 is greater than H_2
39. Which of the following statements do not define the characteristic property of water "Water is a universal solvent"
 (a) It can dissolve maximum number of compounds
 (b) It has very low dielectric constant
 (c) It has high liquid range
 (d) None of these
40. The reaction

$$\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow \text{S} + 2\text{H}_2\text{O}$$
 manifests
 (a) Acidic nature of H_2O_2
 (b) Alkaline nature of H_2O_2
 (c) Oxidising action of H_2O_2
 (d) Reducing action of H_2O_2
41. Triple point of water is
 (a) 273 K (b) 373 K
 (c) 203 K (d) 193 K
42. Which of the following is correct about heavy water ?
 (a) Water at 4°C having maximum density is known as heavy water
 (b) It is heavier than water (H_2O)
 (c) It is formed by the combination of heavier isotope of hydrogen with oxygen
 (d) None of these

43. When sulphur trioxide is heated with heavy water the products are
 (a) Deutero-sulphuric acid
 (b) Deuterium sulphuric acid
 (c) Deuterium and sulphuric acid
 (d) None of the above.
44. The volume strength of 1.5 N H_2O_2 solution is :
 (a) 8.4 (b) 8.0
 (c) 4.8 (d) 3.0
45. The decomposition of H_2O_2 is accelerated by –
 (a) glycerine (b) alcohol
 (c) phosphoric acid (d) Pt powder
46. Commercial 10 volume H_2O_2 is a solution with a strength of approximately
 (a) 15% (b) 3%
 (c) 1% (d) 10%
47. Which of the following statements is not true for hydrogen peroxide?
 (a) Pure H_2O_2 is fairly stable
 (b) It sometimes acts as a reducing agent
 (c) It acts as an oxidising agent
 (d) Aqueous solution of H_2O_2 is weakly basic
48. The structure of H_2O_2 is
 (a) planar (b) non planar
 (c) spherical (d) linear
49. In lab H_2O_2 is prepared by
 (a) Cold $\text{H}_2\text{SO}_4 + \text{BaO}_2$ (b) $\text{HCl} + \text{BaO}_2$
 (c) Conc. $\text{H}_2\text{SO}_4 + \text{Na}_2\text{O}_2$ (d) $\text{H}_2 + \text{O}_2$
50. The reaction of $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + 2\text{H}_2\text{O}$ manifests
 (a) Acidic nature of H_2O_2 (b) Alkaline nature of H_2O_2
 (c) Oxidising nature of H_2O_2 (d) Reducing action of H_2O_2
51. The strength in volumes of a solution containing 30.36 g/L of H_2O_2 is
 (a) 10V (b) 5V
 (c) 20V (d) None of these
52. Which one the following removes temporary hardness of water ?
 (a) Slaked lime (b) Plaster of Paris
 (c) Epsom (d) Hydrolith
53. 20 volume H_2O_2 solution has a strength of about
 (a) 30% (b) 6%
 (c) 3% (d) 10%
54. Which substance does not speed up decomposition of H_2O_2
 (a) Glycerol (b) Pt
 (c) Gold (d) MnO_2
55. H_2O_2 is a
 (a) Weak acid (b) Weak base
 (c) Neutral (d) None of these
56. Hydrogen is not obtained when zinc reacts with
 (a) Cold water (b) dil. HCl
 (c) dil. H_2SO_4 (d) Hot NaOH (20%)
57. H_2O_2 is always stored in black bottles because
 (a) It is highly unstable
 (b) Its enthalpy of decomposition is high
 (c) It undergo auto-oxidation on prolonged standing
 (d) None of these
58. Which of the following is wrong about H_2O_2 ? It is used
 (a) As aerating agent in production of sponge rubber
 (b) As an antichlor
 (c) For restoring white colour of blackened lead painting
 (d) None of these
59. $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$; $E^\circ = -0.68 \text{ V}$. This equation represents which of the following behaviour of H_2O_2 .
 (a) Reducing (b) Oxidising
 (c) Acidic (d) Catalytic
60. Hard water when passed through ion exchange resin containing $\text{R}'\text{COOH}$ groups, becomes free from :
 (a) Cl^- (b) SO_4^{2-}
 (c) H_3O^+ (d) Ca^{2+}
61. H_2O_2 when added to a solution containing KMnO_4 and H_2SO_4 :
 (a) Acts as an oxidizing agent
 (b) Acts as a reducing agent
 (c) Acts both as an oxidizing as well as a reducing agent
 (d) Producing no reaction
62. The O – O – H bond angle in H_2O_2 is
 (a) 106° (b) $109^\circ 28'$
 (c) 120° (d) 94.8°
63. When H_2O_2 is oxidised the product is
 (a) OH^- (b) O_2
 (c) O^{2-} (d) HO_2^-
64. Some statements about heavy water are given below:
 (A) Heavy water is used as a moderator in nuclear reactors.
 (B) Heavy water is more associated than ordinary water.
 (C) Heavy water is more effective solvent than ordinary water.
 Which of the above statements are correct?
 (a) (A) and (C) (b) (A) and (B)
 (c) (A), (B) and (C) (d) (B) and (C)
65. Which of the following reaction produces hydrogen
 (a) $\text{Mg} + \text{H}_2\text{O}$ (b) $\text{BaO}_2 + \text{HCl}$
 (c) $\text{H}_2\text{S}_4\text{O}_8 + \text{H}_2\text{O}$ (d) $\text{Na}_2\text{O}_2 + 2\text{HCl}$
66. Hydrogen can be fused to form helium at
 (a) High temperature and high pressure
 (b) High temperature and low pressure
 (c) Low temperature and high pressure
 (d) Low temperature and low pressure
67. Which of the following gas is insoluble in water ?
 (a) SO_2 (b) NH_3
 (c) H_2 (d) CO_2
68. In which of the following reactions, H_2O_2 acts as a reducing agent
 (a) $\text{PbO}_2(s) + \text{H}_2\text{O}_2(aq) \rightarrow \text{PbO}(s) + \text{H}_2\text{O}(\ell) + \text{O}_2(g)$
 (b) $\text{Na}_2\text{SO}_3(aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{O}(\ell)$
 (c) $2\text{KI}(aq) + \text{H}_2\text{O}_2(aq) \rightarrow 2\text{KOH}(aq) + \text{I}_2(s)$
 (d) $\text{KNO}_2(aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{KNO}_3(aq) + \text{H}_2\text{O}(\ell)$

69. Which one of the following statements is incorrect with regard to ortho- and para-dihydrogen?
- They are nuclear spin isomers
 - The ortho isomer has zero nuclear spin whereas the para isomer has one nuclear spin
 - The para isomer is flavoured at low temperatures
 - The thermal conductivity of the para isomer is 50% greater than that of the ortho isomer
70. Permanent hardness of water is due to the presence of
- bicarbonates of sodium and potassium
 - chlorides and sulphates of sodium and potassium
 - chlorides and sulphates of calcium and magnesium
 - bicarbonates of calcium and magnesium
71. The strength of H_2O_2 (in g/litre) in 11.2 volume solution of H_2O_2 is
- 17
 - 51
 - 34
 - 85
72. The polymeric hydride is
- CaH_2
 - NaH
 - BaH_2
 - MgH_2
73. The volume strength of a 3% w/v H_2O_2 sample is
- 20
 - 15
 - 25
 - 10
74. The sum of the number of neutrons and protons in all the three isotopes of hydrogen is
- 6
 - 5
 - 4
 - 3
75. Which of the following undergoes reduction with hydrogen peroxide in alkaline medium?
- Cl_2
 - I_2
 - PbS
 - Mn^{2+}

EXERCISE - 2

Applied Questions

- At its melting point ice is lighter than water because
 - H_2O molecules are more closely packed in solid state
 - ice crystals have hollow hexagonal arrangement of H_2O molecules.
 - on melting of ice the H_2O molecule shrinks in size
 - ice forms mostly heavy water on first melting.
- Which pair does not show hydrogen isotopes?
 - Ortho and para hydrogen
 - Protium & deuterium
 - Deuterium & tritium
 - Tritium and protium
- The hydride ion, H^- , is a stronger base than the hydroxide ion, OH^- . Which one of the following reactions will occur if sodium hydride (NaH) is dissolved in water?
 - $\text{H}^-(aq) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{O}^-(aq)$
 - $\text{H}^-(aq) + \text{H}_2\text{O}(\ell) \rightarrow \text{OH}^-(aq) + \text{H}_2(g)$
 - $\text{H}^-(aq) + \text{H}_2\text{O}(\ell) \rightarrow \text{OH}^-(aq) + 2\text{H}^+(aq) + 2e^-$
 - $\text{H}^-(aq) + \text{H}_2\text{O}(\ell) \rightarrow \text{No reaction}$
- HCl is added to following oxides. Which one would give H_2O_2
 - MnO_2
 - PbO_2
 - BaO
 - None of these
- Heavy water reacts respectively with CO_2 , SO_3 , P_2O_5 and N_2O_5 to give the compounds :
 - D_2CO_3 , D_2SO_4 , D_3PO_2 , DNO_2
 - D_2CO_3 , D_2SO_4 , D_3PO_4 , DNO_2
 - D_2CO_3 , D_2SO_3 , D_3PO_4 , DNO_2
 - D_2CO_3 , D_2SO_4 , D_3PO_4 , DNO_3
- The H^- ion can be formed in ordinary chemical reaction under proper conditions, but the H^+ ion cannot. The best explanation for this difference is due to
 - the radius of the H nucleus
 - the electronegativity of H atom.
 - the ionisation energy of the H-atom
 - the bond dissociation energy of H-H bond
- D_2O is preferred to H_2O , as a moderator, in nuclear reactors because
 - D_2O slows down fast neutrons better
 - D_2O has high specific heat
 - D_2O is cheaper
 - None of these
- Saline hydrides react explosively with water, such fires can be extinguished by
 - water
 - carbon dioxide
 - sand
 - None of these
- Which of the following chemicals is not present in clear hard water?
 - MgCO_3
 - MgSO_4
 - $\text{Mg}(\text{HCO}_3)_2$
 - CaCl_2
- When same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide solution the ratio of volumes of hydrogen evolved is
 - 1 : 1
 - 1 : 2
 - 2 : 1
 - 9 : 4
- Choose the correct statement :
The reason for use of polyphosphates as water softening agents is, that
 - they form soluble complexes with anionic species
 - they precipitate out cationic species
 - they precipitate out anionic species
 - they form soluble complexes with cationic species

12. Which one of the following processes will produce hard water ?
 (a) Saturation of water with MgCO_3
 (b) Saturation of water with CaSO_4
 (c) Addition of Na_2SO_4 to water
 (d) Saturation of water with CaCO_3
13. Which of the following species is diamagnetic in nature?
 (a) H_2^- (b) H_2^+
 (c) H_2 (d) He_2^+
14. Which of the following statements in relation to the hydrogen atom is correct ?
 (a) 3s, 3p and 3d orbitals all have the same energy
 (b) 3s and 3p orbitals are of lower energy than 3d orbital
 (c) 3p orbital is lower in energy than 3d orbital
 (d) 3s orbital is lower in energy than 3p orbital
15. In context with the industrial preparation of hydrogen from water gas ($\text{CO} + \text{H}_2$), which of the following is the correct statement?
 (a) CO and H_2 are fractionally separated using differences in their densities
 (b) CO is removed by absorption in aqueous Cu_2Cl_2 solution
 (c) H_2 is removed through occlusion with Pd
 (d) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali
16. The critical temperature of water is higher than that of O_2 because H_2O molecule has
 (a) Fewer electrons than oxygen
 (b) Two covalent bonds
 (c) V-shape
 (d) Dipole moment
17. Blackened oil painting can be restored into original form by the action of
 (a) Chlorine (b) BaO_2
 (c) H_2O_2 (d) MnO_2
18. Which of the following is false about H_2O_2
 (a) Act as both oxidising and reducing agent
 (b) Two OH bonds lies in the same plane
 (c) Pale blue liquid
 (d) Can be oxidised by ozone
- DIRECTIONS for Qs. 19 to 25: These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
 (b) Statement-1 is True, Statement -2 is True ; Statement-2 is NOT a correct explanation for Statement -1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement -2 is True
19. **Statement-1** : Decomposition of H_2O_2 is a disproportionation reaction.
Statement-2 : H_2O_2 molecule simultaneously undergoes oxidation and reduction.
20. **Statement-1** : Temporary hardness can be removed by boiling.
Statement-2 : On boiling the soluble bicarbonates change to carbonates which being insoluble, get precipitated.
21. **Statement-1** : H_2O_2 is not stored in glass bottles.
Statement-2 : Alkali oxides present in glass catalyse the decomposition of H_2O_2
22. **Statement-1** : Hydrogen combines with other elements by losing, gaining or sharing of electrons.
Statement-2 : Hydrogen forms electrovalent and covalent bonds with other elements.
23. **Statement-1** : Calgon is used for removing permanent hardness of water.
Statement-2 : Calgon forms precipitates with Ca^{2+} and Mg^{2+} .
24. **Statement-1** : In alkaline solution, H_2O_2 reacts with potassium ferricyanide.
Statement-2 : H_2O_2 is a strong reducing agent.
25. **Statement-1** : Hydrogen peroxide forms two series of salts called peroxides.
Statement-2 : Hydrogen peroxide molecule has two replaceable hydrogen atom.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect?
 (a) Its tendency to lose an electron to form a cation
 (b) Its tendency to gain a single electron in its valence shell to attain stable electronic configuration
 (c) Its low negative electron gain enthalpy value
 (d) Its small size
2. Why does H^+ ion always get associated with other atoms or molecules?
 (a) Ionisation enthalpy of hydrogen resembles that of alkali metals
 (b) Its reactivity is similar to halogens
 (c) It resembles both alkali metals and halogens
 (d) Loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ions. Due to small size it cannot exist free.

3. Metal hydrides are ionic, covalent or molecular in nature. Among LiH, NaH, RbH, CsH, the correct order of increasing ionic character is

(a) LiH > NaH > CsH > KH > RbH
 (b) LiH < NaH < KH < RbH < CsH
 (c) RbH > CsH > NaH > KH > LiH
 (d) NaH > CsH > RbH > LiH > KH

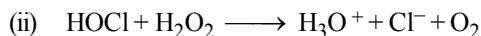
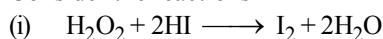
4. Which of the following hydrides is electron-precise hydride?

(a) B₂H₆ (b) NH₃
 (c) H₂O (d) CH₄

5. Radioactive elements emit α , β and γ rays and are characterised by their half-lives. The radioactive isotope of hydrogen is

(a) protium (b) deuterium
 (c) tritium (d) hydronium

6. Consider the reactions



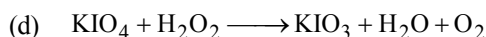
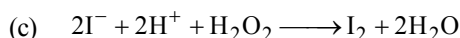
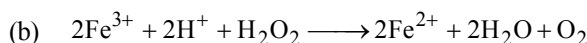
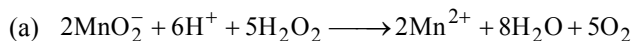
Which of the following statements is correct about H₂O₂ with reference to these reactions? Hydrogen peroxide is

(a) an oxidising agent in both (i) and (ii)
 (b) an oxidising agent in (i) and reducing agent in (ii)
 (c) a reducing agent in (i) and oxidising agent in (ii)
 (d) a reducing agent in both (i) and (ii)

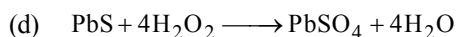
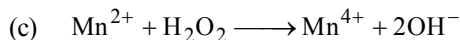
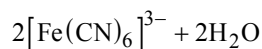
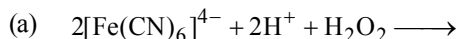
7. The oxide that gives H₂O₂ on treatment with dilute H₂SO₄ is

(a) PbO₂ (b) BaO₂·8H₂O
 (c) MnO₂ (d) TiO₂

8. Which of the following equations depict the oxidising nature of H₂O₂?



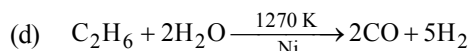
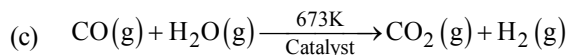
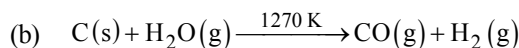
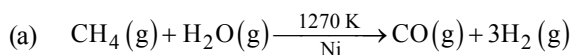
9. Which of the following equation depict reducing nature of H₂O₂?



10. Hydrogen peroxide is

(a) an oxidising agent
 (b) a reducing agent
 (c) both an oxidising and a reducing agent
 (d) neither oxidising nor reducing agent

11. Which of the following reactions increases production of dihydrogen from synthesis gas?



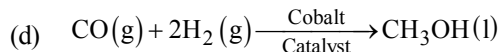
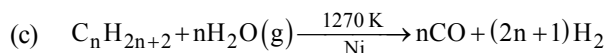
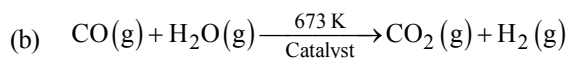
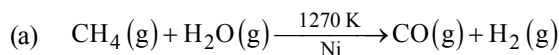
12. When sodium peroxide is treated with dilute sulphuric acid, we get

(a) sodium sulphate and water
 (b) sodium sulphate and oxygen
 (c) sodium sulphate, hydrogen and oxygen
 (d) sodium sulphate and hydrogen peroxide

13. Hydrogen peroxide is obtained by the electrolysis of

(a) water (b) sulphuric acid
 (c) hydrochloric acid (d) fused sodium peroxide

14. Which of the following reactions is an example of use of water gas in the synthesis of other compounds?



15. Which of the following ions will cause hardness in water sample?

(a) Ca²⁺ (b) Na⁺
 (c) Cl⁻ (d) K⁺

16. Which of the following compounds is used for water softening?

(a) Ca₃(PO₄)₂ (b) Na₃PO₄
 (c) Na₆P₆O₁₈ (d) Na₂HPO₄

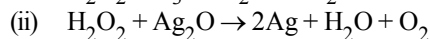
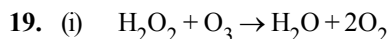
17. Elements of which of the following group(s) of periodic table do not form hydrides?

(a) Groups 7, 8, 9 (b) Group 13
 (c) Groups 15, 16, 17 (d) Group 14

18. Only one element of forms hydride.

(a) group 6 (b) group 7
 (c) group 8 (d) group 9

NEET/AIPMT (2013-2017) Questions



Role of hydrogen peroxide in the above reactions is respectively - [2014]

(a) Oxidizing in (i) and reducing in (ii)
 (b) Reducing in (i) and oxidizing in (ii)
 (c) Reducing in (i) and (ii)
 (d) Oxidizing in (i) and (ii)

20. Which of the following statements about hydrogen is incorrect? [2016]

(a) hydrogen has three isotopes of which tritium is the most common.
 (b) Hydrogen never acts as cation in ionic salts
 (c) Hydronium ion, H₃O⁺ exists freely in solution
 (d) Dihydrogen does not act as a reducing agent

Hints & Solutions

EXERCISE - 1

- (c) Hydrogen is not reactive at ordinary temperature because it is in molecular state i.e., as H_2 with its complete duplet which makes it stable and lesser reactive. At very high temperature, hydrogen exists in atomic form having one electron i.e., incomplete duplet which makes it less stable and highly reactive.
- (d) Hydrogen has high ionisation energy in comparison with alkali metals because it has only one orbital i.e. smaller size. Due to smaller size, hold of nucleus on outermost electron is greater in case of hydrogen.
- (b) $\therefore 22.4 \text{ L of } H_2 \text{ at STP} = 1 \text{ mole of } H_2$
 $\therefore 0.224 \text{ L of } H_2 \text{ at STP} = \frac{1}{22.4} \times 0.224 = 0.01 \text{ moles.}$
- (c) $H(g) \longrightarrow H^+(g) + e^-$.
- (c) Actually hydrogen is in the first group of periodic table due to its much resemblance with alkali metals
- (c) $Fe + \text{dil. } H_2SO_4 \rightarrow FeSO_4 + H_2 \uparrow$
 $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \uparrow$
 Steam
 $Cu + \text{dil. } HCl \rightarrow \text{No reaction}$
 Copper does not evolve H_2 from acid as it is below hydrogen in electrochemical series.
 $2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2 \uparrow$
- (a) Two ice cubes stick to each other due to H-bonding
- (c) The correct option is (c). In H_2O , hydrogen has + 1 oxidation no. In CaH_2 , hydrogen has - 1 oxidation no.
- (a) Hydrogen can be differentiated from after group I elements due to its non-metallic character.
- (d) Chlorine has lone pair which it can donate to form coordinate bond while hydrogen cannot.
- (d) H_2 will not reduce heated Al_2O_3 . As Al is more electro-positive than hydrogen. therefore, its oxide will not be reduced by hydrogen.
- (b) $Mn + 2HNO_3 (\text{dil.}) \rightarrow Mn(NO_3)_2 + H_2$
- (c) By electrolysis of 50% ice cold H_2SO_4 .
 $2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$
 At anode: $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$
 $H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$
 $H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$
- (c) Hydrogen behaves as a metal at very high pressure.
- (d) H_2O_2 can not oxidise O_3 .
 O_3 oxidises H_2O_2
 $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$
 Option (d) is correct.
- (d) Hydrogen is a non-metal while all other members of group 1 (alkali metals) are metals.
- (a) $H + e^- (1s^1) \rightarrow H^- (1s^2 \text{ or } [He])$
 $F + e^- ([He]2s^22p^5) \rightarrow F^- ([He]2s^22p^6 \text{ or } [Ne])$
- (b) $\underbrace{CO + H_2}_{\text{water gas}} \xrightarrow{\text{catalyst}} CO_2 + 2H_2$
- (c) Occlusion is the phenomenon of adsorption of hydrogen by metal.
- (c) Among the given ions, only Cu^{2+} lies below H^+ in electrochemical series.
- (d) Heavy water is stable.
- (a) Polarity of bond depends on difference in electronegativity of the two concerned atoms. H_2O is more polar than H_2S because oxygen (in O-H) is more electronegative than sulphur (in S-H).
- (d) It forms calcium and magnesium complex with Ca^{2+} and Mg^{2+} ions present in hard water.
- (a) The complex salt of metaphosphoric acid sodium hexametaphosphate $(NaPO_3)_6$, is known as calgon. It is represented as $Na_2[Na_4(PO_3)_6]$
- (b) Temporary hardness is due to presence of bicarbonates of calcium and magnesium and permanent hardness is due to the sulphates and chlorides of both of calcium and magnesium.
- (c) Pure hydrogen is evolved by reacting absolute alcohol and Na
 $C_2H_5OH + Na \rightarrow C_2H_5ONa + \frac{1}{2}H_2$
 other statements are correct. See text.
- (c) Sea water is purified by reverse osmosis.
- (d) The hybridisation in water is sp^3 and bond angle 104.5°
- (b) D_2O is used in nuclear reactors as moderator.
- (a) Calgon process is used to remove permanent hardness of water
- (b) $Na \text{ zeolite} + CaCl_2 \rightarrow Ca \text{ zeolite} + 2NaCl$
- (a) % hydrogen in $H_2O_2 = \frac{2}{34} \times 100 = 5.88\%$
- (c) Potash alum is used for purifying water.
- (c) The high boiling point of water is due to H-bonding.
- (a) $CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$
- (b) Due to high dielectric constant, water acts as a good solvent therefore it is also called a universal solvent.
- (c) $Ca(OH)_2$ is used for the softening of temporary hard water.
 $Ca(OH)_2(aq) \xrightarrow{\text{cloudiness}} CaCO_3(s) + H_2O(l)$
- (a) D_2O actually has higher freezing point ($3.8^\circ C$) than water H_2O ($0^\circ C$)
- (b) Water has high dielectric constant i.e., $78.39 \text{ C}^2/\text{Nm}^2$, high liquid range and can dissolve maximum number of compounds. That is why it is used as universal solvent.
- (c) H_2S is oxidised to S by H_2O_2

41. (a) The triple point of any substance is that temperature and pressure at which the material can exist in all three phases (Solid, liquid and gas) in equilibrium specifically the triple point of water is 273.16 K at 611.2 Pa.
42. (c) Heavy water is formed by the combination of heavier isotope (${}_1\text{H}^2$ or D) with oxygen.

$$2\text{D}_2 + \text{O}_2 \rightarrow 2\text{D}_2\text{O}$$
Heavy water
43. (a) $\text{SO}_3 + \text{D}_2\text{O} \longrightarrow \text{D}_2\text{SO}_4$
(Deutero sulphuric acid)
44. (a) Normality of $\text{H}_2\text{O}_2 = \frac{\text{vol. strength}}{5.6}$
Volume of normal (1N) H_2O_2 solution = 5.6 volumes.
 $\therefore$ Volume of strength of 1.5 N H_2O_2
 $= 1.5 \times 5.6 = 8.4$ volumes.
45. (d) Decomposition of H_2O_2 can be accelerated by finely divided metals such as Ag, Au, Pt, Co, Fe etc.
46. (b) Strength of 10V $\text{H}_2\text{O}_2 = \frac{68 \times 10}{22400} \times 100 = 3.035\%$
47. (d) It is weakly acidic in nature and pure hydrogen peroxide turns blue litmus red. ($K_a = 1.57 \times 10^{-12}$ at 293 K). It ionises in two steps.

$$\text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$$

$$\text{HO}_2^- \rightleftharpoons \text{H}^+ + \text{O}_2^{2-}$$
So, option (d) is not true.
48. (b) Structure of H_2O_2 is nonplanar
49. (a) $\text{H}_2\text{SO}_4 + \text{BaO}_2 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
50. (c) $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + 2\text{H}_2\text{O}$
In this reaction H_2O_2 shows oxidising nature.
51. (a) Eq. wt. of $\text{H}_2\text{O}_2 = 17$

$$N = \frac{30.36}{17} = 1.78 \text{ N}$$
Volume strength = $5.6 \times \text{normality}$
 $= 5.6 \times 1.78 = 10 \text{ V}$
52. (a) This method is known as Clark's process. In this method temporary hardness is removed by adding lime water or milk of lime.

$$\text{Ca(OH)}_2 + \text{Ca(HCO}_3)_2 \longrightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$$
ppt.
53. (b) $\therefore$ 22.4 litre O_2 at N.T.P. obtained by 68 gm of H_2O_2
 $\therefore$ 1 litre O_2 at N.T.P. obtained by $\frac{68}{22.4}$ gm of H_2O_2
 $\therefore$ 20 litre O_2 at N.T.P. obtained by
 $\frac{68}{22.4} \times 20$ gm of $\text{H}_2\text{O}_2 = 60.71$ gm of H_2O_2
 $\therefore$ 1000 ml O_2 at N.T.P. obtained by = 60.71 gm of H_2O_2
 $\therefore$ 100 ml O_2 at N.T.P. obtained by
 $= \frac{60.71}{1000} \times 100 = 6.071\%$
54. (a) Glycerol, phosphoric acid or acetanilide is added to H_2O_2 to check its decomposition.
55. (a) $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + [\text{O}]$
weak acid
56. (a) Zinc has no action on cold water.
57. (c) H_2O_2 is unstable liquid and decomposes into water and oxygen either on standing or on heating.
58. (d) H_2O_2 show all these properties.
59. (a) As H_2O_2 is losing electrons so it is acting as reducing agent.
60. (d) An ion exchange resin containing R-COOH group exchange cations like Ca^{2+} , Mg^{2+} , Na^+ , Fe^{2+} with H^+ when hard water is passed through it. This resin is called cation exchange resin.
61. (b) Acidified KMnO_4 (pink or purple) is reduced to colourless Mn^{++} ion :

$$2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5[\text{O}]$$

$$\frac{\text{H}_2\text{O}_2 + [\text{O}] \longrightarrow \text{H}_2\text{O} + \text{O}_2 \times 5}{+7 \quad -1}$$

$$2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}_2 \longrightarrow$$
Pink or purple 0
Colourless

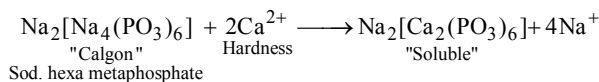
$$\text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$$
62. (d) O-O-H bond angle in H_2O_2 is 94.8° .
63. (b) $\text{H}_2\text{O}_2 + [\text{O}] \xrightarrow{\text{Oxidation}} \text{H}_2\text{O} + \text{O}_2 \uparrow$
64. (b) $\therefore$ Correct choice : (b)
65. (a) $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow$
66. (a) A fusion reaction is difficult to occur because positively charged nuclei repel each other. At very high temperature of the order of 10^6 to 10^7 K, the nuclei may have sufficient energy to overcome the repulsive forces and fuse. It is for this reason, fusion reactions are also called thermonuclear reactions. Hence, hydrogen can be fused to form helium at high temperature and high pressure.
67. (c) Hydrogen is the lightest gas. It is insoluble in water.
68. (a) In the following reaction H_2O_2 acts as a reducing agent.

$$\text{PbO}_2(s) + \text{H}_2\text{O}_2(aq) \rightarrow \text{PbO}(s) + \text{H}_2\text{O}(\ell) + \text{O}_2(g)$$
69. (b) Ortho isomer has one nuclear spin whereas that para isomer has zero nuclear spin.
70. (c) Permanent hardness of water is due to chlorides and sulphates of calcium and magnesium.
71. (c) 1 mL of solution contains 0.03035 g H_2O_2
Strength of 11.2 volume of solutions.
 $= 3.035 \times 11.2 \text{ g/L} = 34 \text{ g/L}$
72. (d) Due to its covalent nature MgH_2 is Polymeric in nature.
73. (d) The volume strength of 1% $\text{H}_2\text{O}_2 = 3.3 \text{ V}$
Then the volume strength of 3% $\text{H}_2\text{O}_2 = 10 \text{ V}$
74. (a) ${}_1\text{H}^1 \quad {}_1\text{D}^2 \quad {}_1\text{T}^3$
no. of neutrons respectively are 0, 1, 2
no. of protons respectively are 1, 1, 1
Hence the sum of protons + neutrons = $1 + 2 + 3 = 6$

75. (b) It reduces iodine to iodine ion in alkaline medium.
 $I_2(s) + H_2O_2(aq) + 2OH^- \longrightarrow 2I^-(aq) + 2H_2O(l) + O_2(g)$

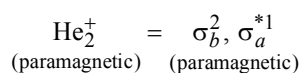
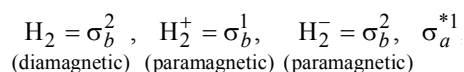
EXERCISE - 2

- (b) In the structure of ice each molecule of H_2O is surrounded by three H_2O molecules in hexagonal honey comb manner which results an open cage like structure. As a result there are a number of 'hole' or open spaces. In such a structure lesser number of molecules are packed per ml. When ice melts a large no. of hydrogen bonds are broken. The molecules therefore move into the holes or open spaces and come closer to each other than they were in solid state. This result sharp increase in the density. Therefore ice has lower density than water.
- (a) Ortho and para hydrogens are two forms of hydrogen (${}_1H^1$) which differ only in the direction of spin of proton.
- (b) $H^-(aq) + H_2O(l) \longrightarrow OH^-(aq) + H_2(g)$
 base 1 acid 1 base 2 acid 2
 In this reaction H^- acts as bronsted base as it accepts one proton (H^+) from H_2O and form H_2 .
- (d) MnO_2 , PbO_2 and BaO will not give H_2O_2 with HCl . MnO_2 and PbO_2 will give Cl_2 and BaO will react with HCl to give $BaCl_2$ and water.
- (d)
- (c) Single e^- of the H atom cannot be readily removed to form H^-
- (d) H_2O absorbs neutrons more than D_2O and this decreases the number of neutrons for the fission process.
- (c) Fire due to action of water on saline hydrides cannot be extinguished with water or CO_2 . These hydrides can reduce CO_2 at high temperature to produce O_2 .
- (a) $MgCO_3$ is insoluble in water.
- (a) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
 $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
 $\therefore$ Ratio of volumes of H_2 evolved is 1 : 1
- (d) Polyphosphates (e.g., sodium hexa metaphosphate) form soluble complexes with cations such as Ca^{2+} , Mg^{2+} and so they are used as water softening agents.



- (b) Permanent hardness of water is due to chlorides and sulphates of calcium and magnesium i.e $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$.
- (c) A diamagnetic substance contains no unpaired electron.

H_2 is diamagnetic as it contains all paired electrons



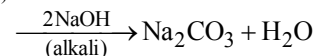
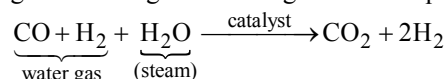
- (a) In one electron species, such as H-atom, the energy of orbital depends only on the principal quantum number, n.

Hence answer (d)

$$\text{i.e., } 1s < 2s = 2p < 3s = 3p = 3d <$$

$$4s = 4p < 4d = 4g$$

- (d) On the industrial scale hydrogen is prepared from water gas according to following reaction sequence



From the above it is clear that CO is first oxidised to CO_2 which is then absorbed in NaOH.

- (d) Critical temperature of water is more than O_2 due to its dipole moment (Dipole moment of water = 1.84 D; Dipole moment of O_2 = zero).
- (c) H_2O_2 . The key reactions are
 $PbO + H_2S \rightarrow PbS + H_2O$
 (black)
 $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
 (white)
 When blackened statues are treated with H_2O_2 , the PbS is oxidised to $PbSO_4$, which is colourless (White).
- (b) The value of dipole moment of H_2O_2 is 2.1 D, which suggest the structure of H_2O_2 cannot be planar. An open-book structure is suggested for H_2O_2 in which O – H bonds lie in different plane.
- (a) Both statement-1 and statement-2 are true and statement-2 is the correct explanation of statement-1.
- (a) 21. (a) 22. (a)
- (c) Both assertion (A) is correct reason (R) is not true.
 Correct Reason : Calgon forms soluble complexes with Ca^{2+} and Mg^{2+} in which properties of these ions are masked.
- (a)
- (a) Both Assertion (A) and reason (R) are true. Hydrogen peroxide forms two series of salts called hydroperoxides and peroxides.

EXERCISE - 3

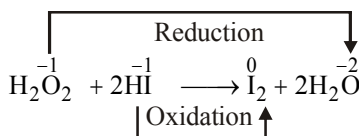
Exemplar Questions

- (b) Hydrogen like halogens accept an electron readily to achieve nearest inert gas configuration.
- (d) H^+ ion always get associated with other atoms or molecules because loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ion. Due to small size it cannot exist free.
- (b) The stability of hydrides decreases from Li to Cs. It is because of the fact that M-H bond becomes weaker due to increase in size of alkali metals down the group. Hence, ionic character increases as the size of the atom

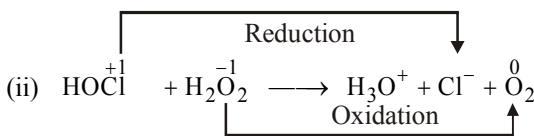
increases i.e., the correct order of increasing ionic character is



4. (d) Electron-precise hydrides are the type of hydrides in which the number of electrons present is equal to the number of electrons required.
5. (c) The radioactive isotope of hydrogen is tritium. Its half life is about 12.32 years.
6. (b)(i)

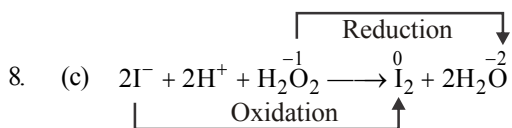
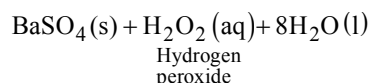
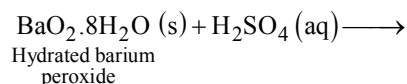


Here H_2O_2 oxidises HI into I_2 hence, behaves as an oxidising agent.



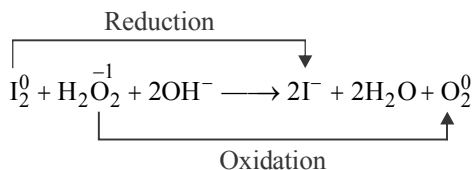
Here, H_2O_2 reduces HOCl to Cl, thus, behaves as reducing agent.

7. (b) Oxides such as BaO_2 , Na_2O_2 etc; which contain peroxide linkage on treatment with dilute H_2SO_4 give H_2O_2 but dioxides such as PbO_2 , MnO_2 , TiO_2 do not give H_2O_2 on treatment with dilute H_2SO_4 .

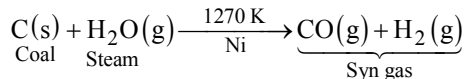


Here H_2O_2 oxidises I^- to I_2 , hence behaves as oxidising agent.

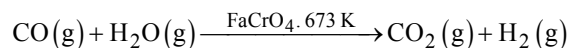
9. (b) The given below reaction show the reducing action in basic medium.



10. (c) Hydrogen peroxide acts as an oxidising as well as reducing agent in both acidic and alkaline media.
11. (c) The production of syn gas or synthesis gas from coal is called coal gasification.



In order to increase the production of hydrogen steam is added to carbon monoxide of the syn gas in the presence of iron chromate as a catalyst at 673 K.



CO_2 is removed by scrubbing with a solution of sodium arsenite.

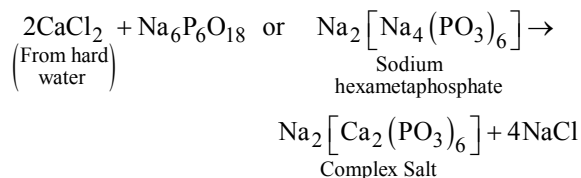
12. (d) $\text{Na}_2\text{O}_2 + \text{dil. H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_2$
13. (b) Hydrogen peroxide is manufactured by electrolysis of 50% sulphuric acid followed by distillation. The distillate is 30% hydrogen peroxide. The first product of electrolysis is peroxy disulphuric acid.

$$2\text{H}_2\text{SO}_4 \longrightarrow 2\text{H}^+ + \text{HSO}_4^-$$

$$2\text{HSO}_4^- (\text{aq}) \xrightarrow{\text{Electrolysis}} \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$$

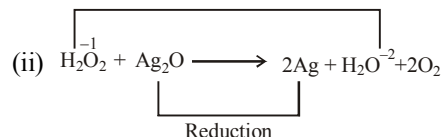
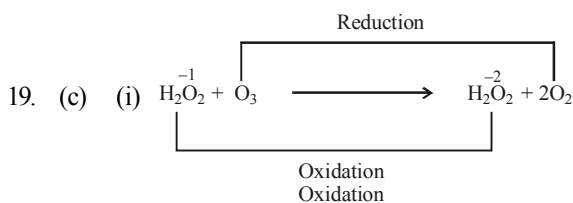
$$\text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 (\text{aq})$$
14. (d) The water gas is a combination of carbon and hydrogen. It is used in manufacturing of methanol.

$$\text{CO(g)} + 2\text{H}_2\text{(g)} \xrightarrow[\text{Cobalt Catalyst}]{} \text{CH}_3\text{OH(l)}$$
15. (a) Bicarbonates, chlorides and sulphates of Ca and Mg are responsible for the hardness of water.
16. (c) Sodium hexametaphosphate also known as Calgon is used.



17. (a) Elements of group 7, 8 and 9 of *d*-block do not form hydrides at all. The inability of metals of group 7, 8 and 9 of periodic table to form hydrides is referred to as hydrides gap of *d*-block. In these compounds H atoms are supposed to occupy interstitial position in the metal lattices. They are also called non-stoichiometric hydrides.
18. (a) Only one element of group 6, i.e., Cr forms hydride.

NEET/AIPMT (2013-2017) Questions



Hence in both the reactions H_2O_2 is acting as an oxidising agent.

20. (a & d) Among the three isotopes of hydrogen, Protium (${}_1\text{H}^1$) is most common. It is an energetic reducing agent. It reduces oxides, chlorides and sulphides of certain metals and produce free metals at ordinary temperature.

$$\text{CuO} + 2\text{H} \longrightarrow \text{Cu} + \text{H}_2\text{O}$$

Chapter 10

The s-Block Elements

GROUP 1 ELEMENTS : ALKALI METALS

(Li, Na, K, Rb, Cs, Fr)

Atomic and Physical Properties

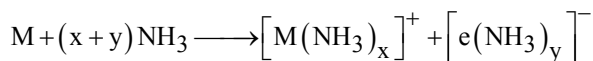
- (i) **General electronic configuration:** General configuration of alkali metals is ns^1 . They are highly electropositive metals, thus not found in free state in nature.
- (ii) **Atomic and ionic radii :** These elements have the largest size in a particular period. Down the group their atomic size increases.
- (iii) **Ionization enthalpy:** Alkali metals have low value of IE which decreases on moving down the group. As a result, Cs is the most electropositive element in the whole of periodic table.
- (iv) **Hydration enthalpy:** Hydration energy decreases on going down in the group, due to increase in the size of metal ion $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
 $\therefore$ Li⁺ has maximum degree of hydration. Due to high degree of hydration, lithium salts are mostly hydrated, example : LiCl. 2H₂O
- (v) **Density :** The density of alkali metals are quite low as compared to other metals. Order of densities of alkali metals $Li < K < Na < Rb < Cs$
- (vi) **Flame test :** Elements and their respective colours imparted to the flame are given below.

Element	Li	Na	K	Rb	Cs
Colour	Crimson red	Golden yellow	Violet	Red violet	Blue
- (vii) **Lustrous surface :** Lustre is due to mobile electrons in the metallic lattice.
- (viii) **Tendency of forming complex compounds :** These metals have weak tendency of forming complex compounds due to large size and low charge density.
- (ix) **Melting point and boiling point :** Their melting and boiling points are low due to weak metallic bonds. Strength of metallic bond decreases in the group from Li to Cs, due to which hardness decreases from Li to Cs.
 $Li > Na > K > Rb > Cs$
- (x) **Photoelectric effect :** Size of Cs and K is large and they possess low I.E. Both contain one electron in outermost shell which got emitted by absorption of visible light

Chemical Properties:

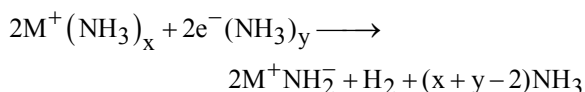
- (i) **Reactivity towards air:**
 Li forms mono oxide (M₂O) and Na forms peroxide (M₂O₂) and K, Rb and Cs form superoxide (MO₂).
 $4Li + O_2 \longrightarrow 2Li_2O$ (oxide)
 $2Na + O \longrightarrow Na_2O_2$ (peroxide)
 $M + O_2 \longrightarrow MO_2$ (superoxide) (M = K, Rb, Cs)
 Basic nature, ionic character and reactivity of these oxides increases from Li to Cs. Due to high reactivity towards air and water, they are normally kept in kerosene oil.
- (ii) **Reactivity towards water:**
 $2M + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2$ (M = alkali metal)
 Due to its small size and high HE, Li reacts less vigorously with water as compared to other alkali metals which react explosively with water. Basic nature of these hydroxides increases from Li to Cs.
 $LiOH < NaOH < KOH < RbOH < CsOH$
 Ionic character, melting point, boiling point, reactivity, thermal stability and solubility in water increases from Li to Cs.
- (iii) **Reactivity towards dihydrogen:**
 $2M + H_2 \longrightarrow 2M^+ + 2H^-$
 These hydrides are ionic solids with high m.pt.s. Thermal stability of LiH is highest. They are ionic hydrides and their stability depends on lattice energy.
 $LiH > NaH > KH > RbH > CsH$
- (iv) **Reactivity towards halogens:**
 Alkali metals directly combine with halogen to form halides (MX)
 $2M + X_2 \longrightarrow 2M^+ + 2X^-$
 Except lithium halides which are covalent, other alkali metal halides are ionic in nature.
 The ionic compounds get dissolved in water, while the covalent compounds get hydrolysed.
 LiCl gets hydrolysed due to its covalent nature. Decreasing order of these halides in undergoing hydrolysis is as follows
 $LiCl > NaCl > KCl > RbCl > CsCl$

- (v) **Reducing nature:** They are strong reducing agents, Li being the strongest and Na the weakest. Electrode potential depends upon sublimation energy, ionization energy and hydration energy. Li due to its small size has the highest hydration energy which accounts for its high negative E° value.
- (vi) **Solution in liquid ammonia:** Alkali metals have low I.E. and large size thus they dissolve in liquid ammonia to give deep blue solution which are conducting in nature.



The ammoniated electrons is responsible for the blue colour of the solution. These solutions are paramagnetic.

On standing or in presence of impurities or catalyst the blue colour solution forms amide.



In concentrated solution, blue colour changes to bronze colour and solution becomes diamagnetic.

(vii) Salts of oxoacids : Metal carbonates :

- (a) All these metals form M_2CO_3 type carbonates. (Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Rb_2CO_3 , Cs_2CO_3)
- (b) Li_2CO_3 is least stable out of all these carbonates, because it is covalent and decomposes to Li_2O and CO_2 at low temperature. Order of their stability is as follows :



Sulphates : $\text{Li}_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{K}_2\text{SO}_4 < \text{RbSO}_3 < \text{Cs}_2\text{SO}_4$

Nitrates : LiNO_3 decomposes to Li_2O at low temperature, whereas NaNO_3 gets decomposed to NaNO_2

Bicarbonates : These metals form MHCO_3 type bicarbonates and thermal stability of these bicarbonates increases from Li to Cs.

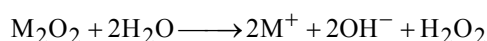
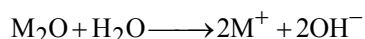
- (viii) Nitrides :** Among all alkali metals, only lithium directly combines with nitrogen to form nitride.

General Characteristics of Compounds of Alkali Metals

- (i) **Oxides and hydroxides:** On combustion in excess of air, Li forms Li_2O , Na forms Na_2O_2 and K, Rb, Cs form superoxides of the formula, MO_2 .

As the size of the metal ion increases, stability of peroxide or superoxide increases due to stabilisation of large anions by larger cations through lattice energy effects.

These oxides are easily hydrolysed by water to form hydroxides:



The pure, oxides and peroxides are colourless while superoxides are yellow or orange in colour. Superoxides are paramagnetic in nature. The alkali metal hydroxides are the strongest of all bases. They dissolve in water to produce large amount of heat due to intense hydration.

- (ii) **Halides:** They are high melting, colourless crystalline solids. They have high $-ve$ enthalpies of formation. M.pts and B.pt. follow the order: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

Note : The low solubility of LiF in water is due to its high lattice enthalpy while the low solubility of CsI is due to small HE of the two ions.

- (iii) **Salts of Oxo-acids :** Oxo acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom. Ex: H_2CO_3 , H_2SO_4 .

Alkali metals form salts with all the oxo-acids. As electropositive character increases down the group, stability of carbonates and hydrogencarbonates increases.

Li_2CO_3 being unstable to heat, decomposes to form Li_2O and CO_2 .

Anomalous Properties of Lithium

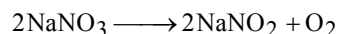
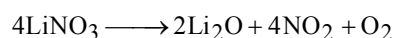
The anomalous behaviour of Li is due to:

- its exceptionally small size
- high polarising power

This give rise to covalent character in Li compounds.

Points of difference between Li and other alkali metals

- Li is much harder. Its m.pt and b.pt. are higher than other alkali metals.
- It is the least reactive and is the strongest reducing agent among all the alkali metals.
- LiCl is deliquescent and crystallises as a hydrate.
- LiHCO_3 is not obtained in solid state while other elements form solid hydrogencarbonates.
- Unlike other alkali metals, Li does not form ethynide with ethyne
- LiNO_3 on heating gives Li_2O while others decompose to nitrite.



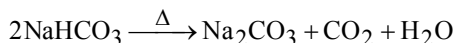
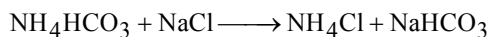
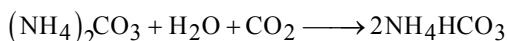
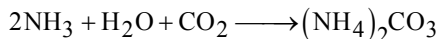
- (vii) LiOH , Li_2CO_3 , LiF and Li_2O are less soluble in water compared to corresponding compounds of other alkali metals.

Diagonal Relationship Between Lithium and Magnesium

- Li and Mg both are hard metals due to the presence of strong metallic bonds in them.
- Li and Mg both are hard, therefore, their melting and boiling points are high.
- LiOH and $\text{Mg}(\text{OH})_2$ both are weak bases.
- LiCl and MgCl_2 are insoluble in water due to their covalent nature, but soluble in organic solvents.
- LiCl and MgCl_2 get hydrolysed due to their covalent nature.
- Li and Mg directly combine with O_2 to form normal oxides (Li_2O and MgO) while other members of their groups form peroxide and super oxide.
- Li and Mg directly combine with N_2 to form Li_3N and Mg_3N_2
- Carbonates and nitrates of Li and Mg are unstable and readily decompose to form oxides.
- Hydration energies of Li^{+1} and Mg^{+2} ions are higher due to small size.

Some Important Compounds of Sodium**(i) Sodium Carbonate (Washing soda); $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$**

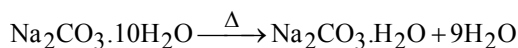
Preparation: It is prepared by solvay process as follows:



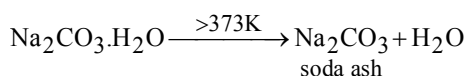
Note : K_2CO_3 cannot be prepared by this method because KHCO_3 is too soluble to be precipitated by addition of NH_4HCO_3 to saturated solution of KCl

Properties:

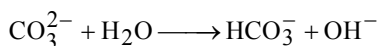
- It is white crystalline solid, existing as a decahydrate.
- It is readily soluble in water.
- On heating, it loses water of crystallisation to form monohydrate.



Above 373 K, monohydrate becomes completely anhydrous.



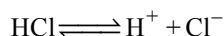
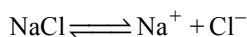
- The carbonate part gets hydrolysed to form alkaline solution

**Uses:**

- It is used in water softening, laundering and cleaning.
- It is used in manufacture of glass, soap, borax and caustic soda.
- It is used in paper, paints and textile industries.
- It is an important laboratory reagent.

(ii) Sodium Chloride; NaCl

Preparation : It is generally obtained by evaporation of sea water. Crude NaCl , obtained by crystallisation of brine solution, contains Na_2SO_4 , CaSO_4 , CaCl_2 and MgCl_2 as impurities. To obtain pure NaCl , crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with HCl gas, crystals of pure NaCl separate out due to common ion effect, leaving behind calcium chloride and magnesium chloride in solution.

**Properties:**

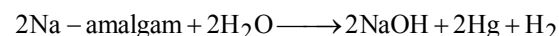
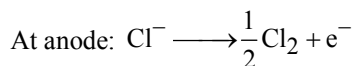
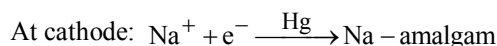
- It melts at 1081 K. It is white crystalline solid.
- Its solubility is 36 g in 100 g of water at 273 K and the solubility does not increase appreciably with increase in temperature.

Uses

- It is used as common salt or table salt for domestic purposes.
- It is used for preparation of Na_2O_2 , NaOH and Na_2CO_3 .

(iii) Sodium Hydroxide, NaOH **Preparation:**

It is prepared by electrolysis of NaCl in castner-kellner cell. Brine solution is electrolysed using Hg cathode and C anode.

**Properties:**

- It is a white, translucent solid which melts at 591 K.
- It dissolves in water to give an alkaline solution.
- Crystals of NaOH are deliquescent.
- It reacts with CO_2 in the atmosphere to form Na_2CO_3 .

Uses: It is used

- in manufacture of soap, paper, artificial silk and chemicals.
- in petroleum refining
- in purification of bauxite
- for preparation of fats and oils
- as a laboratory reagent.

(iv) Sodium Hydrogen Carbonate (Baking Soda), NaHCO_3 **Preparation:**

It is made by saturating a solution of Na_2CO_3 with CO_2 .

**Properties:**

It is known as baking soda because it decomposes on heating to generate bubbles of CO_2 .

Uses :

- It is mild antiseptic for skin infections.
- It is used in fire extinguishers.

Biological Importance of Na and K

Importance of Na^+ : Na^+ ions are found on the outside of cells and participate in transmission of nerve signals, in regulating flow of water across cell membranes and in transport of sugars and amino acids into cell.

Importance of K^+ : K^+ ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP and with sodium, are responsible for the transmission of nerve signals.

GROUP 2 ELEMENTS: ALKALINE EARTH METALS

(Be, Mg, Ca, Sr, Ba, Ra $\rightarrow$ radioactive)

Atomic and Physical Properties

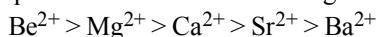
- Electronic Configuration :** General electronic configuration of alkaline earth metals is [noble gas] ns^2 . Their compounds are ionic in nature.
- Atomic and Ionic radii:** Their radii are smaller than alkali metals due to increased nuclear charge. The radii increases down the group with increase in atomic number.

(iii) **Ionization enthalpies:**

They have low IE due to large size and their IE decreases down the group. The first IE of group 2 elements are higher than those of group 1 elements due to their smaller size than group 1 elements. Second IE's of group 2 elements are smaller than those of group 1 elements. This is because removal of second e^- from group 2 elements results in stable noble gas configuration. On other hand, second e^- in group 1 has to be removed from noble gas core which needs large amount of energy.

(iv) **Hydration enthalpies**

Their HE's decreases with increase in ionic size, i.e., HE of group 2 cations will be in following order :



Due to their smaller sizes than group 1 elements, HE's of group 2 elements are larger than those of group 1 elements. As a result, their compounds are more highly hydrated than those of alkali metals.

(v) **Density** : Atomic weight increases from Be to Ba in a group and volume also increases, but increase in atomic weight is more as compared to volume. Therefore, density increases from Be to Ba.**Exception :**

Density of Mg is more as compared to Ca ($\text{Ca} < \text{Mg}$).

Density : $\text{Ca} < \text{Mg} < \text{Be} < \text{Sr} < \text{Ba}$

(vi) **Flame Test** : Elements and their respective colour imparted to the flame are given below :

Element	Be	Mg	Ca	Sr	Ba
Flame	—	—	Brick green	Blood red	Apple red

(vii) **Photoelectric effect** : Due to small size of these metals as compared to alkali metals, their ionisation potential is high. Thus, electrons can be released only by high energy radiations.(viii) **Lustrous Surface** : Lustre is due to mobile electron in the metallic lattice.(ix) **Tendency of forming Complex Compounds** : These metals have higher tendency of forming complex compounds as compared to alkali metals, due to their relatively smaller size. This tendency decreases from Be to Ba.(x) **Melting Point and Boiling Point** : Melting and boiling points of these metals are low, but these metals are harder as compared to metals of IA group.

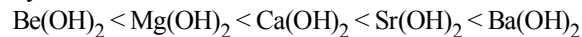
Hardness decreases from Be to Ba, due to which melting and boiling points decrease.

$\text{Be} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$

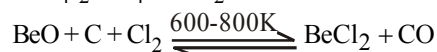
Chemical Properties:

- (i) **Reactivity towards air and water** : Be and Mg form normal MO type oxides, whereas, Ca, Sr and Ba form normal oxides (MO) as well as peroxides MO_2 . On burning in air they give corresponding oxides and nitrides. They react with H_2O (even in cold) to form hydroxides.

Basic nature ($\text{BeO} < \text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$), ionic character, melting point, boiling point, thermal stability reactivity and solubility in water of these oxides increases from Be to Ba, Ionic character, melting point, boiling point, reactivity, thermal stability and solubility in water of hydroxides increases from Be to Ba. Increasing order of basic character of these hydroxides is as follows :

(ii) **Reactivity towards halogens:**

BeF_2 is best prepared by thermal decomposition of $(\text{NH}_4)_2\text{BeF}_4$. BeCl_2 is prepared by :

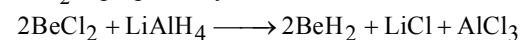


Covalent character of these halides decreases from BeCl_2 to BaCl_2 . Therefore, the amount of hydrolysis also decreases from BeCl_2 to BaCl_2 .

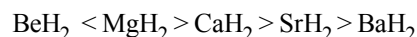
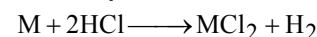
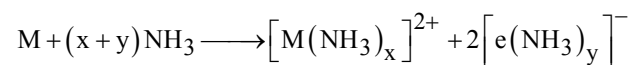
(iii) **Reactivity towards hydrogen:**

Except Be, all elements combine with hydrogen to form hydride, MH_2 .

BeH_2 is prepared by:



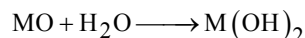
These metals (except Be) combine with hydrogen to form MH_2 type hydrides. Thermal stability of these hydrides is as follows.

(iv) **Reactivity towards acids:**(v) **Reducing nature:** They are strong reducing agents.(vi) **Solutions in liquid ammonia:**

The solution is deep blue black in colour.

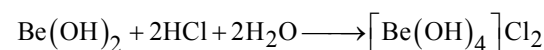
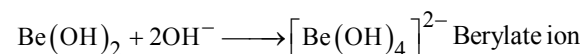
General Characteristics of Group 2 Compounds(i) **Oxides and Hydroxides:**

They have high ΔH_f° values and are thus very stable to heat. BeO is amphoteric while other oxides are basic in nature.



BeO is covalent while other oxides are ionic in nature. The solubility, thermal stability and basic character of these hydroxides increases down the group from $\text{Mg}(\text{OH})_2$ to $\text{Ba}(\text{OH})_2$

$\text{Be}(\text{OH})_2$ is amphoteric as shown below:

(ii) **Halides**

Be-halides are covalent while other group 2 halides are ionic in nature. In solid state, BeCl_2 has chain structure. In vapour phase, BeCl_2 exists as a chloro-bridged dimer. Down the group, tendency to form halide hydrates decreases. Due to high IE, fluorides are less soluble than chlorides.

(iii) Salts of Oxo-acids :

Metal carbonates :

- (1) All these metals form MCO_3 type carbonates (BeCO_3 , MgCO_3 , CaCO_3 , SrCO_3 , BaCO_3)
- (2) BeCO_3 is least stable out of all these carbonates because it is covalent and decomposes to BeO and CO_2 at low temperature. Order of their stability is as follows :
 $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$
- (3) Stability of carbonates of IA group metals > stability of carbonates of IIA group metals.

Sulphates :

Solubility of Sulphates :



Increasing order of thermal stability

**Nitrates :** These metals also form $\text{M}(\text{NO}_3)_2$ and all nitrates give oxides on decomposition.**Bicarbonates :** These metals form $\text{M}(\text{HCO}_3)_2$ type bicarbonates. The thermal stability of bicarbonates increases from Be to Ba.**Different Behaviour of Beryllium as Compared to Other Elements of its Group**

- (i) Ionisation potential and electronegativity of Be are higher than those of other metals.
- (ii) BeCl_2 is insoluble in water, due to its covalent nature, but soluble in organic solvents. Other chlorides (CaCl_2 , SrCl_2 and BaCl_2) get dissolved in water.
- (iii) BeO and $\text{Be}(\text{OH})_2$ are amphoteric in nature. Therefore they react with acids as well as bases. Other oxides react only with acids due to their alkaline nature.
- (iv) Beryllium forms single type of oxide (MO), Ca, Sr and Ba form peroxides also.
- (v) Beryllium does not give flame test, Ca, Sr and Ba impart characteristic colours to the flame.
- (vi) Due to small size, Be forms complex compounds.
- (vii) Hydrides and halides of Be get polymerized.

Diagonal Relationship between Be and Al

- (i) Be and Al both are hard due to strong metallic bonds. Therefore, their melting and boiling points are high.
- (ii) BeCl_2 and AlCl_3 both are covalent compounds. Therefore, they are insoluble in water and soluble in organic solvents.
- (iii) Melting points of BeCl_2 and AlCl_3 are low due to their covalent tendency.
- (iv) Be and Al both have tendency of forming complex compounds due to small size.
- (v) Both BeCl_2 and AlCl_3 are strong Lewis acids and are used as Friedel Crafts catalysts.
- (vi) $\text{Be}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, BeO and Al_2O_3 are amphoteric in nature.
- (vii) BeCl_2 and AlCl_3 form dimers, because both are electron deficient compounds.

Some Important Compounds of Calcium(i) **Calcium Oxide or Quick lime, CaO** **Preparation**

By heating limestone at 1070-1270 K

For the reaction to proceed, CO_2 is removed as soon as it is formed.**Properties:**

- (a) It is a white amorphous solid with a melting point of 2870 K.
- (b) On exposure to air, it absorbs moisture and CO_2

$$\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2$$

$$\text{CaO} + \text{CO}_2 \longrightarrow \text{CaCO}_3$$
- (c) Being basic, it combines with acidic oxides at high temperature.

$$\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$$

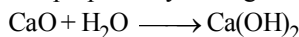
$$6\text{CaO} + \text{P}_4\text{O}_{10} \longrightarrow 2\text{Ca}_3(\text{PO}_4)_2$$
- (d) The process of breaking the lump of lime by addition of limited amount of water is called slaking of lime. Quick lime slaked with soda gives solid sodalime.

Uses: It is used

- (a) for manufacturing cement.
- (b) in the manufacture of Na_2CO_3 from caustic soda.
- (c) in the purification of sugar and manufacture of dye stuffs.
- (d) in the preparation of mortar, a building material.

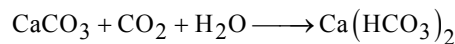
(ii) **Calcium Hydroxide (Slaked lime), $\text{Ca}(\text{OH})_2$**

It is prepared by adding water to quick lime.

**Properties:**

- (a) It is a white amorphous powder.
- (b) It is sparingly soluble in water.
- (c) Its aqueous solution is known as lime water and a suspension of slaked lime in water is called milk of lime.
- (d)
$$\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$$

milky



- (e)
$$2\text{Ca}(\text{OH})_2 + 2\text{Cl}_2 \longrightarrow \text{CaCl}_2 + \text{Ca}(\text{OCl})_2 + 2\text{H}_2\text{O}$$

Bleaching powder

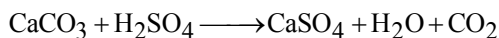
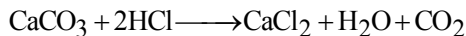
Uses. Calcium hydroxide is used: (i) in the manufacture of bleaching powder and caustic soda, (ii) for white washing buildings and for softening of water, and (iii) in the preparation of soda-lime (mixture of cal. hydroxide and caustic soda)(iii) **Calcium Carbonate, CaCO_3** **Preparation:**

- (a)
$$\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$
- (b)
$$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{NaCl}$$

Properties

- (a) It is a white fluffy powder and is insoluble in water.
- (b) Action of heat :
$$\text{CaCO}_3 \xrightarrow{1200\text{K}} \text{CaO} + \text{CO}_2$$

(c) Action of acids :

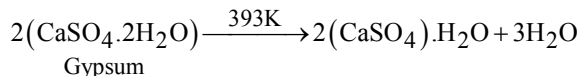


Uses: It is used

- (a) as a building material in form of marble
- (b) in manufacture of quick lime.
- (c) as an antacid, mild abrasive in toothpaste, in chewing gum and a filler in cosmetics.

(iv) **Calcium Sulphate (Plaster of Paris), $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$**

Preparation:



Above 393 K, anhydrous CaSO_4 is formed which is called 'dead burnt plaster'.

Properties:

With adequate quantity of water, it forms a plastic mass that sets into a hard solid.

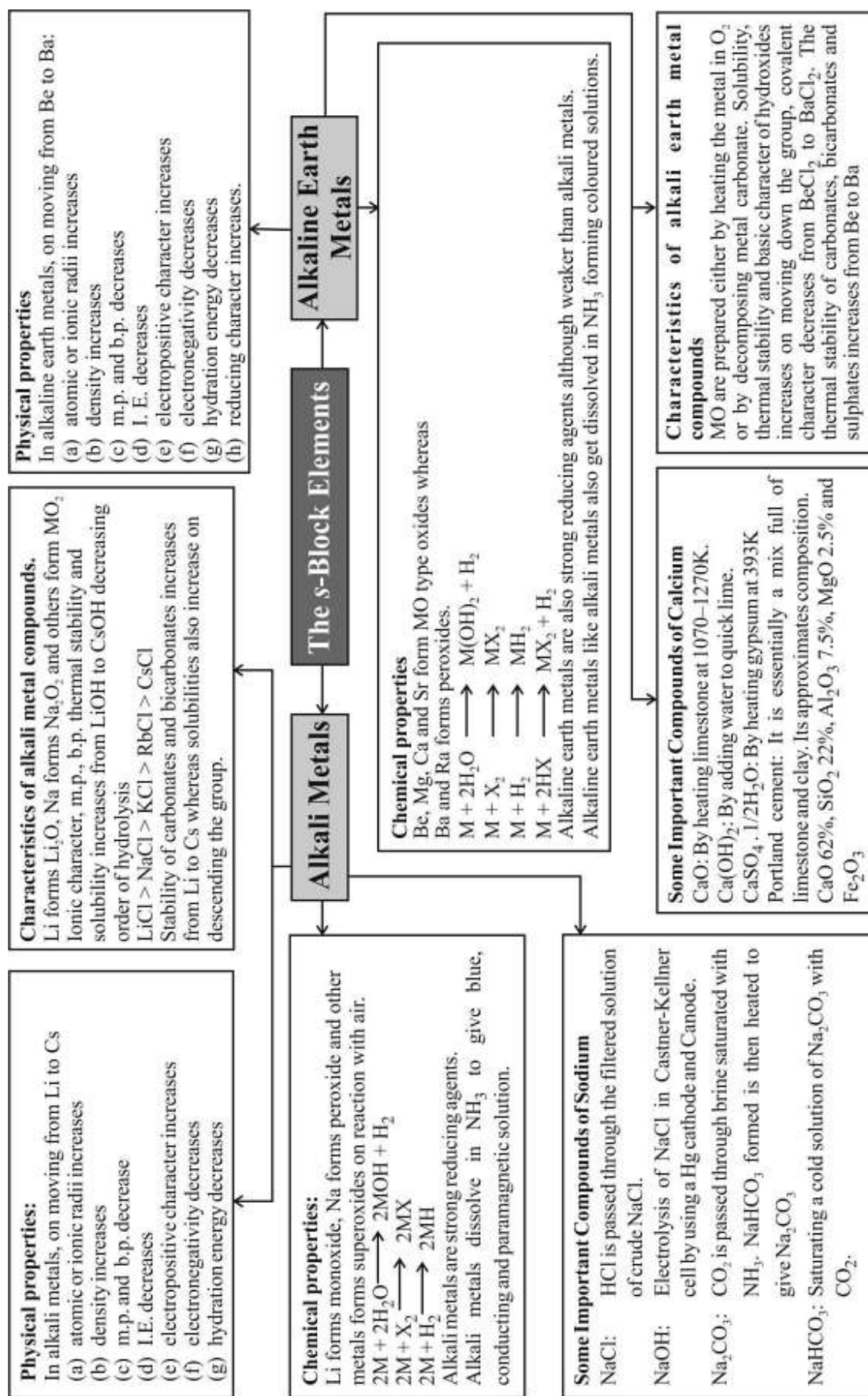
Uses: It is used

- (a) in building industry and in plasters.
- (b) in dentistry, ornamental work and for making casts of statues and busts.

Biological Importance of Ca and Mg

Magnesium is used as a cofactor by enzymes that utilise ATP in phosphate transfer. Chlorophyll, the main pigment for the absorption of light in plants, contains Mg. 99% of body Ca is present in bones and teeth. Ca plays role in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- Which of the following represents a correct sequence of reducing power of the following elements?
(a) $\text{Li} > \text{Cs} > \text{Rb}$ (b) $\text{Rb} > \text{Cs} > \text{Li}$
(c) $\text{Cs} > \text{Li} > \text{Rb}$ (d) $\text{Li} > \text{Rb} > \text{Cs}$
- Nitrolum is:
(a) CaC_2 and graphite (b) CaCN_2 and graphite
(c) $\text{Ca}(\text{CN})_2$ and graphite (d) $\text{CaCN}_2 + \text{N}_2$
- The pair whose both species are used in ant-acid medicinal preparations is :
(a) NaHCO_3 and $\text{Mg}(\text{OH})_2$
(b) Na_2CO_3 and $\text{Ca}(\text{HCO}_3)_2$
(c) $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{OH})_2$
(d) $\text{Ca}(\text{OH})_2$ and NaHCO_3
- Which one of the following properties of alkali metals increases in magnitude as the atomic number rises ?
(a) Ionic radius (b) Melting point
(c) Electronegativity (d) First ionization energy.
- Largest difference in radii is found in case of the pair
(a) Li, Na (b) Na, K
(c) K, Rb (d) Rb, Cs .
- Which compound will show the highest lattice energy ?
(a) RbF (b) CsF
(c) NaF (d) KF
- Strongest bond is in between
(a) CsF (b) NaCl
(c) Both (a) and (b) (d) None of above
- In crystals which one of the following ionic compounds would you expect maximum distance between centres of cations and anions?
(a) LiF (b) CsF
(c) CsI (d) LiI
- Among the following components of cement which is present in highest amount?
(a) Ca_2SiO_4 (b) Ca_3SiO_5
(c) Al_2O_3 (d) $\text{Ca}_3\text{Al}_2\text{O}_6$.
- Which of the following is not correct ?
(a) $2\text{Li}_2\text{O} \xrightarrow[673\text{k}]{\text{heat}} \text{Li}_2\text{O}_2 + 2\text{Li}$
(b) $2\text{K}_2\text{O} \xrightarrow[673\text{k}]{\text{heat}} \text{K}_2\text{O}_2 + 2\text{K}$
(c) $2\text{Na}_2\text{O} \xrightarrow[673\text{k}]{\text{heat}} \text{Na}_2\text{O}_2 + 2\text{Na}$
(d) $2\text{Rb}_2\text{O} \xrightarrow[673\text{k}]{\text{heat}} \text{Rb}_2\text{O}_2 + 2\text{Rb}$
- When potassium dichromate crystals are heated with conc. HCl
(a) O_2 is evolved
(b) chromyl chloride vapours are evolved
(c) Cl_2 is evolved
(d) no reaction takes place
- Which one of the alkaline earth metals shows some anomalous behaviour and has same electronegativity as aluminium?
(a) Sr (b) Ca
(c) Ba (d) Be
- Which of the following does not illustrate the anomalous properties of lithium?
(a) The melting point and boiling point of Li are comparatively high
(b) Li is much softer than the other group I metals
(c) Li forms a nitride Li_3N unlike group I metals
(d) The ion of Li and its compounds are more heavily hydrated than those of the rest of the group
- Which of the following statements is incorrect?
(a) Alkali metal hydroxide are hygroscopic
(b) Dissolution of Alkali metal hydroxide is endothermic
(c) Aqueous solution of alkali metal hydroxides are strongly basic
(d) Alkali metal hydroxides form ionic crystals
- Which property of sodium is being used in street lights ?
(a) It shows photoelectric effect
(b) It has low melting point
(c) Sodium atom emits photons in the yellow region of visible spectrum, due to electrically stimulated transitions
(d) Sodium vapours show golden colour
- Which is most basic in character ?
(a) CsOH (b) KOH
(c) NaOH (d) LiOH
- An inorganic compound which on heating first melts, then solidifies and liberates O_2 gas, the inorganic compound is
(a) Al_2O_3 (b) KMnO_4
(c) MnO_2 (d) KClO_3
- Which of the following has density greater than water?
(a) Li (b) Na
(c) K (d) Rb
- A metal salt solution forms a yellow precipitate with potassium chromate in acetic acid, a white precipitate with dil H_2SO_4 , but gives no precipitate with NaCl . The metal salt solution will consist of
(a) PbCO_3 (b) BaCO_3
(c) MgCO_3 (d) CaCO_3
- When sulphur is heated with $\text{NaOH}(\text{aq})$? The compounds formed are
(a) $\text{Na}_2\text{S} + \text{H}_2\text{O}$
(b) $\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$
(c) $\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$
(d) $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$
- The first (IE_1) and second (IE_2) ionisation energies (kJ/mol) of a few elements designated by Roman numerals are given below. Which of these would be an alkali metal?

	IE_1	IE_2
(a) I	2372	5251
(b) II	520	7300
(c) III	900	1760
(d) IV	16803	380

22. Washing soda has formula
 (a) $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ (b) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
 (c) $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (d) Na_2CO_3
23. Which of the following is known as fusion mixture ?
 (a) Mixture of $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$
 (b) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
 (c) Mixture of $\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$
 (d) NaHCO_3
24. Aqueous solution of sodium carbonate absorbs NO and NO_2 to give
 (a) $\text{CO}_2 + \text{NaNO}_3$ (b) $\text{CO}_2 + \text{NaNO}_2$
 (c) $\text{NaNO}_2 + \text{CO}$ (d) $\text{NaNO}_3 + \text{CO}$
25. Mg on heating to redness in an atmosphere of N_2 and then on treating with H_2O gives:
 (a) NH_3 (b) N_2
 (c) PH_3 (d) MgO
26. Molecular formula of Glauber's salt is :
 (a) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (c) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (d) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
27. A mixture of KCl and KF is added to sodium chloride
 (a) to increase the conductivity of NaCl
 (b) to decrease the melting point of NaCl
 (c) to suppress the melting of dissociation of NaCl
 (d) to decrease the volatility of NaCl
28. What happens when carbonates of group IA elements are heated?
 (a) CO_2 is given out
 (b) Water vapours are given out
 (c) Carbon dioxide and water vapours are evolved
 (d) None of these
29. A well known reagent which contains copper sulphate, sodium potassium tartarate and sodium hydroxide is
 (a) Fenton's reagent (b) Schiff's reagent
 (c) Fehling's solution (d) Nessler's reagent
30. Baking soda is :
 (a) NaHCO_3 (b) K_2CO_3
 (c) Na_2CO_3 (d) NaOH
31. On strong heating sodium bicarbonate changes into:
 (a) sodium monoxide (b) sodium hydroxide
 (c) sodium carbonate (d) sodium peroxide
32. Which of the following compounds transforms baking soda into baking powder?
 (a) KCl (b) KHCO_3
 (c) NaHCO_3 (d) $\text{KHC}_4\text{H}_4\text{O}_6$
33. A certain metal M is used to prepare an antacid, which is used as a medicine in acidity. This metal accidentally catches fire which cannot be put out by using CO_2 based extinguishers. The metal M is
 (a) Ca (b) Mg
 (c) C (d) All of these
34. Which of the following is commercially known as **oxone** ?
 (a) $\text{Na}_2\text{O}_2 + \text{HCl}$ (b) $\text{Na}_2\text{O} + \text{HCl}$
 (c) $\text{Na}_2\text{O}_2 + \text{Na}_2$ (d) none of these
35. Which pair cannot exist together in solution ?
 (a) NaHCO_3 and NaOH (b) NaHCO_3 and NaCl
 (c) NaHCO_3 and Na_2CO_3 (d) NaCl and Na_2CO_3
36. Baking powder contains :
 (a) NaHCO_3 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and starch
 (b) NaHCO_3 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$
 (c) NaHCO_3 , starch
 (d) NaHCO_3
37. Which of the following is used widely in the manufacture of storage battery?
 (a) Arsenic (b) Lithium
 (c) Bismuth (d) Antimony
38. Alkaline earth's metals are denser than alkali metals, because metallic bonding in alkaline earth's metal, is :
 (a) stronger (b) weaker
 (c) volatile (d) not present
39. The order of solubility of sulphates of alkaline earth metals in water is
 (a) $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$
 (b) $\text{Mg} > \text{Be} > \text{Ba} > \text{Ca} > \text{Sr}$
 (c) $\text{Be} > \text{Ca} > \text{Mg} > \text{Ba} > \text{Sr}$
 (d) $\text{Mg} > \text{Ca} > \text{Ba} > \text{Be} > \text{Sr}$
40. Arrange the following compounds in order of increasing solubility
 (i) MgF_2 (ii) CaF_2 (iii) BaF_2
 (a) (i) < (ii) < (iii) (b) (ii) < (i) < (iii)
 (c) (ii) < (iii) < (i) (d) (iii) < (ii) < (i)
41. Potassium is kept in:
 (a) alcohol (b) water
 (c) kerosene (d) liquid ammonia
42. Which of the following atoms will have the smallest size ?
 (a) Mg (b) Na
 (c) Be (d) Li
43. The solubilities of carbonates decrease down the magnesium group due to a decrease in
 (a) hydration energies of cations
 (b) inter-ionic attraction
 (c) entropy of solution formation
 (d) lattice energies of solids
44. Which of the following relations is correct with respect to first (I) and second (II) ionization potentials of sodium and magnesium?
 (a) $I_{\text{Mg}} = II_{\text{Na}}$ (b) $I_{\text{Mg}} < II_{\text{Na}}$
 (c) $I_{\text{Na}} > I_{\text{Mg}}$ (d) $II_{\text{Na}} > II_{\text{Mg}}$
45. Epsom salt is
 (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (b) $\text{BaSO}_4 \cdot 2\text{H}_2\text{O}$
 (c) $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ (d) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
46. Which of the following has maximum ionization energy
 (a) $\text{Ba} \longrightarrow \text{Ba}^+ + e^-$ (b) $\text{Be} \longrightarrow \text{Be}^+ + e^-$
 (c) $\text{Ca} \longrightarrow \text{Ca}^{2+} + 2e^-$ (d) $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2e^-$
47. The value of x is maximum for
 (a) $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$
 (b) $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$
 (c) $\text{BaSO}_4 \cdot x\text{H}_2\text{O}$
 (d) All have the same value of x.
48. Of the metals Be, Mg, Ca and Sr of group II A. In the periodic table the least ionic chloride would be formed by
 (a) Be (b) Mg
 (c) Ca (d) Sr

49. Which of the following is the component of most of the kidney stones?
 (a) $(\text{COO})_2\text{Ca}$ (b) $(\text{COO})_2\text{Ba}$
 (c) $(\text{COONa})_2$ (d) $(\text{COO})_2\text{Mg}$
50. Which one is known as barytes?
 (a) BaSO_4 (b) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
 (c) BaO (d) BaCO_3
51. Which one of the following salts does not impart colour to the flame?
 (a) Kl (b) LiCl
 (c) CaCl_2 (d) MgCl_2
52. The Formula of Mohar's Salt; $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot \text{XH}_2\text{O}$ the value of X :
 (a) 5 (b) 10
 (c) 6 (d) 8
53. Which of the following compounds is used in preparation of green fire?
 (a) K_2SO_4 (b) NaNO_3
 (c) $\text{Ba}(\text{NO}_3)_2$ (d) None of these
54. Amongst LiCl , RbCl , BeCl_2 and MgCl_2 the compounds with the greatest and least ionic character respectively are :
 (a) LiCl and RbCl (b) MgCl_2 and BeCl_2
 (c) RbCl and BeCl_2 (d) RbCl and MgCl_2
55. Lithopone is
 (a) $\text{BaO} + \text{ZnSO}_4$ (b) $\text{BaS} + \text{ZnSO}_4$
 (c) $\text{ZnS} + \text{BaSO}_4$ (d) $\text{ZnO} + \text{BaSO}_4$
56. Mixture of MgCl_2 and MgO is called :
 (a) Portland cement (b) Sorel's cement
 (c) double salt (d) none of these
57. K_2CS_3 can be called potassium
 (a) Sulphocyanide (b) Thiocarbide
 (c) Thiocarbonate (d) Thiocyanate
58. Estimation of calcium and magnesium is done by
 (a) EDTA (b) oxalate
 (c) Phosphate (d) none of these
59. Philosopher's wool on heating with BaO at 1100°C produces:
 (a) $\text{Ba} + \text{ZnCl}_2$ (b) BaCdO_2
 (c) BaZnO_2 (d) $\text{BaO}_2 + \text{Zn}$
60. Which one of the following processes will produce hard water?
 (a) Saturation of water with MgCO_3
 (b) Saturation of water with CaSO_4
 (c) Addition of Na_2SO_4 to water
 (d) Saturation of water with CaCO_3
61. In Solvay ammonia process, sodium bicarbonate is precipitate due to
 (a) presence of NH_3
 (b) reaction with CO_2
 (c) reaction with brine solution
 (d) reaction with NaOH
62. In India at the occasion of marriages, the fire works used give green flame. Which one of the following radicals may be present?
 (a) Na^+ (b) K^+
 (c) Ba^{2+} (d) Ca^{2+}
63. Which one of the following is flourspar?
 (a) CaF_2 (b) CaO
 (c) H_2F_2 (d) CaCO_3
64. Plaster of Paris is :
 (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (b) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$
 (c) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (d) $\text{CaSO}_4 \cdot 4\text{H}_2\text{O}$
65. Gypsum on heating at $120 - 130^\circ\text{C}$ gives :
 (a) anhydrous salt (b) hemihydrate
 (c) monohydrate (d) dihydrate
66. Plaster of Paris on making paste with little water sets to hard mass due to formation of
 (a) CaSO_4 (b) $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
 (c) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (d) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
67. Which of the following compounds of cement sets at the slowest rate?
 (a) Dicalcium silicate
 (b) Tricalcium silicate
 (c) Tricalcium aluminate
 (d) Tetracalcium aluminoferrite.
68. The chemical which is used for plastering the broken bones is
 (a) $(\text{CaSO}_4)_2\text{H}_2\text{O}$ (b) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
 (c) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (d) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
69. Colemanite is
 (a) $\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_2] \cdot 2\text{H}_2\text{O}$ (b) $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
 (c) $\text{Ca}(\text{OH})_2$ (d) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$
70. Dead burn plaster is
 (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (b) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
 (c) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (d) CaSO_4
71. Bone ash contains
 (a) CaO (b) CaSO_4
 (c) $\text{Ca}_3(\text{PO}_4)_2$ (d) $\text{Ca}(\text{H}_2\text{PO}_4)_2$
72. The wire of flash bulb is made of
 (a) Mg (b) Cu
 (c) Ba (d) Ag
73. Calcium cyanamide is
 (a) CaCHNH_2 (b) CaCN_2
 (c) CaC_2N_2 (d) $\text{Ca}(\text{CN})_2$
74. Calcium is obtained by
 (a) roasting of lime stone
 (b) reduction of CaCl_2 with carbon
 (c) electrolysis of a solution of CaCl_2 in water
 (d) electrolysis of molten CaCl_2
75. Mortar is a mixture of
 (a) CaCO_3 , sand and water
 (b) slaked lime and water
 (c) slaked lime, sand and water
 (d) CaCO_3 and CaO

EXERCISE - 2

Applied Questions

- Lithium can not be stored in kerosene oil because
 - it is an alkali metal
 - it reacts with kerosene oil
 - it floats to the surface of kerosene oil
 - none of the above is correct
- Which one out of the NaOH and KOH, is a better absorber of CO_2 ?
 - NaOH
 - KOH
 - both absorb CO_2 equally
 - can not be predicted
- Which one of the following has minimum value of cation/anion ratio ?
 - NaCl
 - KCl
 - MgCl_2
 - CaF_2
- All of the following substances react with water. The pair that gives the same gaseous product is
 - K and KO_2
 - Na and Na_2O_2
 - Ca and CaH_2
 - Ba and BaO_2
- Which of the following is neither deliquescent nor efflorescent and is used for wool washing ?
 - NaOH
 - KOH
 - NaHCO_3
 - $\text{Na}_2\text{CO}_3 \cdot \text{NaCO}_3 \cdot 2\text{H}_2\text{O}$
- Among the following oxides, which one is most basic
 - ZnO
 - MgO
 - Al_2O_3
 - N_2O_5
- Which of the following statement is false ?
 - Strontium decomposes water readily than beryllium
 - Barium carbonate melts at a higher temperature than calcium carbonate
 - Barium hydroxide is more soluble in water than magnesium hydroxide
 - Beryllium hydroxide is more basic than barium hydroxide.
- The general formula of an alum is $\text{M}_2\text{SO}_4 \cdot \text{M}'_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ where M is univalent and M' is a trivalent metal which of the following does not form alum ?
 - Li
 - Na
 - K
 - all of these form alum
- What is the function of potassium nitrate in gun powder ?
 - It is a sublime substance
 - It is added to act as instant explosive
 - It is added to provide oxygen
 - It reacts with sulphur to form another compound that is highly explosive in nature
- If NaOH is added to an aqueous solution of Zn^{2+} ions, a white precipitate appears and on adding excess NaOH, the precipitate dissolves. In this solution zinc exists in the :
 - cationic part
 - anionic part
 - both in cationic and anionic parts
 - there is no zinc left in the solution
- Among LiI, NaI, KI, the one which is more ionic and more soluble in water is :
 - KI
 - NaI
 - LiI
 - None of these
- A metal M readily forms its sulphate MSO_4 which is water-soluble. It forms its oxide MO which becomes inert on heating. It forms an insoluble hydroxide $\text{M}(\text{OH})_2$ which is soluble in NaOH solution. Then M is
 - Mg
 - Ba
 - Ca
 - Be
- In curing cement plasters water is sprinkled from time to time. This helps in
 - developing interlocking needle-like crystals of hydrated silicates
 - hydrating sand and gravel mixed with cement
 - converting sand into silicic acid
 - keeping it cool
- On heating anhydrous Na_2CO_3 , ... is evolved
 - CO_2
 - Water vapour
 - CO
 - No gas
- The metals A and B form oxide but B also forms nitride when both burn in air. The A and B are
 - Cs, K
 - Mg, Ca
 - Li, Na
 - K, Mg
- Based on lattice energy and other considerations which one of the following alkali metal chlorides is expected to have the highest melting point
 - LiCl
 - NaCl
 - KCl
 - RbCl
- An aqueous solution of salt 'R' when treated with dil HCl, a colourless gas is given out. The gas so evolved when passed through acidified KMnO_4 decolourises KMnO_4 solution. The salt 'R' is
 - Na_2CO_3
 - NaClO_3
 - NaNO_2
 - Na_2SO_3
- Which of the following sulphates have the highest solubility in water?
 - MgSO_4
 - BaSO_4
 - CaSO_4
 - BeSO_4

19. On being placed in water, sodium peroxide not only produces an alkaline solution but also some bubbles. If we assume that the peroxide ion picks up two protons from water to produce a compound that can be seen as the dibasic conjugate acid of peroxide ion and then this compound undergoes a redox disproportion.
- Using the above information complete the following equation.
- $$\text{Na}_2\text{O}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow (\text{A}) + (\text{B})$$
- (A) and (B) are
- (a) H_2O_2 and NaOH (b) H_2O and O_2
 (c) NaOH and O_2 (d) Na_2O and NaOH
20. The metal X is prepared by the electrolysis of fused chloride. It reacts with hydrogen to form a colourless solid from which hydrogen is released on treatment with water. The metal is :
- (a) Ca (b) Al (c) Zn (d) Cu
21. The correct order of radii is –
- (a) $\text{Li} < \text{Be} < \text{Mg}$ (b) $\text{H}^+ < \text{Li}^+ < \text{H}^-$
 (c) $\text{Mn}^{3+} < \text{Mn}^{2+} < \text{Mn}^{+7}$ (d) $\text{K}^+ > \text{Cl}^- > \text{S}^{2-}$
22. Select the correct statements :
- I. Cs^+ is more highly hydrated than the other alkali metal ions
 II. Among the alkali metals Li, Na, K and Rb, lithium has the highest melting point
 III. Among the alkali metals only lithium forms a stable nitride by direct combination with nitrogen
- (a) I, II and III (b) I and II
 (c) I and III (d) II and III
23. The melting point of lithium (181°C) is just double the melting point of sodium (98°C) because –
- (a) down the group, the hydration energy decreases
 (b) down the group, the ionization energy decreases
 (c) down the group the cohesive energy decreases
 (d) None of these
24. Magnesium form Mg^{2+} and Mg^+ because :
- (a) ionic radius of $\text{Mg}(\text{II})$ is smaller than of $\text{Mg}(\text{I})$.
 (b) hydration energy of divalent magnesium ion is higher.
 (c) magnesium (II) carbonate is insoluble in water.
 (d) generally higher oxidation states are preferred by metals.
25. A metal 'M' reacts with N_2 to give a compound 'A' (M_3N). 'A' on heating at high temperature gives back 'M' and 'A'; on reacting with H_2O gives a gas B. 'B' turns CuSO_4 solution blue on passing through it. M and B can be
- (a) Al and NH_3 (b) Li and NH_3
 (c) Na and NH_3 (d) Mg and NH_3
26. Which is not correctly matched
- (1) Basic strength $\text{Cs}_2\text{O} < \text{Rb}_2\text{O} < \text{K}_2\text{O} < \text{Na}_2\text{O} < \text{Li}_2\text{O}$ of oxides
 (2) Stability of $\text{Na}_2\text{O}_2 < \text{K}_2\text{O}_2 < \text{Rb}_2\text{O}_2 < \text{Cs}_2\text{O}_2$ peroxides
 (3) Stability of $\text{LiHCO}_3 < \text{NaHCO}_3 < \text{KHCO}_3$ bicarbonates $< \text{RbHCO}_3 < \text{CsHCO}_3$
 (4) Melting point $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$
- (a) 1 and 4 (b) 1 and 3
 (c) 1 and 2 (d) 2 and 3
27. On being placed in water, sodium peroxide not only produces an alkaline solution but also some bubbles. If we assume that the peroxide ion picks up two protons from water to produce a compound that can be seen as the dibasic conjugate acid of peroxide ion and then this compound undergoes a redox disproportion.
- Using the above information complete the following equation.
- $$\text{Na}_2\text{O}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow (\text{A}) + (\text{B})$$
- (A) and (B) are
- (a) H_2O_2 and NaOH (b) H_2O and O_2
 (c) NaOH and O_2 (d) Na_2O and NaOH
28. BaSO_4 is used in the X-ray investigation of intestinal track because it is opaque to X-rays. For this, one adds solid BaSO_4 in water to obtain a saturated solution with $\text{BaSO}_4(\text{s})$ suspended in saturated solution.
- $$\text{BaSO}_4(\text{solid}) \longrightarrow \text{BaSO}_4(\text{Soln.})$$
- $$\longrightarrow \text{Ba}^{++} + \text{SO}_4^{2-}$$
- However one patient is allergic to Ba^{2+} ions and one has to reduce the concentration of Ba^{2+} ions from the saturated solution. The method adopted for this is :
- (a) Heat the system because ionization reaction $\text{BaSO}_4 = \text{Ba}^{++} + \text{SO}_4^{2-}$ is endothermic
 (b) Add more BaSO_4 solid to the solution
 (c) reduce the volume of saturated solution over the solid BaSO_4
 (d) Add enough Na_2SO_4 to solution so that Ba^{2+} ion can be precipitate due to excess SO_4^{2-} ions.
29. In which of the following the hydration energy is higher than the lattice energy?
- (a) MgSO_4 (b) RaSO_4
 (c) SrSO_4 (d) BaSO_4
30. The alkali metals form salt-like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders ?
- (a) $\text{CsH} > \text{RbH} > \text{KH} > \text{NaH} > \text{LiH}$
 (b) $\text{KH} > \text{NaH} > \text{LiH} > \text{CsH} > \text{RbH}$
 (c) $\text{NaH} > \text{LiH} > \text{KH} > \text{RbH} > \text{CsH}$
 (d) $\text{LiH} > \text{NaH} > \text{KH} > \text{RbH} > \text{CsH}$
31. Which of the following oxides is **not** expected to react with sodium hydroxide?
- (a) CaO (b) SiO_2
 (c) BeO (d) B_2O_3
32. Which of the following alkaline earth metal sulphates has hydration enthalpy higher than the lattice enthalpy?
- (a) CaSO_4 (b) BeSO_4
 (c) BaSO_4 (d) SrSO_4
33. The compound A on heating gives a colourless gas and a residue that is dissolved in water to obtain B. Excess of CO_2 is bubbled through aqueous solution of B, C is formed which is recovered in the solid form. Solid C on gentle heating gives back A. The compound is
- (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (b) CaCO_3
 (c) Na_2CO_3 (d) K_2CO_3

34. Which of the following compounds has the lowest melting point ?
 (a) CaCl_2 (b) CaBr_2
 (c) CaI_2 (d) CaF_2
35. Which one of the following is present as an active ingredient in bleaching powder for bleaching action ?
 (a) CaOCl_2 (b) $\text{Ca}(\text{OCl})_2$
 (c) CaO_2Cl (d) CaCl_2
36. Which of the following statements is **incorrect** ?
 (a) Pure sodium metal dissolves in liquid ammonia to give blue solution.
 (b) NaOH reacts with glass to give sodium silicate
 (c) Aluminium reacts with excess NaOH to give $\text{Al}(\text{OH})_3$
 (d) NaHCO_3 on heating gives Na_2CO_3
37. Match List – I with List –II for the compositions of substances and select the correct answer using the code given below the lists :
- | List - I | List - II |
|----------------------|--|
| Substances | Composition |
| (A) Plaster of paris | (i) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
| (B) Epsomite | (ii) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ |
| (C) Kieserite | (iii) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ |
| (D) Gypsum | (iv) $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ |
| | (v) CaSO_4 |
- Code :
- | | | | |
|-----------|-------|-------|------|
| (A) | (B) | (C) | (D) |
| (a) (iii) | (iv) | (i) | (ii) |
| (b) (ii) | (iii) | (iv) | (i) |
| (c) (i) | (ii) | (iii) | (v) |
| (d) (iv) | (iii) | (ii) | (i) |
38. Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value ?
 (a) BaCl_2 (b) AlCl_3
 (c) LiCl (d) BeCl_2
39. The ease of adsorption of the hydrated alkali metal ions on an ion-exchange resins follows the order :
 (a) $\text{Li}^+ < \text{K}^+ < \text{Na}^+ < \text{Rb}^+$
 (b) $\text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$
 (c) $\text{K}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Li}^+$
 (d) $\text{Na}^+ < \text{Li}^+ < \text{K}^+ < \text{Rb}^+$
40. KO_2 (potassium super oxide) is used in oxygen cylinders in space and submarines because it
 (a) absorbs CO_2 and increases O_2 content
 (b) eliminates moisture
 (c) absorbs CO_2
 (d) produces ozone.
41. The products obtained on heating LiNO_2 will be :
 (a) $\text{Li}_2\text{O} + \text{NO}_2 + \text{O}_2$ (b) $\text{Li}_3\text{N} + \text{O}_2$
 (c) $\text{Li}_2\text{O} + \text{NO} + \text{O}_2$ (d) $\text{LiNO}_3 + \text{O}_2$
42. What is the best description of the change that occurs when $\text{Na}_2\text{O}(\text{s})$ is dissolved in water ?
 (a) Oxide ion accepts sharing in a pair of electrons
 (b) Oxide ion donates a pair of electrons
 (c) Oxidation number of oxygen increases
 (d) Oxidation number of sodium decreases
43. Which of the following on thermal decomposition yields a basic as well as acidic oxide ?
 (a) NaNO_3 (b) KClO_3
 (c) CaCO_3 (d) NH_4NO_3
44. The sequence of ionic mobility in aqueous solution is :
 (a) $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$ (b) $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$
 (c) $\text{Rb}^+ > \text{K}^+ > \text{Cs}^+ > \text{Na}^+$ (d) $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
45. Property of the alkaline earth metals that increases with their atomic number is
 (a) solubility of their hydroxides in water
 (b) solubility of their sulphates in water
 (c) ionization energy
 (d) electronegativity
- DIRECTIONS for Qs. 46 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
46. **Statement-1** : Potassium and caesium are used in photoelectric cells.
Statement-2 : Potassium and caesium emit electrons on exposure to light.
47. **Statement-1** : LiCl is predominantly a covalent compound.
Statement-2 : Electronegativity difference between Li and Cl is too small.
48. **Statement-1** : Sulphate is estimated as BaSO_4 and not as MgSO_4 .
Statement-2 : Ionic radius of Mg^{2+} is smaller than that of Ba^{2+} .
49. **Statement-1** : Mg continue to burn in nitric oxide
Statement-2 : During burning, heat evolved do not decompose NO.
50. **Statement-1** : Superoxides of alkali metals are paramagnetic.
Statement-2 : Superoxides contain the ion O_2^{2-} which has one unpaired electron.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- The alkali metals are low melting. Which of the following alkali metal is expected to melt if the room temperature rises to 30°C ?
(a) Na (b) K
(c) Rb (d) Cs
- Alkali metals react with water vigorously to form hydroxides and dihydrogen. Which of the following alkali metals reacts with water least vigorously?
(a) Li (b) Na
(c) K (d) Cs
- The reducing power of a metal depends on various factors. Suggest the factor which makes Li, the strongest reducing agent in aqueous solution.
(a) Sublimation enthalpy
(b) Ionisation enthalpy
(c) Hydration enthalpy
(d) Electron-gain enthalpy
- Metal carbonates decompose on heating to give metal oxide and carbon dioxide. Which of the metal carbonates is most stable thermally?
(a) MgCO_3 (b) CaCO_3
(c) SrCO_3 (d) BaCO_3
- Which of the following carbonates given below is unstable in air and is kept in CO_2 atmosphere to avoid decomposition?
(a) BeCO_3 (b) MgCO_3
(c) CaCO_3 (d) BaCO_3
- Metals form basic hydroxides. Which of the following metal hydroxide is the least basic?
(a) Mg(OH)_2 (b) Ca(OH)_2
(c) Sr(OH)_2 (d) Ba(OH)_2
- Some of the Group 2 metal halides are covalent and soluble in organic solvents. Among the following metal halides, the one which is soluble in ethanol is
(a) BeCl_2 (b) MgCl_2
(c) CaCl_2 (d) SrCl_2
- The order of decreasing ionisation enthalpy in alkali metals is
(a) $\text{Na} > \text{Li} > \text{K} > \text{Rb}$ (b) $\text{Rb} < \text{Na} < \text{K} < \text{Li}$
(c) $\text{Li} > \text{Na} > \text{K} > \text{Rb}$ (d) $\text{K} < \text{Li} < \text{Na} < \text{Rb}$
- The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of Li in water is due to
(a) ionic nature of lithium fluoride
(b) high lattice enthalpy
(c) high hydration enthalpy for lithium ion
(d) low ionisation enthalpy of lithium atom
- Amphoteric hydroxides react with both alkalies and acids. Which of the following Group 2 metal hydroxides is soluble in sodium hydroxide?
(a) Be(OH)_2 (b) Mg(OH)_2
(c) Ca(OH)_2 (d) Ba(OH)_2
- In the synthesis of sodium carbonate, the recovery of ammonia is done by treating NH_4Cl with Ca(OH)_2 . The by-product obtained in this process is
(a) CaCl_2 (b) NaCl
(c) NaOH (d) NaHCO_3
- When sodium is dissolved in liquid ammonia, a solution of deep blue colour is obtained. The colour of the solution is due to
(a) ammoniated electron (b) sodium ion
(c) sodium amide (d) ammoniated sodium ion
- By adding gypsum to cement
(a) setting time of cement becomes less
(b) setting time of cement increases
(c) colour of cement becomes light
(d) shining surface is obtained
- Dead burnt plaster is
(a) CaSO_4 (b) $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$
(c) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (d) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- Suspension of slaked lime in water is known as
(a) lime water
(b) quick lime
(c) milk of lime
(d) aqueous solution of slaked lime
- Which of the following elements does not form hydride by direct heating with dihydrogen?
(a) Be (b) Mg
(c) Sr (d) Ba
- The formula of soda ash is
(a) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (b) $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$
(c) $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (d) Na_2CO_3
- A substance which gives brick red flame and breaks down on heating to give oxygen and a brown gas is
(a) magnesium nitrate (b) calcium nitrate
(c) barium nitrate (d) strontium nitrate
- Which of the following statements is true about Ca(OH)_2 ?
(a) It is used in the preparation of bleaching powder.
(b) It is a light blue solid.
(c) It does not possess disinfectant property.
(d) It is used in the manufacture of cement.
- A chemical 'A' is used for the preparation of washing soda to recover ammonia. When CO_2 is bubbled through an aqueous solution of 'A', the solution turns milky. It is used in white washing due to disinfectant nature. What is the chemical formula of 'A'?
(a) $\text{Ca(HCO}_3)_2$ (b) CaO
(c) Ca(OH)_2 (d) CaCO_3

21. Dehydration of hydrates of halides of calcium, barium and strontium i.e., $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ can be achieved by heating. These become wet on keeping in air. Which of the following statements is correct about these halides?
- (a) Act as dehydrating agent
 - (b) Can absorb moisture from air
 - (c) Tendency to form hydrate decreases from calcium to barium
 - (d) All of the above
22. In Castner-Kellner cell for production of sodium hydroxide: **[NEET Kar. 2013]**
- (a) Brine is electrolyzed with Pt electrodes
 - (b) Brine is electrolyzed using graphite electrodes
 - (c) Molten sodium chloride is electrolysed
 - (d) Sodium amalgam is formed at mercury cathode
23. Solubility of the alkaline earth's metal sulphates in water decreases in the sequence :- **[2015]**
- (a) $\text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$
 - (b) $\text{Sr} > \text{Ca} > \text{Mg} > \text{Ba}$
 - (c) $\text{Ba} > \text{Mg} > \text{Sr} > \text{Ca}$
 - (d) $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$
24. The function of "Sodium pump" is a biological process operating in each and every cell of all animals. Which of the following biologically important ions is also a constituent of this pump : **[2015]**
- (a) Mg^{2+}
 - (b) K^+
 - (c) Fe^{2+}
 - (d) Ca^{2+}
25. On heating which of the following releases CO_2 most easily ? **[2015 RS]**
- (a) K_2CO_3
 - (b) Na_2CO_3
 - (c) MgCO_3
 - (d) CaCO_3
26. Which of the following statements is false ? **[2016]**
- (a) Mg^{2+} ions form a complex with ATP
 - (b) Ca^{2+} ions are important in blood clotting
 - (c) Ca^{2+} ions are not important in maintaining the regular beating of the heart.
 - (d) Mg^{2+} ions are important in the green parts of plants.

Hints & Solutions

EXERCISE - 1

- (a) A reducing agent is a substance which can lose electron and hence a reducing agent should have low ionisation energy. Now since ionisation energy decreases from Li to Cs, the reducing property should increase from Li to Cs. The only exception to this is lithium. This is because the net process of converting an atom to an ion takes place in 3 steps.
 - $M(s) \rightarrow M(g)$ $\Delta H =$ Sublimation energy
 - $M(g) \rightarrow M^+(g) + e^-$ $\Delta H =$ Ionisation energy
 - $M^+(g) + H_2O \rightarrow M^+(aq)$ $\Delta H =$ Hydration energy
 The large amount of energy liberated in hydration of Li (because of its small size) makes the overall ΔH negative. This accounts for the higher oxidation potential of lithium i.e., its high reducing power.
- (b) Nitrolim is $CaCN_2 + C$. It is used as fertilizer since it reacts with H_2O to form NH_3 .

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$
- (a) $NaHCO_3$ is used in medicine to neutralise the acidity in the stomach. $Mg(OH)_2$ is basic in nature and dissolves in acids forming corresponding salts. So both are used in antacid medicinal preparations.
- (a) Within a group, ionic radius increases with increase in atomic number. The melting points decrease down the group due to weakening of metallic bond. The electronegativity and the 1st ionization energy also decreases down the group.
- (b) Radii of atoms increase as we go down the group due to the addition of extra energy shell. Nuclear charge also increases on moving down the group but the influence of addition of energy shell predominates. This predomination is larger in case when we move from Na to K among all the options given.
- (c) With the same anion, smaller the size of the cation, higher is the lattice energy. The correct order of size of cations is –

$$Na^+ < K^+ < Rb^+ < Cs^+$$
 Hence, the lattice energy of NaF will be maximum. i.e., NaF.
- (a) According to Fajan rules, ionic character increases with increase in size of the cation and decrease in size of the anion. Thus, CsF has higher ionic character than NaCl and hence bond in CsF is stronger than in NaCl.
- (c) As Cs^+ ion has larger size than Li^+ and I^- has larger size than F^- , therefore maximum distance between centres of cations and anions is in CsI.
- (b) Composition of cement depends upon its type. Portland cement is most common kind and contains 51% tricalcium silicate, 24% of dicalcium silicate and 6% of tricalcium aluminate.
- (a) Lithium does not form peroxide.
- (c)
- (d) Be shows diagonal relationship with Al
- (b) Li is much softer than the other group I metals. Actually Li is harder than other alkali metals
- (b) During the dissolution of alkali metal hydrides energy is released in large amount, i.e., it is exothermic in nature.
- (c) The property of sodium atom to emit photons in yellow region of visible spectrum, due to electrically stimulated electron transitions is used in street lights.
- (a) Since the ionization energies of alkali metals decrease down the group, the ionic character and consequently basic property of their hydroxides increases in the same order, i.e. from LiOH to CsOH.
- (d) $2KClO_3 \xrightarrow[\text{solid}]{\text{heat melts}} 2KCl + 3O_2$
- (d) Li, Na, K are lighter than water but Rb is heavier than water.
- (b) $BaCO_3$ forms a yellow ppt of barium chromate. $BaCO_3$ forms a white precipitate of $BaSO_4$. $BaCl_2$ is soluble in water.
- (c) $4S + 6NaOH \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$
- (b) As outermost electronic configuration of alkali metals is ns^1 and also their size are largest in their respective periods so their 1st I.E. will be lowest among the given options. As second electron is to be removed from complete shell or noble gas core, so the 2nd I.E. must be highest among the given options. So, option (b) is correct choice.
- (b) Washing soda is $Na_2CO_3 \cdot 10H_2O$.
- (c) Mixture of K_2CO_3 and Na_2CO_3 is called fusion mixture
- (b) $Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$
- (a) Magnesium on heating to redness in an atmosphere of N_2 gives magnesium nitride.

$$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$
 Then magnesium nitride is rapidly hydrolysed by water to give magnesium hydroxide and ammonia.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$
- (d) Glauber's salt is $Na_2SO_4 \cdot 10H_2O$.
- (b)
- (d) Carbonates of group IA are fairly stable and will melt before they eventually decompose into oxides at temperature above $1000^\circ C$. Li_2CO_3 is considerably less stable than other carbonates of group IA and on decomposition by heating, it gives CO_2 .

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
 So, option (d) is more probable.
- (c) Fehling's solution is a mixture of Alk. $CuSO_4 + Na-K$ tartarate (Rochelle salt)
- (a) $NaHCO_3$ (baking soda) is one of the major constituents of baking powder.
- (c) Sodium bicarbonate on heating changes into sodium carbonate by the loss of CO_2 and H_2O .

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

Sodium bicarbonate
Sodium carbonate
- (d)
- (b) Magnesium hydroxide is used to prepare an antacid which is used as medicine. Hence, the metal M is Mg.

34. (a) ($\text{Na}_2\text{O}_2 + \text{HCl}$) is commercially known as oxone and is used for bleaching of delicate fibres.

35. (a) NaHCO_3 and NaOH cannot exist together. NaHCO_3 being acid salt will react with alkali to form normal salt.

36. (a) Baking powder has starch, NaHCO_3 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

37. (d) Lithium is widely used in the manufacture of storage battery.

38. (a) Metallic bonding in alkaline earth's metals is stronger because of larger number of electrons in the outer shell in alkaline earth's metal atoms.

39. (a)

40. (b) $\text{BaF}_2 > \text{MgF}_2 > \text{CaF}_2$

41. (c) Potassium is kept in kerosene as it is highly reactive and reacts with all other options given above namely alcohol forming alkoxide, water forming hydroxide and ammonia forming a complex but does not react with kerosene.

42. (c) Within a period, the size decreases from left to right, i.e., $\text{Na} > \text{Mg} > \text{Li} > \text{Be}$. Atomic size increases down the group.

43. (a) As we move down the group, the lattice energies of carbonates remain approximately the same. However the hydration energies of the metal cation decreases from Be^{++} to Ba^{++} , hence the solubilities of carbonates of the alkaline earth metal decrease down the group mainly due to decreasing hydration energies of the cations from Be^{++} to Ba^{++} .

44. (d) The IInd ionisation potential of Na is higher than Mg because it requires more energy to remove an electron from a saturated shell or stable (fully filled) orbital.

$$\begin{aligned} {}_{11}\text{Na} &\longrightarrow 1s^2, 2s^2 2p^6, 3s^1 \xrightarrow{\text{I}} \\ &\quad 1s^2, 2s^2 2p^6, 3s^0 \xrightarrow{\text{II}} 1s^2, 2s^2 2p^5, 3s^0 \\ {}_{12}\text{Mg} &\longrightarrow 1s^2, 2s^2 2p^6, 3s^2 \xrightarrow{\text{I}} \\ &\quad 1s^2, 2s^2 2p^6, 3s^1 \xrightarrow{\text{II}} 1s^2, 2s^2 2p^6, 3s^0 \end{aligned}$$

Here $\text{Na-I} < \text{Mg-I}$ and $\text{Na-II} > \text{Mg-II}$.
Option (d) is correct.

45. (d) 46. (d)

47. (a) Because of smaller size, Mg^{2+} ions are extensively hydrated.

48. (a) Because of small atomic size and high I.E. Be forms covalent chloride.

49. (a) 50. (a)

51. (d) Halides of group I and II impart characteristic colour to the flame due to low IE of the central atom. However, ionization energy of Be and Mg atoms is high due to their small size, hence they can't be excited to higher levels by Bunsen burner flame. Thus, their halides don't impart colour to flame.

52. (c) The Mohr's salt is represented by the molecular formula $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Hence, it has six molecules of water.

53. (c) $\text{Ba}(\text{NO}_3)_2$ is used in preparation of green fire.

54. (c) According to Fajan's rule,
Size of cation $\propto$ Ionic character.
Recall that size of metal (ion) increases while going down the group, and decreases on crossing the periods from left to right. Thus Rb^+ (group I) is largest and Be^{2+} (group II) is smallest in size. Hence RbCl has greatest, and BeCl_2 has lowest ionic character.

55. (c) $\text{ZnS} + \text{BaSO}_4$ is lithopone. It is used as white pigment.

56. (b) Mixture of MgO and MgCl_2 is called Sorel's cement. It is used for making magnesia cement.

57. (c) In K_2CO_3 replacement of O by S gives K_2CS_3 which is called potassium thiocarbonate.

58. (a) Calcium and magnesium are estimated by EDTA.

59. (c) Philosopher's wool is ZnO

$$\text{ZnO} + \text{BaO} \xrightarrow{1100^\circ\text{C}} \text{BaZnO}_2$$

60. (b) Permanent hardness of water is due to chlorides and sulphates of calcium and magnesium i.e. CaCl_2 , CaSO_4 , MgCl_2 and MgSO_4 .

61. (c) $\text{NH}_4\text{HCO}_3 + \text{NaCl} \xrightarrow[\text{Brine}]{\text{Sod. bicarbonat ppt.}} \text{NaHCO}_3 \downarrow + \text{NH}_4\text{Cl}$

62. (c) 63. (a)

64. (c) Chemically plaster of Paris is $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.

65. (b) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{120^\circ\text{C}} \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
Plaster of Paris is hemihydrate.

66. (d) Plaster of Paris ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) on making paste with little water sets to a hard mass due to formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

$$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Heat}$$

Plaster of Paris Gypsum

67. (a) Dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$ contains more SiO_2 as compared to tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$. Therefore, it has slow setting rate.

68. (a) $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ – Plaster of paris is used for plastering the broken bones.

69. (b) Colemanite is a mineral of boron having composition as $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

70. (d) 71. (c) 72. (a) Mg. 73. (b)

74. (d) $\text{CaCl}_2 \rightarrow \underset{\text{Cathode}}{\text{Ca}^{+2}} + \underset{\text{Anode}}{2\text{Cl}^-}$
Cathode : $\text{Ca}^{+2} + 2e^- \rightarrow \text{Ca}$
Anode : $2\text{Cl}^- \rightarrow 2e^- + \text{Cl}_2$

75. (c)

EXERCISE - 2

1. (c) Because of its very low density lithium floats to the surface of kerosene oil.
2. (b) KOH is better absorber of CO_2 because K_2CO_3 formed is more soluble and does not separate out.
3. (c) Atomic size of $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and that of $\text{Cl}^- > \text{F}^-$. Therefore, $\text{Mg}^{2+}/\text{Cl}^-$ ratio has the minimum value.
4. (c) Ca and CaH_2 both react with H_2O to form H_2 gas,

$$\text{Ca} + 2\text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{H}_2$$

$$\text{CaH}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + 2\text{H}_2$$
 whereas K gives H_2 while KO_2 gives O_2 and H_2O_2

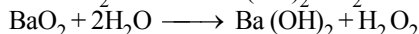
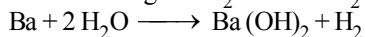
$$2\text{K} + 2\text{H}_2\text{O} \longrightarrow 2\text{KOH} + \text{H}_2$$

$$2\text{KO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{KOH} + \text{O}_2 + \text{H}_2\text{O}_2$$
 Similarly, Na gives H_2 while Na_2O_2 gives H_2O_2

$$2\text{Na} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2$$

$$\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$$

Likewise Ba gives H_2 while BaO_2 gives H_2O_2



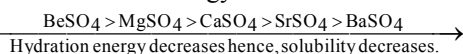
5. (d) Sodium sesquicarbonate ($Na_2CO_3 \cdot NaCO_3 \cdot 2H_2O$) is neither deliquescent nor efflorescent and is used for wool washing.
6. (b) MgO , N_2O_5 is strongly acidic, ZnO and Al_2O_3 are amphoteric, therefore, MgO is most basic.
7. (d) $Be(OH)_2$ is amphoteric, but the hydroxides of other alkaline earth metals are basic. The basic strength increases gradually.
8. (a) Li does not form alum because of its small size.
9. (c) KNO_3 is included in gun powder to provide a supply of oxygen.
10. (b) $Zn^{2+} + 2NaOH \longrightarrow 2Na^+ + Zn(OH)_2$
 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$
 Thus Na_2ZnO_2 forms $2Na^+$ and $[ZnO_2]^{2-}$ ions.
11. (a) Larger cation (K^+) develops less polarisation in anion and thus KI has more ionic nature and more soluble in water.
12. (d) Sulphate of alkaline earth metal are sparingly soluble or almost not soluble in water whereas $BeSO_4$ is soluble in water due to high degree of solvation. $Be(OH)_2$ is insoluble in water but soluble in $NaOH$.
13. (a) Setting of cement is exothermic process which develops interlocking crystals of hydrated silicates
14. (d) Anhydrous form of Na_2CO_3 does not decompose on heating even to redness. It is a amorphous powder called soda ash.
15. (d) K and Mg, both form oxides



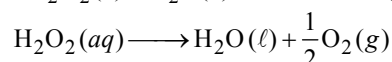
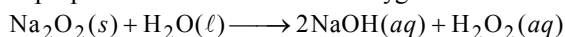
Mg form nitride also $3Mg + N_2 \rightarrow Mg_3N_2$

K does not form nitride.

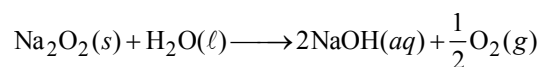
16. (b) Although lattice energy of $LiCl$ is higher than $NaCl$ but $LiCl$ is covalent in nature and $NaCl$ ionic there after, the melting point decreases as we move towards $NaCl$ because the lattice energy decreases as a size of alkali metal atom increases (lattice energy $\propto$ melting point of alkali metal halide)
17. (d) Since 'R' gives a colourless gas on reaction with dil HCl , so it contains CO_3^{2-} or SO_3^{2-} as anion (i.e., CO_2 or SO_2 is evolved)
 Since the gas decolourises acidified $KMnO_4$ solution so it is SO_2 and thus the anion present is SO_3^{2-} i.e., the salt 'R' is Na_2SO_3 .
18. (d) $BeSO_4$ is most soluble because hydration energy is more than lattice energy.



19. (c) From the given information, we can see that the reaction proceeds via formation of H_2O_2 (which is diabasic conjugate acid of peroxide ion), H_2O_2 then disproportionates into water and oxygen.

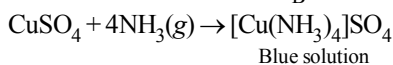
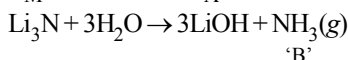
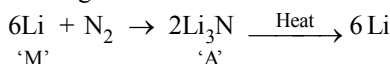


Thus over all reaction is



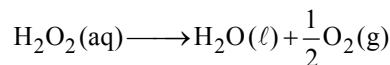
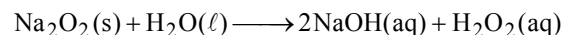
20. (a) $Ca + H_2 \longrightarrow CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + H_2$
21. (b) H^+ cation is smaller than parent H-atom. H^- and Li^+ are isoelectronic species so Li^+ with higher nuclear charge (i.e. 3) will be smaller than H^- having smaller nuclear charge (i.e. 1).
22. (d) Amongst alkali metal Li ions are highly hydrated.
23. (c) The atom becomes larger on descending the group, so the bonds becomes weaker (metallic bond), the cohesive force/energy decreases and accordingly melting point also decreases.
24. (b) Statement (b) is correct.
25. (b) From the given data 'M' is a metal from group 1 as it forms M_3N . Since on heating to high temperature, M_3N gives back the metal 'M' the metal is most likely to be Li.

Writing various reactions

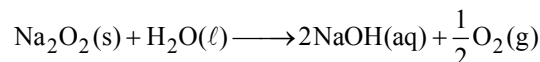


Thus M is Li and B is $NH_3(g)$.

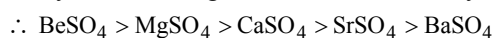
26. (a) Basic strength of the oxides increase in the order $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$. The increase in basic strength is due to the decrease in I.E. and increase in electropositive character.
 The melting points of the halides decrease in the order $NaF > NaCl > NaBr > NaI$, as the size of the halide ion increases. The decrease in melting point is due to increase in the covalent character with increase in the size of anion according to Fajan's rule.
27. (c) From the given information, we can see that the reaction proceeds via formation of H_2O_2 (which is diabasic conjugate acid of peroxide ion), H_2O_2 then disproportionates into water and oxygen.



Thus over all reaction is



28. (d) To reduce the concentration of Ba^{+2} ions, add enough Na_2SO_4 to solution. As the concentration of SO_4^{--} increases, Ba^{+2} combine with SO_4^{--} and are precipitated.
29. (a) In alkaline earth metals ionic size increases down the group. The lattice energy remains constant because sulphate ion is so large, so that small change in cationic sizes do not make any difference. On moving down the group the degree of hydration of metal ions decreases very much leading to decrease in solubility

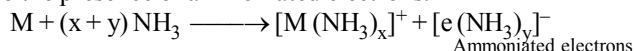


30. (d) The stability of alkali metal hydrides decreases from Li to Cs. It is due to the fact that M-H bonds become weaker with increase in size of alkali metals as we move down the group from Li to Cs. Thus the order of stability of hydrides is
 $\text{LiH} > \text{NaH} > \text{KH} > \text{RbH} > \text{CsH}$
 i.e. option (d) is correct answer.
31. (a) NaOH is a strong alkali. It combines with acidic and amphoteric oxides to form salts. Since CaO is a basic oxide hence does not react with NaOH.
32. (b) Be^{2+} is very small, hence its hydration enthalpy is greater than its lattice enthalpy
33. (b) $\text{CaCO}_{3(s)} \xrightarrow{\Delta} \text{CO}_{2(g)} \uparrow + \text{CaO}_{(s)}$
 A colourless B
 $\text{CaO}_{(s)} + \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_{2(aq)}$
 B
 $\text{Ca}(\text{OH})_2 + 2\text{CO}_2 \longrightarrow \text{Ca}(\text{HCO}_3)_{2(aq)}$
 C
 $\text{Ca}(\text{HCO}_3)_{2(s)} \xrightarrow{\Delta} \text{CaCO}_{3(s)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(g)}$
 A
 $\therefore$ Correct choice : (b)
34. (c) Melting points of halides decreases as the size of the halogen increases. The correct order is
 $\text{CaF}_2 > \text{CaCl}_2 > \text{CaBr}_2 > \text{CaI}_2$
35. (b) Active ingredient in bleaching powder for bleaching action is $\text{Ca}(\text{OCl})_2$
36. (c) $2\text{Al}(s) + 2\text{NaOH}(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$
 sod. meta aluminate
37. (b) (A) Plaster of paris = $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$
 (B) Epsomite = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
 (C) Kieserite = $\text{MgSO}_4 \cdot \text{H}_2\text{O}$
 (D) Gypsum = $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
38. (a) $(\text{AlCl}_3, \text{LiCl} \text{ \& \; } \text{BeCl}_2)$ all these solutions are acidic due to cationic hydrolysis, whereas BaCl_2 is salt of strong base and strong acid, hence its solution will almost neutral i.e., $\text{pH} \approx 7$.
39. (b) All alkali metal salts are ionic (except Lithium) and soluble in water due to the fact that cations get hydrated by water molecules. The degree of hydration depends upon the size of the cation. Smaller the size of a cation, greater is its hydration energy.
 Relative ionic radii : $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
 Relative degree of hydration:
 $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
40. (a) $4\text{KO}_2 + 2\text{CO}_2 \rightarrow 2\text{K}_2\text{CO}_3 + 3\text{O}_2$.
 KO_2 is used as an oxidising agent. It is used as air purifier in space capsules. Submarines and breathing masks as it produces oxygen and remove carbon dioxide.
41. (a) $4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$
42. (b)
43. (c) Calcium carbonate on thermal decomposition gives CaO (Basic oxide) and CO_2 (Acidic oxide)
 $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2 \uparrow$
 Basic oxide Acidic oxide
44. (b) Smaller the ion more is its ionic mobility in aqueous solution. Ionic radii of the given alkali metals is in the order $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ and thus expected ionic mobility will be in the order $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$. However due to high degree of solvation (or hydration) because of lower size or high charge density, the hydrated ion size follows the order $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$ and thus conductivity order is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$ i.e. option (b) is correct answer.
45. (a) Lattice energy decreases more rapidly than hydration energy for alkaline earth metal hydroxides. On moving down a group $\therefore$ solubility of their hydroxides increases.

Sol. For Qs. 46-50

The thermal stabilities of carbonates increase down the group due to increase in metallic character i.e. electropositive character. Further bigger cation stabilises bigger anion through crystal lattice energy effect.

Solution of alkali in liquid ammonia has high electrical conductivity due to the presence of ammoniated electrons.



Sodium carbonate is prepared by solvay process not potassium carbonate, as KHCO_3 is quite soluble in water.

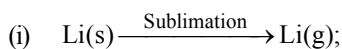
46. (a) K and Cs emit electrons on exposure of light due to low ionisation potential.
47. (c) Statement-1 is true but statement-2 is false.
 Due to high polarizing power of Li^+ , LiCl is a covalent compound.
48. (b) Sulphate is estimated as BaSO_4 because Ba^{2+} being larger ion is hydrated to a lesser extent hence it has high lattice energy group.
49. (c) When Mg is burnt in nitric oxide, it continues to burn because during burning the heat evolved decomposes NO to N_2 and O_2 . Oxygen thus, produced helps Mg to burn.
50. (a) Presence of unpaired electrons in superoxides of alkali metals make them paramagnetic.

EXERCISE - 3

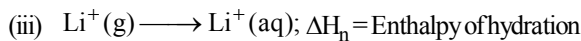
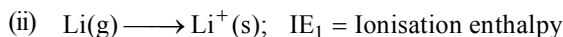
Exemplar Questions

1. (d) Alkali metals have low melting and boiling points. The melting point of alkali metals decreases from Li to Cs as cohesive force decreases with increase in atomic size.
2. (a) The reactivity of alkali metals with water increases on moving down the group from Li to Cs due to increase in electropositive character.
3. (c) Reducing character is measured by tendency of an element to lose electron in aqueous solution. Higher the negative E_{RP}° value, greater is the ability to lose electrons.
 E_{RP}° depends on:
 (i) enthalpy of sublimation
 (ii) ionisation of enthalpy
 (iii) enthalpy of hydration
 Thus, in aqueous medium, order of reactivity of alkali metals is $\text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{Li}$. E_{RP}° value of Li is least (-3.04 V) among all alkali metals.

The formation of Li^+ (aq) from Li involves following steps:



ΔH_s = Enthalpy of sublimation

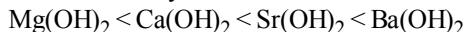


For alkali metals, enthalpies of sublimation are almost same. IE_1 value of Li is positive & highest and hydration enthalpy is negative and maximum for smallest Li^+ which makes it strongest reducing agent.

4. (d) BaCO_3 is thermally most stable due to the small size of resulting oxide ion. As the atomic number increases the stability of the metal ion decreases hence, stability of carbonates increases.

5. (a) BeCO_3 is unstable due to high polarising power of smallest Be^{2+} ion. Also, it shows reversible reaction, because of more stability of oxide formed. Hence, BeCO_3 has least stability and it is stable only in CO_2 atmosphere.

6. (a) The basic character of the given hydroxides increases down the group due to decrease in ionization enthalpies. On moving down the group, the ionic size increases, so M–O bond in metal hydroxides gets weaker and easily gives OH^- in the solution and I.E. further decreases. Hence, Mg(OH)_2 will be least basic. The order of basicity will be:



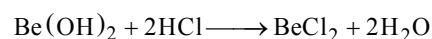
7. (a) Ethanol is a covalent compound and only a compound which has more covalent character can be dissolved in it. Also the group ionic character increases and beryllium halide have covalent character due to its small size and high effective nuclear charge. Hence, among the given halides, BeCl_2 can be soluble in ethanol.

8. (c) On moving down the group from Li to Rb increased screening effect makes the removal of electron easier. Thus, the order of decreasing ionization enthalpy will be: $\text{Li} > \text{Na} > \text{K} > \text{Rb}$

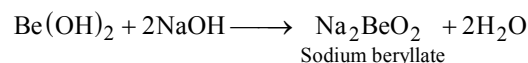
9. (b) Among fluorides, the order of solubility is $\text{LiF} < \text{NaF} < \text{KF} < \text{RbF} < \text{CsF}$. On moving down the group solubility increases because lattice energy decreases. Also, LiF exhibit very high lattice energy.

10. (a) Be(OH)_2 is an amphoteric hydroxide thus gets dissolve both in acids and alkalies.

Basic nature :

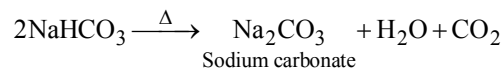
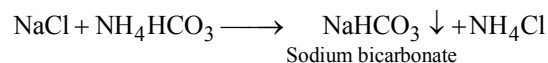
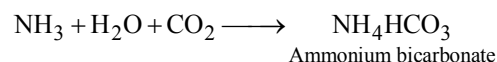


Acidic nature:

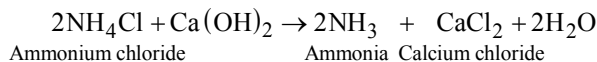
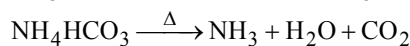


11. (a) Sodium carbonate can be synthesised by Solvay ammonia soda process.

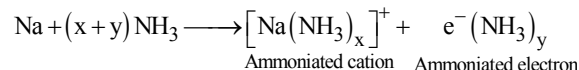
The reactions involved in the process are :



NH_3 is recovered from NH_4HCO_3 and NH_4Cl



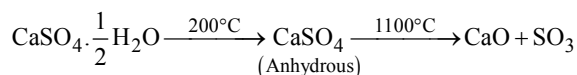
12. (a) Alkali metals dissolve in liquid NH_3 giving deep blue coloured solution.



When light fall on the solution, the ammoniated electrons get excite to higher energy level by absorbing certain wavelength and transmit blue colour.

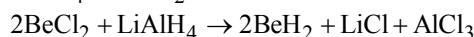
13. (b) Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added to cement to increase its setting time so that it gets sufficiently hardened. Setting of cement is an exothermic process and involves hydration of calcium aluminates and silicates.

14. (a) On heating plaster of Paris at certain temperature, it forms anhydrous calcium sulphate which is known to be dead burnt plaster and has no setting property as it absorbs water very slowly.

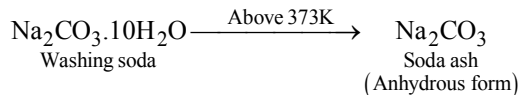


15. (c) Slaked lime [Ca(OH)_2] is sparingly soluble in water and it forms a suspension of slaked lime in water which is called milk of lime and a clear solution obtained after the suspension settles is known as lime water.

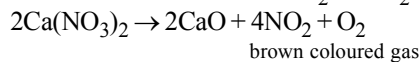
16. (a) Except Be, all alkaline earth metals form hydrides (MH_2) on directly heating with H_2 . BeH_2 can't be prepared by direct heating but it can be prepared by the action of LiAlH_4 on BeCl_2 .



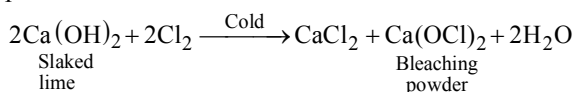
17. (d) On heating washing soda, it loses its water of crystallisation. Above 373 K, it becomes completely anhydrous white powder called soda ash.



18. (b) Calcium gives brick red coloured flame. Also, calcium nitrate on heating decomposes into calcium oxide and evolution of a mixture of NO_2 and O_2 takes place.



19. (a) Ca(OH)_2 is used in the manufacture of bleaching powder.



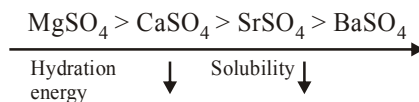
20. (c) To recover NH_3 in Solvay process Ca(OH)_2 is used. On passing CO_2 through Ca(OH)_2 , it turns milky due to the formation of CaCO_3 . Also, Ca(OH)_2 is used for white washing due to its disinfectant nature.



21. (d) Chlorides of alkaline earth metals are hydrated salts. Due to their hygroscopic nature, they can be used as a dehydrating agent and can absorb moisture from air. Extent of hydration decreases from Ca to Ba.

NEET/AIPMT (2013-2017) Questions

22. (d) In Castner Kellner cell, sodium amalgam is formed at mercury cathode.
23. (d) Solubility of alkaline earth metal sulphates decreases down the group due decrease in hydration energy.



24. (b) K^+ ion is a constituent of sodium pump.
25. (c) Carbonates becomes more thermally stable down the group, therefore MgCO_3 will leave CO_2 easily.
26. (c)

Chapter 11 The *p*-block elements (Group 13 and 14)

GROUP 13 ELEMENTS : THE BORON FAMILY

It includes	Boron	(B)	non-metal
	Aluminium	(Al)	metal
	Gallium	(Ga)	metals
	Indium	(In)	
	Thallium	(Tl)	

Atomic and Physical Properties

(i) Electronic Configuration

All these elements have three electrons in the outermost energy levels and their outer electronic configuration is $ns^2 np^1$.

(ii) Atomic Radii

The atomic radii are smaller than group 1 and 2 elements due to increased nuclear charge.

Atomic radius increases B to Tl. The abrupt increase in the atomic radius of Al is due to greater screening effect in Al than in B. Atomic radius of Ga is less than that of Al. This is due to presence of $d-e^{-1}$ s in Ga which have a poor shielding effect thus resulting in poor screening of outer e^{-1} s from nuclear charge. As a result, size of Ga < Al.

(iii) Ionization enthalpy

In spite of the large nuclear charge and small size, *the first ionisation energies of these elements are less than the corresponding value of s-block elements*. This is because *p*-electrons are less penetrating and more shielded than *s*-electrons, i.e., they are farther from the nucleus and hence held less tightly than free *s*-electrons and thus can be easily removed.

(iv) Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is due to difference in atomic size of the elements.

(v) Density : Density increases from B to Tl due to increase in size of the atom. Aluminium has an extremely low density and hence used as an important structural material.

(vi) Melting and boiling points : Melting points do not vary regularly due to structural changes in the elements. Boron has a very high melting point because it exists as a giant covalent polymer in both solid and liquid states. The melting point decreases from B to Ga and then increases. Due to its unusually low m. pt. (303 K), Ga can exist as liquid during summers.

Chemical Properties

(i) Oxidation states

Al forms Al^{3+} ions. Down the group, stability of +3 O.S. decreases while that of +1 O.S. increases. This is because of inert pair effect (i.e. due to poor shielding effect of intervening *d*- and *f*-orbitals, the $ns e^{-1}$ s becomes inert towards bonding)

(ii) Tendency of forming ionic compounds

The tendency of formation of ionic compounds increases from B to Tl. Boron forms only covalent compounds. This is due to its extremely high ionisation energy which is not compensated either by the lattice energies of its ionic compounds or by the hydration energies of ions in aqueous solution.

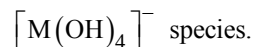
(iii) Trends in chemical reactivity

In trivalent state, they form e^{-} deficient compounds. Thus, they show tendency to accept e^{-} pair and hence act as Lewis acids. This tendency decreases down the group.

Ex

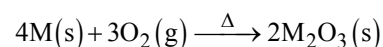
(a) BCl_3 accepts lone pair of e^{-} s from NH_3 to form $BCl_3 \cdot NH_3$.

(b) $AlCl_3$ becomes stable by forming a dimer Al_2Cl_6 . In trivalent state, most of their compounds are hydrolysed in water. For ex: the trichlorides on hydrolysis form



(iv) Complex formation : On account of their smaller size and greater charge, these elements have a much greater tendency to form complexes than the *s*-block elements.

(v) Reactivity towards air:



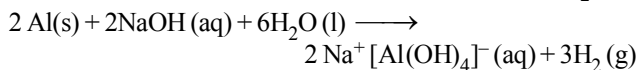
Aluminium forms a very thin oxide layer on surface which protect the metal from further attack.

Boron trioxide is acidic. Al and Ga oxides are amphoteric and those of In and Tl are basic in their properties.

Crystalline boron is unreactive. It is the amorphous boron which reacts with air.

(vi) **Reactivity towards acids and alkalis:**

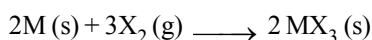
B does not react with acids and alkalis. Al shows amphoteric character and reacts with both acids and alkalis.



Conc HNO_3 renders Al and Ga passive by forming a protective oxide layer on the surface.

(vii) **Reactivity towards halogens:**

With halogens they form trihalides of formula MX_3



(X = F, Cl, Br, I)

Anomalous Behaviour of Boron

Owing to its extremely small size, high electron density, high electronegativity and non-availability of d-electrons, boron exhibits following anomalous properties:

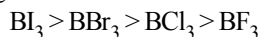
- Boron is a typical non-metal, while other members of the group are metals.
- It forms only covalent compounds while other members can form covalent as well as ionic compounds. The maximum covalency of B is four while that of Al is six.
- Its oxides and hydroxides have acidic nature while that of other members have amphoteric and basic nature.
- Its hydrides are quite stable while that of other members are not so stable.
- Like non-metals, it combines with metals to form metal borides (eg. Mg_3B_2) while other members form alloy with metals.
- It does not decompose steam while other members do so.

Trihalides of Boron:

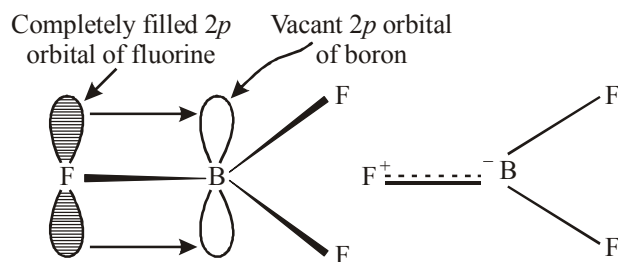
Due to small size and high electronegativity of boron, all boron halides are covalent.

Boron atom, in BX_3 , has six electrons in the outermost orbit and thus it can accept a pair of electrons from a donor atom like N, O, P or S to complete its octet. Hence boron halides function as very efficient **Lewis acids**.

The relative Lewis acid character of boron trihalides is found to follow the following order.



This anomalous behaviour can be explained on the basis of the *relative tendency of the halogen atom to back donate its unutilised electrons to the vacant p-orbitals of boron atom*.

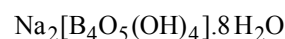


Formation of back bonding between boron and fluorine in BF_3 molecule.

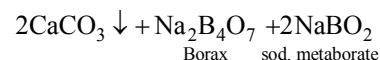
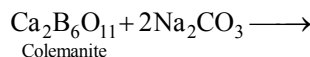
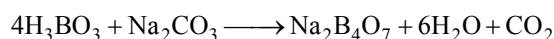
Some Important Compounds of Boron**Borax:**

It is a white crystalline solid with formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

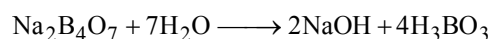
It contains tetranuclear units and the correct formula is therefore



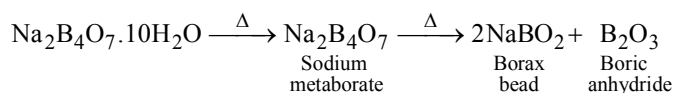
It dissolves in water to give an alkaline solution.

Preparation:(i) *From colemanite:*(ii) *From boric acid:***Properties:**

- Aqueous solution of borax is alkaline due to hydrolytic decomposition which produces NaOH and H_3BO_3 .



- On heating, borax loses water and swells into a white mass which on further heating melts to form a transparent glassy solid called **borax glass** and **borax bead**.



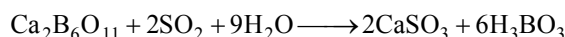
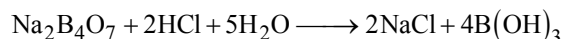
The metaborates of many transition metals have characteristic colours therefore borax bead test is used for qualitative analysis of various cation.

Uses

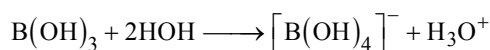
- Borax is used in the manufacture of enamels, glazes, pyrex glass.
- It is also used as a cleansing and stiffening agent in laundry work and in candle industry.
- It is used for glazing paper, playing cards and also as an antiseptic.
- It is also used in water softening.

Orthoboric Acid

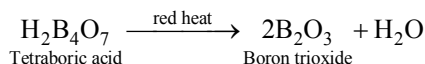
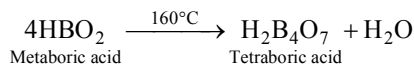
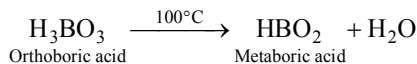
It is white crystalline solid with a soapy touch.

Preparation(i) *From colemanite,*(ii) *It is prepared by acidifying an aqueous solution of borax:***Properties**

- It is a weak monobasic acid and acts as a Lewis acid.



(ii) *Action of heat :*



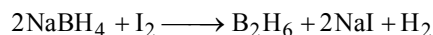
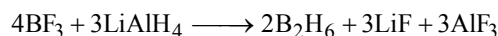
Uses

- (i) It is used as an antiseptic, as eye-wash (eye-lotion) and as a food preservative.
- (ii) It is used in the preparation of glass, glazes and enamels.
- (iii) It is also used in leather industry.

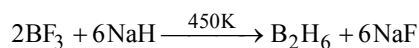
Diborane

Its formula is B_2H_6 .

Preparation :



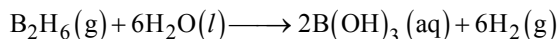
(Lab method)



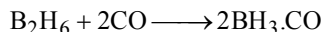
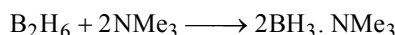
(Industrial method)

Properties :

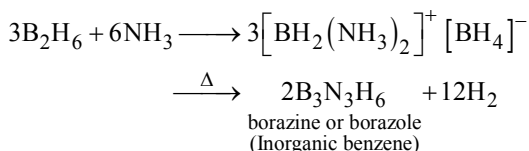
- (i) It is a colourless, highly toxic gas.
- (ii) It catches fire spontaneously on exposure to air.
- (iii) Action of oxygen : $\text{B}_2\text{H}_6 + 3\text{O}_2 \longrightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$
- (iv) Hydrolysis :



- (v) Reaction with Lewis base :

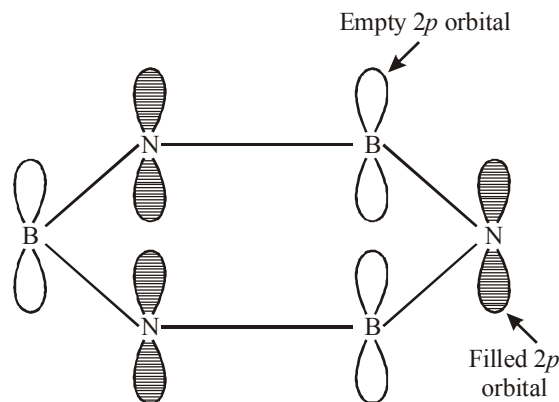
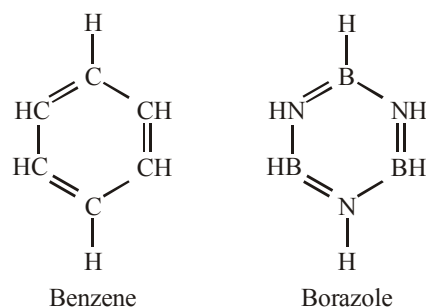


- (vi) Action of ammonia :

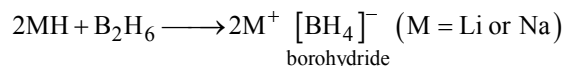


Borazole has been called as **inorganic benzene** because it is very close to benzene in structure and properties.

Borazole is isoelectronic with benzene. It is a planar molecule in which B and H atoms are sp^2 hybridized. The difference is that in borazole the π -bonding is dative and it arises from overlap of empty p -orbitals of boron with filled p -orbitals of nitrogen.



- (vii) Formation of complex borohydride :



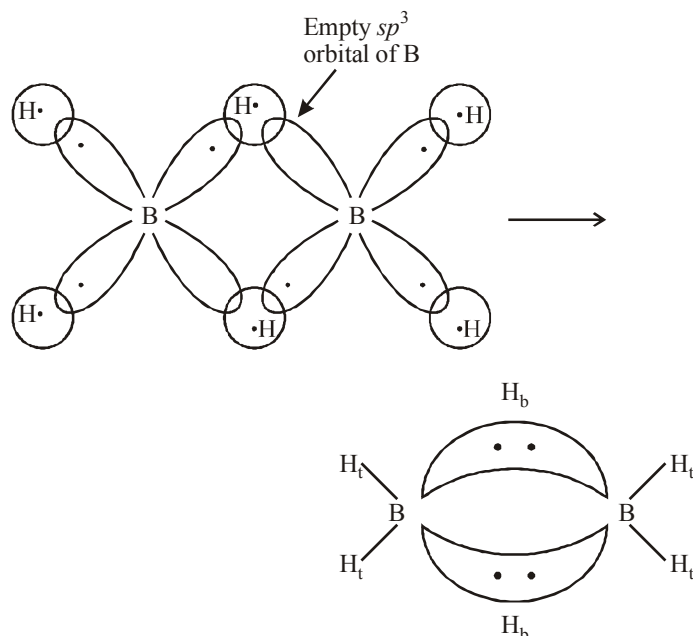
Uses of diborane

- (i) It is used as a catalyst in polymerisation reactions.
- (ii) It is used as a reducing agent in organic reactions.
- (iii) It is used for welding torches.
- (iv) Diborane is also used for preparing substances such as high energy fuels and propellants.
- (v) Hydroboration is a useful method for preparing hydrocarbons, alcohols, ketones and acids.

Structure and bonding in diborane :

Each B atom uses sp^3 hybrid orbitals for bonding. Two of the four sp^3 orbitals of each of the boron atom overlap with 1 s orbitals of two terminal hydrogen atoms forming two normal B – H σ bonds. One of the remaining sp^3 hybrid orbital ((either filled or empty) of one of the boron atoms, the 1 s orbital of the bridge hydrogen atom and one of the sp^3 hybrid orbitals (empty or filled respectively) of the second boron atom overlap to form a delocalised orbital covering the three nuclei. Thus a pair of electrons (one electron from B and other from H) acts as a bond between three atoms (centres) ; such bond is known as *three-centre two electron bonds* ($3c - 2e$ bonds).

The 3-centre – $2e^-$ bridge bonds are also referred to as banana bonds.



Structure of diborane showing two three centre - two electron bonds.
 H_t represents terminal H atom
 H_b represents bridged H atom

GROUP 14 ELEMENTS : THE CARBON FAMILY

It includes

- Non-metal : [Carbon (C)
 Silicon (Si)]
 Semi-metal : [Germanium (Ge)]
 Metal : [Tin (Sn)
 Lead (Pb)]

Carbon is the important constituent of all organic matter while silicon is the main constituent of inorganic matter.

Atomic and Physical Properties

- Electronic Configuration :**
 The valence shell electronic configuration of these elements is $ns^2 np^2$.
- Covalent Radius :**
 The radius increases from C to Si due to addition of a new shell.
 From Si to Pb, increase in size is small. This is due to presence of d- and f- e^- s which have a poor screening effect.
- Ionization enthalpy :**
 The 1st ionisation energy of group 14 members is higher than group 13 members.
 Ionisation energy decreases down the group. Small decreases in ionisation energy from Si to Ge to Sn and slight increase in ionisation energy from Sn to Pb is due to poor shielding effect of intervening d and f orbitals and increase in size of atom.
- Electronegativity**
 Due to small size, they are more electronegative than group 13 elements. The electronegativity decreases from C to Pb but not in regular manner due to filling of d- and f-orbitals.

(v) Physical properties

All the members of this group are solids. Their melting point and boiling points decreases from carbon to lead. C and Si are non-metals, Ge is a metalloid while Sn and Pb are soft metals with low m. pts.

Chemical Properties

(i) Oxidation states and trends in chemical reactivity :

Their common O. S. are +4 and +2. C exhibits negative O. S. also. Due to inert pair effect, the stability of +4 O.S. decreases down the group while that of +2 O.S. increases. Thus, $PbCl_2$ is more stable than $PbCl_4$.

Except C, other elements can expand their covalency beyond 4 due to presence of d-orbitals in them. Thus, their halides undergo hydrolysis and have tendency to form complexes by accepting e^- pairs from donor species.

For example : SiF_6^{2-} , $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$

(ii) Reactivity towards oxygen :

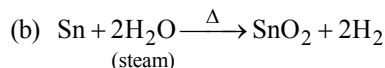
They form two types of oxides : monoxide (MO) and dioxide (MO_2)

Oxides in higher oxidation state are more acidic than those in lower oxidation state. Down the group the acidic character decreases.

CO_2 , SiO_2 , GeO_2 are acidic while SnO_2 and PbO_2 are amphoteric. CO is neutral, GeO is acidic, SnO and PbO are amphoteric.

(iii) Reactivity towards water:

(a) C, Si and Ge are not affected by water.

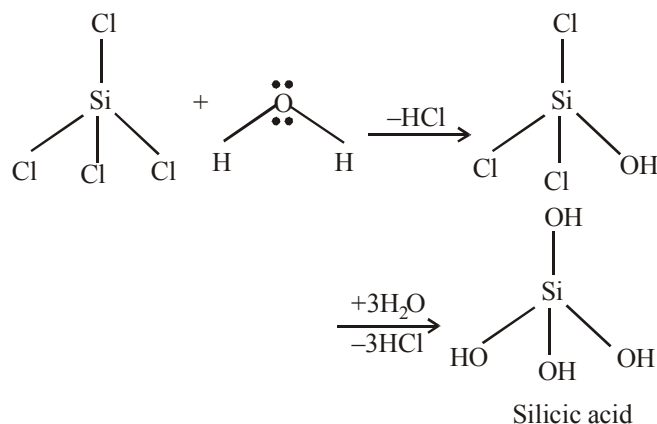


(c) Pb is unaffected by water due to oxide film formation on its surface.

(iv) Reactivity towards halogens

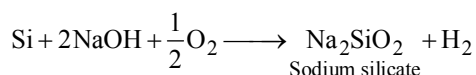
They form two types of halides : MX_2 and MX_4 .

Most of the MX_4 are covalent in nature. However, SnF_4 and PbF_4 are ionic in nature. PbI_4 does not exist. Stability of dihalides increases down the group. Thus, GeX_4 is more stable than GeX_2 but PbX_2 is more stable than PbX_4 . Except CCl_4 , other tetrachlorides are easily hydrolysed by water due to presence of d-orbitals in them. Ex: hydrolysis of $SiCl_4$.



Important Trends and Anomalous Behaviour of Carbon

- Due to its smaller size, higher electronegativity, higher ionisation energy and unavailability of d-orbitals, carbon differs from rest of the members of its group.
- Due to absence of d-orbitals, the maximum covalency of C is 4 while for other members, it can be more than 4 due to presence of d-orbitals.
- Carbon forms $p\pi - p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Examples are $C=C$, $C\equiv C$, $C=O$, $C=S$ and $C\equiv N$. Heavier elements do not form $p\pi-p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.
- Carbon shows the property of catenation i.e. self-linking of the atoms through covalent bonds. This is because C–C bonds are very strong. Down the group, catenation tendency decreases.
- Carbon remains unaffected by alkalis while other members reacts with alkali as



Allotropes of Carbon

Carbon exhibits many allotropic forms: both crystalline and amorphous. Diamond, graphite and fullerenes are the allotropes of carbon.

Diamond

It has a rigid 3D network of C–atoms.

It has directional covalent bonds throughout the lattice.

It is very difficult to break extended covalent bonding and hence diamond is the hardest substance known. It is used as an abrasive for sharpening hard tools, in making dies and in the manufacture of tungsten filaments for electric light bulbs.

In diamond all the electrons are used in bond formation, there is no mobile electron in the system and hence the **diamond crystals are non-conductor of electricity**.

Graphite

It has a layered structure and the layers are held by van der Waals forces. The C atoms undergo sp^2 hybridisation, forming 3 σ -bonds. The fourth e^- forms a π -bond and is delocalised over the whole sheet. Electrons are mobile and this makes graphite a good conductor of electricity. It is soft and slippery and is thus used as a dry lubricant in machines running at high temperature. Graphite is thermodynamically the most stable allotrope of carbon and thus, $\Delta_f H^\circ$ for graphite is taken to be zero.

Graphite is used (i) in making electrodes and carbon arcs, (ii) as a lubricant, (iii) in crucible, (iv) in lead pencils, and (v) as a moderator in nuclear reactors.

Fullerenes

They are made by heating graphite in an electric arc in presence of inert gases such as He or Ar. They are pure form of carbon.

Fullerenes are large cage like spheroidal molecules with general formula C_{2n} (where $n \geq 30$). Two important member are C_{60} and C_{70} . C_{60} fullerene looks like a soccer ball (so called bucky ball). C_{60} is called Buckminsterfullerene.

Some Important Compounds of C and Si Oxides of Carbon

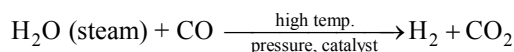
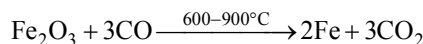
(i) Carbon monoxide (CO)

(a) Preparation :

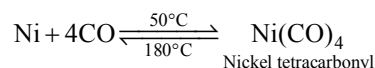
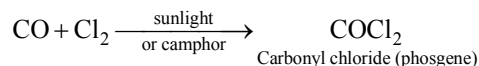
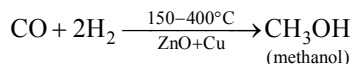
- $2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$
- $HCOOH \xrightarrow[\text{conc. } H_2SO_4]{373\text{ K}} H_2O + CO$
- $C(s) + H_2O(g) \xrightarrow[1273\text{ K}]{473\text{ K}} CO(g) + H_2(g)$
Water or synthesis gas
- $2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\text{ K}} 2CO(g) + 3N_2(g)$
Producer gas
- $CO_2 + C \longrightarrow 2CO$; $CO_2 + Zn \longrightarrow ZnO + CO$
- $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(b) Properties :

- It is colourless, odourless, water insoluble gas.
- It is a powerful reducing agent.
- It combines with haemoglobin (Hb) in the blood thus forming carboxyhaemoglobin which decreases oxygen carrying capacity of Hb.
- As a reducing agent

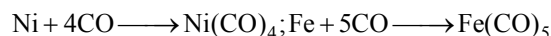


- It behaves as an unsaturated compound and gives addition product with a number of substances.

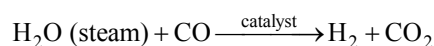
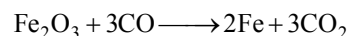


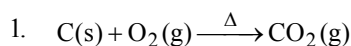
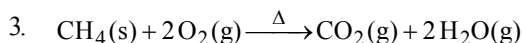
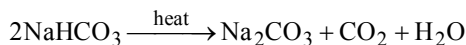
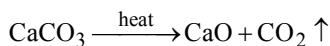
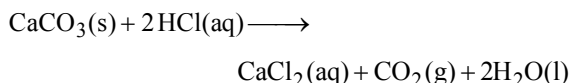
Uses :

- Carbon monoxide is used as a fuel in the form of *water gas* ($CO + H_2$) and *producer gas* ($CO + N_2$).
- It is used in making carbonyls which in turn are used in the extraction of iron and nickel.

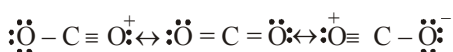


- It is used in the manufacture of methanol, synthetic petrol and phosgene.
- It is used as a reducing agent in metallurgy of iron and in the manufacture of hydrogen.

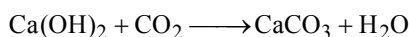


(ii) Carbon dioxide (CO₂)**(a) Preparation :****2. Commercial method :****4. Laboratory method :****(b) Properties :**

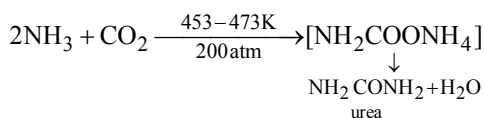
- It is one of the gases responsible for greenhouse effect. It is not poisonous as CO.
- It is obtained as a solid in form of dry ice by allowing liquefied CO₂ to expand rapidly.
- It exists as a resonance hybrid of two structures :



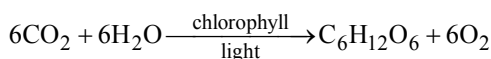
- It turns lime water milky



- Action of NH₃ :



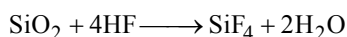
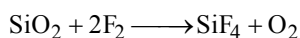
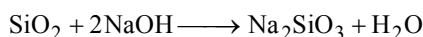
- Photosynthesis :

**Uses :**

- Dry ice is used as a refrigerant.
- Gaseous CO₂ is used in cold drinks, in fire extinguisher and to manufacture urea.
- It is used in manufacture of white lead and Na₂CO₃

Silicon Dioxide, SiO₂

- It is commonly known as silica.
- It is a covalent, 3D network solid in which each Si atom is covalently bonded in a tetrahedral manner to four O-atoms.
- In normal form, silica is non-reactive due to high Si-O bond enthalpy.
- It is attacked by F₂, HF and NaOH.

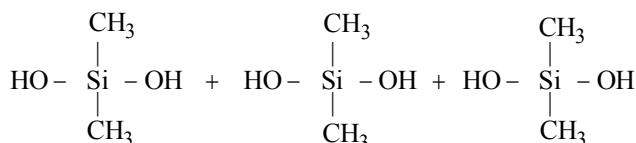
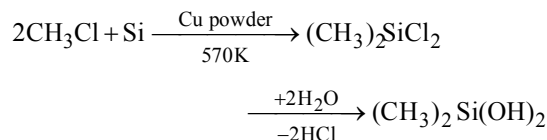


- Quartz (crystalline form of silica) is used as a piezoelectric material and has helped to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.

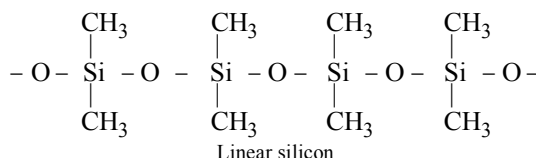
- Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.
- Kieselgur, an amorphous form of silica, is used in filtration plants.

Silicones

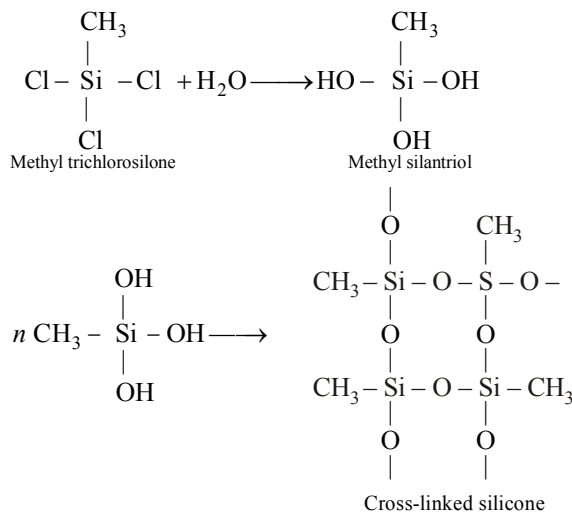
They are a group of organosilicon polymers having $\text{-(R}_2\text{SiO)-}$ as a repeating unit. The starting materials for their preparation are alkyl or aryl substituted silicon chlorides R_nSiCl_(4-n).

(i) Preparation of linear silicones :

$-\text{H}_2\text{O} \downarrow$ Polymerisation



- Preparation of cyclic silicones:** Cyclic (ring) silicones are formed when water is eliminated from the terminal -OH groups of linear silicones.
- Preparation of cross linked silicones :** Hydrolysis of alkyl trichlorosilane, CH₃SiCl₃ gives the monomethylsillantriol which then undergoes polymerisation to a very complex *cross linked polymer*.

**Properties :**

- Being surrounded by non-polar alkyl groups, silicones are water repelling in nature.
- They have high thermal stability, high dielectric strength and resistance to oxidation.
- Silicone is non-toxic.

- (iv) Silicone products may be fluids, greases, resins or rubbers depending upon the size and type of polymer.

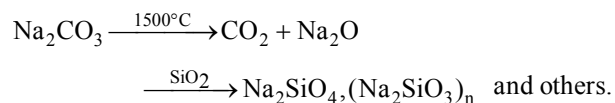
Uses

They are used as sealant, greases, electrical insulators and for water proofing of fabrics.

They are also used as non-stick coating for pans, and are used in paints and varnish.

Silicates

- (i) Its examples are feldspar, zeolites, mica and asbestos.
- (ii) Their basic structural unit is SiO_4^{4-} . Each Si atom is bonded to four O-atoms in tetrahedral fashion.
- (iii) Silicates can be prepared by fusing an alkali metal carbonate with silica.



- (iv) The various types of silicates are

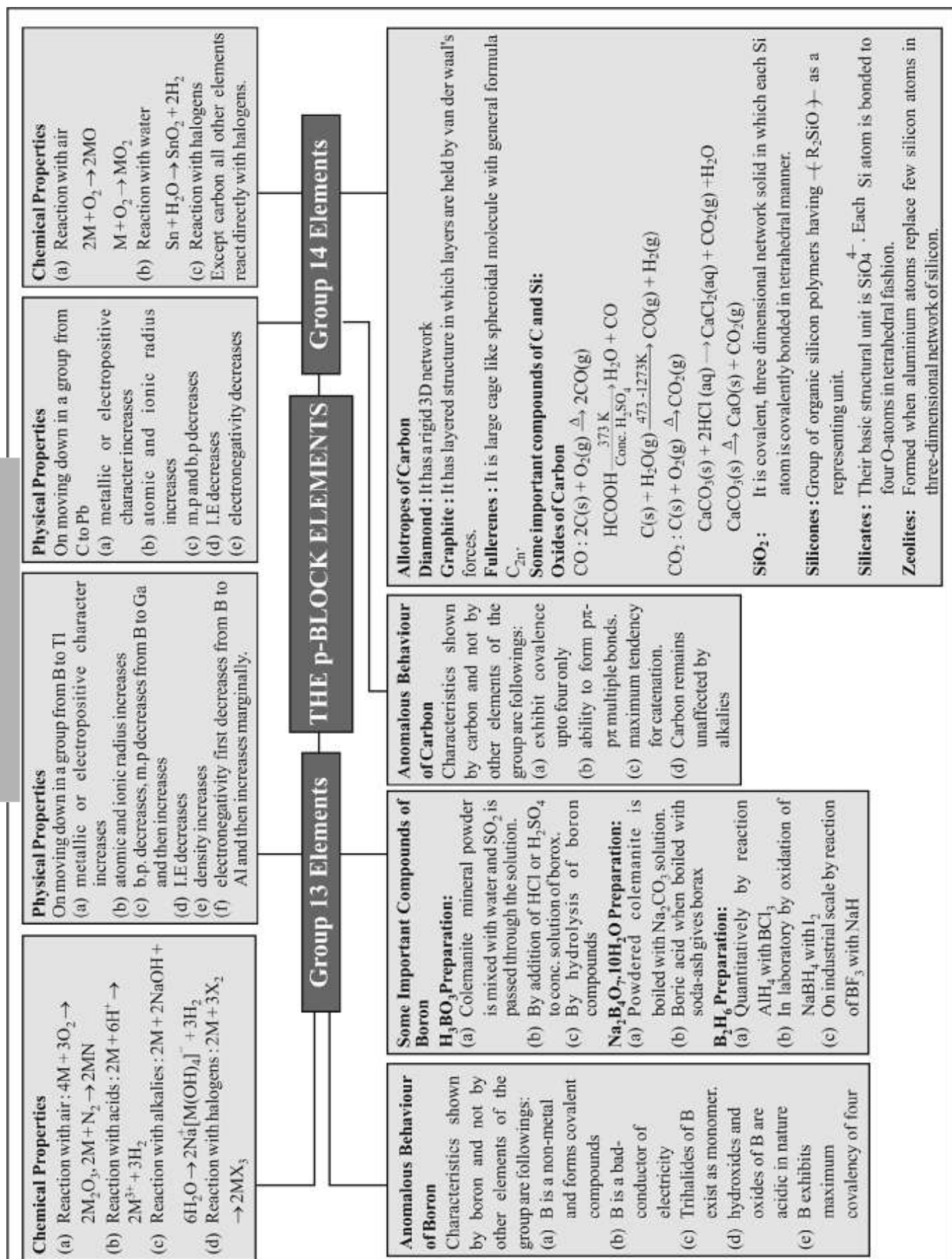
- (a) Orthosilicates
- (b) Pyrosilicates
- (c) Cyclic or ring silicates
- (d) Chain silicates
- (e) Sheet silicates
- (f) Three dimensional silicates

- (v) Two man-made silicates are glass and cement.

Zeolites

- (i) They are formed when Al - atoms replace few Si-atoms in 3D network of SiO_2 such that the overall structure acquires a negative charge which is balanced by cations such as Na^+ , K^+ or Ca^{2+} .
- (ii) They act as molecular sieves by trapping small molecules in their interstices reversibly.
- (iii) They are used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation.
- (iv) Hydrated zeolites are used as ion exchangers in softening of hard water.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- Alum is :
 - $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$
 - $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
 - NaAlO_2
- In borax bead test which compound is formed?
 - Ortho-borate
 - Meta-borate
 - Double oxide
 - Tetra-borate
- Alum helps in purifying water by
 - forming Si complex with clay particles
 - sulphate part which combines with the dirt and removes it
 - coagulating the mud particles
 - making mud water soluble.
- Which of the following halides is least stable and has doubtful existence?
 - Cl_4
 - GeI_4
 - SnI_4
 - PbI_4
- Unlike the other elements of its group carbon does not form CX_2 type molecules because :
 - energetically this is not possible
 - carbon undergoes catenation
 - it is non-metallic
 - carbon does not contain d-orbital
- AlI_3 , when react with CCl_4 , gives
 - AlCl_3
 - Cl_4
 - Al_4C_3
 - Al_2O_3
- Which of the following statements about anhydrous aluminium chloride is correct?
 - It exists as AlCl_3 molecules
 - It is not easily hydrolysed
 - It sublimes at 180°C
 - It is a strong Lewis base
- Orthoboric acid –
 - donate proton to form H_2BO_3^-
 - accept proton of form H_4BO_3^+
 - donate OH^- to form H_2BO_2^+
 - accept OH^- to form $[\text{B}(\text{OH})_4]^-$
- The approximate percentage of silica in cement is:
 - 5 – 10%
 - 15 – 20%
 - 20 – 25%
 - 25 – 30%
- The strongest Lewis acid is –
 - BF_3
 - BCl_3
 - BBr_3
 - BI_3
- Bell metal is an alloy of:
 - Sn and Pb
 - Cu and Pb
 - Sn and Cu
 - In, Sn and Cu
- In the Hoopé's process of aluminium extraction, the fused materials remain in three different layers. These layers remain separated even in electrolytic reduction, because :
 - cell has the arrangement for separation
 - all the layers have different densities
 - all the layers are at different temperatures
 - upper layer is attracted by cathode and lower layer is attracted by anode.
- Thermite is a mixture of :
 - $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$
 - $\text{Fe}_2\text{O}_3 + \text{Al}$
 - $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$
 - $\text{Al}_2\text{O}_3 + 2\text{Cr}$
- Thermite is a mixture of iron oxide and
 - zinc powder
 - potassium metal
 - sodium shavings
 - aluminium powder
- Inorganic benzene is :
 - $\text{B}_3\text{H}_3\text{N}_3$
 - BH_3NH_3
 - $\text{B}_3\text{H}_6\text{N}_3$
 - $\text{H}_3\text{B}_3\text{N}_6$
- An aqueous solution of potash alum gives :
 - two types of ions
 - only one type of ion
 - four types of ions
 - three types of ions
- Ionisation enthalpy ($\Delta_i H_1 \text{ kJ mol}^{-1}$) for the elements of Group 13 follows the order.
 - $\text{B} > \text{Al} > \text{Ga} > \text{In} > \text{Tl}$
 - $\text{B} < \text{Al} < \text{Ga} < \text{In} < \text{Tl}$
 - $\text{B} < \text{Al} > \text{Ga} < \text{In} > \text{Tl}$
 - $\text{B} > \text{Al} < \text{Ga} > \text{In} < \text{Tl}$
- The liquefied metal which expands on solidification is :
 - Ga
 - Al
 - Zn
 - In
- Amphoteric oxide among the following is –
 - B_2O_3
 - Ga_2O_3
 - In_2O_3
 - Tl_2O_3
- Which of the following has the least melting point ?
 - B
 - Al
 - Ga
 - In
- Borax is used as cleansing agent because on dissolving in water it gives
 - Alkaline solution
 - Acidic solution
 - Bleaching solution
 - Colloidal solution
- Which of the following properties of aluminium makes it useful for food packaging ?
 - Good electrical conductivity
 - Good thermal conductivity
 - Low density
 - Non toxicity
- Aluminium reacts with caustic soda to form:
 - aluminium hydroxide
 - aluminium oxide
 - sodium meta-aluminate
 - sodium tetra-aluminate
- In the reaction $\text{B}_2\text{O}_3 + \text{C} + \text{Cl}_2 \rightarrow \text{A} + \text{CO}$. The A is
 - BCl_3
 - BCl_2
 - B_2Cl_2
 - CCl_2

25. Non-oxide ceramics can be
 (a) B_4C (b) SiC
 (c) Si_3N_4 (d) All of these
26. Which of the following metals burn in air at high temperature with the evolution of heat?
 (a) Cu (b) Hg
 (c) Pb (d) Al
27. Which of the following product is formed when SiF_4 reacts with water?
 (a) SiF_3 (b) H_4SiO_4
 (c) H_2SO_4 (d) H_2SiF_4
28. Boron forms covalent compound due to
 (a) higher ionization energy
 (b) lower ionization energy
 (c) small size
 (d) Both (a) and (c)
29. Which metal is protected by a layer of its own oxide
 (a) Al (b) Ag
 (c) In (d) Fe
30. When Al is added to KOH solution
 (a) no action takes place (b) oxygen is evolved
 (c) water is produced (d) hydrogen is evolved
31. Which of the following is not true about potash alum?
 (a) Its empirical formula is $KAl(SO_4)_2 \cdot 12H_2O$.
 (b) Its aqueous solution is basic
 (c) It is used in dyeing industries
 (d) All are correct.
32. $AlCl_3$ acts as a strong Lewis acid because $AlCl_3$ is :
 (a) easily hydrolysed
 (b) a covalent compound
 (c) an ionic compound
 (d) an electron deficient compound
33. Which one of the following is a metalloid?
 (a) phosphorous (b) antimony
 (c) nitrogen (d) bismuth
34. In the electrolytic extraction of aluminium, cryolite is used
 (a) to obtain more aluminium
 (b) to decrease temperature to dissolve bauxite
 (c) to protect the anode
 (d) as reducing agent
35. Select the correct statements for diborane :
 1. Boron is approximately sp^3 hybridized
 2. $B-H-B$ angle is 180°
 3. There are two terminal B-H bonds for each boron atom
 4. There are only 12 bonding electrons
 (a) 1, 2 and 4 (b) 1, 2 and 3
 (c) 2, 3 and 4 (d) 1, 3 and 4
36. Action of concentrated nitric acid (HNO_3) on metallic tin produces
 (a) stannic nitrate (b) stannous nitrite
 (c) stannous nitrate (d) hydrated stannic oxide
37. Which of the following statements about anhydrous aluminium chloride is correct?
 (a) It fumes in moist air
 (b) It exists as dimer both in the vapour state below $350^\circ C$ and in non-polar solvents
 (c) It is prepared by heating Al_2O_3 in a stream of sulphur chloride (S_2Cl_2) vapours and chlorine.
 (d) All of these
38. Aqueous solution of orthoboric acid can be titrated against sodium hydroxide using phenolphthalein indicator only in presence of –
 (a) trans-glycerol (b) catechol
 (c) cis-glycerol (d) Both (b) and (c)
39. Which of the following statement is correct with respect to the property of elements with an increase in atomic number in the carbon family (group 14)?
 (a) atomic size decrease
 (b) ionization energy increase
 (c) metallic character decrease
 (d) stability of +2 oxidation state increase
40. H_3BO_3 on heating up to 373 K yields:
 (a) boric anhydride (b) orthoboric acid
 (c) metaboric acid (d) tetraboric acid
41. Which of the following statements about H_3BO_3 is not correct?
 (a) It is a strong tribasic acid
 (b) It is prepared by acidifying an aqueous solution of borax
 (c) It has a layer structure in which planar BO_3 units are joined by hydrogen bonds
 (d) It does not act as proton donor but acts as a Lewis acid by accepting a lone pair of electrons
42. Boron halides behave as Lewis base, because of their :
 (a) ionic nature (b) acidic nature
 (c) covalent nature (d) electron deficient nature
43. Aluminium chloride exists as dimer, (Al_2Cl_6) in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives
 (a) $[Al(OH)_6]^{3-} + 3HCl$ (b) $[Al(H_2O)_6]^{3+} + 3Cl^-$
 (c) $Al^{3+} + 3Cl^-$ (d) $Al_2O_3 + 6HCl$
44. Among the following the hardest is :
 (a) Peat (b) Lignite
 (c) Graphite (d) Anthracite
45. Which one of the following exist in the oxidation state other than +3?
 (a) B (b) Al
 (c) Ce (d) Ga
46. In aqueous solution $GaCl$ disproportionates to
 (a) $GaCl_2$ and $GaCl_3$ (b) Ga and $GaCl_3$
 (c) $GaCl_2$ and Ga (d) $GaCl_3$ and $GaCl_5$
47. Which of the following is a semiconductor?
 (a) C (b) Pb
 (c) Ge (d) Sn
48. Ordinary glass is :
 (a) Sodium silicate
 (b) Calcium silicate
 (c) Sodium and calcium silicate
 (d) Mixed salt of Na and Ca
49. Which of the following types of forces bind together the carbon atoms in diamond?

- (a) Ionic (b) Covalent
(c) Dipolar (d) Van der Waals.
50. Water gas is produced by
(a) passing steam through a red hot coke bed
(b) saturating hydrogen with moisture
(c) mixing oxygen and hydrogen in the ratio of 1 : 2
(d) heating a mixture of CO_2 and CH_4 in petroleum refineries.
51. Activated charcoal is employed to remove colouring matter from pure substances. It works by :
(a) Bleaching (b) Oxidation
(c) Reduction (d) Adsorption
52. In graphite, electrons are
(a) localised on every third C-atom
(b) present in anti-bonding orbital
(c) localised on each C-atom
(d) spread out between the structure
53. Glass reacts with HF to produce
(a) SiF_4 (b) H_2SiF_6
(c) H_2SiO_3 (d) Na_3AlF_6
54. The oxide of lead used in lead accumulators is :
(a) PbO (b) Pb_2O_3
(c) Pb_3O_4 (d) PbO_2
55. Producer gas is the mixture of :
(a) $\text{CO} + \text{N}_2$ (b) $\text{CO} + \text{H}_2$
(c) $\text{CO} + \text{water vapours}$ (d) $\text{N}_2 + \text{CH}_4$
56. Coal gas is a mixture of :
(a) H_2O and CO (b) $\text{H}_2, \text{CO}, \text{N}_2$ and CH_4
(c) H_2 and CO (d) CH_4 and CO
57. The chemical name of phosgene is
(a) Phosphorus
(b) Carbonyl chloride
(c) Phosphorus oxychloride
(d) Phosphorus trichloride
58. Least thermally stable is –
(a) CCl_4 (b) SiCl_4
(c) GeCl_4 (d) GeBr_4
59. Be_2C and Al_4C_3 are called –
(a) ethanides (b) methanides
(c) carbonides (d) acetylides
60. Which one of the following has the lowest m.p.?
(a) B (b) Al
(c) Ga (d) Tl.
61. Red lead is:
(a) Pb_3O_4 (b) Pb_2O_3
(c) Pb_2O (d) PbO
62. Silicon dioxide is formed by the reaction of
(a) $\text{SiCl}_4 + \text{H}_2\text{O}$ (b) $\text{SiO}_2 + \text{HF}$
(c) $\text{SiO}_2 + \text{NaOH}$ (d) $\text{SiCl}_4 + \text{NaOH}$
63. In laboratory silicon can be prepared by heating
(a) carbon in electric furnace
(b) silica with sodium carbonate
(c) silica with magnesium
(d) None of these
64. In the manufacture of glass addition of MnO_2 gives :
(a) yellow colour (b) red colour
(c) violet colour (d) pink colour
65. Carborundum is
(a) SiC (b) CaC_2
(c) Mg_2C_3 (d) None of these
66. White lead is
(a) PbCO_3 (b) $\text{PbCO}_3 \cdot \text{PbO}$
(c) $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ (d) $2\text{PbSO}_4 \cdot \text{PbO}$
67. Pb reacts with dilute HNO_3 and produces
(a) NO (b) NH_4NO_3
(c) N_2O_5 (d) NO_2
68. In silica (SiO_2), each silicon atom is bonded to
(a) two oxygen atoms
(b) four oxygen atoms
(c) one silicon and two oxygen atoms
(d) one silicon and three oxygen atoms
69. The inert pair effect is most prominent in –
(a) C (b) Pb
(c) Ge (d) Si
70. Consider the following chemical reaction –
$$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \longrightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$$

(a) CO is an oxidising agent
(b) CO is reducing agent
(c) CO is neutral towards litmus
(d) CO acts as catalyst
71. Tetra ethyl lead is used as :
(a) fire extinguisher (b) antiknock compound
(c) pain killer (d) mosquito killer
72. To a piece of charcoal, sulphuric acid is added. Then:
(a) there is no reaction
(b) water gas is formed
(c) SO_2 and CO_2 are evolved
(d) CO and SO_2 are evolved
73. Which of the following has the highest calorific value ?
(a) Coal gas (b) Water gas
(c) Producer (d) Carbon dioxide gas
74. Which one of the following statements about the zeolites is false ?
(a) They are used as cation exchangers
(b) They have open structure which enables them to take up small molecules
(c) Zeolites are aluminosilicates having three dimensional network
(d) None of the above
75. When vapours of SiCl_4 are passed over hot Mg, the product formed is :
(a) MgSiCl_6 (b) $\text{SiCl}_2 + \text{MgCl}_2$
(c) $\text{Si} + \text{MgCl}_2$ (d) $\text{MgSi} + \text{Cl}_2$

EXERCISE - 2

Applied Questions

- $$\text{PbS} \xrightarrow[\text{in air}]{\text{Heat}} \text{A} + \text{PbS} \xrightarrow[\text{No air}]{\text{High temp.}} \text{Pb} + \text{SO}_2$$

Identify A

 - PbO
 - PbSO₄
 - None
 - (a) or (b)
- Aluminium hydroxide is soluble in excess of sodium hydroxide forming the ion
 - AlO₂³⁻
 - AlO₂⁻³
 - AlO₂⁻
 - AlO₃⁻
- The hardest substance amongst the following is
 - Be₂C
 - titanium
 - SiC
 - B₄C
- Moissan boron is
 - amorphous boron of ultra purity
 - crystalline boron of ultra purity
 - amorphous boron of low purity
 - crystalline boron of low purity
- Silicon carbide is used as a/an
 - abrasive
 - dehydrating agent
 - solvent
 - catalyst
- Which of the following does not exist in free form
 - BF₃
 - BCl₃
 - BBr₃
 - BH₃
- The role of fluorspar (CaF₂) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na₃AlF₆) is
 - As a catalyst
 - To make the fused mixture very conducting
 - To increase the temperature of the melt.
 - To decrease the rate of oxidation of carbon at the anode.
- The precious Ruby stone is
 - Alumina
 - Aluminium silicate
 - Sodium aluminium silicate
 - Sodium silicate
- Anhydrous AlCl₃ cannot be obtained from which of the following reactions?
 - Heating AlCl₃·6H₂O
 - By passing dry HCl over hot aluminium powder
 - By passing dry Cl₂ over hot aluminium powder
 - Bypassing dry Cl₂ over a hot mixture of alumina and coke
- The factor responsible for weak acidic nature of B-F bonds in BF₃ is
 - Large electronegativity of fluorine
 - Three centred two electron bonds in BF₃
 - p π - d π back bonding
 - p π - p π back bonding
- Aluminium vessels should not be washed with materials containing washing soda since
 - washing soda is expensive
 - washing soda is easily decomposed
 - washing soda reacts with aluminium to form soluble aluminate.
 - washing soda reacts with aluminium to form insoluble aluminium oxide
- Which one of the following is correct statement?
 - The hydroxide of aluminium is more acidic than that of boron
 - The hydroxide of boron is basic, while that of aluminium is amphoteric
 - The hydroxide of boron is acidic, while that of aluminium is amphoteric
 - The hydroxide of boron and aluminium are amphoteric
- Newly shaped glass articles when cooled suddenly become brittle, therefore these are cooled slowly, this process is known as
 - Tempering
 - Annealing
 - Quenching
 - Galvanising
- CO₂ and N₂ are non-supporters of combustion. However for putting out fires CO₂ is preferred over N₂ because CO₂
 - Does not burn
 - Forms noncombustible products with burning substances
 - Is denser than nitrogen
 - Is a more reactive gas
- Aluminium has a great affinity for oxygen and its oxidation is an exothermic process. This fact is used in
 - preparing thin foils of aluminium
 - making utensils
 - preparing duralumin alloy
 - thermite welding
- Tin plague is the
 - Conversion of stannous to stannic
 - Conversion of white tin to grey tin
 - Emission of sound while bending a tin rod
 - Atmospheric oxidation of tin
- Tin cry refers to
 - Conversion of white to grey tin
 - Tin plating
 - Conversion of white tetrahedral tin to white rhombohedral tin
 - Emission of sound while bending a tin rod.
- Lead is not affected by dil. HCl in cold because
 - Pb is less electronegative than H
 - PbO film is formed which resists chemical attack by acid
 - A protective coating of PbCl₂ is formed on Pb surface
 - PbO₂ film is always present on Pb surface, which resist chemical attack
- Carbon and silicon belong to group 14. The maximum coordination number of carbon in commonly occurring compounds is 4, whereas that of silicon is 6. This is due to
 - large size of silicon
 - more electropositive nature of silicon
 - availability of d-orbitals in silicon
 - Both (a) and (b)

20. A kettle which becomes furred-up in use has inside it a deposit composed mainly of:
 (a) Magnesium bicarbonate (b) Magnesium sulphate
 (c) Sodium sulphate (d) Calcium carbonate
21. Colour is imparted to glass by mixing
 (a) synthetic dyes (b) metal oxides
 (c) oxides of non-metals (d) coloured salts
22. The form of BN which is as hard as diamond is
 (a) hexagonal form
 (b) Cubic form with ZnS structure
 (c) both of these
 (d) none of these
23. The type of glass used in making lenses and prisms is
 (a) Flint glass (b) Jena glass
 (c) Pyrex glass (d) Quartz glass
24. SiF_4 gets hydrolysed giving.....
 (a) SiO_2 (b) $\text{Si(OH)}_2\text{F}_2$
 (c) H_2SiF_6 (d) Si(OH)_4
25. When alumina is heated with carbon in the atmosphere of nitrogen then products formed are
 (a) $\text{Al} + \text{CO}$ (b) $\text{Al} + \text{CO} + \text{N}_2$
 (c) $\text{Al} + \text{CO}_2$ (d) $\text{AlN} + \text{CO}$
26. Soldiers of Napoleon army while at alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to
 (a) a change in the partial pressure of oxygen in the air
 (b) a change in the crystalline structure of tin
 (c) an interaction with nitrogen of the air at very low temperatures
 (d) an interaction with water vapours contained in the humid air
27. On controlled hydrolysis and condensation R_3SiCl yields
 (a) $\text{R}_3\text{Si}-\text{O}-\text{SiR}_3$ (b) $\{\text{R}_3\text{Si}-\text{O}-\text{SiR}_3\}_n$
- $$\begin{array}{c} \text{R} \quad \text{R} \\ | \quad | \\ -\text{Si}-\text{O}-\text{Si}- \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ -\text{Si}-\text{O}-\text{Si}- \\ | \quad | \\ \text{R} \quad \text{R} \end{array}$$

$$\begin{array}{c} \text{R} \quad \text{R} \\ | \quad | \\ -\text{Si}-\text{O}-\text{Si}- \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ -\text{Si}-\text{O}-\text{Si}- \\ | \quad | \\ \text{R} \quad \text{R} \end{array}$$
- (c) R_3SiOH (d) $\text{R}_3\text{Si}-\text{O}-\text{SiR}_3$
28. Carborundum is obtained when silica is heated at high temperature with
 (a) carbon (b) carbon monoxide
 (c) carbon dioxide (d) calcium carbonate
29. Maximum $\pi\pi$ - $\pi\pi$ back bonding exists in
 (a) BCl_3 (b) BF_3
 (c) BBR_3 (d) BI_3
30. Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of:
 (a) $\text{Al}_2\text{O}_3 + \text{HF} + \text{NaAlF}_4$
 (b) $\text{Al}_2\text{O}_3 + \text{CaF}_2 + \text{NaAlF}_4$
 (c) $\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6 + \text{CaF}_2$
 (d) $\text{Al}_2\text{O}_3 + \text{KF} + \text{Na}_3\text{AlF}_6$
31. Heating an aqueous solution of aluminium chloride to dryness will give
 (a) Al(OH)Cl_2 (b) Al_2O_3
 (c) Al_2Cl_6 (d) AlCl_3
32. In view of the signs of $\Delta_r G^\circ$ for the following reactions:
 $\text{PbO}_2 + \text{Pb} \rightarrow 2\text{PbO}, \quad \Delta_r G^\circ < 0$
 $\text{SnO}_2 + \text{Sn} \rightarrow 2\text{SnO}, \quad \Delta_r G^\circ > 0$
 Which oxidation states are more characteristics for lead and tin?
 (a) For lead +2, for tin +2 (b) For lead +4, for tin +4
 (c) For lead +2, for tin +4 (d) For lead +4, for tin +2
33. When PbO_2 reacts with conc. HNO_3 the gas evolved is
 (a) NO_2 (b) O_2
 (c) N_2 (d) N_2O
34. How can the following reaction be made to proceed in forward direction?
 $\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4] + \text{H}_2\text{O}$
 (a) addition of borax (b) addition of *cis*-1,2-diol
 (c) addition of Na_2HPO_4 (d) addition of *trans*-1,2-diol
35. The species present in solution when CO_2 is dissolved in water are
 (a) $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$
 (b) $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$
 (c) $\text{CO}_3^{2-}, \text{HCO}_3^-$
 (d) $\text{CO}_2, \text{H}_2\text{CO}_3$
36. Unlike the other elements of its group carbon and silicon does not form MX_2 type molecules because:
 (a) energetically this is not possible
 (b) carbon undergoes catenation
 (c) it is non-metallic
 (d) carbon does not contain d-orbital
37. Gas A is bubbled through slaked lime when a white precipitate is formed. On prolonged bubbling the precipitate is dissolved. On heating the resultant solution, the white precipitate appears with evolution of gas B. The gases A and B respectively are
 (a) CO and CO (b) CO_2 and CO
 (c) CO and CO_2 (d) CO_2 and CO_2
38. Nitrolim is a mixture of
 (a) CaC_2 & Ga (b) CaCN_2 & C
 (c) Ca(CN)_2 & Ga (d) CaCN_2 & N_2
39. The straight chain polymer is formed by
 (a) hydrolysis of CH_3SiCl_3 followed by condensation polymerisation
 (b) hydrolysis of $(\text{CH}_3)_4\text{Si}$ by addition polymerisation
 (c) hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ followed by condensation polymerisation
 (d) hydrolysis of $(\text{CH}_3)_3\text{SiCl}$ followed by condensation polymerisation
40. The tendency of BF_3 , BCl_3 and BBR_3 to behave as Lewis acid decreases in the sequence:
 (a) $\text{BCl}_3 > \text{BF}_3 > \text{BBR}_3$ (b) $\text{BBR}_3 > \text{BCl}_3 > \text{BF}_3$
 (c) $\text{BBR}_3 > \text{BF}_3 > \text{BCl}_3$ (d) $\text{BF}_3 > \text{BCl}_3 > \text{BBR}_3$
41. Name the type of the structure of silicate in which one oxygen atom of $[\text{SiO}_4]^{4-}$ is shared?
 (a) Linear chain silicate (b) Sheet silicate
 (c) Pyrosilicate (d) Three dimensional

42. In silicon dioxide
- there are double bonds between silicon and oxygen atoms
 - silicon atom is bonded to two oxygen atoms
 - each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
 - each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.
43. The structure of diborane (B_2H_6) contains
- four 2c-2e bonds and four 3c-2e bonds
 - two 2c-2e bonds and two 3c-3e bonds
 - two 2c-2e bonds and four 3c-2e bonds
 - four 2c-2e bonds and two 3c-2e bonds
44. Which one of the following is the correct statement?
- Boric acid is a protonic acid
 - Beryllium exhibits coordination number of six
 - Chlorides of both beryllium and aluminium have bridged structures in solid phase
 - $B_2H_6 \cdot 2NH_3$ is known as 'inorganic benzene'
45. Name of the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared.
- Pyrosilicate
 - Sheet silicate
 - Linear chain silicate
 - Three dimensional silicate
46. Lead pipes are not suitable for drinking water because
- A layer of lead dioxide is deposited over pipes
 - Lead reacts with air to form litharge
 - Lead reacts with water containing air to form $Pb(OH)_2$
 - Lead forms basic lead carbonate
- DIRECTIONS for Qs. 47 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1
 - Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement - 1
 - Statement-1 is True, Statement-2 is False
 - Statement-1 is False, Statement-2 is True
47. **Statement-1** : Boron is metalloid.
Statement-2 : Boron shows metallic nature.
48. **Statement-1** : Benzene is reactive while inorganic benzene is unreactive compound.
Statement-2 : Inorganic benzene is, borazine, $B_3N_3H_6$.
49. **Statement-1** : Silicones are hydrophobic in nature.
Statement-2 : Si – O – Si linkages are moisture sensitive.
50. **Statement-1** : Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.
Statement-2 : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

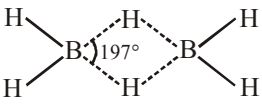
- The elements which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is
 - B
 - Al
 - Ga
 - In
- Which of the following is a Lewis acid?
 - $AlCl_3$
 - $MgCl_2$
 - $CaCl_2$
 - $BaCl_2$
- The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[B(OH_4)]^-$ and the geometry of the complex are respectively.
 - sp^3 , tetrahedral
 - sp^3 , square planar
 - sp^3d^2 , octahedral
 - dsp^2 , square planar
- Which of the following oxides is acidic in nature?
 - B_2O_3
 - Al_2O_3
 - Ga_2O_3
 - In_2O_3
- The exhibition of highest coordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in MF_6^{3-} ?
 - B
 - Al
 - Ga
 - In
- Boric acid is an acid because its molecule
 - contains replaceable H^+ ion
 - gives up a proton
 - accepts OH^- from water releasing proton
 - combines with proton from water molecule
- Catenation i.e., linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in group 14 elements follows the order
 - $C > Si > Ge > Sn$
 - $C > > Si > Ge \approx Sn$
 - $Si > C > Sn > Ge$
 - $Ge > Sn > Si > C$
- Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding.
 - $MeSiCl_3$
 - Me_2SiCl_2
 - Me_3SiCl
 - Me_4Si

9. Ionisation enthalpy ($\Delta_i H$ kJ mol⁻¹) for the elements of group 13 follows the order
 (a) $B > Al > Ga > In > Tl$ (b) $B < Al < Ga < In < Tl$
 (c) $B < Al > Ga < In > Tl$ (d) $B > Al < Ga > In < Tl$
10. In the structure of diborane,
 (a) All hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane
 (b) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane
 (c) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane
 (d) All the atoms are in the same plane
11. A compound X, of boron reacts with NH_3 on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating BF_3 with lithium aluminium hydride. The compounds X and Y are represented by the formulas.
 (a) B_2H_6 , $B_3N_3H_6$ (b) B_2O_3 , $B_3N_3H_6$
 (c) BF_3 , $B_3N_3H_6$ (d) $B_3N_3H_6$, B_2H_6
12. Quartz is extensively used as a piezoelectric material, it contains
 (a) Pb (b) Si
 (c) Ti (d) Sn
13. The most commonly used reducing agent is
 (a) $AlCl_3$ (b) $PbCl_2$
 (c) $SnCl_4$ (d) $SnCl_2$
14. Dry ice is
 (a) solid NH_3 (b) solid SO_2
 (c) solid CO_2 (d) solid N_2
15. Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group (s) are present in the mixture?
 (a) Group 2 (b) Groups 2, 13 and 14
 (c) Group 2 and 13 (d) Groups 2 and 14

NEET/AIPMT (2013-2017) Questions

16. Which of the following structure is similar to graphite? [2013]
 (a) B (b) B_4C
 (c) B_2H_6 (d) BN
17. Which of these is not a monomer for a high molecular mass silicone polymer? [2013]
 (a) Me_2SiCl_2 (b) Me_3SiCl
 (c) $PhSiCl_3$ (d) $MeSiCl_3$
18. The basic structural unit of silicates is : [2013]
 (a) SiO_4^{4-} (b) SiO_3^{2-}
 (c) SiO_4^{2-} (d) SiO
19. Which statement is wrong? [NEET Kar. 2013]
 (a) Feldspars are not aluminosilicates
 (b) Beryl is an example of cyclic silicate
 (c) Mg_2SiO_4 is orthosilicate
 (d) Basic structural unit in silicates is the SiO_4 tetrahedron
20. The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence : [2015 RS]
 (a) $Ga < In < Al < Tl$ (b) $Al < Ga < In < Tl$
 (c) $Tl < In < Ga < Al$ (d) $In < Tl < Ga < Al$
21. It is because of inability of ns^2 electrons of the valence shell to participate in bonding that:- [2017]
 (a) Sn^{2+} is oxidising while Pb^{4+} is reducing
 (b) Sn^{2+} and Pb^{2+} are both oxidising and reducing
 (c) Sn^{4+} is reducing while Pb^{4+} is oxidising
 (d) Sn^{2+} is reducing while Pb^{4+} is oxidising

27. (b) In reaction with water, SiF_4 (like SiCl_4) gets hydrolysed to form H_4SiO_4 (silicic acid).

$$\text{SiF}_4 + 4\text{H}_2\text{O} \longrightarrow \text{Si(OH)}_4 \text{ or } \text{H}_4\text{SiO}_4 + 4\text{HF}$$
(Silicic acid)
28. (d) 29. (a)
30. (d) $2\text{KOH} + 2\text{Al} + 2\text{H}_2\text{O} \rightarrow 2\text{KAlO}_2 + 3\text{H}_2$
31. (a) $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is a molecular formula of potash alum.
32. (d) AlCl_3 acts as a strong Lewis acid because AlCl_3 is an electron deficient compound. Al has three electrons in outer most electron. Through sharing it gets 3 electrons. Still it requires 2 electrons to complete its octet.
33. (b) Antimony is a metalloid because it has some characters of metals and some of non-metals.
34. (b) Cryolite Na_3AlF_6 is added
 (1) to decrease the melting temperature from 2323 K to 1140 K
 (2) to increase the electrical conductivity of solution
35. (d) 
 B is sp^3 hybridized
 Only 12 bonding electrons available
 BHB angle is 97° not 180° .
36. (d) Action of concentrated nitric acid (HNO_3) on metallic tin produces hydrated tin oxide ($\text{SnO}_2 \cdot 2\text{H}_2\text{O}$) which is also called meta stannic acid

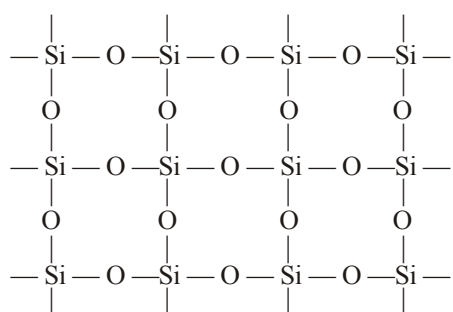
$$\text{Sn} + 4\text{HNO}_3 \longrightarrow \text{SnO}_2 \cdot \text{H}_2\text{O} + 4\text{NO}_2 + \text{H}_2\text{O}$$
37. (d) (A) $\text{AlCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Al(OH)}_3 + 3\text{HCl} \uparrow$ (fumes)
 (B) It exists as dimer in non-polar solvents like benzene and in vapour state below 400°C .
 (C) $4\text{Al}_2\text{O}_3 + 3\text{S}_2\text{Cl}_2 + 9\text{Cl}_2 \longrightarrow 8\text{AlCl}_3 + 6\text{SO}_2 \uparrow$
 So all options are correct.
38. (d) It forms a stable cyclic complex with polyhydroxy compounds like cis-glycerol, cathechol, etc. This helps in the release of H^+ as H_3O^+ and, therefore, boric acid acts as a strong acid and hence can be titrated with sodium hydroxide using phenolphthalein.
39. (d) In the carbon family the stability of +2 oxidation state increases with increase in atomic number due to inert pair effect.
 Therefore SnCl_4 is more stable than SnCl_2 & PbCl_2 is more stable than PbCl_4 .
40. (c) H_3BO_3 on heating at 373K yields metaboric acid (HBO_2)

$$\text{H}_3\text{BO}_3 \xrightarrow[\Delta]{373\text{K}} \text{HBO}_2 + \text{H}_2\text{O}$$
metaboric acid (orthorhombic form)
41. (a) H_3BO_3 is a weak monobasic acid.
42. (d) Boron halides behave as Lewis acid because of their electron deficient nature. Boron halide like BCl_3 has only six electrons around Boron, which is less than required for octet rule. So it has a tendency to attract electron from others. Thus it behaves as an acid.
43. (b) $\text{Al}_2\text{Cl}_6 + 12\text{H}_2\text{O} \rightleftharpoons 2[\text{Al(H}_2\text{O)}_6]^{3+} + 6\text{Cl}^-$
44. (d) Anthracite is a coal of hard variety burning with little flame & smoke. Graphite layers are held together by weak van der waal forces so it is very soft. Lignite is soft brown coal showing traces of plant structure, intermediate between coal & Peat. peat is vegetable matter decomposed in water and partly carbonized.
45. (c) Boron (B), aluminium (Al) and gallium (Ga) are present in group 13. They show + 3 oxidation state. While cerium (Ce) is a lanthanoid. It presents in lanthanide series. It shows + 3 and + 4 oxidation states.
46. (b)
47. (c) Ge is used as a semiconductor in transistors.
48. (c) Normal glass is calcium alkali silicate glass made by fusing the alkali metal carbonate, CaCO_3 and SiO_2 .
49. (b) In diamond each carbon atom is sp^3 hybridized and thus forms covalent bonds with four other carbon atoms lying at the corners of a regular tetrahedron.
50. (a)
$$\text{H}_2\text{O} + \text{C} \longrightarrow \text{H}_2 + \text{CO}$$
Steam Red hot coke water gas
51. (d) Activated charcoal is an allotropic form of carbon made by heating or chemically oxidizing sawdust or peat. It has large surface area and acts as adsorbant.
52. (d) In graphite, each carbon is sp^2 -hybridized and one singly occupied unhybridized p -orbitals of C-atoms overlap sidewise to form a π -electron cloud which is delocalized and thus the electrons are spread out between the structure.
53. (b) $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$
54. (d) PbO_2 is a strong oxidising agent and is produced in situ in lead storage batteries. The anode is oxidized to PbO_2 and cathode is reduced to spongy Pb.
55. (a) Producer gas is a fuel gas and is mixture of CO and N_2 .
56. (b) Coal gas is a mixture of $\text{H}_2 + \text{CO} + \text{N}_2 + \text{CH}_4$
57. (b) Carbonyl chloride (COCl_2) is known as phosgene.
58. (d) The thermal stability of tetrahalides decreases in order $\text{CX}_4 > \text{SiX}_4 > \text{GeX}_4 > \text{SnX}_4$ and in terms of same metal with different halides is in order of

$$\text{MF}_4 > \text{MCl}_4 > \text{MBr}_4 > \text{MI}_4$$
59. (b) Because they react with water to form methane gas

$$\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \longrightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4$$
Aluminium carbide Methane
- $$\text{Be}_2\text{C} + 4\text{H}_2\text{O} \longrightarrow 2\text{Be(OH)}_2 + \text{CH}_4$$
Beryllium carbide Methane
60. (c) The m.p decreases from B to Ga, hence gallium (Ga) has least m.p. (303 K) among group of 13 element.
61. (a) Red lead is Pb_3O_4 . It is a mixed oxide of Pb (II) and Pb (IV). It acts as a powerful oxidising agent.
62. (a)
$$\text{SiCl}_4(s) + 2\text{H}_2\text{O}(\ell) \xrightarrow[\text{-4HCl}]{\Delta} \text{Si(OH)}_4(aq)$$
Silicic acid
- $$\xrightarrow{\Delta} \text{SiO}_2 \cdot x\text{H}_2\text{O}(s)$$
Silica gel
63. (c) $\text{SiO}_2 + 2\text{Mg} \rightarrow \text{Si} + 2\text{MgO}$

64. (c) Manganese salts are violet or purple coloured. So MnO_2 gives violet colour to the glass. Fe^{3+} gives yellow colour mixture of Fe^{3+} & Fe^{2+} gives green colour. CO^{2+} gives deep blue and colloidal particle of Cu gives ruby-red colour.
65. (a)
66. (c) White lead is $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ also known as basic lead carbonate.
67. (a) $3\text{Pb} + 8\text{HNO}_3(\text{dil}) \longrightarrow 2\text{NO} + 3\text{Pb(NO}_3)_2 + 4\text{H}_2\text{O}$
nitric oxide
Therefore, Pb reacts with dil HNO_3 to produce NO.
68. (b) In silica (SiO_2); each Si atom is surrounded by four oxygen atom.

Structure of SiO_2

Only Si – O bonds exist and no Si = O.

69. (b) The inert pair effect is most prominent in the heavier members of the group. Inert pair effect increases as we move the group down the group.
70. (b) CO is reducing agent because it readily accepts oxygen to form CO_2 . CO is used as reducing agent to reduce many metallic oxides into metals in metallurgy.
71. (b) Knocking (metallic sound or rattle) decreases the power and increases the wear of the engine. Knocking is more if petrol contains greater percentage of straight chain hydrocarbon. It is least in case of alkene / branched chain HC/ aromatic HC. Tetra ethyl lead dissociates into ethyl radicals which combine with some straight chain HC and thus lowering the knocking property of fuel by forming branched chain HC.
72. (c) Charcoal is a pure form of carbon, its reaction with hot conc. H_2SO_4 is as follows :
 $\text{C} + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{H}_2\text{O} + 2\text{SO}_2 + \text{CO}_2$
73. (a) The larger the percentage of hydrogen present in a fuel, the higher will be its calorific value. Thus the calorific values of coal gas, water gas and producer gas are of the order of 500, 350 and 103 BTH (British Thermal Unit) per cubic foot respectively.
1BTH = 252 calories.
74. (d)
75. (c) $\text{SiCl}_4 + 2\text{Mg} \longrightarrow \text{Si} + 2\text{MgCl}_2$
(vapours) hot.

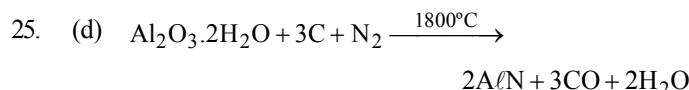
EXERCISE - 2

- (d)
- (c) $\text{Al(OH)}_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$
Sodium meta-aluminate
- (d) B_4C is the hardest substance after diamond and BN.
- (c) Moissan boron is amorphous boron, obtained by reduction of B_2O_3 with Na or Mg. It has 95-98% boron and is black in colour.
- (a) Abrasive is tough material used for sharpening and grinding the uneven surfaces and silicon carbide is used for grinding glass
- (d) Boron form different hydride of general formula B_nH_{n+4} and B_nH_{n+6} but BH_3 is unknown.
- (b) CaF_2 when added to fused Cryolite, lowers the m.p. and increases the conductivity.
- (a) Alumina Al_2O_3 is known as Ruby stone
- (a) $2\text{Al} + 6\text{HCl} \xrightarrow{\Delta, \text{air}} 2\text{AlCl}_3 + 3\text{H}_2$
 $2\text{Al} + 3\text{Cl}_2 \longrightarrow 2\text{AlCl}_3$
 $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \xrightarrow{1000^\circ\text{C}} 2\text{AlCl}_3 + 3\text{CO}$
vapours
 $\downarrow$ Cooling
Anhydrous AlCl_3
 $\text{AlCl}_3 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{Al(OH)}_3 + 3\text{HCl} + 3\text{H}_2\text{O}$
Thus AlCl_3 cannot be obtained by this method
- (d) It is $p\pi - P\pi$ back bonding involving B and F. The smaller atoms show more back bonding.
- (c) $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2$
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2 \uparrow$
Sodium meta-aluminate (soluble)
- (c) $\text{B(OH)}_3 \rightleftharpoons \text{H}_3\text{BO}_3$ Boric acid
 $\text{Al(OH)}_3 \rightleftharpoons$ Amphoteric
- (b) Annealing makes the glass soft.
- (c) CO_2 being more dense covers the igniting material more effectively than N_2 .
- (d)
- (b) It is the conversion of white tin to grey tin at low temperature which crumbles into powder.
- (d) Tin cry is the emission of sound on bending the tin.
- (c) Pb with dil HCl forms protective coating of PbCl_2
- (c) Due to non-availability of vacant *d*-orbitals, it cannot exceed its coordination number more than four. Thus carbon never forms complexes e.g., $[\text{CCl}_6]^{2-}$ does not exist but $[\text{SiCl}_6]^{2-}$ exists.
- (d) The bicarbonates of Ca and Mg are decomposed to Ca and Mg carbonates by boiling.
- (b) Metal oxides or some salts are fused with glass to impart colour.

22. (b) The cubic form of BN with ZnS structure is as hard as diamond.

23. (a)

24. (d) It is hydrolysed with water to form a $\text{Si}(\text{OH})_4$.

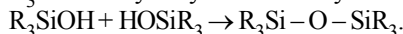


26. (b) $\alpha\text{-tin} \xrightleftharpoons{15.2^\circ\text{C}} \beta\text{-Sn} \xrightleftharpoons{164^\circ\text{C}} \gamma\text{-Sn} \xrightleftharpoons{232^\circ\text{C}} \text{Liquid tin}$
(Grey) (White) (Brittle)

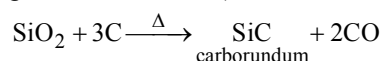
(most common and stable) (Rhombic)

Although transitions of white to grey tin occurs at any temperature below 15.2°C , it becomes rapid only at -50°C , unless a catalyst is present. During the conversion of white tin to grey tin (in cold countries) volume increases. Grey Sn is very brittle easily crumbles down to powder. This phenomenon is called tin diseases, tin pest or tin plague.

27. (a) R_3SiCl on hydrolysis forms only a dimer.



28. (a) Silica on heating with carbon at elevated temperature, gives carborundum (silicon carbide)

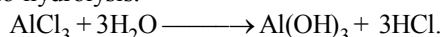


Carborundum is a very hard substance.

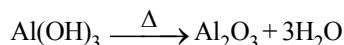
29. (b) In BF_3 , boron atom has vacant $2p_z$ A.O. and fluorine atom has electron pair in $2p$ A.O. so, maximum overlapping is possible between vacant $2p_z$ A.O. of boron and fully filled $2p$ A.O. of fluorine due to similar size of A.O's.

30. (c) Fused alumina (Al_2O_3) is a bad conductor of electricity. Therefore, cryolite (Na_3AlF_6) and fluorspar (CaF_2) are added to purified alumina which not only make alumina a good conductor of electricity but also reduce the melting point of the mixture to around 1140 K.

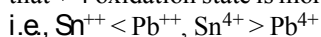
31. (b) The solution of aluminium chloride in water is acidic due to hydrolysis.



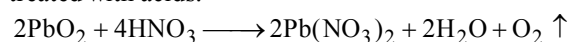
On heating it till dryness $\text{Al}(\text{OH})_3$ is converted into Al_2O_3



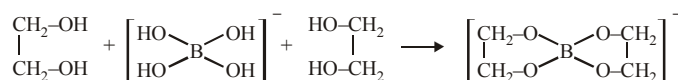
32. (c) Negative $\Delta_r G^\circ$ value indicates that +2 oxidation state is more stable for Pb. Also it is supported by inert pair effect that +2 oxidation state is more stable for Pb and as $\Delta_r G^\circ$ value is positive in second reaction it indicates that +4 oxidation state is more stable for Sn.



33. (b) PbO_2 is a powerful oxidizing agent and liberate O_2 when treated with acids.

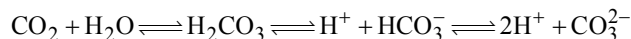


34. (b) *cis*-1,2-diol forms chelated complex ion with the product, $[\text{B}(\text{OH})_4]^-$ causing the reaction to proceed in forward direction.

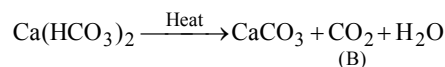
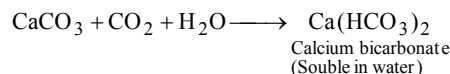
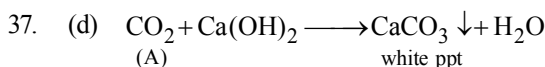


Stable chelated complex ion

35. (a)



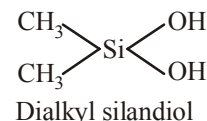
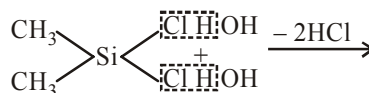
36. (a) The stability of dihalides (MX_2) increases down the group. Except C and Si, the other members form dihalides.



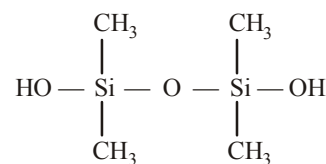
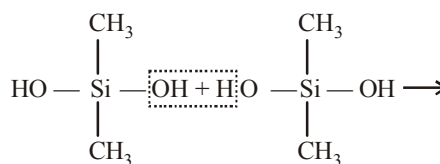
A and B are CO_2 and CO_2 .

38. (b) Nitrolim is a mixture of CaCN_2 and graphite (C) which is used as fertilizer.

39. (c) Hydrolysis of substituted chlorosilanes yield corresponding silanols which undergo polymerisation.

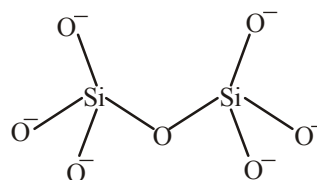


Polymerisation of dialkyl silandiol yields linear thermoplastic polymer.



40. (b) *p-p* overlap between B and F is maximum due to identical size and energy of *p*-orbitals, so electron deficiency in boron of BF_3 is neutralized partially to the maximum extent by back donation. Hence BF_3 is least acidic.

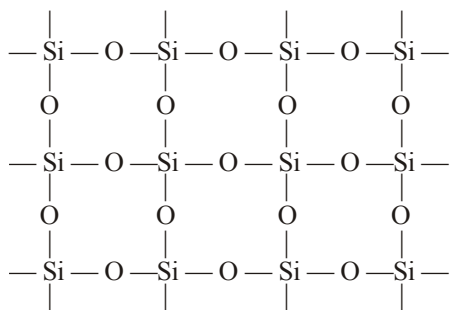
As the size of halogen atom increases from F to I, the extent of overlap between $2p$ -orbital of B and a bigger *p*-orbital of halogen decreases. Therefore the electron deficiency of B increases.



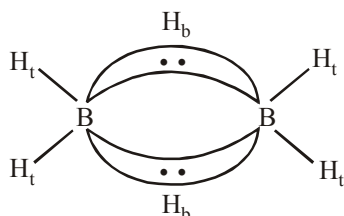
41. (c)

Pyrosilicate $[\text{Si}_2\text{O}_7]^{6-}$

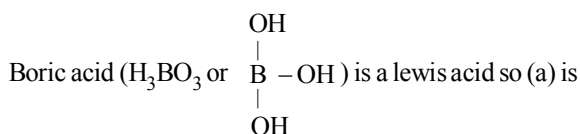
42. (d) In SiO_2 (quartz), each of O-atom is shared between two SiO_4^{4-} tetrahedra.

Structure of SiO_2

43. (d) In diborane (B_2H_6) structure there are four 2c-2e bonds and two 3c-2e bonds (see structure of diborane). Structure of B_2H_6 :



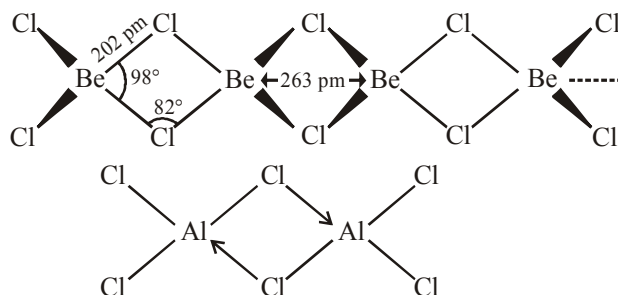
44. (c) The correct formula of inorganic benzene is $\text{B}_3\text{N}_3\text{H}_6$ so (d) is incorrect statement



incorrect statement.

The coordination number exhibited by beryllium is 4 and not 6 so statement (b) is incorrect.

Both BeCl_2 and AlCl_3 exhibit bridged structures in solid state so (c) is correct statement.



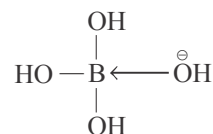
45. (b) Two dimensional sheet structures of the formula $(\text{SiO}_5)^{2n-}$ are formed when tetrahedral are shared.
46. (c)
47. (c) Boron is metalloid. Thus assertion is correct. Metalloids possess, metallic as well as non-metallic nature. Hence, reason is false.
48. (d) Borazine has more polarity as compared to benzene because nitrogen is more and boron is less electronegative than carbon. Thus due to polarity inorganic benzene, borazine is highly reactive while benzene is much less reactive.

49. (b)
50. (c) Assertion is true because lower oxidation state becomes more & more stable for heavier elements in p-block due to inert pair effect. Hence Reason is false.

EXERCISE - 3

Exemplar Questions

1. (c) Among these elements, in gallium, the crystal structure is different which suggests that Ga consists of almost discrete Ga_2 molecule, so its melting point is lowest. Ga exists as liquid from 30°C upto 2000°C and hence, it is used in high temperature measurement.
2. (a) Alkaline earth metals (Mg, Ca, Ba) form ionic chloride whereas aluminium form covalent chloride. Despite of sharing electrons with chlorine, the octet of aluminium is incomplete. To complete the octet, it needs electrons and thus, acts as a Lewis acid.
3. (a) Structure of $\text{B}(\text{OH})_4^-$ is

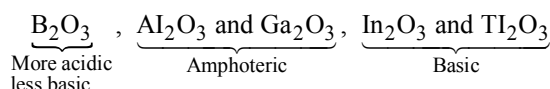


4 bond pair + 0 lone pair

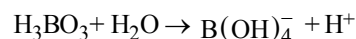
Hybridisation — sp^3

Geometry — Tetrahedral

4. (a) On moving down the group the acidic nature of oxides changes from acidic to basic through amphoteric



5. (a) Among these elements boron has the lowest atomic number. It has atomic number 5 and do not have vacant d -orbital. Boron can show maximum coordination number of 4. The element M in the complex ion MF_6^{3-} has a coordination number of six. Hence, B can not form complex of the type MF_6^{3-} .
6. (c) Boric acid is a monobasic weak acid. It does not liberate H^+ ion but accepts electrons from OH^- ion.

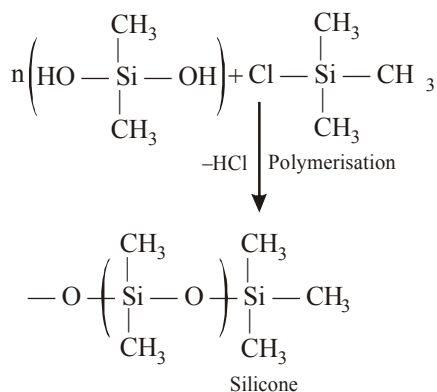


7. (b) The tendency of forming long open or closed chains by combination of some atoms in themselves is known as catenation. The tendency of catenation is maximum in carbon and decreases on moving down the group.

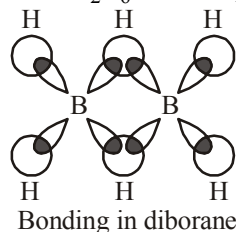


This is due to high bond energy of C — C bonds. On moving down the group, atomic size increases and electronegativity decreases, hence, tendency to show catenation decreases.

8. (c) Silicon has a strong tendency to form polymers like silicones. The chain length of silicon polymer can be controlled by adding $(\text{CH}_3)_3\text{SiCl}$ which block the ends as shown below

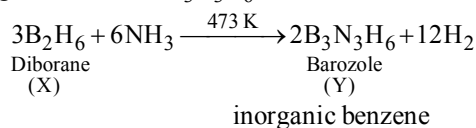


9. (d) On moving down a group the ionization enthalpies generally decreases due to increase in atomic size and screening effect which is more than to compensate the effect of increase in nuclear charge. Consequently the electron becomes less and less tightly held by the nucleus as we move down the group. The sharp decrease in ionization enthalpy from B to Al is due to increase in size. In case of Ga, there are 10 *d*-electrons in its inner electronic configuration. Since the *d*-electrons shield the nuclear charge less effectively than the *s* & *p* electrons, the outer electron are held strongly by the nucleus. As a result the ionization enthalpy increases slightly inspite of the increase in atomic size as we move from Al to Ga. The similar increase is also observed from In to Tl, which is due to presence of 14*f* electrons in inner electronic configuration of Tl which has poor shielding effect.
10. (b) In diborane, there are 12 valence electrons, three from each boron atoms and six from the six hydrogen atoms. The structure of B₂H₆ can be represented as

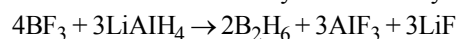


The four terminal hydrogen atoms and two boron atoms lie in the same plane. These four terminal B-H bonds are regular 3C-2e bonds. Above and below the plane, there are two bridging hydrogen atoms. Each boron atom forms two bonds even though it has only three electrons. The terminal B—H bonds are regular bonds but the bridge B—H bonds are different. Each bridge hydrogen is bonded to the two boron atoms only by sharing of two electrons. Such covalent bond is called banana bond.

11. (a) (i) Reaction of ammonia with diborane gives initially B₂H₆.2NH₃ which is represented as [BH₂(NH₃)₂]⁺[BH₄][−] which on further heating gives borazine, B₃N₃H₆ also called borazole.



- (ii) Diborane can be prepared by the reaction of BF₃ with lithium aluminium hydride in diethyl ether.



12. (b) Quartz, is a crystalline forms of silica. Quartz is extensively used as a piezoelectric material.
13. (d) Sn and Pb can show two oxidation states i.e. +2 and +4. These elements in +4 oxidation state behave as oxidising agent, where as in +2 oxidation state behave as reducing agent. The stability of +2 oxidation state increases on moving down in a group i.e., reducing character decreases from Ge (I) to Pb (II). i.e., Germanium salts are strongest reducing agent and Pb(II) salt the weakest. Ge is much less abundant than tin in nature. hence Sn (II) salts are widely used as reducing agent.
14. (c) Carbon dioxide can be obtained as a solid in the form of dry ice allowing the liquified CO₂ to expand rapidly. It is used to maintain the low temperature in laboratory. Dry ice is solid CO₂
15. (b) Cement is obtained by combining a material rich in lime (CaO) with other material like silica SiO₂ alongwith the oxides of aluminium, iron and magnesium. The average composition of cement is
- CaO (50 – 60%)
SiO₂ (20 – 25%)
Al₂O₃ (5 – 10%)
Fe₂O₃ (1 – 2%)
SO₂ (1 – 2%)
MgO (2 – 3%)

Thus, it contains elements of group 2(Ca), group 13 (Al) and group 14 (Si).

NEET/AIPMT (2013-2017) Questions

16. (d) Boron nitride (BN) is known as inorganic graphite. The most stable form is hexagonal one. It has layered structure similar to graphite.
17. (b) Since Me₃SiCl contains only one Cl, therefore it can't form high molecular mass silicon polymer. It can form only dimer.
18. (a) SiO₄^{4−} is basic structural unit of silicates.
19. (a) Feldspars are 3-dimensional alumino-silicates.
20. (b) Lower oxidation state become more stable on moving down the group
Al < Ga < In < Tl
21. (d) Inertness of *ns*² electrons of the valence shell to participate in bonding on moving down the group in heavier p-block elements is called inert pair effect. As a result, Pb(II) is more stable than Pb(IV)
Sn(IV) is more stable than Sn(II)
∴ Pb(IV) is easily reduced to Pb(II) and can acts as an oxidising agent whereas Sn(II) is easily oxidised to Sn(IV) and can acts as a reducing agent.

Chapter 12 Organic Chemistry : Some Basic Principles and Techniques

TETRAVALENCY AND SHAPES OF ORGANIC MOLECULES

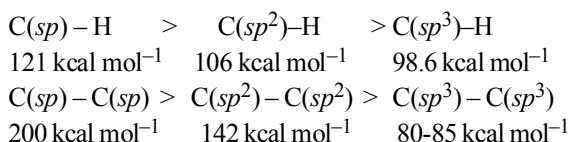
The tetravalence, formation of covalent bond and catenation property of carbon results in the formation of a large number of compounds of carbon. These compounds are covalent in nature and are studied under a branch of chemistry called organic chemistry. Carbon atoms present in organic compounds are either

sp , sp^2 or sp^3 hybridised.

Hybridisation influences the bond length and bond strength in organic compounds. The sp hybrid orbital contains more s -character and hence, it is closer to its nucleus and forms shorter and stronger bonds than sp^3 hybrid orbital.

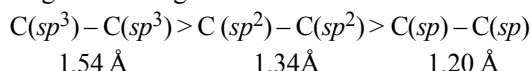
The bond angles and geometry associated with the three types of hybridization are summarized below :

Hybridisation	sp^3	sp^2	sp
Angle	$109^\circ 28'$	120°	180°
Geometry	Tetrahedral	Trigonal	Linear
Example	Alkane, Cycloalkane and in saturated part of all organic molecules	Alkenes and other compounds containing $C=C$, $C=O$, $C=N$ and $C=S$ double bonds	Alkynes and all other compounds containing $C\equiv C$ and $C\equiv N$ triple bonds,
Bond	Four- σ	Three- σ One- π	Two- σ Two- π
s%	25	33.3	50
p%	75	66.7	50
Electronegativity	2.48	2.75	3.25



Note : (i) Greater is the s -character of the hybrid orbitals, greater is the electronegativity. Thus, a C -atom having an sp hybrid orbital with 50% s -character is more electronegative than sp^2 (33% s -character) or sp^3 (25% s -character) hybrid orbitals.

(ii) Since a bigger orbital forms a longer bond, therefore, $C-C$ single bond length decreases in the order:



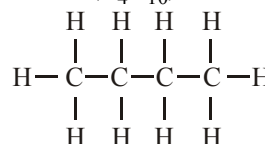
STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

(i) **Complete, Condensed and Bond - line Structural Formulas :**

For example few compounds are represented in all three formulas below :

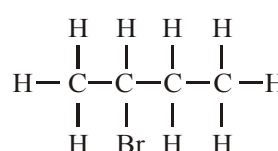
Ex:

(a) Butane (C_4H_{10})



Complete

(b) 2 - Bromobutane



Complete



Condensed



Bond line

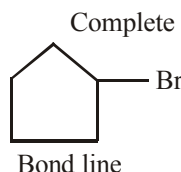
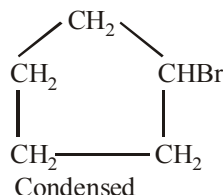
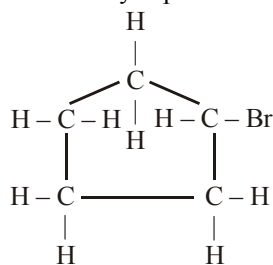


Condensed



Br
Bond - line

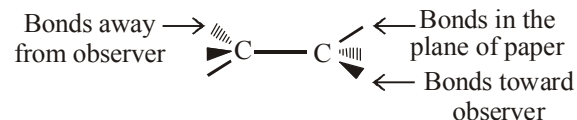
(c) 1-Bromocyclopentane



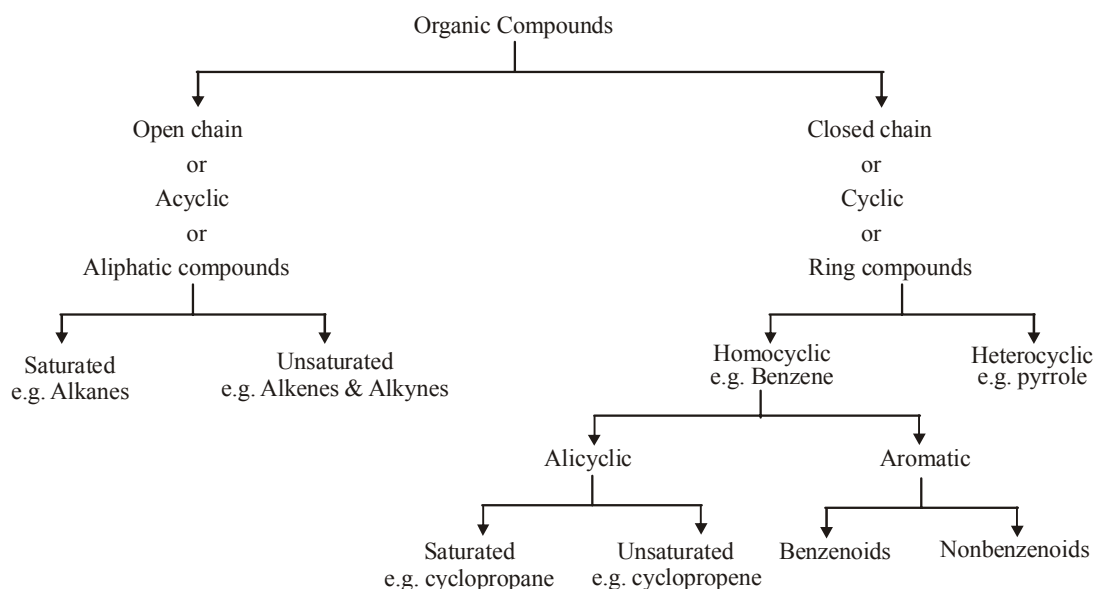
(ii) 3D Representation

By using solid () and dashed () wedge formula, 3-D image of a molecule can be shown from 2D picture. The dashed line depicts the bond projecting out of the plane of paper and away from the observer while solid-wedge depicts the bond projecting out of the plane of paper and towards the observer. The bonds lying in plane of paper are depicted by using a normal line (—).

Ex: Ethane



CLASSIFICATION OF ORGANIC COMPOUNDS



NOMENCLATURE OF ORGANIC COMPOUNDS

Nomenclature of Alkanes

(i) Straight chain hydrocarbons:

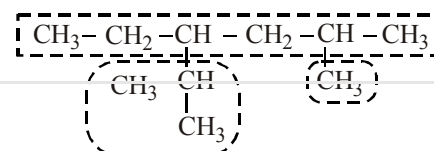
The names of such compounds are based on their chain structure, and end with suffix 'ane' and carry a prefix indicating the number of C - atoms present in the chain. The alkanes differ from each other by no. of $-\text{CH}_2$ groups in the chain.

Some names are:

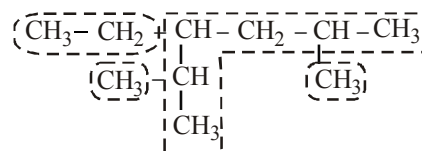
Methane	CH_4	Butane	C_4H_{10}
Ethane	C_2H_6	Pentane	C_5H_{12}
Propane	C_3H_8	Hexane	C_6H_{14}

(ii) Branched chain hydrocarbons: The rules for naming are:

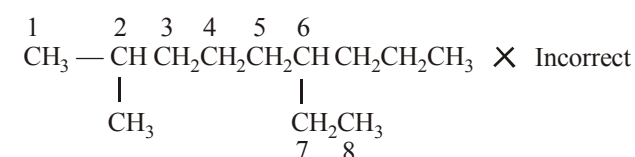
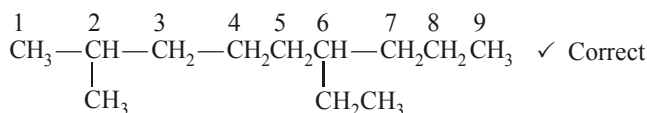
- (a) The longest C - chain in the molecule is identified. Out of all the possible chains. If there are the possibilities of more than one longest chain the chain which possesses more than one side chain is selected.



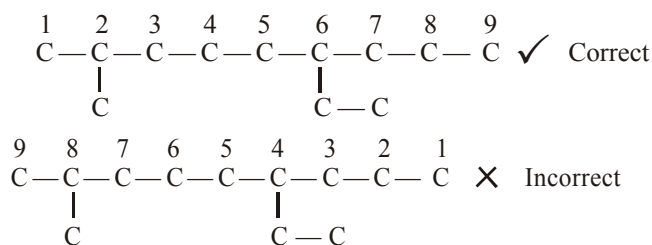
2 side chains (wrong)



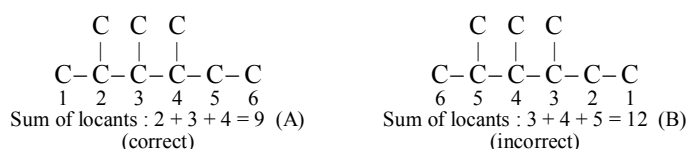
3-side chains (correct)



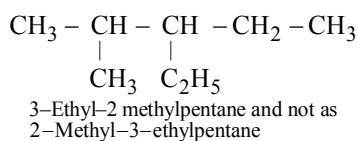
- (b) The numbering is done in such a way that branched carbon atoms get the lowest possible numbers.



In case, the parent chain has two or more substituents, numbering must be done in such a way that the sum of the locants on the parent chain is the lowest possible. Thus in following structures A and B numbering may be done in two ways : in one (A), the sum of locants is 9 while in other (B), it is 12, hence the former is correct while the latter is wrong.

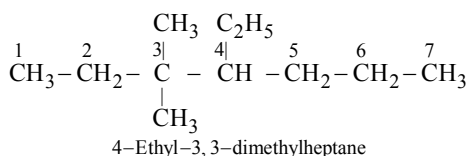
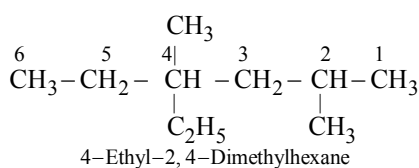


- (c) The names of alkyl groups attached as a branch are prefixed to the name of parent alkane and position of substituents is indicated by appropriate numbers. If different alkyl groups are present they are listed in alphabetical order. For example



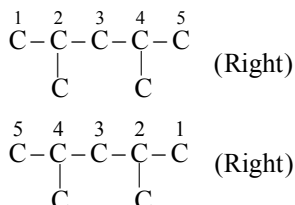
- (d) If two or more identical substituent groups are present, then numbers are separated by commas. The names of identical substituents are indicated with prefixes such as di, tri, tetra, penta, hexa, etc. While writing names of substituents spelling of these prefixes are not considered.

For example :



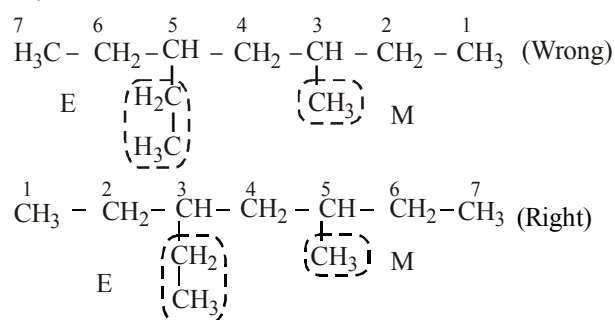
- (e) If side chains are at same carbon from both sides, following rules are adopted :

- (1) For same side chains numbering may be given from any end.

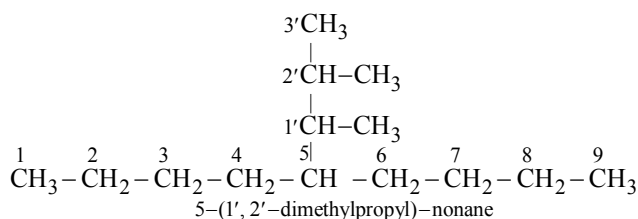


- (2) If side chains are different numbering is given in alphabetical preference order.

Ex.



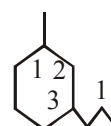
(f) Naming the complex substituent : In case the substituent on the parent chain is complex (i.e., it has itself branched chain) then it is named as a substituted alkyl group and its carbon chain is numbered from the carbon atom attached to the main chain. The name of this complex substituent is written in bracket to avoid confusion with the numbers of the main chain. e.g.,



Nomenclature of Cyclic Compounds

A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are given, then rules given above are applied.

For example : Cyclobutane

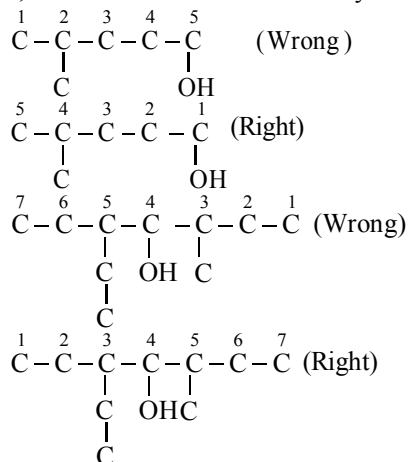


1-methyl-3-propylcyclo-hexane

Nomenclature of Organic Compounds Containing Functional Groups

- Numbering is given from the end from which functional group is closest.
- If the functional group is situated at same carbon from both sides, follow the rules of saturated hydrocarbons.

Ex.

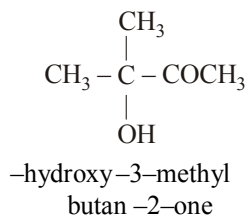
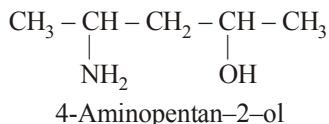


- (iii) If the organic compound contains two or more functional groups, one of the group is selected as principal functional group containing longest possible chain of carbon atom and all the remaining functional groups are treated as substituents.

Order of preference used while selecting the principal functional group

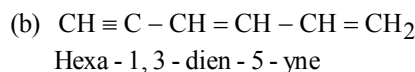
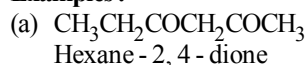
Carboxylic acids > Sulphonic acids > anhydrides > esters > acid chlorides > acid amides > nitriles > aldehydes > cyanides > isocyanides > ketones > alcohols > phenols > thiols > amines > ethers > alkenes > alkynes.

For example :



- (iv) — R, — C₆H₅, halogens (F, Cl, Br, I), —NO₂, —OR etc. are always prefix substituents.
- (v) If more than one functional group of same type is present, their number is indicated by adding di-, tri-, etc. before the class suffix.

Examples :



See the following table for IUPAC names of certain organic compounds

Class of compounds	Functional group structure	Functional group prefix	Functional group suffix
Alkanes	—	—	-ane
Alkenes	>C=C<	—	-ene
Alkynes	—C≡C—	—	-yne
Arenes	—	—	-
Halides	—X (X = F, Cl, Br, I)	halo	-
Alcohols	—OH	hydroxy	-ol
Aldehydes	—CHO	formyl, or oxo	-al
Ketones	>C=O	oxo	-one
Nitriles	—CN≡	cyano	nitrile
Ethers	R-O-R	alkoxy	-
Carboxylic acids	—COOH	carboxy	-oic acid
Carboxylate ions	—COO [−]	—	-oate
Esters	—COOR	alkoxycarbonyl	-oate
Acyl halides	—COX (X = F, Cl, Br, I)	halocarbonyl	-oyl halide
Amines	—NH ₂ , >NH, >N—	amino	-amine
Amides	—CONH ₂ —CONHR, —CONR ₂	carbamoyl	-amide
Nitro compounds	—NO ₂	nitro	-
Sulphonic acids	—SO ₃ H	sulpho	sulphonic acid
Thio alcohol	—SH	Mercapto—	—thiol
Anhydride	$\begin{array}{c} \text{—CO—} \\ \text{—CO—} \end{array} \text{O}$	—	—oic anhydride
Isocyanide	—N≡C	Carbylamine	—iso nitrile

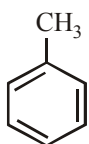
Note : $\text{—}\overset{\text{O}}{\parallel}\text{C—H}$, $\text{—}\overset{\text{O}}{\parallel}\text{C—OH}$, $\text{—}\overset{\text{O}}{\parallel}\text{C—Cl}$, $\text{—}\overset{\text{O}}{\parallel}\text{C—NH}_2$ & $\text{—C}\equiv\text{N}$

are the groups of which carbons are also included in the longest chain. If these are alone in a compound they come on first carbon, if double, comes on first and last positions.

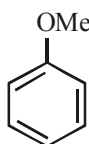
Nomenclature of Aromatic Compounds

- (i) The substituent is placed as prefix to the word benzene.

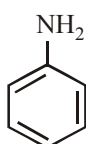
Examples :



Methyl benzene
(Toluene)



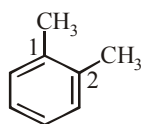
Methoxy benzene
(Anisole)



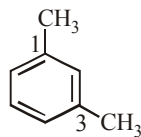
Amino benzene
(Aniline)

- (ii) If benzene ring is disubstituted, position of substituents is defined by numbering the C-atoms of ring such that substituents are located at lowest numbers possible.

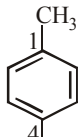
Example :



1,2-Dimethylbenzene
(*o*-Xylene)



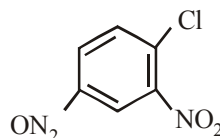
1,3-Dimethylbenzene
(*m*-xylene)



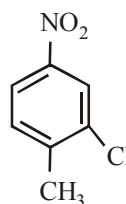
1,4-Dimethylbenzene
(*p*-xylene)

- (iii) For tri - or higher substituted benzene derivatives, the compounds are named by identifying substituent positions on the ring by following lowest locant rule. In some cases, common name of benzene derivatives is taken as base compound. Substituent of base compound is assigned no. 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents should be numbered according to alphabetical order.

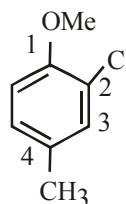
ex:



1 - Chloro - 2, 4 - dinitrobenzene



2 - Chloro - 1 - methyl - 4 - nitrobenzene

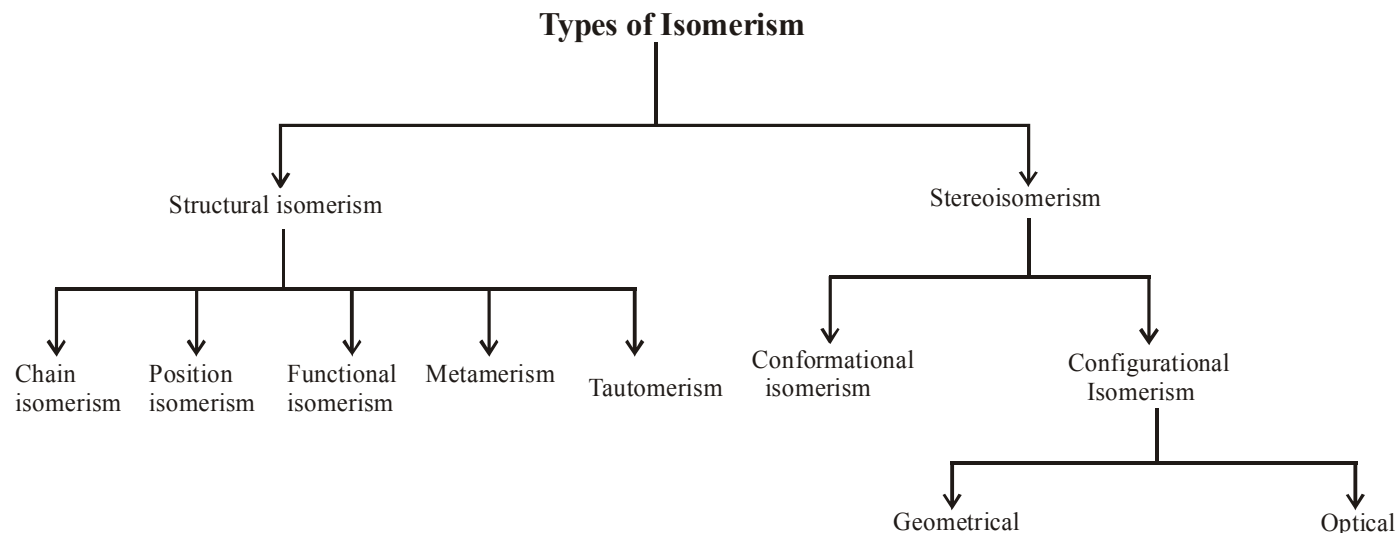


2 - Chloro - 4 - methyl anisole

- (iv) When benzene ring is attached to an alkane with a functional group, it is considered as substituent instead of parent and its name as a substituent is phenyl

ISOMERISM

The phenomenon of existence of two or more compounds possessing same molecular formula but different properties is called isomerism and the compounds are called isomers. The following chart shows different types of isomerism.



Structural Isomerism: It arises when compounds have same molecular formula but different structures. It arises because of the difference in the sequence of covalently bonded atoms in the molecule without reference to space.

Types of Structural Isomerism

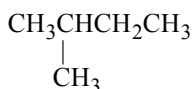
- (i) **Chain isomerism** : Two or more compounds with same molecular formula but different carbon skeletons are called chain isomers and the phenomena is known as chain isomerism.

Examples :

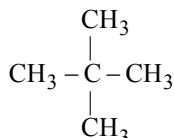
Pentane : C_5H_{12}



n-Pentane



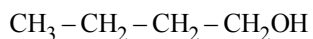
Isopentane



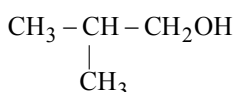
Neopentane

n-Pentane, isopentane and neopentane possess the chain of five, four and three carbons, respectively. Hence they are chain isomers.

Butyl alcohol : C_4H_9OH



n-Butyl alcohol



Isobutyl alcohol

These two butyl alcohols are chain isomers.

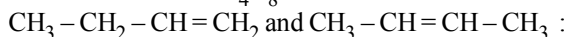
- (ii) **Position isomerism** : It is shown by the compounds in which there is difference in the position of attachment of functional group, multiple bond or substituent along the same chain length of carbon atoms.

Examples : $CH_3 - CH_2 - CH_2Cl$ & $CH_3 - \underset{\substack{| \\ Cl}}{CH} - CH_3$

1-Chloropropane

2-Chloropropane

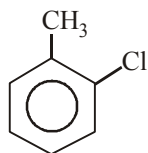
Molecular formula : C_4H_8



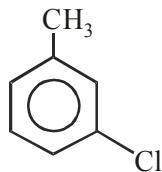
1-Butene

2-Butene

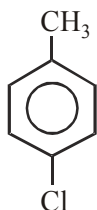
Note : In the disubstituted benzene derivatives also position isomerism exists because of the relative position occupied by the substituents on the benzene ring. Thus, Chlorotoluene, $C_6H_4(CH_3)Cl$ exists in three isomeric forms - ortho, meta and para.



o-Chlorotoluene



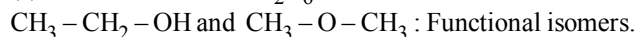
m-Chlorotoluene



p-Chlorotoluene

- (iii) **Functional group isomerism** : When two or more compounds have same molecular formula but different functional groups. Such compounds are called functional group isomers

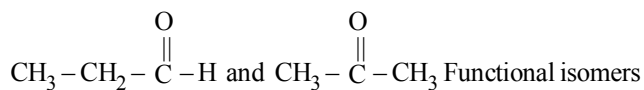
(a) Molecular formula : C_2H_6O



Ethyl alcohol Dimethyl ether

(Alcohol) (Ether)

(b) Molecular formula : C_3H_6O



Propanal

Propanone

(Aldehyde)

(Ketone)

(c) Molecular formula : $C_3H_6O_2$



:Functional isomers

Propanoic acid

Methyl acetate

(Acid)

(Ester)

- (iv) **Metamerism** : This type of isomerism is due to unequal distribution of substituents on either side of the polyvalent functional group.

Members belong to the same homologous series.

Ex.

(a) Diethyl ether and methyl propyl ether



Diethyl ether



Methyl propyl ether

(b) Diethyl amine and methyl propyl amine



Diethyl amine



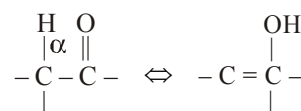
Methyl propyl amine

- (v) **Tautomerism** : Tautomerism is a special type of functional group isomerism which arises due to the migration of H-atom as proton from a polyvalent atom to other polyvalent atom with reshuffling of π bond.

Keto-Enol Tautomerism :

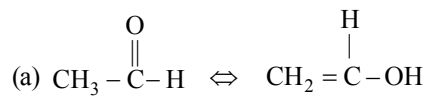
When the tautomers exist in the two forms keto & enol then, such type of tautomerism is called keto-enol tautomerism.

Keto means the compound has a keto group $>C=O$, and the enol form has both double bond and OH (hydroxy) group joined to the same carbon.



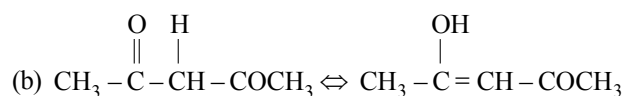
Keto form

Enol form



Acetaldehyde

Vinyl alcohol



(Keto)

(Enol)

Stereoisomerism

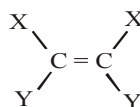
Two or more compounds which have the same molecular formula and the same connectivity of atoms but different three dimensional arrangement of their constituent atoms or groups are said to be stereoisomers and the phenomenon is termed as stereoisomerism.

(i) **Geometrical isomerism** : Arises due to different geometries of compounds, i.e., different arrangement of atoms or groups around doubly bonded C - atoms.

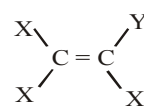
Two types:

Cis-isomer

Two identical atoms or groups lie on same side of double bond i.e.

**Trans-isomer**

Two identical atoms or groups lie on opposite side of double bond, i.e.



If the two atoms or groups linked to same doubly linked carbon are similar as in the molecule $a_aC = C_{bb}$, the compound does not show geometrical isomerism.

(ii) **Optical isomerism** : It is shown by compounds which rotates the plane of polarised light either towards right i.e clockwise or towards left, i.e., anti - clockwise.

Optical activity : It is the ability of a substance to rotate the plane of polarisation of plane polarised light.

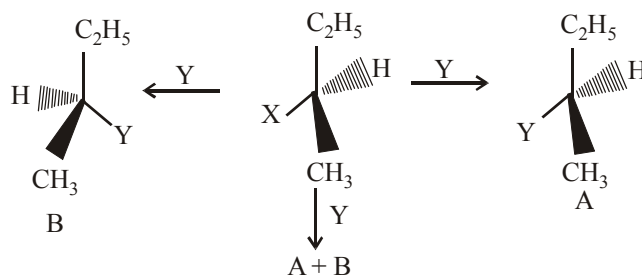
- One rotating the plane of polarised light to the left. This form is named as laevorotatory. (Latin, laevous = left) or direction (–) form
- One rotating the plane of polarized light exactly to the same extent but to the right is named dextrorotatory (Latin Dexter – right) or direction (+) – form.
- An inactive form which does not rotate the plane of polarized light at all. This is a mixture of equal amounts of (+) and (–) – forms and hence it is optically inactive. It is named (±) - mixture or Racemic mixture. (Latin, Racemic - mixture of equal compounds) **Asymmetric carbon atom** : A carbon atom attached to four different atoms and groups is called asymmetric carbon atom. e.g. $CH_3^*CHOHCOOH$.

Chirality : If the mirror image of the molecule is different from the molecule it is said to be a chiral molecule. In such case if one configuration of the molecule is placed above its mirror image configuration, the similar atoms and groups do not fall over each other and the configurations are said to be *nonsuperimposable*. Chirality is the necessary condition for a compound to be optically active.

Enantiomers : Pairs of nonsuperimposable mirror images are called enantiomers. Enantiomers are non superimposable mirror image isomers. They have identical physical properties (bpt, mpt, density etc.) except for their rotation of plane polarised light. They are much more difficult to separate. In nature very often only one enantiomer is produced. Living organisms are one of the best sources of optically active compounds (plants, enzymes, animals, cells etc.).

Diastereo Isomers : Stereo isomers which are not mirror images of each other are called diastereo isomers. They have different physical properties (mpt, bpt, solubility) and are often easy to separate by distillation, recrystallisation, chromatography etc.).

Racemixture : A mixture containing equal amounts of two enantiomers will have zero optical rotation and is called *racemic mixture*



if only (A) is obtained, process is called retention of configuration. If only (B) is obtained, process is called inversion of configuration. If 50:50 mixture of above two is obtained then the process is called racemisation and the product is optically inactive.

REACTION MECHANISM

A general reaction is depicted as:

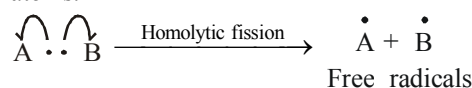


A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products is referred to as reaction mechanism.

Fission of a Covalent Bond

A covalent bond can be cleaved in two ways:

- Homolytic cleavage** : On bond breaking, one of the electrons of shared pair in covalent bond goes with each of the bonded atoms.

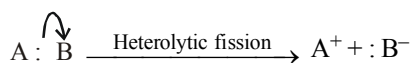


It results in the formation of free radicals which contain an odd or unpaired electron. Such reactions are called free radical or homopolar or non-polar reactions.

Favourable conditions :

- High temperature
- Light of suitable wavelength
- Non polar solvent
- Presence of peroxide or oxygen
- Ability of substrate and attacking reagent to produce free-radicals.

- (ii) **Heterolytic cleavage** : When a covalent bond joining two atoms A and B breaks in such a way that both the electrons of the covalent bond (i.e., shared pair) are taken away by one of the bonded atoms, the mode of bond cleavage is called heterolytic fission or heterolysis.



(when B is more electronegative than A)

It results in formation of cations and anions

Favourable conditions : (a) Low temperature (b) Polar solvent (c) Presence of acid or base catalyst (d) Polar nature of the substrate and attacking reagent.

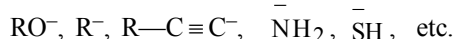
Nucleophiles and Electrophiles

A reagent that brings an electron pair is called a nucleophile i.e. nucleus seeking and the reaction is called nucleophilic.

They are of two types :

(a) **Charged Nucleophiles** :

All the negative ions qualify as nucleophiles.



(b) **Neutral Nucleophiles** : Central atom has electron pair.

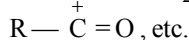
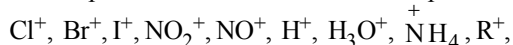


A reagent that takes away an electron pair is called an electrophile (E^+) i.e., electron seeking and the reaction is called electrophilic. Electrophiles may be neutral or positively charged.

(a) **Neutral electrophiles** : Central atom has deficiency of electrons. ex. $BF_3, BCl_3, AlCl_3, BeCl_2, FeCl_3, SO_3$, etc..

(b) **Charged electrophiles** :

All the positive ions behave like electrophiles.



Electrophiles are generated by heterolysis of a covalent bond.

Transition metal cations are electrophiles

For example : $Fe^{3+}, Fe^{2+}, Ag^+, Hg^{2+}, Cd^{2+}$, etc.

Electron Displacement

The electron displacement in an organic molecule may take place either in ground state under the influence of an atom or a group or in presence of an appropriate attacking reagent.

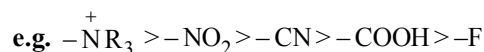
Electron displacement due to influence of an atom or group present in molecule cause permanent polarisation of the bond. Example: Inductive effect and resonance effect.

Temporary electron displacement effects are seen in a molecule when a reagent approaches attack it.

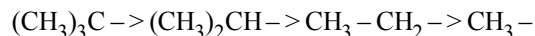
Example: electromeric or polarisability effect.

- (i) **Inductive Effect** : The polarisation of σ - bond caused by polarisation of adjacent σ - bond is called inductive effect. It is a permanent effect. The effect decreases as the number of intervening bonds increases and becomes very small after three C - atoms. Inductive effect (I-effect) is of two types.

- (a) **-I effect** : Atoms or group of atoms which attract the bonded electrons more strongly than hydrogen atom, are said to have -I effect and are termed as electron attracting (-I groups). Such groups when linked with a carbon chain make it electron poor.



- (b) **+I Effect** : Those atoms or group of atoms which attract the shared electron pair (bond pair) less strongly than hydrogen atom are said to have +I (electron repelling) effect. Such groups when attached with a carbon chain displace the shared σ electrons towards the chain and make it electron rich.



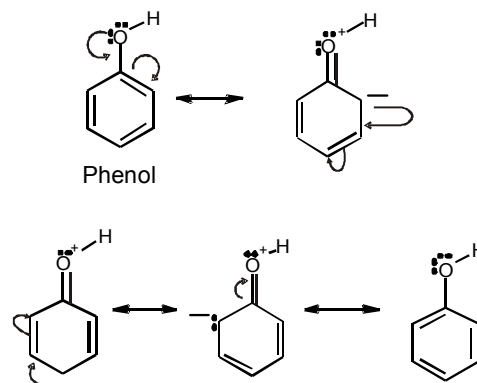
- (ii) **Resonance effect** : It is defined as the polarity produced in a molecule by the interaction of two π - bonds or between a π - bond and lone pair of e^- s present on an adjacent atom. It is also called mesomeric effect. It is a permanent effect.

Two types of resonance effects:

(a) **Positive resonance effect (+ R effect)**

In this effect, transfer of electrons is away from an atom group attached to the conjugated system. This effect results into increase in electron density at certain positions in molecule.

Example : Phenol



Examples : halogen, $-OH, -OR, -OCOR, -NH_2, -NHR, -NR_2, -NHR, -NR_2, -NHCOR$

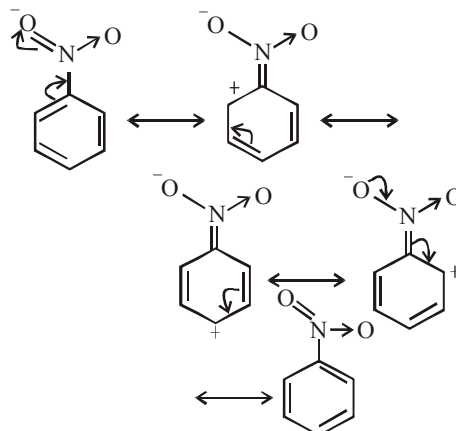
Decreasing order of activating (+R) groups

$-O-, -NH_2, -NHR, -NR_2, -OH, -OR, -NHCOR, -R, -Ar, -X$ (Till $-OH$ they are very strong activating groups)

(b) **Negative resonance effect (- R effect)**

In this effect, transfer of electrons occurs towards atom or group attached to the conjugated system.

Example : Nitrobenzene



Examples : $-\text{COOH}$, $-\text{CHO}$, $\text{C}=\text{O}$, $-\text{CN}$, $-\text{NO}_2$

The very strong deactivating ($-\text{R}$) groups are

$-\text{NO}_2$, $-\text{CF}_3$, $-\text{NR}_3^+$

Conditions for Resonance :

- (1) The atomic arrangement is the same in all the canonical forms.
- (2) Same number of paired or unpaired electrons must be present in each canonical form.
- (3) The canonical forms must possess same or nearly same energy.
- (4) The molecule must have a planar structure.

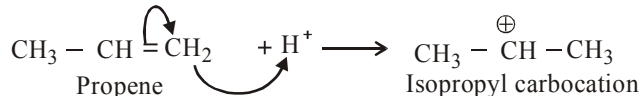
(iii) **Electromeric effect (E - Effect)** : It is defined as the complete transfer of a shared pair of π - electrons to one of the atoms (more electronegative) joined by a multiple bond on demand of an attacking reagent. It is a temporary effect.

Two types of electromeric effect:

(a) +E effect

In this, π - electrons of multiple bond are transferred to that atom to which reagent gets attached.

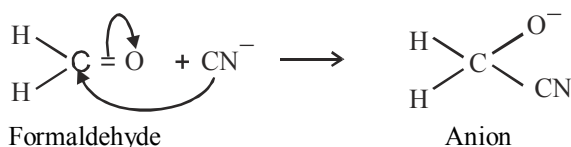
For example :



(b) -E effect

In this, π - electrons of multiple bond are transferred to that atom to which attacking reagent does not get attached

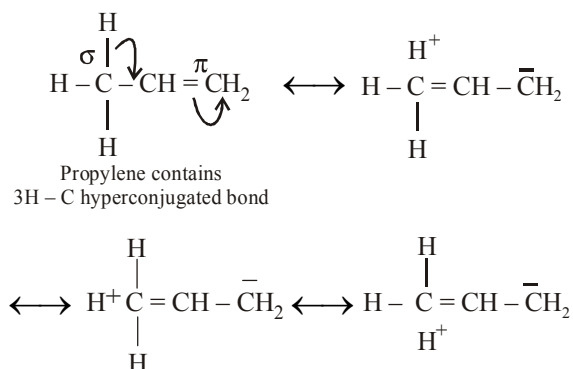
For example :



Oxygen being more electronegative pulls π electrons of multiple bond toward itself. Carbonyl C acquires positive charge thus got attacked by nucleophile.

(iv) **Hyperconjugation** : It involves delocalisation of σ - electrons of C - H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p - orbital. It is a permanent effect. Hyperconjugation is also called no - bond resonance.

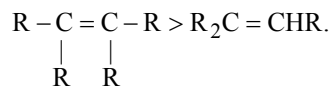
In propylene, there are three H—C sigma bonds in conjugation with the π bond. So, only three resonating forms can be written.



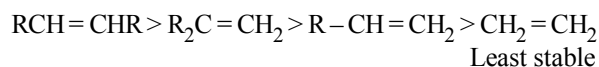
Effects of hyperconjugation :

(1) Stability of alkenes :

(a) Alkylated alkenes are more stable than others.



[Tetraalkyl ethylene]



(b) Greater the number of α C - H bonds in an alkene, greater will be the number of hyperconjugated structures, hence greater will be the stability.

(2) **Bond lengths** : Hyperconjugation in a molecule results in a change in bond lengths.

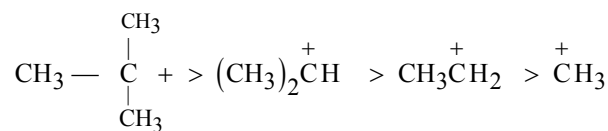
(3) Stability of alkyl free radicals :

t -alkyl > $sec.$ alkyl > primary alkyl > CH_3 (methyl radical)

Greater the number of hyperconjugative structures of an alkyl radical, higher is the stability.

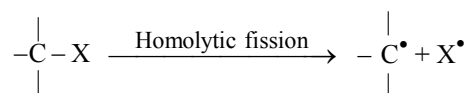
(4) **Stability of alkyl carbonium ions** : Greater the number of alkyl groups attached to positively charged carbon atom, greater is the hyperconjugation interaction and stabilisation of the cation.

The relative stability of carbocations follows the order:



INTERMEDIATES

Free Radicals



If EN of C $\approx$ EN of X

It is an atom or group of atoms possessing an odd or unpaired electron. It is electrically neutral and shows paramagnetism.

Stability of free radicals is due to following reasons :

(i) Resonance (ii) Hyperconjugation

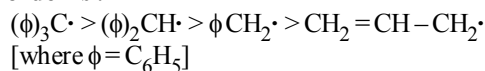
Order of stability of free radicals :

t -butyl > isopropyl > ethyl > methyl

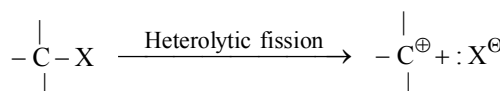
Stability on the basis of resonance :

Stability $\propto$ Number of resonating structures

The order is :



Carbonium ion or Carbocation

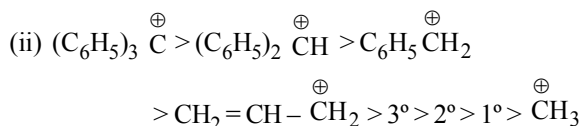
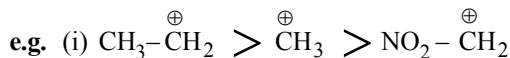


If EN of X > EN of C

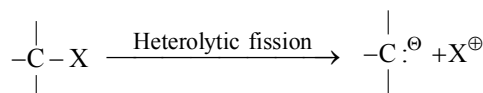
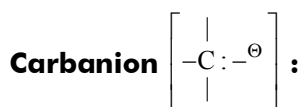
Organic species containing positively charged carbon atom is known as carbonium ion. The positively charged carbon atom contains six electrons in its valence shell.

Stability of carbonium ions :

$$\text{Stability of carbocation} \propto +I \propto \frac{1}{-I}$$



Stability $\propto$ No. of resonating structures



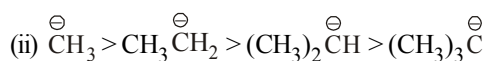
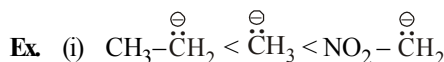
If EN of C > EN of X

An organic species containing negatively charged carbon atom is called carbanion.

Stability of carbanion is due to following reasons

- Inductive effect
- Resonance
- s-character in Hybridisation

$$\text{Stability of Carbanion} \propto -I, \propto \frac{1}{+I}$$



Note : Carbanions are nucleophiles.

TYPES OF ORGANIC REACTIONS

(i) Substitution or Displacement Reactions

Substitution or displacement reactions are those reactions in which an atom or group of atoms attached to a carbon atom in a substrate molecule is replaced by another atom or group of atoms.

(ii) Addition Reactions

Addition reactions are those in which the attacking reagent adds up to the substrate molecule. Such reactions are given by those compounds which possess double or triple bonds.

(iii) Elimination Reactions

The reverse of addition reactions are termed as elimination reactions. In these reactions generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed.

(iv) Rearrangement Reactions

The reactions which involve the migration of an atom or group from one site to another within the molecule (nothing is added from outside and nothing is eliminated) resulting in a new molecular structure are known as rearrangement reactions.

PURIFICATION OF ORGANIC COMPOUNDS

A large number of methods are available for the purification of substances. The choice of method, however depends upon the nature of substance (whether solid or liquid) and the types of impurities present in it. Following are some of the important methods which are commonly employed for the purification of organic compounds:

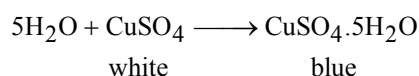
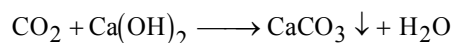
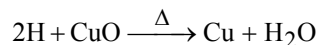
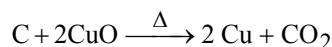
- (1) Filtration, (2) Crystallization, (3) Fractional crystallization, (4) Sublimation, (5) Distillation, (6) Fractional Distillation, (7) Distillation under reduced pressure, (8) Steam Distillation, (9) Differential extraction, (10) Chromatography

QUALITATIVE AND QUANTITATIVE ANALYSIS

Qualitative Analysis

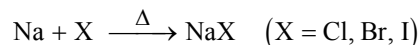
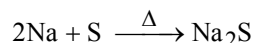
The elements present in organic compounds are C and H. In addition to these, they may also contain O, N, S, halogens and P.

Detection of C and H: They are detected by heating the compound with copper (II) oxide. C is oxidised to CO_2 and H to H_2O . CO_2 turns white lime water milky, while water formed turn white anhydrous CuSO_4 to blue hydrated CuSO_4 .



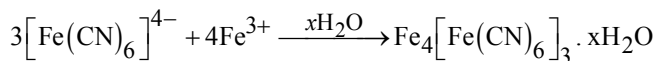
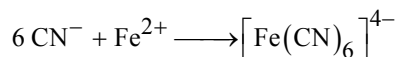
Detection of other elements

Preparation of Lassaigne's extract : N, S halogens and P are detected by Lassaigne's test. The elements present in organic compounds are converted to ionic form by fusing with Na-metal. The reactions involved are:

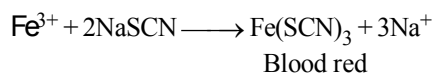


They are extracted from fused mass by boiling with distilled water. The extract is known as sodium fusion extract (Lassaigne's extract).

- (a) **Test for N :** The extract is boiled with FeSO_4 and then acidified with conc. H_2SO_4 . Prussian blue colour confirms presence of nitrogen.

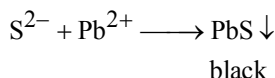


But if sulphur is also present along with nitrogen one gets blood red colouration due to formation of ferric thiocyanate.

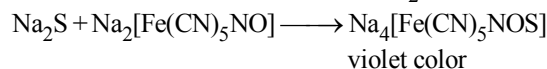
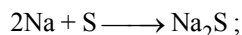


(b) Test for S:

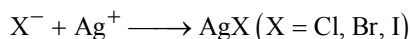
- (i) To extract, add CH_3COOH and lead acetate. A black ppt of PbS confirms S.



- (ii) Take small portion of Lassaigne's extract and add few drops of sodium nitroprusside solution, a violet colouration is obtained which fades away on standing.

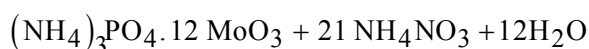
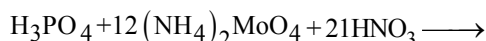
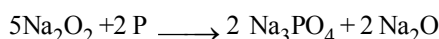
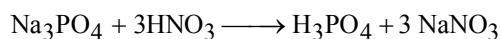


- (c) Test for halogens :** The extract is acidified with HNO_3 and then treated with AgNO_3 . A white ppt, soluble in NH_4OH indicates the presence of Cl. A yellowish ppt, sparingly soluble in NH_4OH indicates the presence of Br. A yellow ppt, insoluble in NH_4OH indicates the presence of I



If N or S is also present, then extract is first boiled with conc. HNO_3 to decompose CN^- and S^{2-} (they would otherwise interfere with AgNO_3 test for halogens).

- (d) Test for P :** Phosphorus is detected by fusing the organic compound with an oxidising agent like Na_2O_2 . P in the compound is oxidised to PO_4^{3-} which is then extracted with water. The solution is boiled with HNO_3 and then treated with ammonium molybdate. A yellow coloured ppt indicates presence of phosphorus.



Ammonium
phosphomolybdate

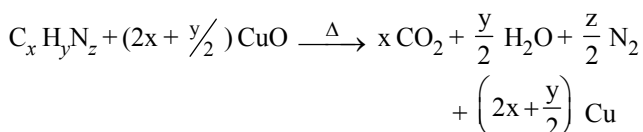
Quantitative Analysis

The percentage composition of elements present in an organic compound is determined in following ways:

(i) Carbon and Hydrogen

A known mass of an organic compound is burnt in presence of excess of O_2 and CuO , when C and H are oxidised to CO_2 and H_2O . Let mass of organic compound be 'W' g, mass of H_2O and CO_2 produced be W_1 and W_2 g. Then,

$$\text{Percentage of C} = \frac{12 \times W_2 \times 100}{44 \times W}$$



$$\text{Percentage of H} = \frac{2 \times W_1 \times 100}{18 \times W}$$

(ii) Nitrogen

- (a) Dumas method:** The N-containing organic compound, when heated with CuO in an atmosphere of CO_2 , yields free N_2 in addition to CO_2 and H_2O .

Let mass of organic compound = Wg

Volume of nitrogen collected = V_1 mL

Room temp = T_1 K

$$\text{Volume of N}_2 \text{ at STP} = \frac{P_1 V_1 \times 273}{760 \times T_1} \quad (\text{Let it be } V \text{ mL})$$

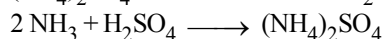
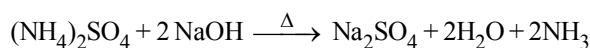
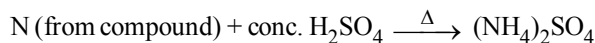
P_1 = Atm. pressure - Aqueous tension

22400 mL N_2 at STP weighs 28 g.

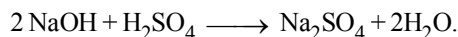
$$V \text{ mL N}_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{ g}$$

$$\% \text{ of N}_2 = \frac{28 \times V \times 100}{22400 \times W}$$

- (b) Kjeldhal's method:** The compound is heated with conc H_2SO_4 when nitrogen gets converted to $(\text{NH}_4)_2\text{SO}_4$. The mixture is then heated with excess of NaOH . The liberated NH_3 gas is absorbed in an excess of standard solution of H_2SO_4 .



The volume of the acid left unused is found by titration against a standard alkali solution.



The difference between initial amount of acid taken and that left after reaction gives the amount of acid reacted with NH_3 .

$$\% \text{ of N} = \frac{14 \times M \times 2 \left(V - \frac{V_1}{2} \right)}{1000} \times \frac{100}{W}$$

Where M $\rightarrow$ molarity

V $\rightarrow$ volume of H_2SO_4 taken

$V_1 \rightarrow$ volume of NaOH used for titration of excess of H_2SO_4

W $\rightarrow$ mass of organic compound

$$2 \left(v - \frac{v_1}{2} \right) \rightarrow \text{volume of NH}_3 \text{ solution}$$

(iii) Halogens

Carius method: A known mass of organic compound is heated with fuming HNO_3 in presence of AgNO_3 . C and H in the compound are oxidised to CO_2 and H_2O . The halogen present forms AgX which is filtered, washed, dried and weighed.

Let mass of organic compound = Wg

mass of AgX formed = W_1 g

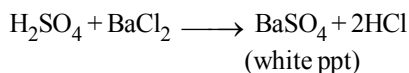
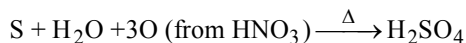
1 mol of AgX contains 1 mol of X

$$\text{mass of X in } W_1 \text{ g of Ag} = \frac{\text{atomic mass of X} \times W_1 \text{g}}{\text{molecular mass of AgX}}$$

$$\% \text{ of X} = \frac{\text{at. mass of X} \times W_1 \times 100}{\text{molecular mass of AgX} \times W}$$

(iv) **Sulphur**

A known mass of organic compound is heated with sodium peroxide or fuming HNO_3 . S in the compound is oxidised to H_2SO_4 . It is precipitated as BaSO_4 by adding excess BaCl_2 solution in water.



The ppt is filtered, washed, dried and weighed.

The % of S is calculated from mass of BaSO_4 .

Let mass of organic compound taken = W g

mass of BaSO_4 formed = W_1 g

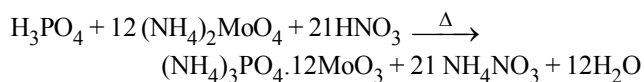
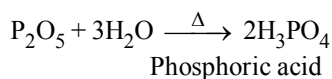
1 mol of $\text{BaSO}_4 = 233$ g $\text{BaSO}_4 = 32$ g S

W_1 g BaSO_4 contains $\frac{32 \times W_1}{233}$ g S

$$\% \text{ of S} = \frac{32 \times W_1 \times 100}{233 \times W}$$

(v) **Phosphorus**

A known mass of an organic compound is heated with fuming HNO_3 . Carbon and hydrogen are oxidised to CO_2 and H_2O respectively while P in compound is oxidised to H_3PO_4 . It is precipitated as ammonium phosphomolybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ by adding ammonium molybdate. The precipitate of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ is then filtered, washed, dried and weighed.



Let mass of organic compound = W g

mass of ammonium phosphomolybdate = W_1 g

Molar mass of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 = 1877$ g

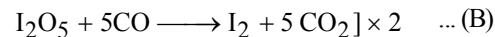
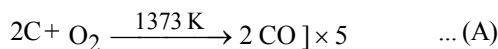
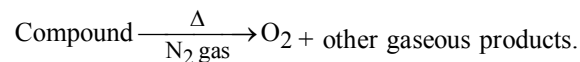
$$\% \text{ of P} = \frac{31 \times W_1 \times 100}{1877 \times W} \%$$

If P is estimated as $\text{Mg}_2\text{P}_2\text{O}_7$.

$$\% \text{ of P} = \frac{62 \times W_1 \times 100}{222 \times W} \%$$

(vi) **Oxygen**

$\% \text{ of O}_2 = 100 - (\text{sum of \% of all other elements})$



On solving (A) and (B), we find that each mole of O_2 liberated produces 2 moles of CO_2 .

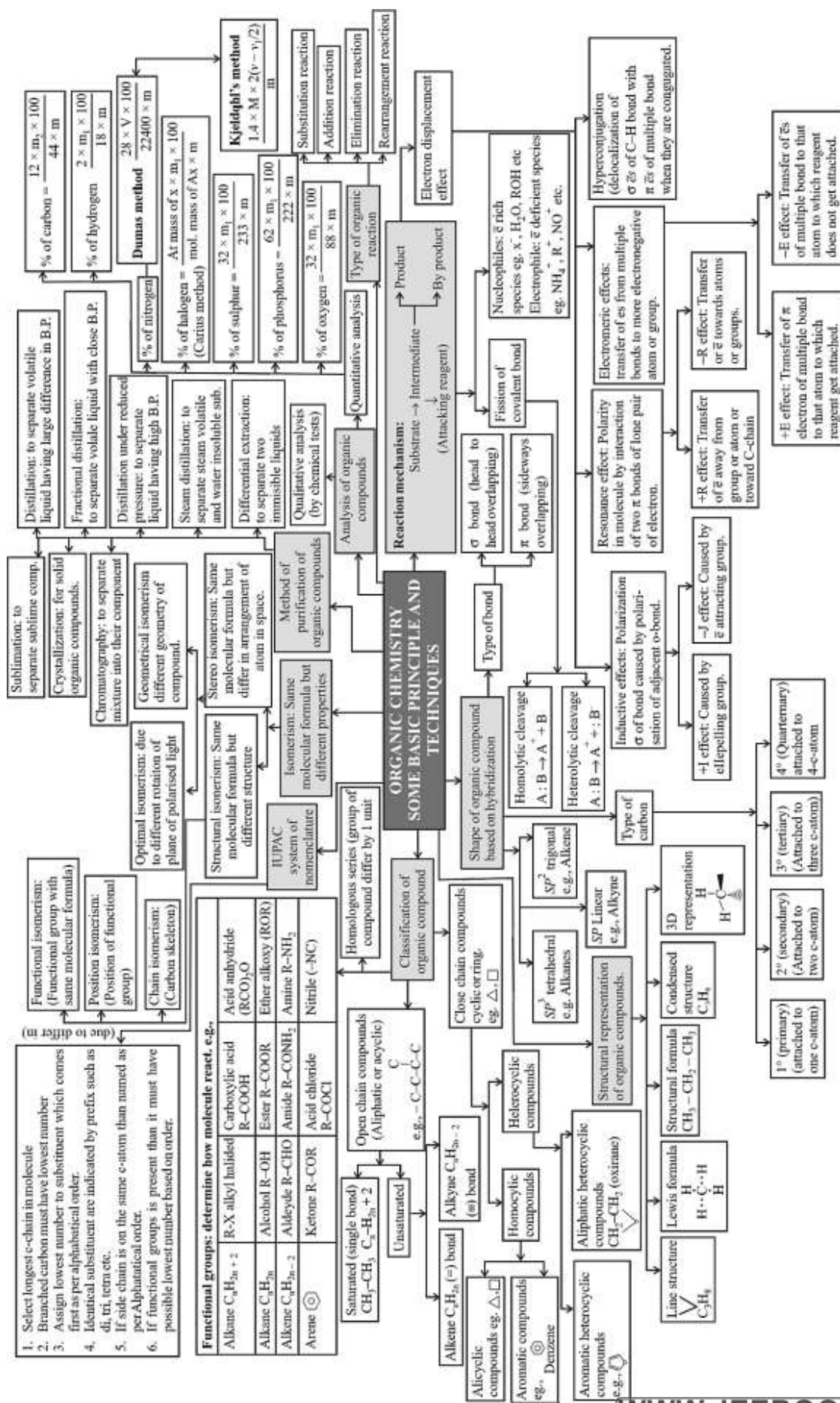
Let mass of organic compound = W g

mass of CO_2 produced = W_1 g

$$\therefore m_1 \text{ g of CO}_2 \text{ is obtained from } \frac{32 \times W_1}{88} \text{ g O}_2$$

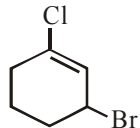
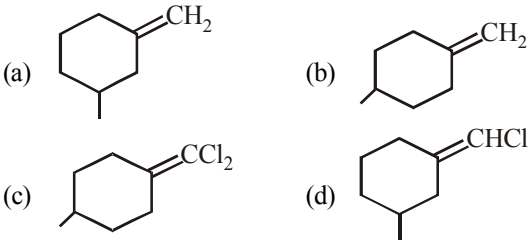
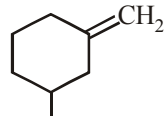
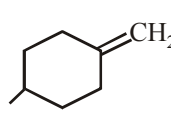
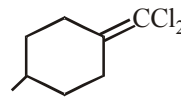
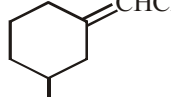
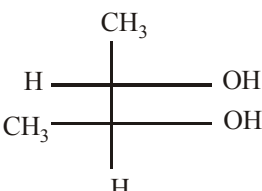
$$\therefore \% \text{ of O}_2 = \frac{32 \times W_1 \times 100}{88 \times W} \%$$

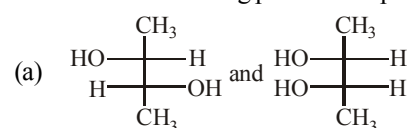
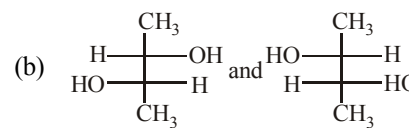
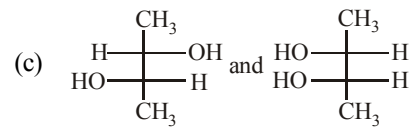
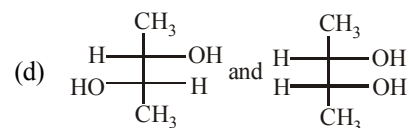
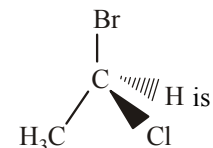
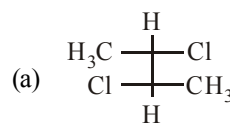
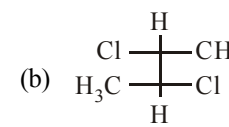
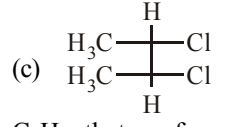
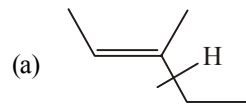
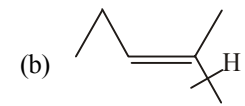
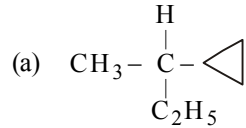
CONCEPT MAP



EXERCISE - 1

Conceptual Questions

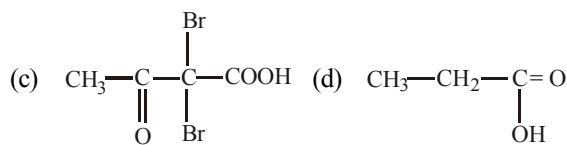
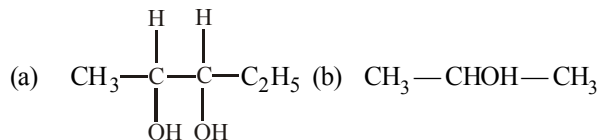
- The number of enantiomers of the compound $\text{CH}_3\text{CHBrCHBrCOOH}$ is :
 (a) 2 (b) 3
 (c) 4 (d) 6
- The IUPAC name of $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}(\text{CH}_3)_2$ is :
 (a) 4-methyl-2-pentyne
 (b) 4,4-dimethyl-2-butyne
 (c) methyl isopropyl acetylene
 (d) 2-methyl-4-pentyne
- Which pairs have same percentage of carbon?
 (a) CH_3COOH and $\text{C}_6\text{H}_{12}\text{O}_6$
 (b) CH_3COOH and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 (c) CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$
 (d) $\text{C}_6\text{H}_{12}\text{O}_6$ and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- The IUPAC name of the compound :
 $\text{CH}_2 - \text{CH} - \text{CH}_2$ is
 $\begin{array}{ccc} | & | & | \\ \text{CN} & \text{CN} & \text{CN} \end{array}$
 (a) 1, 2, 3-trinitropropane
 (b) 1, 2, 3-tricyanopropane
 (c) 3-cyanopentane-1, 5-dinitrile
 (d) 1, 2, 3-pentanetrinitrile
- The IUPAC name of the compound $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ is :
 (a) 3-ethoxy-1-methoxypropane
 (b) 1-ethoxy-3-methoxypropane
 (c) 2, 5-dioxyhexane
 (d) ethoxypropane oxymethane
- The absolute configuration of the following :
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{Cl} \\ | \\ \text{Cl} - \text{C} - \text{H} \\ | \\ \text{C}_2\text{H}_5 \end{array}$ is
 (a) 2S, 3R (b) 2S, 3S
 (c) 2R, 3S (d) 2R, 3R
- Which of the following compounds has wrong IUPAC name?
 (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \text{CH}_2\text{CH}_3 \rightarrow$ ethyl butanoate
 (b) $\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CHO} \rightarrow$ 3-methyl-butanal
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH} \\ | \\ \text{OH} \end{array}$
 (c) $\text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \rightarrow$ 2-methyl-3-butanol
 $\begin{array}{c} \text{OH} \quad \text{CH}_3 \\ | \quad | \end{array}$
 (d) $\text{CH}_3 - \text{CH} - \text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_3$
 $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3 \end{array}$
 $\rightarrow$ 2-methyl-3-pentanone
- The IUPAC name of the compound shown below is :

 (a) 3-bromo-1-chlorocyclohexene
 (b) 1-bromo-3-chlorocyclohexene
 (c) 2-bromo-6-chlorocyclohex-1-ene
 (d) 6-bromo-2-chlorocyclohexene
- In Lassaigne test a violet colour obtained indicates the presence of
 (a) sulphur (b) halogen
 (c) nitrogen (d) None of these
- IUPAC name of the compound is :
 $\begin{array}{c} \text{O} \\ || \\ \text{H} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{OCH}_3 \end{array}$
 (a) 2-methoxypropanal (b) methoxypropanal
 (c) 3-methoxypropanal (d) 2-formyl methoxyethane
- The number of secondary hydrogens in 2, 2-dimethylbutane is :
 (a) 8 (b) 6 (c) 4 (d) 2
- The geometrical isomerism is shown by

 (a)  (b) 
 (c)  (d) 
- The IUPAC name for
 $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3 \\ | \\ \text{H} \end{array}$ is
 (a) 5-chlorohex-2-ene
 (b) 2-chlorohex-5-ene
 (c) 1-chloro-1-methylpent-3-ene
 (d) 5-chloro-5-methylpent-2-ene
- Among the following the most stable compound is :
 (a) *cis*-1, 2-cyclohexanediol
 (b) *trans*-1, 2-cyclohexanediol
 (c) *cis*-1, 3-cyclohexanediol
 (d) *trans*-1, 3-cyclohexanediol
- Which of the following compounds contains 1° , 2° , 3° as well as 4° carbon atoms ?
 (a) Neopentane (b) 2-methyl pentane
 (c) 2,3-dimethyl butane (d) 2,2,3-trimethyl pentane
- Correct configuration of the following is

 (a) 1S, 2S (b) 1S, 2R (c) 1R, 2R (d) 1R, 2S

17. The correct name for the following hydrocarbon is
 (a) Tricyclo [4.1.0] heptane
 (b) Bicyclo [5.2.1] heptane
 (c) Bicyclo [4.1.0] heptane
 (d) Bicyclo [4.1.0] hexane
18. The Beilstein test for organic compounds is used to detect
 (a) nitrogen (b) sulphur (c) carbon (d) halogens
19. Which of the following is an optically active compound ?
 (a) 1-Butanol (b) 1-Propanol
 (c) 2-Chlorobutane (d) 4-Hydroxyheptane
20. An important chemical method to resolve a racemic mixture makes use of the formation of
 (a) a meso compound (b) enantiomers
 (c) diastereomers (d) racemates
21. Lassaigne's test is used in qualitative analysis to detect
 (a) nitrogen (b) sulphur
 (c) chlorine (d) All of these
22. The process of separation of a racemic modification into *d* and *l*-enantiomers is called
 (a) Resolution (b) Dehydration
 (c) Revolution (d) Dehydrohalogenation
23. Tautomerism will be exhibited by
 (a) $(\text{CH}_3)_2\text{NH}$ (b) $(\text{CH}_3)_3\text{CNO}$
 (c) R_3CNO_2 (d) RCH_2NO_2
24. Lassaigne's test for the detection of nitrogen fails in
 (a) $\text{NH}_2\text{CONHNH}_2 \cdot \text{HCl}$ (b) $\text{NH}_2\text{NH}_2 \cdot \text{HCl}$
 (c) NH_2CONH_2 (d) $\text{C}_6\text{H}_5\text{NHNH}_2 \cdot \text{HCl}$
25. A compound of molecular formula of C_7H_{16} shows optical isomerism, compound will be
 (a) 2, 3-Dimethylpentane (b) 2, 2-Dimethylpentane
 (c) 2, 4 - Dimethylpentane (d) None of these
26. $\text{CH}_2=\text{C}(\text{O})-\text{CH}_3$ and $\text{CH}_2=\text{C}(\text{O})-\text{CH}_3$ are
 (a) resonating structures (b) tautomers
 (c) geometrical isomers (d) optical isomers
27. Which of the following pairs of compounds are enantiomers?
 (a) 
 (b) 
 (c) 
 (d) 
28. Kjeldahl's method is used in the estimation of
 (a) nitrogen (b) halogens
 (c) sulphur (d) oxygen
29. The chirality of the compound
 is
 (a) R (b) S (c) E (d) Z
30. Among the following four structures I to IV,
 (I) $\text{C}_2\text{H}_5-\text{CH}(\text{CH}_3)-\text{C}_3\text{H}_7$, (II) $\text{CH}_3-\text{C}(\text{O})-\text{CH}(\text{CH}_3)-\text{C}_2\text{H}_5$
 (III) $\text{H}-\text{C}^+(\text{H})_2$, (IV) $\text{C}_2\text{H}_5-\text{CH}(\text{CH}_3)-\text{C}_2\text{H}_5$
 it is true that
 (a) only I and II are chiral compounds
 (b) only III is a chiral compound
 (c) only II and IV are chiral compounds
 (d) all four are chiral compounds
31. Which of the following is optically inactive?
 (a)  (b) 
 (c)  (d) none of these.
32. C_8H_{16} that can form *cis-trans* geometrical isomers and also has a chiral centre, is
 (a)  (b) 
 (c) Both of these (d) None of these
33. Which of the following will have a mesoisomer also?
 (a) 2, 3- Dichloropentane (b) 2, 3-Dichlorobutane
 (c) 2-Chlorobutane (d) 2-Hydroxypropanoic acid
34. Amongst the following compounds, the optically active alkane having lowest molecular mass is
 (a) 
 (b) $\text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_3$
 (c) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
 (d) $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$
35. The most suitable method for separation of a 1 : 1 mixture of ortho and para nitrophenols is
 (a) sublimation (b) chromatography
 (c) crystallization (d) steam distillation

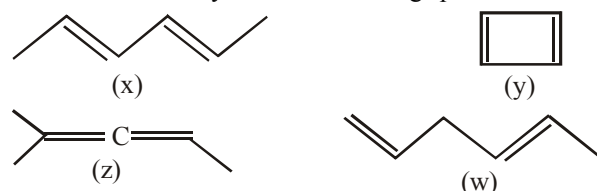
36. Which one of the following is a technique most suitable for purification of cyclohexanone from a mixture containing benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone?

- (a) Crystallization (b) Sublimation
(c) IR spectroscopy (d) Gas chromatography

37. Which of the following is optically active?



38. The correct stability order of following species is –



- (a) $x > y > w > z$ (b) $y > x > w > z$
(c) $x > w > z > y$ (d) $z > x > y > w$

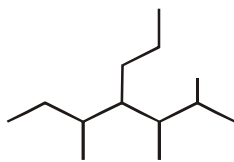
39. An aromatic compound of formula $\text{C}_7\text{H}_7\text{Cl}$ has in all isomers:

- (a) 5 (b) 2 (c) 4 (d) 3

40. How many optically active stereoisomers are possible for lactic acid?

- (a) 1 (b) 2 (c) 4 (d) 3

41. The correct IUPAC name for



- (a) 5-methyl-4-(1'-2'-demethylpropyl) heptane
(b) 3-methyl-4-(1',2'-dimethylpropyl) heptane
(c) 2,3,5-trimethyl-4-propylheptane
(d) 4-propyl-2,3,5-trimethylheptane

42. Geometrical isomerism is possible in:

- (a) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$
(b) $\text{CH}_3\text{CH} = \text{CHCH}_3$
(c) $\text{CH}_3\text{CH} = \text{CH}_2$
(d) $\text{ClH}_2\text{C} - \text{CH}_2\text{Cl}$

43. How many acyclic structural isomers are possible for the compound with molecular formula $\text{C}_3\text{H}_3\text{Cl}_3$?

- (a) 3 (b) 2 (c) 5 (d) 6

44. The number of optical enantiomorphs of tartaric acid is/are:

- (a) 1 (b) 4 (c) 3 (d) 2

45. Which of the cations is more stable?

- (a) $\begin{array}{c} \text{H} \\ | \\ \text{R}' - \text{C}^+ - \text{OR} \end{array}$ (b) $\begin{array}{c} \text{H} \\ | \\ \text{R}' - \text{C} = \text{OR}^+ \end{array}$
(c) both equal (d) both are unstable

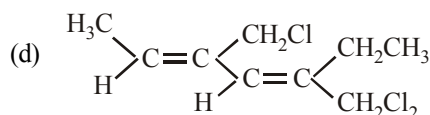
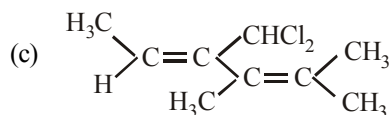
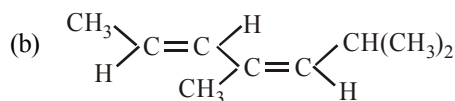
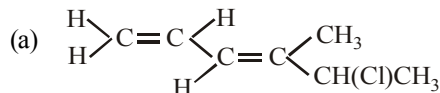
46. Geometrical isomerism is possible in case of:

- (a) pentene-2 (b) propane
(c) pentane (d) ethene

47. The number of isomers of the compound with molecular formula $\text{C}_2\text{H}_2\text{Br}_2$ is

- (a) 4 (b) 3 (c) 5 (d) 2

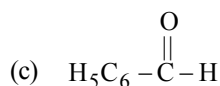
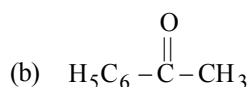
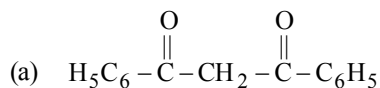
48. One among the following will show optical activity?



49. The number of ether isomers possible for $\text{C}_4\text{H}_{10}\text{O}$ are:

- (a) 2 (b) 5 (c) 4 (d) 3

50. Keto-enol tautomerism is observed in:



(d) Both (a) and (b)

51. The best method for the separation of naphthalene and benzoic acid from their mixture is:

- (a) distillation (b) sublimation
(c) chromatography (d) crystallisation

52. Isomerism due to rotation around C–C single bond is:

- (a) Enantiomerism (b) Position isomerism
(c) Conformation (d) Diastereoisomerism

53. If a compound has n asymmetric carbon atoms, then maximum number of optical isomers are given by the formula

- (a) 2^n (b) $\left(\frac{1}{2}\right)^n$ (c) $\sqrt{2n}$ (d) $2\sqrt{n}$

54. Which is a chiral molecule?

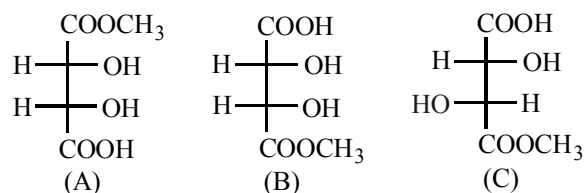
- (a) 2,2-dimethylbutanoic acid
(b) 4-methylpentanoic acid
(c) 3-methylpentanoic acid
(d) 3,3-dimethylbutanoic acid

55. In Kjeldahl's method, CuSO_4 acts as

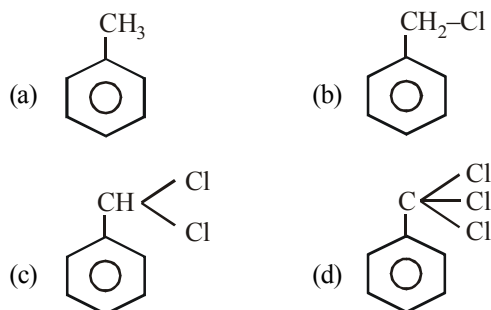
- (a) oxidising agent (b) reducing agent
(c) hydrolysing agent (d) catalytic agent

56. The following compounds differ in
- $\begin{array}{c} \text{H} & & \text{Cl} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{Cl} \end{array}$

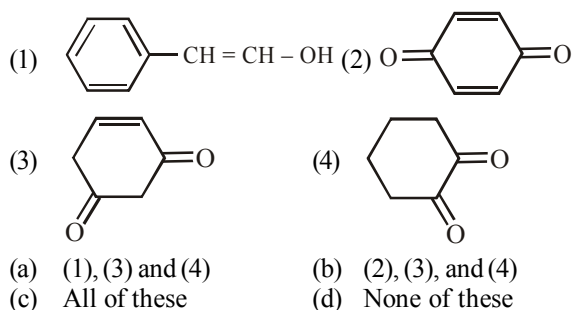
$\begin{array}{c} \text{H} & & \text{Cl} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{Cl} & & \text{H} \end{array}$
- (a) configuration (b) conformation
(c) structure (d) chirality
57. A mixture of methyl alcohol and acetone can be separated by
- (a) distillation
(b) fractional distillation
(c) steam distillation
(d) distillation under reduced pressure
58. The correct statement about the compounds (A), (B) and (C) is :



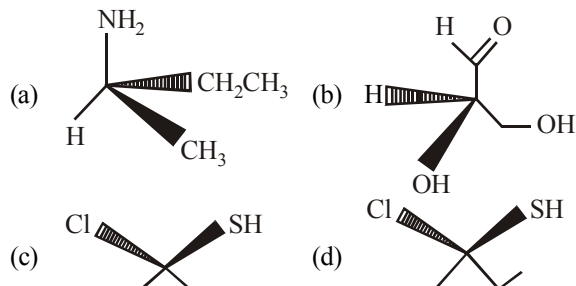
- (a) (A) and (B) are identical
(b) (A) and (B) are diastereomers
(c) (A) and (C) are enantiomers
(d) (A) and (B) are enantiomers
59. Which compound on nitration will give highest amount of m-substituted product ?



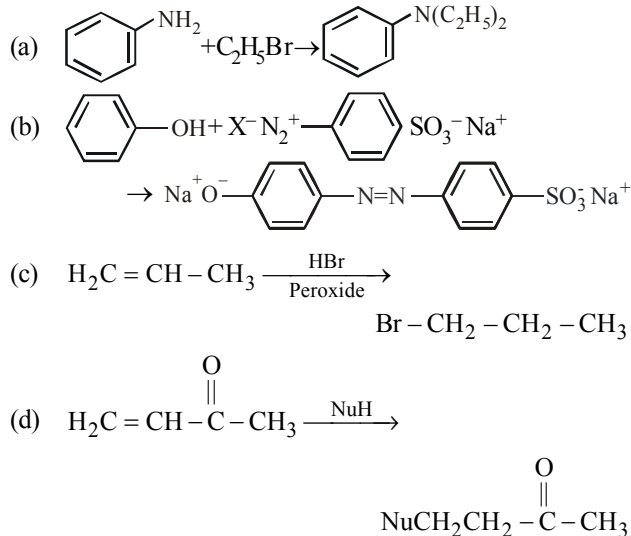
60. The molecular formula of diphenyl methane, $\text{C}_6\text{H}_5\text{-CH}_2\text{-C}_6\text{H}_5$, is $\text{C}_{13}\text{H}_{12}$. How many structural isomers are possible when one of the hydrogens is replaced by a chlorine atom?
- (a) 6 (b) 4 (c) 8 (d) 7
61. Nitroethane can exhibit one of the following kind of isomerism:
- (a) metamerism (b) optical activity
(c) tautomerism (d) position isomerism
62. Tautomerism is exhibited by –



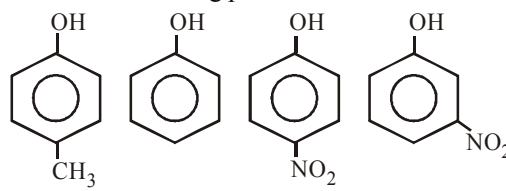
63. Which of the substance is purified by sublimation?
- (a) Benzoic acid (b) Camphor
(c) Naphthalene (d) All of these
64. The most reactive compound for electrophilic nitration is
- (a) Benzene (b) Nitrobenzene
(c) Benzoic acid (d) Toluene.
65. Which of the following molecules is achiral?

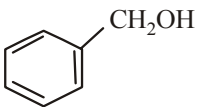
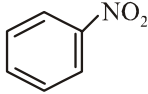
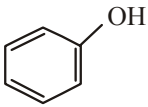
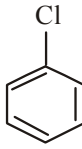
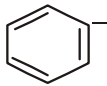
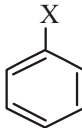
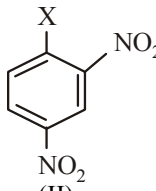
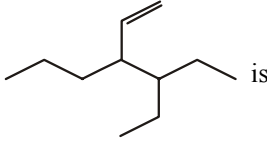


66. Which one of the following is a free-radical substitution reaction?
- (a) $\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{CN}$
- (b) $\text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{Boiling}} \text{C}_6\text{H}_5\text{CH}_2\text{Cl}$
- (c) $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow{\text{Anh. AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3$
- (d) $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{AgNO}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$
67. Which of the following undergoes nucleophilic substitution exclusively by $\text{S}_{\text{N}}1$ mechanism?
- (a) Ethyl chloride (b) Isopropyl chloride
(c) Chlorobenzene (d) Benzyl chloride
68. Styrene can be purified by
- (a) Simple distillation (b) Fractional distillation
(c) Steam distillation (d) Vacuum distillation
69. The correct order regarding the electronegativity of hybrid orbitals of carbon is
- (a) $sp > sp^2 > sp^3$ (b) $sp < sp^2 > sp^3$
(c) $sp < sp^2 < sp^3$ (d) $sp > sp^2 < sp^3$
70. The example of an electrophilic substitution reaction is :



71. Which one of the following does not have sp^2 hybridized carbon ?
 (a) Acetonitrile (b) Acetic acid
 (c) Acetone (d) Acetamide
72. Rate of the reaction

$$R-\overset{\overset{O}{\parallel}}{C}-Z + Nu^- \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-Nu + Z^-$$
 is fastest when Z is
 (a) OC_2H_5 (b) NH_2 (c) Cl (d) $OCOCH_3$
73. The increasing order of stability of the following free radicals is
 (a) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
 (b) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$
 (c) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$
 (d) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
74. Steam distillation is used for the purification of :
 (a) covalent compounds
 (b) electrovalent compounds
 (c) co-ordinate compounds
 (d) volatile compounds
75. Which of the following is strongest nucleophile –
 (a) Br^- (b) $:OH^-$
 (c) $:CN^-$ (d) $C_2H_5O^-$
76. Strongest acid among the following is :
 (a) CCl_3COOH (b) CH_3COOH
 (c) CF_3COOH (d) CBr_3COOH
77. The prussian blue colour obtained in the Lassaigne's test for nitrogen is due to the formation of
 (a) Iron (II) hexacyanoferrate (III)
 (b) Iron (III) hexacyanoferrate (II)
 (c) Iron (III) hexacyanoferrate (III)
 (d) Iron (II) hexacyanoferrate (II)
78. Which one of the following species is isoelectronic with ammonia ?
 (a) CH_2^- (b) $^+CH_2$ (c) $^-CH_3$ (d) $^+CH_3$
79. A *meta*-directing functional group is :
 (a) $-COOH$ (b) OH
 (c) $-CH_3$ (d) $-Br$
80. The following compound will undergo electrophilic substitution more readily than benzene :
 (a) Nitrobenzene (b) Benzoic acid
 (c) Benzaldehyde (d) Phenol
81. In Kjeldahl's method for the estimation of nitrogen, the formula used is
 (a) $\%N = \frac{1.4VW}{N}$ (b) $\%N = \frac{1.4VW}{V}$
 (c) $\%N = \frac{VNW}{1.8}$ (d) $\%N = \frac{1.4VN}{W}$
82. The number of σ and π bonds in a molecule of acetonitrile are respectively
 (a) 2, 5 (b) 3, 4 (c) 4, 3 (d) 5, 2
83. An asymmetric carbon atom is that in which :
 (a) three similar and one dissimilar groups
 (b) two similar and two dissimilar groups
 (c) all the different groups
 (d) none of the above
84. Which of the following pairs represent electrophiles?
 (a) $AlCl_3, H_2O$ (b) SO_3, NO_2^+
 (c) BF_3, H_2O (d) NH_3, SO_3
85. Chromatography is a valuable method for the separation, isolation, purification and identification of the constituents of a mixture and it is based on general principle of
 (a) phase rule (b) phase distribution
 (c) interphase separation (d) phase operation
86. The shape of methyl carbanion is similar to that of –
 (a) BF_3 (b) NH_3
 (c) methyl free radical (d) methyl carbocation
87. The replacement of chlorine of chlorobenzene to give phenol requires drastic conditions, but the chlorine of 2,4-dinitrochlorobenzene is readily replaced since,
 (a) nitro groups make the aromatic ring electron rich at ortho/para positions
 (b) nitro groups withdraw electrons from the meta position of the aromatic ring
 (c) nitro groups donate electrons at meta position
 (d) nitro groups withdraw electrons from ortho/para positions of the aromatic ring
88. The optical inactivity due to internal compensation can be exhibited by :
 (a) dextro-tartaric acid (b) laevo-tartaric acid
 (c) racemic-tartaric acid (d) meso-tartaric acid
89. Consider the following phenols :
- 
- The decreasing order of acidity of the above phenols is
 (a) $III > IV > II > I$ (b) $II > I > IV > III$
 (c) $I > IV > II > III$ (d) $III > IV > I > II$
90. Absolute alcohol cannot be obtained by simple fractional distillation because
 (a) Pure C_2H_5OH is unstable
 (b) C_2H_5OH form hydrogen bonds with water
 (c) Boiling point of C_2H_5OH is very close to that of water
 (d) Constant boiling azeotropic mixture is formed with water
91. Impure glycerine can be purified by
 (a) Steam distillation (b) Simple distillation
 (c) Vacuum distillation (d) Extraction with a solvent
92. Consider the acidity of the carboxylic acids :
 (A) $PhCOOH$ (B) $o-NO_2C_6H_4COOH$
 (C) $p-NO_2C_6H_4COOH$ (D) $m-NO_2C_6H_4COOH$
 Which of the following order is correct ?
 (a) $B > D > A > C$ (b) $B > D > C > A$
 (c) $A > B > C > D$ (d) $B > C > D > A$
93. The decreasing order of nucleophilicity among the nucleophiles
 (A) $CH_3C(=O)O^-$ (B) CH_3O^-
 (C) CN^-
 (D) $H_3C-C_6H_4-S(=O)_2O^-$ is

- (a) (C), (B), (A), (D) (b) (B), (C), (A), (D)
 (c) (D), (C), (B), (A) (d) (A), (B), (C), (D)
94. 1,2-Dihydroxybutane has the formula
 (a) C(OH)-C(OH)-C-C (b) $\text{C-C(OH)}_2\text{-C-C}$
 (c) (OH)C-C-C-C(OH) (d) C-C(OH)-C(OH)-C
95. Which of the following represents the correct order of stability of the given carbocations ?
 (a) $\text{F}_3\text{C}^+ > \text{F}_3\text{C}-\text{C}^+ > \text{CH}_3^+$ (b) $\text{H}_3\text{C}^+ > \text{F}_3\text{C}-\text{C}^+ > \text{F}_3\text{C}^+$
 (c) $\text{F}_3\text{C}-\text{C}^+ > \text{F}_3\text{C}^+ > \text{H}_3\text{C}^+$ (d) $\text{F}_3\text{C}-\text{C}^+ > \text{H}_3\text{C}^+ > \text{F}_3\text{C}^+$
96. A bottle containing two immiscible liquids is given to you. They may be separated by using a
 (a) Fractionating column (b) Separating funnel
 (c) Vacuum distillation (d) Steam distillation
97. Distillation is used to separate liquids which differ in the b.p by
 (a) 5°C (b) 10°C
 (c) $30-80^\circ\text{C}$ (d) 100°C
98. Example of chain isomerism are :
 (a) Ortho and meta toluic acids
 (b) Methyl acetate and ethyl formate
 (c) Pentanoic acid and 2-methyl butanoic acid
 (d) 2-pentanone and 3-pentanone
99. $\text{CH}_3-\text{CHCl}-\text{CH}_2-\text{CH}_3$ has a chiral centre. which one of the following represents its R-configuration?
 (a) $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{H}-\text{C}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$ (b) $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{Cl}-\text{C}-\text{CH}_3 \\ | \\ \text{H} \end{array}$
 (c) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{C}_2\text{H}_5 \end{array}$ (d) $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{H}_3\text{C}-\text{C}-\text{Cl} \\ | \\ \text{H} \end{array}$
100. For (i) I^- , (ii) Cl^- , (iii) Br^- , the increasing order of nucleophilicity would be
 (a) $\text{Cl}^- < \text{Br}^- < \text{I}^-$ (b) $\text{I}^- < \text{Cl}^- < \text{Br}^-$
 (c) $\text{Br}^- < \text{Cl}^- < \text{I}^-$ (d) $\text{I}^- < \text{Br}^- < \text{Cl}^-$
101. The order of decreasing reactivity towards an electrophilic reagent, for the following would be
 (i) benzene (ii) toluene
 (iii) chlorobenzene (iv) phenol
 (a) (ii) > (iv) > (i) > (iii) (b) (iv) > (iii) > (ii) > (i)
 (c) (iv) > (ii) > (i) > (iii) (d) (i) > (ii) > (iii) > (iv)
102. Which one of the following is most reactive towards electrophilic attack ?
 (a)  (b) 
 (c)  (d) 
103. How many stereoisomers does this molecule have?
 $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CHBrCH}_3$
 (a) 4 (b) 6 (c) 8 (d) 2
104. The stability of carbanions in the following :
 (I) $\text{RC}=\bar{\text{C}}$ (II) 
 (III) $\text{R}_2\text{C}=\bar{\text{C}}\text{H}$ (IV) $\text{R}_3\text{C}-\bar{\text{C}}\text{H}_2$
 is in the order of :
 (a) (I) > (II) > (III) > (IV) (b) (II) > (III) > (IV) > (I)
 (c) (IV) > (II) > (III) > (I) (d) (I) > (III) > (II) > (IV)
105. In the hydrocarbon
 $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$
 6 5 4 3 2 1
 The state of hybridization of carbons 1, 3 and 5 are in the following sequence :
 (a) sp^2, sp, sp^3 (b) sp, sp^3, sp^2
 (c) sp, sp^2, sp^3 (d) sp^3, sp^2, sp
106. The state of hybridization of C_2 , C_3 , C_5 and C_6 of the hydrocarbon,
 $\begin{array}{ccccccc} & & \text{CH}_3 & & & \text{CH}_3 & \\ & & | & & & | & \\ \text{CH}_3 & - & \text{C} & - & \text{CH} & = & \text{CH} & - & \text{CH} & - & \text{C} & \equiv & \text{CH} \\ & 7 & 6 & & 5 & 4 & 3 & & 2 & 1 \\ & & | & & & & & & & & & & \\ & & \text{CH}_3 & & & & & & & & & & \end{array}$
 is in the following sequence:
 (a) sp^3, sp^2, sp^2 and sp (b) sp, sp^2, sp^2 and sp^3
 (c) sp, sp^2, sp^3 and sp^2 (d) sp, sp^3, sp^2 and sp^3
107. Which of the following compounds will exhibit cis-trans (geometrical) isomerism?
 (a) Butanol (b) 2-Butyne
 (c) 2-Butenol (d) 2-Butene
108. Cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV) are given. In these the order of decreasing acidic character will be :
 (a) III > II > IV > I (b) II > III > I > IV
 (c) II > III > IV > I (d) III > IV > II > I
109. The correct order of increasing reactivity of C - X bond towards nucleophile in the following compounds is:
 
 (I) (II) (III) (IV)
 (a) I < II < IV < III (b) II < III < I < IV
 (c) IV < III < I < II (d) III < II < I < IV
110. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is:
 (a) $\text{CH}_3\text{COOCH}_3$ (b) CH_3CONH_2
 (c) $\text{CH}_3\text{COOCOCH}_3$ (d) CH_3COCI
111. The correct IUPAC name of the compound
 is

- (a) 4-Ethyl-3-propyl hex-1-ene
 (b) 3-Ethyl-4-ethenyl heptane
 (c) 3-Ethyl-4-propyl hex-1-ene
 (d) 3-(1-ethylpropyl) hex-1-ene
112. The IUPAC name of the following compound is
-
- (a) trans-2-chloro-3-iodo-2-pentene
 (b) cis-3-iodo-4-chloro-3-pentene
 (c) trans-3-iodo-4-chloro-3-pentene
 (d) cis-2-chloro-3-iodo-2-pentene
113. The IUPAC name of is
- (a) 3-ethyl-4,4-dimethylheptane
 (b) 1,1-diethyl-2,2-dimethylpentane
 (c) 4,4-dimethyl-5,5-diethylpentane
 (d) 5,5-diethyl-4,4-dimethylpentane
114. Presence of a nitro group in a benzene ring
- (a) deactivates the ring towards electrophilic substitution
 (b) activates the ring towards electrophilic substitution
 (c) renders the ring basic
 (d) deactivates the ring towards nucleophilic substitution.
115. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is
- (a) $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{CONH}_2$, $-\text{CHO}$
 (b) $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{CONH}_2$, $-\text{CHO}$
 (c) $-\text{CHO}$, $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{CONH}_2$
 (d) $-\text{CONH}_2$, $-\text{CHO}$, $-\text{SO}_3\text{H}$, $-\text{COOH}$
116. The IUPAC name of neopentane is
- (a) 2,2 dimethylpropane (b) 2 methylpropane
 (c) 2,2 dimethylbutane (d) 2-methylbutane

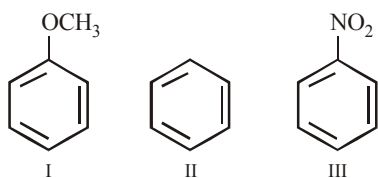
117. The alkene that exhibits geometrical isomerism is :
- (a) 2-methyl propene (b) 2-butene
 (c) 2-methyl-2-butene (d) propene
118. The number of stereoisomers possible for a compound of the molecular formula $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{Me}$ is:
- (b) 2 (c) 4 (d) 6 (d) 3
119. Out of the following, the alkene that exhibits optical isomerism is
- (a) 3-methyl-2-pentene (b) 4-methyl-1-pentene
 (c) 3-methyl-1-pentene (d) 2-methyl-2-pentene
120. The IUPAC name of the following compound is
-
- (a) 4-Bromo-3-cyanophenol
 (b) 2-Bromo-5-hydroxybenzonitrile
 (c) 2-Cyano-4-hydroxybromobenzene
 (d) 6-Bromo-3-hydroxybenzonitrile
121. Hyperconjugation involves overlap of the following orbitals
- (a) $\sigma-\sigma$ (b) $\sigma-\pi$ (c) p-p (d) $\pi-\pi$
122. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) :
- (a) sp and sp^3 (b) sp and sp^2
 (c) only sp^3 (d) sp^2 and sp^3
123. Which one of the following conformations of cyclohexane is chiral?
- (a) Boat (b) Twist boat (c) Rigid (d) Chair.
124. Directing influence of the methyl group can be explained on the basis of
- (a) inductive effect (b) electromeric effect
 (c) resonance effect (d) no-bond resonance
125. The number of isomers of the compound C_2BrFCl is
- (a) 3 (b) 4 (c) 5 (d) 6

EXERCISE - 2

Applied Questions

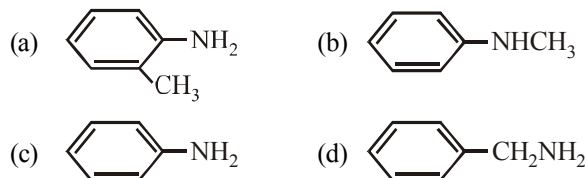
1. Which of the following is true?
- (a) A *cis* isomer has lower b.p. than the *trans*
 (b) A *cis* isomer has lower m.p. than the *trans*
 (c) All isomers of nitrophenols are equal soluble in water
 (d) All the three are correct
2. Which is weakest base :
- (a) $\text{C}_6\text{H}_5-\text{CH}_2-\text{NH}_2$ (b) $\text{C}_6\text{H}_5-\text{CH}_2-\text{NH}-\text{CH}_3$
 (c) $\text{O}_2\text{N}-\text{CH}_2-\text{NH}_2$ (d) $\text{CH}_3-\text{NH}-\text{CHO}$
3. Which of the following is maximum stable
- (a) Conjugated alkadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$)
 (b) Isolated alkadiene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$)
 (c) Cumulated alkadiene ($\text{CH}_2=\text{C}=\text{CH}_2$)
 (d) All are equal
4. Which is true regarding the relative basic character of the following two pairs?
- (a) $\text{NH}_3 > \text{NH}_2\text{OH}$ (b) $-\text{CCl}_3 > -\text{CF}_3$
 (c) Both are true (d) Neither is true
5. Decreasing order of reactivity towards nucleophilic addition to carbonyl group among cyclopentanone, 3-pentanone and n-pentanal is
- (a) 3-pentanone, cyclopentanone, n-pentanal
 (b) n-pentanal, 3-pentanone, cyclopentanone
 (c) n-pentanal, cyclopentanone, 3-pentanone
 (d) cyclopentanone, 3-pentanone, n-pentanal
6. The reaction :
-
- is described as
- (a) $\text{S}_{\text{E}}2$ (b) $\text{S}_{\text{N}}1$ (c) $\text{S}_{\text{N}}0$ (d) $\text{S}_{\text{N}}2$
7. Which of the following is not correct?
- Order of basicity** **Order of nucleophilicity**
- (a) $\text{F}^- > \text{Cl}^- > \text{Br}^-$ $\text{Br}^- > \text{Cl}^- > \text{F}^-$
 (b) $\text{H}-\text{O}-\text{O}^- > \text{OH}^-$ $\text{H}-\text{O}-\text{O}^- > \text{OH}^-$
 (c) $-\text{CH}_3 > \text{NH}_2^- > \text{OH}^-$ $-\text{CH}_3 > \text{NH}_2^- > \text{OH}^-$
 (d) $\text{H}_2\text{O} > \text{H}_2\text{S}$ $\text{H}_2\text{O} < \text{H}_2\text{S}$

8. Among the following compounds (I - III), the ease of their reaction with electrophiles is,

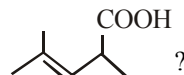


- (a) $\text{II} > \text{III} > \text{I}$ (b) $\text{III} > \text{II} > \text{I}$
 (c) $\text{II} > \text{I} > \text{III}$ (d) $\text{I} > \text{II} > \text{III}$
9. Which one of the following compounds is resistant to nucleophilic attack by hydroxyl ions ?
 (a) Methyl acetate (b) Acetonitrile
 (c) Diethyl ether (d) Acetamide
10. Which one of the following orders is correct regarding the $-I$ effect of the substituents ?
 (a) $-\text{NR}_2 > -\text{OR} > -\text{F}$ (b) $-\text{NR}_2 > -\text{OR} > -\text{F}$
 (c) $-\text{NR}_2 < -\text{OR} < -\text{F}$ (d) $-\text{NR}_2 > -\text{OR} < -\text{F}$
11. Which of the following is false regarding a good contributor of a resonance hybrid?
 (a) It must have as many bonds as possible
 (b) It must have as many octets as possible
 (c) Negative charge, if any, should be on electronegative atom
 (d) None of the three
12. Correct order of stability is :
 (a) cis-2-butene > 1-butene > trans-2-butene
 (b) trans-2-butene > cis-2-butene > 1-butene
 (c) 1-butene > cis-2-butene > trans-2-butene
 (d) cis-2-butene > trans-2-butene > 1-butene
13. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is
 (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{III} > \text{II} > \text{I}$
 (c) $\text{II} > \text{III} > \text{I}$ (d) $\text{I} < \text{II} > \text{III}$
14. Which of the following is least reactive in a nucleophilic substitution reaction.
 (a) $(\text{CH}_3)_3\text{C}-\text{Cl}$ (b) $\text{CH}_2=\text{CHCl}$
 (c) $\text{CH}_3\text{CH}_2\text{Cl}$ (d) $\text{CH}_2=\text{CHCH}_2\text{Cl}$
15. Which of the following is true regarding hyperconjugation, also known as no-bond resonance?
 (i) Like inductive effect it involves donation of electrons through σ bonds
 (ii) Hyperconjugation involves overlapping of filled orbitals with the empty p orbital of the carbocation
 (iii) Like resonance, it involves displacement of π or lone pair of electrons to the carbon bearing positive charge
 (iv) It involves delocalisation of σ and π -electrons
 (a) (ii) and (iv) (b) (ii)
 (c) (iii) (d) none
16. In the anion HCOO^- the two carbon-oxygen bonds are found to be of equal length. what is the reason for it ?
 (a) The $\text{C}=\text{O}$ bond is weaker than the $\text{C}-\text{O}$ bond
 (b) The anion HCOO^- has two resonating structures
 (c) The anion is obtained by removal of a proton from the acid molecule
 (d) Electronic orbitals of carbon atom are hybridised

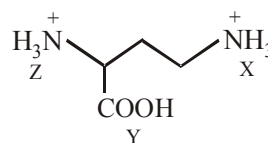
17. Which of the following is the strongest base ?



18. Which type of isomerism is possible in the compound

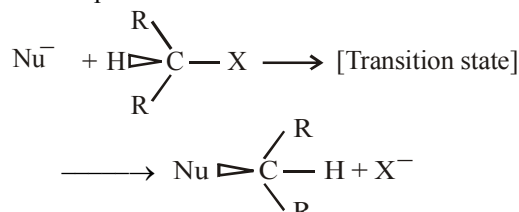


- (a) Geometrical (b) Optical
 (c) Both (d) None
19. Which pair of isomerism is not possible together?
 (a) Ring-chain and functional
 (b) Geometrical and optical
 (c) Metamerism and functional
 (d) Metamerism and chain
20. $\text{CH}_3\text{Br} + \text{Nu}^- \longrightarrow \text{CH}_3 - \text{Nu} + \text{Br}^-$
 The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is
 $[\text{Nu}^- = (\text{A}) \text{PhO}^-, (\text{B}) \text{AcO}^-, (\text{C}) \text{HO}^-, (\text{D}) \text{CH}_3\text{O}^-]$
 (a) $\text{A} > \text{B} > \text{C} > \text{D}$ (b) $\text{B} > \text{D} > \text{C} > \text{A}$
 (c) $\text{D} > \text{C} > \text{A} > \text{B}$ (d) $\text{D} > \text{C} > \text{B} > \text{A}$
21. Lassaigne's test is used to detect
 (a) nitrogen and halogens (b) sodium and halogens
 (c) halogens and sulphur (d) All of these
22. The reason for the loss of optical activity of lactic acid when OH group is changed by H is that :
 (a) Chiral centre of the molecule is destroyed
 (b) Molecule acquires asymmetry
 (c) Due to change in configuration
 (d) Structural change occurs
23. Which of the following does not exhibit *cis-trans* isomerism?
 (a) $\text{C}_6\text{H}_5\text{CH}=\text{NOH}$ (b) $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$
 (c) (d) None of the three
24. C-H bond energy is about 101 kcal/mol for methane, ethane and other alkanes but is only 77 kcal/mol for C-H bond of CH_3 in toluene. This is because :
 (a) of inductive effect due to $-\text{CH}_3$ in toluene
 (b) of the presence of benzene ring in toluene.
 (c) of resonance among the structures of benzyl radical in toluene
 (d) of aromaticity of toluene
25. In Carius method 0.099 g organic compound gave 0.287 g AgCl . The percentage of chlorine in the compound will be
 (a) 28.6 (b) 71.7 (c) 35.4 (d) 64.2
26. Select the appropriate relation with respect to acidity of X, Y, Z for the given compound, with increasing order.



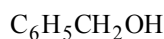
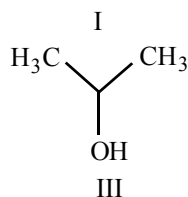
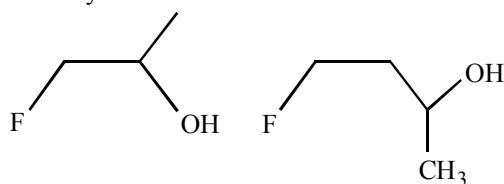
- (a) $\text{Z} > \text{X} > \text{Y}$ (b) $\text{Y} > \text{Z} > \text{X}$
 (c) $\text{Z} < \text{X} > \text{Y}$ (d) $\text{X} > \text{Y} > \text{Z}$

27. The shape of transition state is –



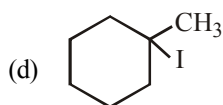
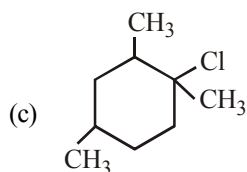
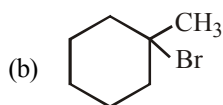
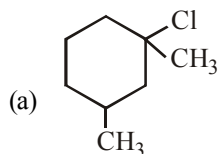
- (a) Triangular planar (b) Square pyramidal
(c) Trigonal bipyramidal (d) Tetrahedral

28. Arrange the following alcohols in order of their decreasing tendency to form carbocation.



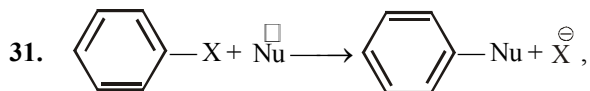
- (a) I > II > III > IV (b) IV > III > I > II (c) IV > III > II > I
(d) II > I > IV > III

29. Which molecule will be most reactive for $\text{S}_{\text{N}}1$ reaction –



30. Diazo compounds, sometimes do not respond Lassaigne's test for nitrogen because

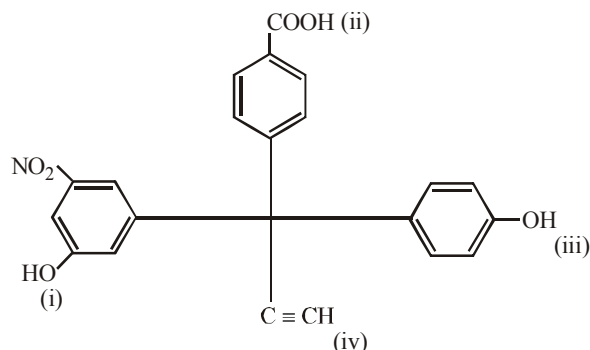
- (a) these are quite stable compounds and do not decompose to elemental nitrogen
(b) these contain very little carbon
(c) these form organometallic compounds with sodium
(d) their nitrogen contents is removed, during heating, in the form of nitrogen gas



the reaction is not possible because –

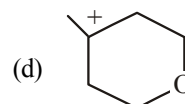
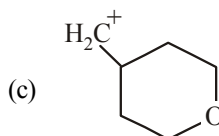
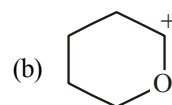
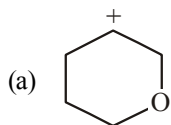
- (a) Nu faces steric hinderance on attacking the leaving group
(b) electrons are delocalised in the benzene ring
(c) reaction is thermodynamically controlled
(d) C – X bond possesses a double bond character

32. Which of the following represent the decreasing order of K_{a} values?



- (a) (ii) > (i) > (iii) > (iv) (b) (ii) > (iii) > (i) > (iv)
(c) (i) > (ii) > (iii) > (iv) (d) (ii) > (iv) > (i) > (iii)

33. Which of the following is most stable?



34. Sodium nitroprusside, when added to an alkaline solution of sulphide ions, produces purple colour ion due to the formation of

- (a) $\text{Na}[\text{Fe}(\text{H}_2\text{O})_5\text{NOS}]$ (b) $\text{Na}_2[\text{Fe}(\text{H}_2\text{O})_5\text{NOS}]$
(c) $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NOS}]$ (d) $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$

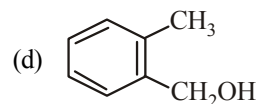
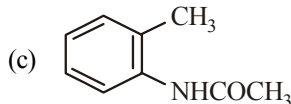
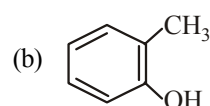
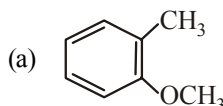
35. Base strength of:

- (A) $\text{H}_3\text{C}\bar{\text{C}}\text{H}_2$, (B) $\text{H}_2\text{C}=\bar{\text{C}}\text{H}$ and (C) $\text{H}-\text{C}\equiv\bar{\text{C}}$

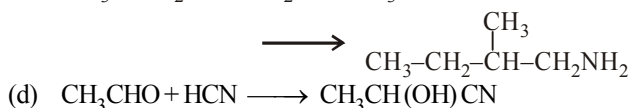
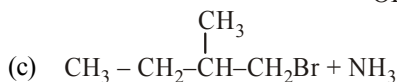
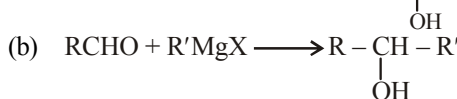
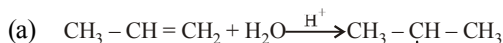
is in the order of:

- (a) (B) > (A) > (C) (b) (C) > (B) > (A)
(c) (A) > (C) > (B) (d) (A) > (B) > (C)

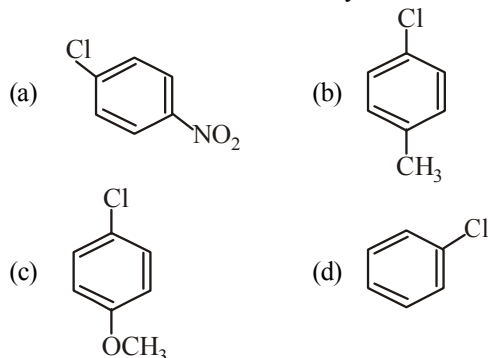
36. Which one of the following is most reactive towards electrophilic reagent?



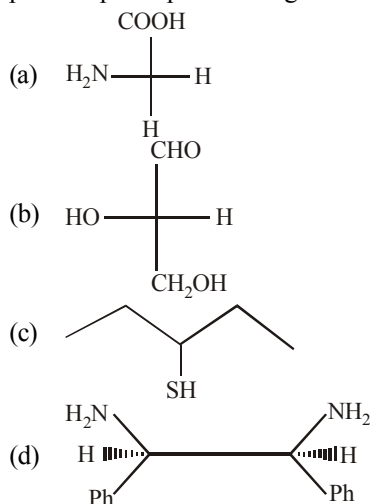
37. Which one is a nucleophilic substitution reaction among the following?



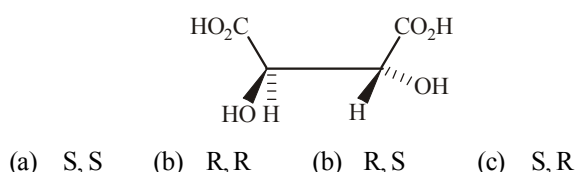
38. Which of the following compounds undergoes nucleophilic substitution reaction most easily?



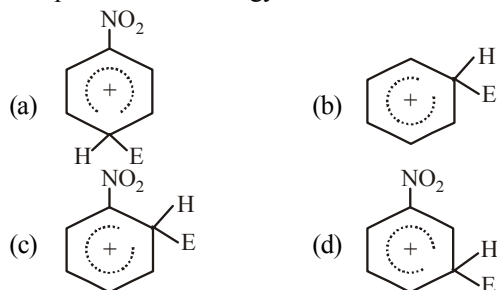
39. Which of the following molecules is expected to rotate the plane of plane-polarised light?



40. The absolute configuration of



41. The electrophile, E^+ attacks the benzene ring to generate the intermediate σ -complex. Of the following, which σ -complex is lowest energy?



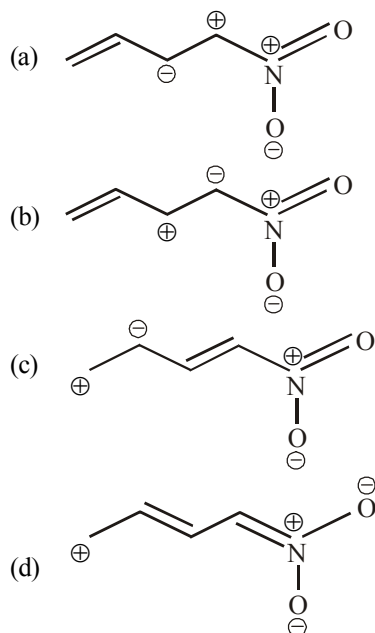
42. Arrange the carbanions, $(CH_3)_3\bar{C}$, $\bar{C}Cl_3$, $(CH_3)_2\bar{C}H$, $C_6H_5\bar{C}H_2$ in order of their decreasing stability:
- (a) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$
 (b) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

- (c) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$
 (d) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$

43. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is

- (a) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$
 (b) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$
 (c) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$
 (d) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

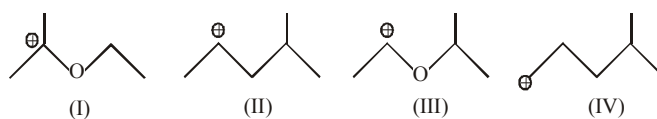
44. Among the following, the least stable resonance structure is



45. The number of stereoisomers obtained by bromination of *trans*-2-butene is

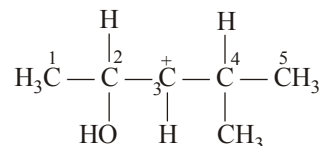
- (a) 1 (b) 2 (c) 3 (d) 4

46. The correct stability order for the following species is



- (a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)
 (c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

47. In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is



- (a) CH_3 at C-4 (b) H at C-4
 (c) CH_3 at C-2 (d) H at C-2

DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: **Statement-1 (Assertion)** and **Statement-2 (Reason)**. Answer these questions from the following four options.

- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True

48. Statement-1 : Aniline is better nucleophile than anilium ion.

Statement-2 : Anilium ion have +ve charge.

49. Statement-1 : Trans-2-butene on reaction with Br_2 gives meso-2, 3-dibromobutane.

Statement-2 : The reaction involves syn-addition of bromine.

50. Statement-1 : Different number of electron pairs are present in resonance structures.

Statement-2 : Resonance structures differ in the location of electrons around the constituent atoms.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

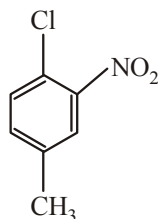
1. Which of the following is the correct IUPAC name?

- (a) 3-ethyl-4, 4-dimethylheptane
 (b) 4, 4-dimethyl-3-ethylheptane
 (c) 5-ethyl-4, 4-dimethylheptane
 (d) 4, 4-bis(methyl)-3-ethylheptane

2. The IUPAC name for $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{OH}$ is

- (a) 1-hydroxypentane-1, 4-dione
 (b) 1, 4-dioxopentanol
 (c) 1-carboxybutan-3-one
 (d) 4-oxopentanoic acid

3. The IUPAC name for



- (a) 1-chloro-2-nitro-4-methylbenzene
 (b) 1-chloro-4-methyl-2-nitrobenzene
 (c) 2-chloro-1-nitro-5-methylbenzene
 (d) *m*-nitro-*p*-chlorotoluene
4. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative?
- (a) $\text{CH}_3 - \text{CH}_2 - \text{*CH}_2 - \text{CH}_3$
 (b) $\text{CH}_3 - \text{*CH} = \text{CH} - \text{CH}_3$
 (c) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{*CH}$
 (d) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{*CH}_2$
5. In which of the following functional groups, isomerism is not possible?
- (a) Alcohols (b) Aldehydes
 (c) Alkyl halides (d) Cyanides
6. The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils.

These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is

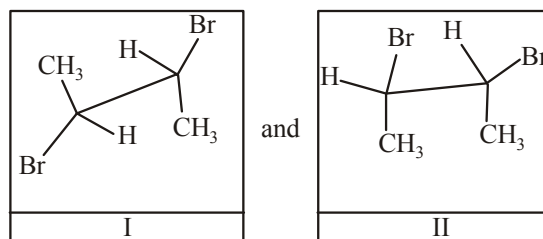
- (a) distillation
 (b) crystallisation
 (c) distillation under reduced pressure
 (d) steam distillation
7. During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?
- (a) Column chromatography
 (b) Solvent extraction
 (c) Distillation
 (d) Thin layer chromatography
8. The principle involved in paper chromatography is
- (a) adsorption (b) partition
 (c) solubility (d) volatility
9. What is the correct order of decreasing stability of the following cations?



- (a) II > I > III (b) II > III > I
 (c) III > I > II (d) I > II > III
10. Correct IUPAC name for $\text{H}_3\text{C} - \underset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}} - \underset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}} - \text{CH}_3$ is

- (a) 2-ethyl-3-methylpentane
 (b) 3, 4-dimethylhexane
 (c) 2-sec-butylbutane
 (d) 2, 3-dimethylbutane
11. In which of the following compounds the carbon marked with asterisk is expected to have greatest positive charge?
- (a) $\text{*CH}_3 - \text{CH}_2 - \text{Cl}$ (b) $\text{*CH}_3 - \text{CH}_2 - \text{Mg}^+\text{Cl}^-$
 (c) $\text{*CH}_3 - \text{CH}_2 - \text{Br}$ (d) $\text{*CH}_3 - \text{CH}_2 - \text{CH}_3$

12. Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable?
- (a) $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O}^-$ (b) $\text{Cl} - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O}^-$
- (c) $\text{F} - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O}^-$ (d) $\text{F} \diagup \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{O}^-$
13. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction. $\text{H}_3\text{C} - \text{HC} = \text{CH}_2 + \text{H}^+ \longrightarrow ?$
- (a) 2° carbanion (b) 1° carbocation
(c) 2° carbocation (d) 1° carbanion
14. Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of $\text{CH}_3 - \text{Br}$ is
- (a) $\text{CH}_3 - \text{Br} \longrightarrow \overset{+}{\text{C}}\text{H}_3 + \text{Br}^-$
(b) $\text{CH}_3 - \text{Br} \longrightarrow \overset{+}{\text{C}}\text{H}_3 + \text{Br}^-$
(c) $\text{CH}_3 - \text{Br} \longrightarrow \overset{+}{\text{C}}\text{H}_3 + \text{Br}^-$
(d) $\text{CH}_3 - \text{Br} \longrightarrow \overset{+}{\text{C}}\text{H}_3 + \overset{-}{\text{Br}}$
15. The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to $>\text{C} = \text{C}<$ portion which can be shown as
- (a) $\text{H}^+ \curvearrowright >\text{C} = \text{C}<$
(b) $\text{H}^+ \curvearrowright >\text{C} = \text{C}<$
(c) $\text{H}^+ \curvearrowright >\text{C} = \text{C}<$
(d) All of these are possible
17. Some *meta*-directing substituents in aromatic substitution are given. Which one is most deactivating? [2013]
- (a) $-\text{SO}_3\text{H}$ (b) $-\text{COOH}$
(c) $-\text{NO}_2$ (d) $-\text{C}\equiv\text{N}$
18. Which of the following compounds will not undergo Friedel-Craft's reaction easily? [2013]
- (a) Xylene (b) Nitrobenzene
(c) Toluene (d) Cumene
19. The structure of isobutyl group in an organic compound is : [2013]
- (a) $\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3$
(b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 -$
(c) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} -$
(d) $\text{CH}_3 - \text{CH} - \text{CH}_2 -$
20. Arrange the following in increasing order of stability [NEET Kar. 2013]
- (A) $(\text{CH}_3)_2\overset{+}{\text{C}} - \text{CH}_2\text{CH}_3$ (B) $(\text{CH}_3)_3 - \overset{+}{\text{C}}$
(C) $(\text{CH}_3)_2 - \overset{+}{\text{C}}\text{H}$ (D) $\text{CH}_3 - \overset{+}{\text{C}}\text{H}_2$
(E) $\overset{+}{\text{C}}\text{H}_3$
(a) $\text{E} < \text{D} < \text{C} < \text{B} < \text{A}$ (b) $\text{E} < \text{D} < \text{C} < \text{A} < \text{B}$
(c) $\text{D} < \text{E} < \text{C} < \text{A} < \text{B}$ (d) $\text{A} < \text{E} < \text{D} < \text{C} < \text{B}$
21. Given

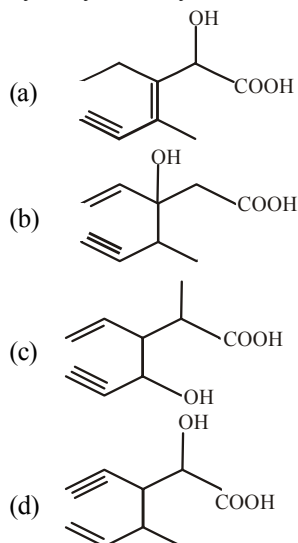


I and II are [NEET Kar. 2013]

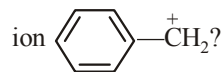
- (a) A pair of optical isomers
(b) Identical
(c) A pair of conformers
(d) A pair of geometrical isomers
22. Homolytic fission of the following alkanes forms free radicals $\text{CH}_3 - \text{CH}_3$, $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$, $(\text{CH}_3)_2\text{CH} - \text{CH}_3$, $\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$. Increasing order of stability of the radicals is [NEET Kar. 2013]
- (a) $(\text{CH}_3)_3\dot{\text{C}} < (\text{CH}_3)_2\dot{\text{C}} - \text{CH}_2\text{CH}_3 < \text{CH}_3 - \dot{\text{C}}\text{H} - \text{CH}_3 < \text{CH}_3 - \dot{\text{C}}\text{H}_2$
(b) $(\text{CH}_3)_2\dot{\text{C}} - \text{CH}_2\text{CH}_3 < \text{CH}_3 - \dot{\text{C}}\text{H} - \text{CH}_3 < \text{CH}_3 - \dot{\text{C}}\text{H}_2 < (\text{CH}_3)_3\dot{\text{C}}$
(c) $\text{CH}_3 - \dot{\text{C}}\text{H}_2 < \text{CH}_3 - \dot{\text{C}}\text{H} - \text{CH}_3 < (\text{CH}_3)_2\dot{\text{C}} - \text{CH}_2 - \text{CH}_3 < (\text{CH}_3)_3\dot{\text{C}}$
(d) $\text{CH}_3 - \dot{\text{C}}\text{H}_2 < \text{CH}_3 - \dot{\text{C}}\text{H} - \text{CH}_3 < (\text{CH}_3)_3\dot{\text{C}} < (\text{CH}_3)_2\dot{\text{C}} - \text{CH}_2\text{CH}_3$

NEET/AIPMT (2013-2017) Questions

16. Structure of the compound whose IUPAC name is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is : [2013]

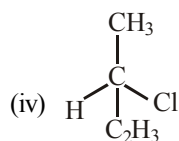
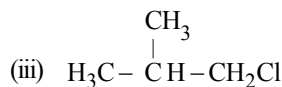
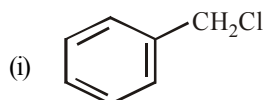


23. What is the hybridisation state of benzyl carbonium



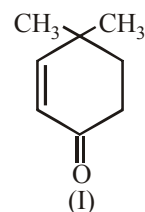
[NEET Kar. 2013]

- (a) sp^3 (b) sp^2
(c) sp^2d (d) sp^2d
24. Nitrogen detection in an organic compound is carried out by Lassaigne's test. The blue colour formed corresponds to which of the following formulae? [NEET Kar. 2013]
- (a) $Fe_3[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_3$ (d) $Fe_4[Fe(CN)_6]_2$
25. Which of the following compounds will undergo racemisation when solution of KOH hydrolyses? [2014]

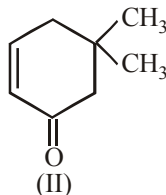


- (a) (i) and (ii) (b) (ii) and (iv)
(c) (iii) and (iv) (d) (i) and (iv)
26. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M H_2SO_4 . The percentage of nitrogen in the soil is : [2014]
- (a) 37.33 (b) 45.33
(c) 35.33 (d) 43.33
27. Two possible stereo-structures of $CH_3CHOH.COOH$, which are optically active, are called. [2015 RS]
- (a) Diastereomers (b) Atropisomers
(c) Enantiomers (d) Mesomers
28. Which of the following statements is not correct for a nucleophile? [2015 RS]
- (a) Nucleophile is a Lewis acid
(b) Ammonia is a nucleophile
(c) Nucleophiles attack low e^- density sites
(d) Nucleophiles are not electron seeking.

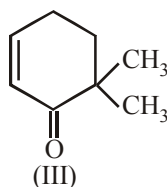
29. Given



(I)



(II)

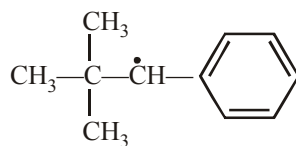


(III)

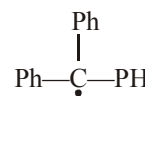
Which of the given compounds can exhibit tautomerism?

- (a) I and III (b) II and III [2015]
(c) I, II and III (d) I and II

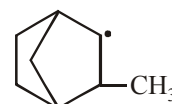
30. Consider the following compounds [2015]



(I)



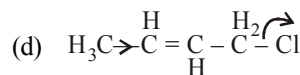
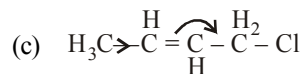
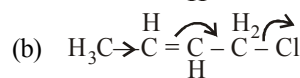
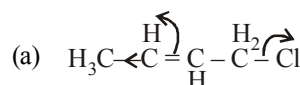
(II)



(III)

Hyperconjugation occurs in :

- (a) II only (b) III only
(c) I and III (d) I only
31. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place? [2015]



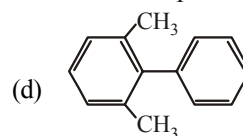
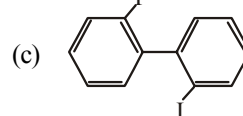
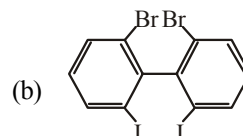
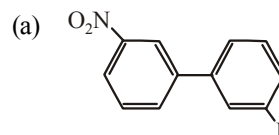
32. In Duma's method for estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is : [2015]

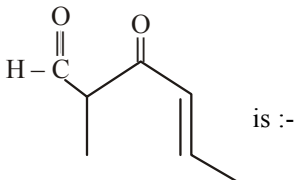
- (a) 18.20 (b) 16.76
(c) 15.76 (d) 17.36

33. The pair of electron in the given carbanion, $CH_3C \equiv C^-$, is present in which of the following orbitals ? [2016]

- (a) $2p$ (b) sp^3
(c) sp^2 (d) sp

34. Which of the following biphenyls is optically active ? [2016]

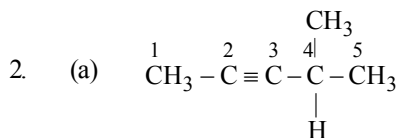


35. The correct statement regarding the comparison of staggered and eclipsed conformation of ethane, is **[2016]**
- The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain
 - The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain
 - The eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
 - The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain.
36. The most suitable method of separation of 1 : 1 mixture of ortho and para-nitrophenols is : **[2017]**
- Chromatography
 - Crystallisation
 - Steam distillation
 - Sublimation
37. The IUPAC name of the compound **[2017]**
- 
- is :-
- 5-formylhex-2-en-3-one
 - 5-methyl-4-oxohex-2-en-5-al
 - 3-keto-2-methylhex-5-enal
 - 3-keto-2-methylhex-4-enal
38. The correct statement regarding electrophile is:- **[2017]**
- Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile
 - Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
 - Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile
 - Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile

Hints & Solutions

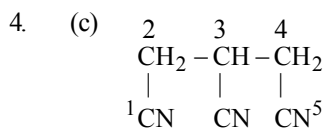
EXERCISE - 1

1. (c) No. of asymmetric carbon = 2
No. of enantiomers = $2^2 = 4$.



4-methyl-2-pentyne

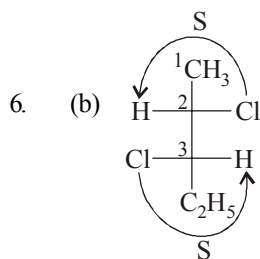
3. (a) is the answer.
Molecular formula of $\text{CH}_3\text{COOH} = \text{C}_2\text{H}_4\text{O}_2$
Both the compounds given have same empirical formula that is CH_2O . So, percentage of carbon in both of them will be same.



IUPAC name is 3-cyanopentane-1,5-dinitrile

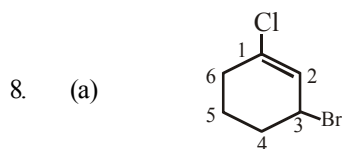
5. (a)
$$\text{CH}_3 - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{CH}_2\text{CH}_3$$

3-ethoxy-1-methoxypropane



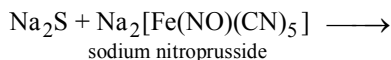
So compound is (2S, 3S)

7. (c) The correct name is 3-methylbutan-2-ol

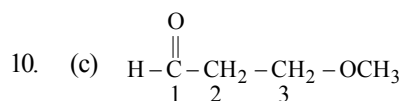


3-bromo-1-chlorocyclohexene

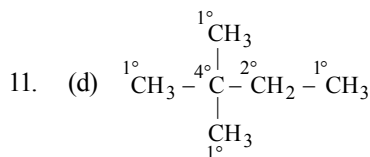
9. (a) Violet colour in Lassaigne's test indicates the presence of sulphur.



sodium nitroprusside

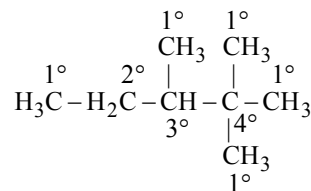


3-methoxypropanal



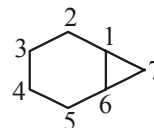
Thus number of secondary hydrogens is two.

12. (d) Geometrical isomerism is observed when different groups are attached to each of the doubly bonded carbon atom.
13. (a) The IUPAC name of the given compound is 5-chlorohex-2-ene.
14. (d) Among 1, 2- and 1, 3- configurations, 1, 3- is more stable due to less repulsion.
Further among *cis* and *trans* isomers, *trans* is more stable due to less crowding.
15. (d) 2, 2, 3-trimethyl pentane



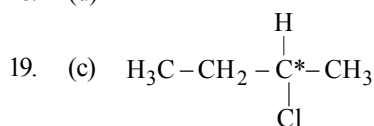
16. (a)

17. (c)



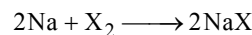
Bicyclo [4, 1, 0] heptane

18. (d)



The compound containing a chiral carbon atom i.e., (a carbon atom which is attached to four different atoms is known as a chiral carbon atom) is optically active. As 2-chlorobutane contains a chiral C^* atom hence it is optically active.

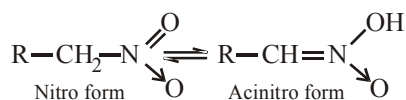
20. (c) Diastereomers since they have different melting points, boiling points, solubilities etc.
21. (d) Nitrogen, sulphur and halogens are tested in an organic compound by Lassaigne's test. The organic compound is fused with sodium metal as to convert these elements into ionisable inorganic substances,



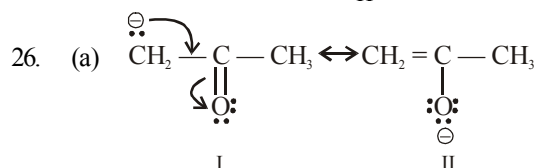
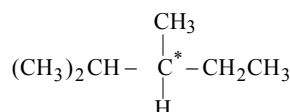
The cyanide, sulphide or halide ions can be confirmed in aqueous solution by usual test.

22. (a) Resolution.
23. (d) Tautomerism is exhibited by the oscillation of hydrogen atom between two polyvalent atoms present in the molecule. As (d) has α -hydrogen atom therefore it

shows tautomerism whereas other structures do not.

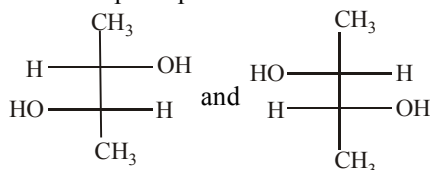


24. (b) Hydrazine (NH_2NH_2) does not contain carbon and hence on fusion with Na metal, it cannot form NaCN; consequently hydrazine does not show Lassaigne's test for nitrogen.
25. (a) A compound is said to exhibit optical isomerism if it at least contains one chiral carbon atom, which is an atom bonded to 4 different atoms or groups.



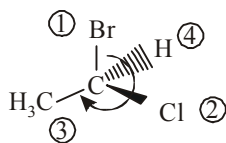
both are resonating structures.

27. (b) Compound which are mirror image of each other and are non superimposable are termed as enantiomers.



These are enantiomers

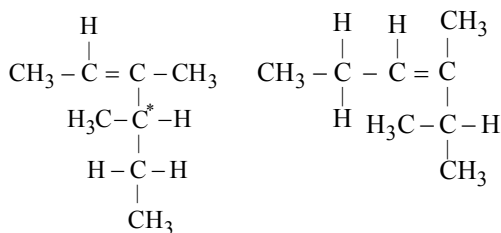
28. (a) Kjeldahl's method is suitable for estimating nitrogen in those compounds in which nitrogen is linked to carbon and hydrogen. The method is not used in case of nitro, azo and azoxy compound. This method is basically used for estimating nitrogen in food fertilizers and agricultural products.
29. (a) Clockwise rotation.



Hence configuration is R.

If the eye travel in a clockwise direction, the configuration is R as the order of priority is $\text{Br} > \text{Cl} > \text{CH}_3 > \text{H}$

30. (a) Carbon atom is connected with four different groups in chiral structure.
31. (c) It has centre of symmetry, so optically inactive.
32. (a) Redrawing the given structures we get,

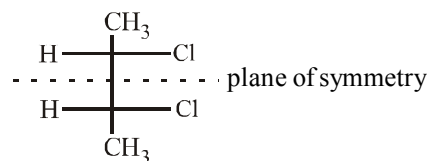


(a)

(b)

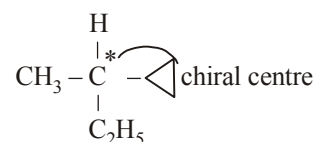
From the above structure, it is evident than structure (a) will show *cis-trans* isomerism and it also has a chiral carbon. On the other hand, structure (b) although shows *cis-trans* isomerism, it has no chiral carbon.

33. (b) The compound has two similar asymmetric C-atoms. It has plane of symmetry and exist in Meso form.

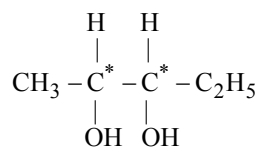


Meso - 2, 3 dichlorobutane

34. (a) Only 2-cyclopropyl butane has a chiral centre.

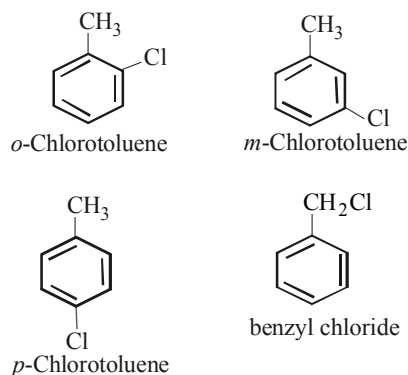


35. (d) The boiling point of *o*-nitrophenol is less than *para*-nitrophenol due to presence of intramolecular hydrogen bonding. Since *p*-nitrophenol is less volatile in steam than *o*-nitrophenol hence they can be separated by steam distillation.
36. (c) IR spectroscopy is used for the purification of cyclohexanone from a mixture of benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone. because in this method, each functional group appear at a certain peak. So, cyclohexane can be identified by carbonyl peak.
37. (a) Optically active compound has asymmetric carbon atom

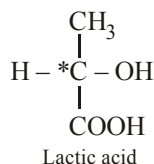


It has two asymmetric carbon (marked as *) atoms and is optically active.

38. (c) x is a conjugated diene system, w is an isolated diene system, z is a cumulated diene system, y is antiaromatic system.
39. (c) $\text{C}_7\text{H}_7\text{Cl}$ has 4 isomers

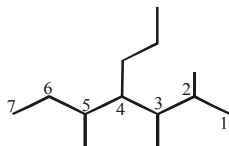


40. (b) No. of optical isomers = 2^x (where x = No. of asymmetric atoms)



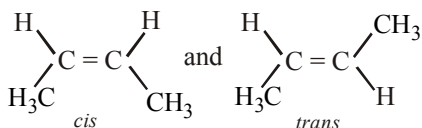
$\therefore$ No. of optical isomers of lactic acid = $(2)^1 = 2$

41. (c) In case two or more chains are of equal length, then the chain with greater number of side chains is selected as the principal chain.

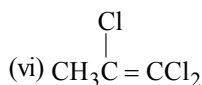
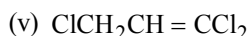
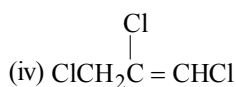
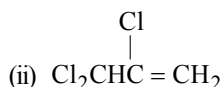


2, 3, 5-Trimethyl-4-propylheptane

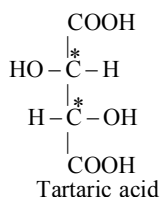
42. (b) Geometrical isomerism is shown by compounds which have $\text{C}=\text{C}$ and two groups attached to same C atoms are different. Choice (b) fulfills both conditions.



43. (d) The parent hydrocarbon of $\text{C}_3\text{H}_3\text{Cl}_3$ is C_3H_6 , i.e. $^3\text{CH}_3\text{CH}=\text{CH}_2$. Three chlorine atoms can be present in following ways.



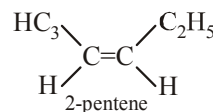
44. (d)



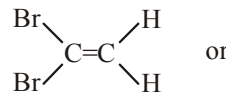
Tartaric acid is an example of a symmetrical molecule, having two asymmetric carbon atoms. In such cases Number of optical enantiomorphs (d and l isomers) = $2^{(n-1)} = 2^1 = 2$

45. (b) Although (b) has positive charge on O (an electronegative element), it is more stable because here every atom has octet of electrons.

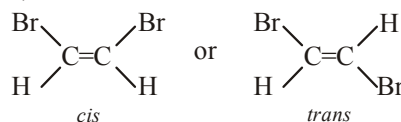
46. (a) Geometrical isomerism is shown by compounds having $\text{C}=\text{C}$ and the two groups attached to each of carbon atom are different



47. (b) The parent hydrocarbon is C_2H_4 or $\text{CH}_2=\text{CH}_2$, so, $\text{C}_2\text{H}_2\text{Br}_2$ can be obtained by replacing two H by two Br for which there are three possibilities.

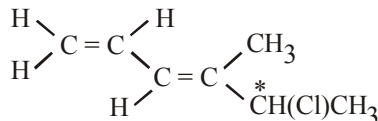


1, 1-dibromoethene



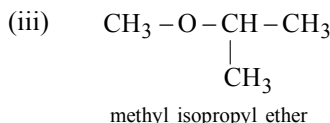
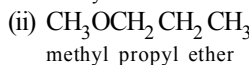
1, 2-dibromoethene

48. (a) Optical activity is the result of chirality (which comes from the presence of chiral carbon in molecule) or the non-superimposability of certain molecules on their mirror images. So, the compound given in option (a) which contains a chiral carbon atom(*) is the only chiral molecule and hence is optically active among the given molecules.

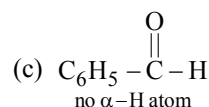
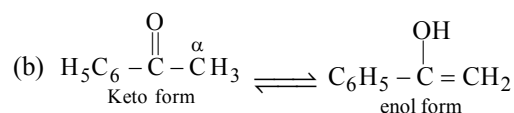
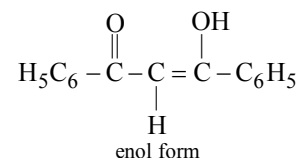
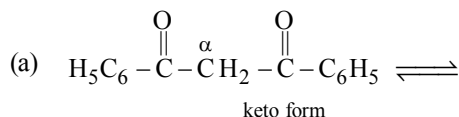


* marked carbon atom is chiral.

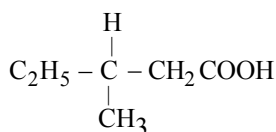
49. (d) (i) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
diethyl ether



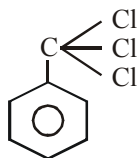
50. (d) Keto-enol tautomerism is shown by carbonyl compounds having α -hydrogen atom.



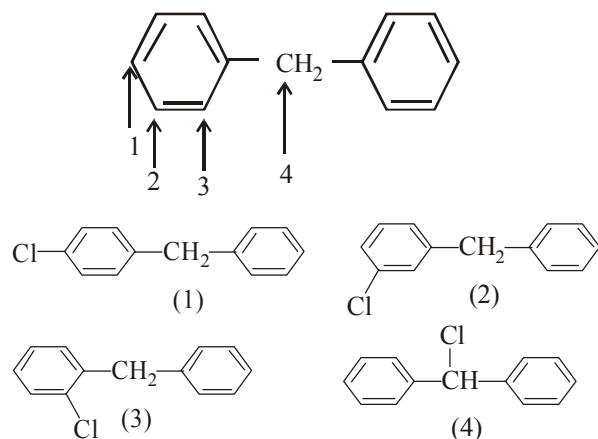
51. (b) Among the given compounds naphthalene is volatile but benzoic acid is non-volatile (it forms a dimer). So, the best method for their separation is sublimation, which is applicable to compounds which can be converted directly into the vapour phase from its solid state on heating and back to the solid state on cooling. Hence it is the most appropriate method.
52. (c) The free rotation across C – C gives rise to many spatial arrangements. These arrangements are called conformers and property is called conformation.
53. (a) Maximum number optical isomers of a compound having n asymmetric carbon atoms is 2^n .
54. (c) Chiral molecules are those molecules which have atleast one asymmetric carbon atom (a carbon atom attached to 4 different groups). This is true in case of 3-methylpentanoic acid.



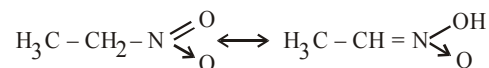
55. (d) Kjeldahl's method depends upon the fact that most of the organic compounds containing nitrogen are quantitatively decomposed to give $(\text{NH}_4)_2\text{SO}_4$ when heated strongly with conc. H_2SO_4 . In this method CuSO_4 acts as catalytic agent.
56. (a) Given structures are representing *cis-trans* isomerism (geometrical) hence differ only in configuration.
57. (a)
58. (d) A and B are enantiomers.
59. (d) $-\text{CH}_3$ group has electron donating inductive effect which decreases with replacement of each hydrogen atom by chlorine atom. Hence highest amount of m -substituted product will be obtained on nitration of



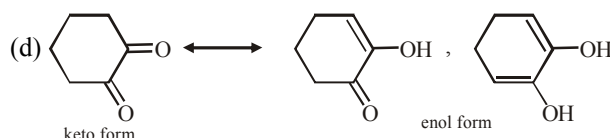
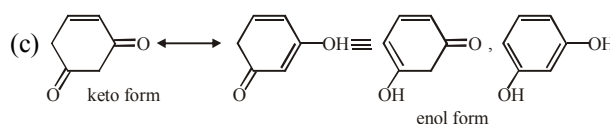
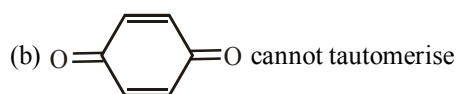
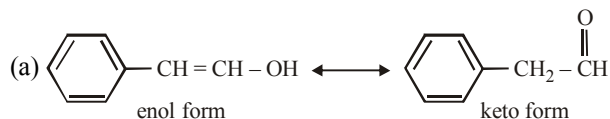
60. (b) In diphenylmethane monochlorination at following positions will produce structured isomers



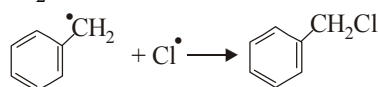
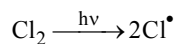
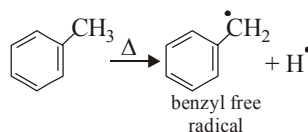
61. (c) Nitroethane ($\text{C}_2\text{H}_5\text{NO}_2$) can exhibit tautomerism among the given kinds of isomerism due to the presence of α -hydrogen which is labile and form nitrolic acid.



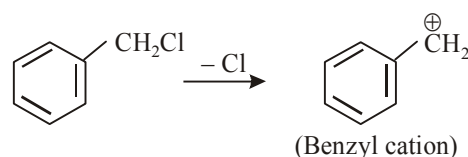
62. (a).



63. (d) Benzoic acid, camphor and naphthalene sublime on heating hence, they are purified by sublimation method.
64. (d) Due to +I-effect of the CH_3 group, toluene has much higher electron density in the ring than benzene, nitrobenzene and benzoic acid as they show –I-effect and hence is most reactive towards nitration.
65. (c) Compound given in option (c) is the only compound which do not have any chiral carbon atom. Thus, it is achiral i.e. do not show optical activity.
66. (b) In the presence of UV rays or energy, by boiling chlorine, free radical is generated which attack the methyl carbon atom of the toluene.

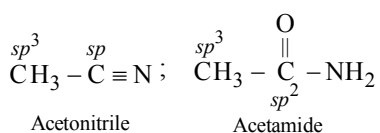
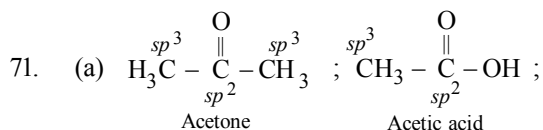


67. (d) $\text{S}_{\text{N}}1$ reactions involve the formation of carbocation, more is stability of carbocation, higher will be the probability of alkyl halide to undergo $\text{S}_{\text{N}}1$ mechanism. Thus decreasing order of $\text{S}_{\text{N}}1$ mechanisms follows order Benzyl > allyl > tertiary alkyl halide > secondary alkyl halide > primary alkyl halides

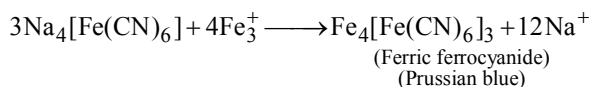
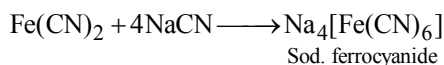
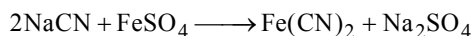
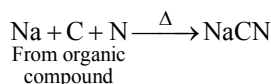


Obtained from $\text{S}_{\text{N}}1$ path. This molecule is resonance stabilised.

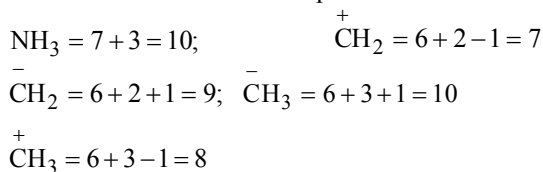
68. (d) Styrene can be purified by vacuum distillation.
69. (a) Among the three given hybrid orbitals, sp hybrid orbital is most electronegative. Contribution of s in sp hybrid orbital is maximum so this orbital is closer to nucleus. Naturally it will have greater tendency to pull electron towards it. Hence it becomes more electronegative and sp^3 becomes least electronegative.
70. (b) It is a coupling reaction of diazonium salt. In it the aromatic ring undergoing attack by diazonium ion must contain a powerful electron releasing group, generally $-OH$, $-NR_2$, $-NHR$ or $-NH_2$. Substitution usually secures para- to the activating group. It has been established experimentally that coupling is electrophilic aromatic substitutions.



72. (c) Cl^- is the best leaving group among the given option.
73. (b) The order of stability of free radicals
 $(\text{C}_6\text{H}_5)_3\dot{\text{C}} > (\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{H} > (\text{CH}_3)_3\dot{\text{C}} > (\text{CH}_3)_2\dot{\text{C}}\text{H}$
 The stabilisation of first two is due to resonance and last two is due to inductive effect.
74. (d) Steam distillation is used for the purification of volatile compounds.
75. (c) The strength of nucleophile depends upon the nature of alkyl group R on which nucleophile has to attack and also on the nature of solvent. The order of strength of nucleophiles follows the order :
 $\text{CN}^- > \text{I}^- > \text{C}_6\text{H}_5\text{O}^- > \text{OH}^- > \text{Br}^- > \text{Cl}^-$
76. (c) CF_3COOH has highest acidity due to $-I$ effect of F.
77. (b) The chemistry of the Lassaigne's test of nitrogen is

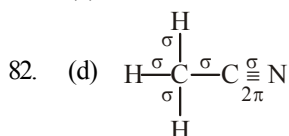


78. (c) Isoelectronic species has same number of electrons. No. of electrons in different species



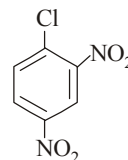
79. (a) In present case, $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ is the only group whose key atom (atom attached to benzene carbon) is having a multiple bond (one of the characteristics of m -directing groups).
80. (d) Due to +M effect of the $-\text{OH}$ group in phenol, electron density in the ortho and para positions of the phenol nucleus increases hence phenol will undergo electrophilic substitution easily than benzene. The other three compounds have electron withdrawing groups, hence they will undergo electrophilic substitution with a difficulty than benzene.

81. (d)



Therefore, the number of σ and π bonds in acetonitrile are 5 and 2 respectively.

83. (c) An asymmetric carbon atom is that in which all different groups are attached with carbon. Option (c) is correct.
84. (b) Electrophiles are electron deficient or positively charged species.
85. (b)
86. (b) Methyl carbanion is sp^3 hybridised, with three bond pairs and one lone pair same is the case with NH_3 .
87. (d) $-\text{NO}_2$ group is electron attractive group, so it is able to deactivate the benzene ring.

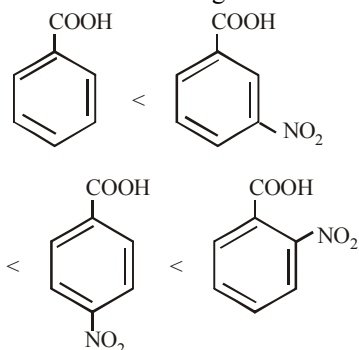


hence withdrawal of electrons from ortho and para position cause easy removal of $-\text{Cl}$ atom due to development of +ve charge on o - and p positions.

88. (d) Optical inactivity due to internal compensation is exhibited by meso-tartaric acid. Option (d) is correct.
89. (a) Electron withdrawing group ($-\text{NO}_2$) increases acidity while electron releasing group ($-\text{CH}_3$, $-\text{H}$) decreases acidity. Also effect will be more if functional group present at para position then ortho and then meta.
90. (d) Absolute alcohol cannot be obtained by simple fractional distillation because a Constant boiling azeotropic mixture is formed. It is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% of ethanol. This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapour composition is exactly the same as the liquid.
91. (c) Simple distillation is suitable for liquids which boil without decomposition at atmospheric pressure. In case of liquids which decompose before their boiling point is reached, vacuum distillation is used. Glycerine decomposes at its boiling point (298°C) but can be distilled unchanged at 12 mm pressure at 180°C .

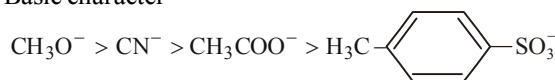
92. (d) In aromatic acids presence of electron withdrawing substituent e.g. $-\text{NO}_2$ disperses the negative charge of the anion and stabilises it and hence increases the acidity of the parent benzoic acid.

Further o-isomer will have higher acidity than corresponding m and p isomers. Since nitro group at p-position have more pronounced electron withdrawing than NO_2 group at m-position hence the correct order is the one given above.



93. (b) The stronger the base the more is the nucleophilic character and vice versa.

Basic character



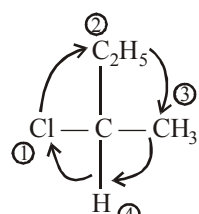
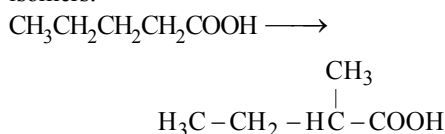
94. (a) 1,2-dihydroxybutane has longest carbon atom chain of 4 atoms and OH groups attached on it at first and second carbon atoms. So the choice (a) is correct.

95. (b) – I group destabilises carbocation and since inductive effect decreases with increasing length of carbon chain. Therefore (b) is the correct option.

96. (b) Being immiscible liquids, they form different layers hence can be separated with the help of separating funnel.

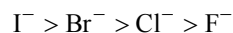
97. (c) Simple distillation can be applied for the separation and purification of a mixture of two or more liquids provided their boiling points differ at least by 30 K. In such cases, the low boiling (more volatile) liquid of the mixture will distil over first. The temperature of the distillation flask is then raised when high boiling (less volatile) liquid of the mixture will distil, it is collected in a separate flask.

98. (c) Pentanoic acid and 2-methyl butanoic acid are chain isomers.

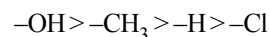


R-configuration

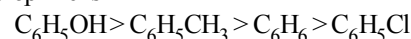
100. (a) Nucleophilicity increases down the periodic table.



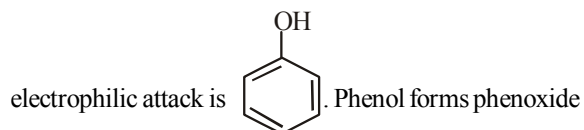
101. (c) Electrophiles have high affinity for electrons. They attack at the site where electron-density is highest. Electron donating groups increases the electron density. The electron donating tendency decreases in the order :



Therefore, the correct order of reactivity towards electrophile is

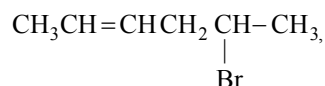


102. (c) Out of the given compounds the most reactive towards



ion which is stable due to resonance i.e. the correct answer is option (c).

103. (a) In the molecule



the number of stereoisomers is given by sum of geometrical isomers (because of presence of $C = C$) and optical isomers (because of presence of chiral carbon atom).

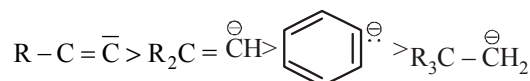
Number of geometrical isomers = 2 (one C = C is present).

Number of optical isomers = 2 (one chiral carbon atom).

Total number of stereoisomers = $2 + 2 = 4$

104. (d) The stability of carbanions is affected due to resonance, inductive effect and s - character of orbitals. Greater the number of groups having + I group (alkyl group) lesser stable would be the carbanion.

Further stability of carbanion decreases with decrease in s-character. Benzene carbanions are stabilized due to resonance, hence the correct order is



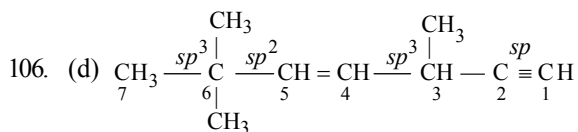
The correct order of stability of given carbanion is in the order I > III > II > IV.

105. (b) C-1 is sp hybridized ($C \equiv C$)

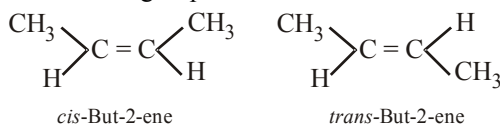
C-3 is sp^3 hybridized (C-C)

C-5 is sp^2 hybridized (C=C)

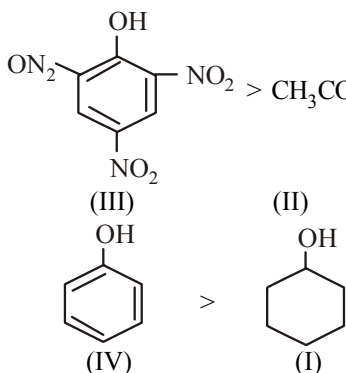
Thus the correct sequence is sp, sp^3, sp^2 .



107. (d) Alkenes with double bonds cannot undergo free rotation and can have different geometrical shapes with two different groups on each end of the double bond.



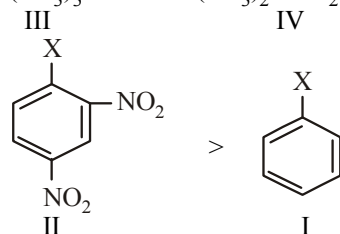
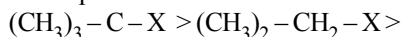
108. (a) Oc1cc([N+](=O)[O-])cc([N+](=O)[O-])cc1[N+](=O)[O-] > CC(=O)O >



Explanation : Presence of three —NO₂ groups in *o*-, *p*- positions to phenolic groups (in III) makes phenol strongly acidic because its corresponding conjugate base is highly stabilised due to resonance. Conjugate base of CH₃COOH, II (*i.e.* CH₃COO⁻) is resonance hybrid of two equivalent structures. The conjugate base of phenol, IV is stabilized due to resonance (note that here all resonating structures are not equivalent). The conjugate base of cyclohexanol, I does not exhibit resonance, hence not formed.

109. (a) Tertiary alkyl halide is most reactive towards nucleophilic substitution because the corresponding carbocation (3°) is most stable. Aryl halide is least reactive due to partial double bond character of the C — Cl bond.

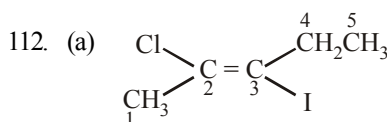
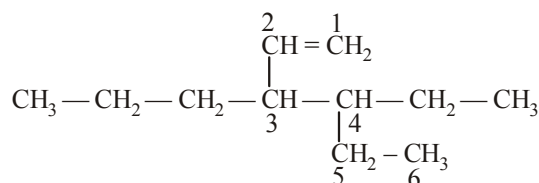
Presence of —NO₂ groups in *ortho* and *para* positions increases the reactivity of the —Cl towards nucleophiles.



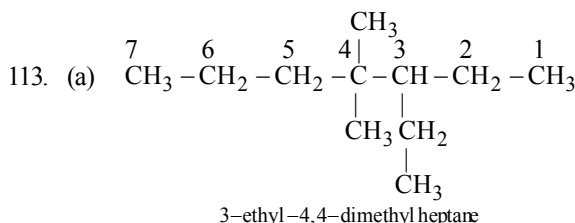
or I < II < IV < III

110. (d) Cl⁻ is the weakest base and hence better leaving group

111. (a) The given compound is

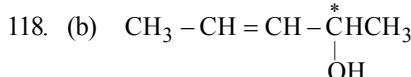
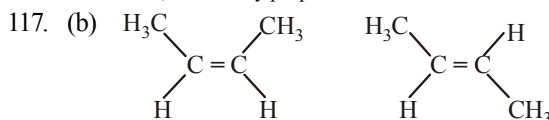
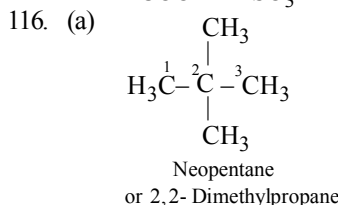
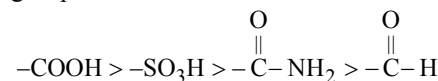


Correct IUPAC name of above compound is *trans*-2-chloro-3-iodo-2-pentene



114. (a) Nitro group is electron withdrawing group, so it deactivates the ring towards electrophilic substitution.

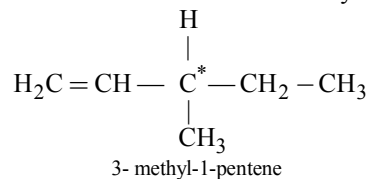
115. (a) The correct order of priority for the given functional group is



exhibits both geometrical as well as optical isomerism.

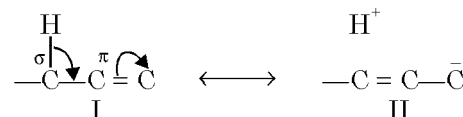
cis - R *cis* - S
trans - R *trans* - S

119. (c) For a compound to show optical isomerism, presence of chiral carbon atom is a necessary condition.



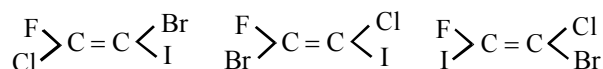
120. (b) —CN has highest priority. Further the sum of locants is 7 in (b) and 9 in (d).

121. (b) Alkyl groups with at least one hydrogen atom on the α-carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.



Note that the delocalisation involves σ and π bond orbitals (or *p* orbitals in case of free radicals) ; thus it is also known as σ — π conjugation. This type of *electron release due to the presence of the system H—C—C=C* is known as hyperconjugation

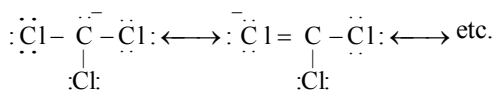
122. (b) Allene (C_3H_4) is $H_2\overset{sp^2}{C}=\overset{sp}{C}=\overset{sp^2}{CH_2}$
123. (b) Chiral conformation will not have plane of symmetry. Since twist boat does not have plane of symmetry it is chiral.
124. (d) Methyl group can't produce electromeric and resonance effects. Inductive effect affects all the three positions of the ring in decreasing order of *ortho* > *meta* > *para*. It shows hyperconjugation (no-bond resonance) which explains beautifully the *o*, *p*-directing influence of the $-CH_3$ group.
125. (d) Taking any two halogens, the possible structural isomers for the alkene can be three.



Each of the three alkene can exist as *E* and *Z* isomer, making total number of isomers as six.

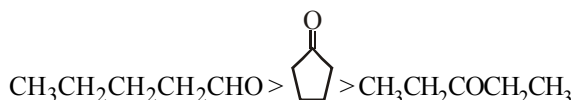
EXERCISE - 2

1. (b) A *cis*-isomer has higher b.p. due to polar (or more polar) nature but lower m.p. due to asymmetry than the *trans*-isomer. Among three isomeric nitrophenols, *o*-isomer forms intramolecular bonding so H-bonding with water will be restricted.
2. (d) Due to resonance of lone pair.
3. (a) Due to resonance conjugated alkadiene is maximum stable. Isolated is more stable than cumulated alkadiene.
4. (a) NH_2OH is less basic than NH_3 because of $-I$ effect of OH . However $^-CF_3$ is more basic than $^-CCl_3$ because in $^-CCl_3$ the unshared electron pair of C in the *p* orbital undergoes extended *p-d* bonding into an empty *d* AO of the three chlorines, hence it is less available for protonation.

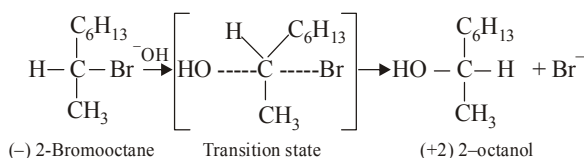


Since F lies in the 2nd period, it has no *d* orbital, hence such dispersal of electrons of C is not possible. Remember resonance stabilization is generally more important than the inductive effect.

5. (c) More is the electron - deficiency on the carbonyl carbon, greater will be the reactivity of the carbonyl compounds towards nucleophilic addition.

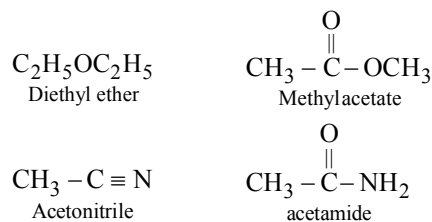


6. (d) When (–) 2-bromooctane is allowed to react with sodium hydroxide under conditions, where second order kinetics are followed, (+) 2-octanol is obtained.



In this reaction Walden Inversion takes place so it is an example of S_N2 -reaction.

7. (b) Peroxide ion is more nucleophilic but less basic than OH^- .
8. (d) $-OCH_3$ activates the benzene ring. $-NO_2$ deactivates the ring. Hence the reaction of the given compounds with electrophiles is in the order, I > II > III.
9. (c) The compound is diethyl ether $(CH_3CH_2)_2O$ which is resistant to nucleophilic attack by hydroxyl ion due to absence of double or triple bond, whereas all other compounds given are unsaturated

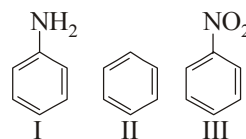


10. (c) The atom or group which has more power to attract electrons in comparison to hydrogen is said to have $-I$ effect. Thus higher the electronegativity of atom stronger will be the $-I$ effect. As electronegativity of N, O and F follow the order $N < O < F$ hence based upon electronegative character order of $-I$ effect is $-NR_2 < -OR < -F$.
11. (d) All statements are true.
12. (b) Stability of an alkene depends upon the heat of hydrogenation of an alkene. The heat of hydration is the standard enthalpy change in hydrogenation of an alkene. The lower the heat of hydrogenation of an alkene higher will be stability.

Order of stability Heat of hydrogenation

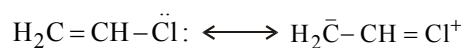
	(kJ/mol)
trans-2-butene	–115.5
cis-2-butene	–119.6 and
1-butene	–126.8 respectively.

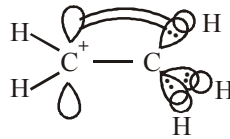
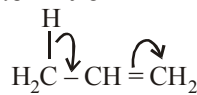
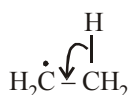
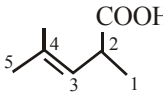
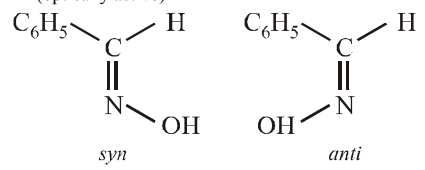
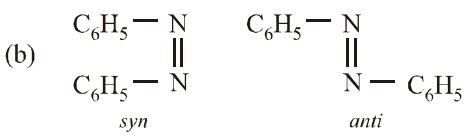
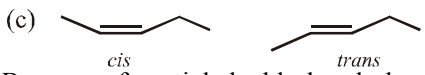
13. (a) Amino group is activating while nitro group is deactivating. Hence, correct order is aniline > benzene > nitrobenzene. I > II > III

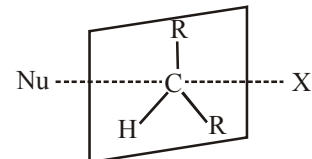


$-NO_2$ is an electron attracting group hence decrease the electron density on ring, whereas $-NH_2$ group is electron releasing group hence increases electron density on ring. Benzene is also electron rich due to delocalization of electrons.

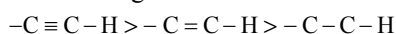
14. (b) $H_2C=CHCl$ is capable of showing resonance which develops a partial double bond character on C–Cl bond, thereby making it less reactive toward nucleophilic substitution.



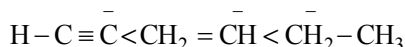
15. (a) 
Carbocation Alkyl group
Hyperconjugation in CH_2CH_3
- 
Hyperconjugation in propene
- 
Hyperconjugation in free radical
16. (b) HCOO^- exists in following resonating structures
- $$\text{H}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}^- \leftrightarrow \text{H}-\overset{\overset{\text{O}^-}{\parallel}}{\text{C}}=\text{O}$$
- Hence in it both the carbon oxygen bonds are found equal.
17. (d) Lone pair of electrons present on the nitrogen of benzyl amine is not involved in resonance.
18. (b) . Here C_2 is chiral, hence optical isomerism is possible. However, the doubly bonded C_4 has two similar ($-\text{CH}_3$) groups, hence geometrical isomerism is not possible.
19. (c) Metamerism shown among compounds of the same functional group.
20. (c) The stronger the acid, the weaker the conjugate base formed.
The acid character follows the order :
 $\text{CH}_3\text{COOH} > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{CH}_3\text{OH}$
The basic character will follow the order
 $\text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^- < \text{OH}^- < \text{CH}_3\text{O}^-$
Hence, decreasing order of rate of given reactions with Nu^- is
 $\text{D} > \text{C} > \text{A} > \text{B}$
21. (d)
22. (a) $\text{CH}_3^* \text{CH}(\text{OH})\text{COOH} \xrightarrow[-\text{H}]{+\text{OH}} \text{CH}_3\text{CH}(\text{H})\text{COOH}$
Lactic acid No chiral carbon
Chiral carbon is present (optically inactive)
(optically active)
23. (d) (a) 
syn *anti*
- (b) 
syn *anti*
- (c) 
cis *trans*
24. (c) Because of partial double bond character (due to resonance), C – H bond energy is less for toluene.

25. (b) $\% \text{ of chlorine} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl}}{\text{Mass of substance}} \times 100$
 $= \frac{35.5}{143.5} \times \frac{0.287}{0.099} \times 100 = 71.71\%$
26. (b) Carboxylic acids are stronger acids than $-\text{NH}_3^+$ because the corresponding conjugate base ($-\text{COO}^-$) is more stable than $-\text{NH}_2$. Hence Y is the strongest acid. Since $-\text{COOH}$ has $-I$ effect which decreases with distance, therefore, effect is more pronounced in Z than in X. As a result, Z is more acidic than X. Hence the true option is $\text{Y} > \text{Z} > \text{X}$.
27. (c) Shape of transition state is as follows:
- 
Trigonal bipyramidal
28. (c) $\text{C}_6\text{H}_5\text{CH}_2^+ > \text{CH}_3\text{C}^+(\text{CH}_3)_2 > \text{FCH}_2\text{CH}_2\text{CH}^+(\text{CH}_3) > \text{FCH}_2\text{CH}^+(\text{CH}_3)$
Benzyl 3° 2° (more stable)
- F is more away from +ve charge
29. (d) Order of stability of carbocation $3^\circ > 2^\circ > 1^\circ$ and I is the best leaving group among halogens.
30. (d) Since diazo compounds may lose nitrogen in the form of nitrogen gas, they sometimes do not respond Lassaigne's test for nitrogen.
31. (d) Lone pair present at X can enter in the ring. This gives rise to double bond character in C – X bond attached to the ring.
32. (a) In given structures –
After releasing H^+ from (ii) group it forms a more stable resonating structure of carboxylate ion. In case of (i) the anion formed after release of H^+ is more stable due to presence of e^- withdrawing NO_2 in benzene ring. In (iii) phenoxide ion formed after release of H^+ is more stable in comparison to Acetylide ion of group (iv) which is formed after releasing of (iv) H^+ ion so acidic structure of K_a is
 $(\text{ii}) > (\text{i}) > (\text{iii}) > (\text{iv})$
33. (b)
34. (d) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] + \text{S}^{2-} \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$
Sodium thio-nitroprusside
(violet)
35. (d) The amount of s-character in various hybrid orbitals is as follows.
 $sp = 50\%$, $sp^2 = 33\%$ and $sp^3 = 25\%$

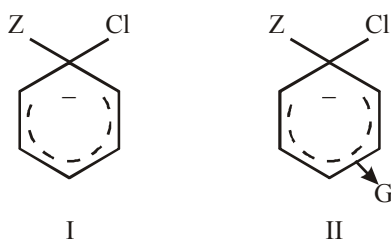
Therefore s character of the C – H bond in acetylene (sp) is greater than that of the C – H bond in alkene (sp^2 hybridized) which in turn has greater s character of the C – H bond than in alkanes. Thus owing to a high s character of the C – H bond in alkynes, the electrons constituting this bond are more strongly held by the carbon nucleus with the result the hydrogen present on such a carbon atom can be easily removed as proton. The acidic nature of three types of C – H bonds follows the following order



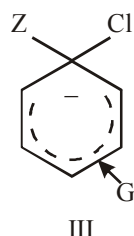
Further, as we know that conjugate base of a strong acid is a weak base, hence the correct order of basicity is



36. (b) Due to +M effect of –OH group and hyperconjugation of –CH₃ group.
37. (c) Because of high electronegativities of the halogen atom, the carbon halogen (C – X) is highly polarised covalent bond. Thus, the carbon atom of the C – X bond becomes a good site for attack by nucleophiles (electron rich species). Nucleophilic substitution reactions are the most common reactions of alkyl halides.
38. (a) In S_NAr reactions, a carbanion is formed as an intermediate, so any substituent that increases the stability of carbanion and hence the transition state leading to its formation will enhance the S_NAr reactions. To compare the rates of substitution in chlorobenzene, chlorobenzene having electron-withdrawing group, and chlorobenzene having electron-releasing group, we compare the structures carbanion I (from chlorobenzene), II (from chlorobenzene containing electron-withdrawing group) and III (from chlorobenzene containing electron-releasing group).



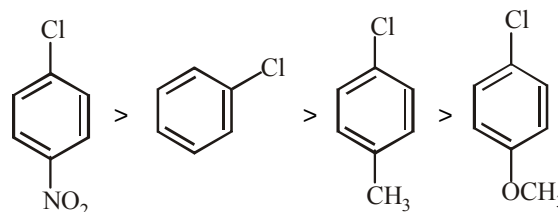
G withdraws electrons, neutralises (disperses) –ve charge of the ring, stabilises carbanion, facilitates S_N reaction (activation effect)



G releases electrons, intensifies –ve charge, destabilizes carbanion, retards S_N reaction (deactivation)

NO_2 is activating group and CH_3 and OCH_3 are deactivating group.

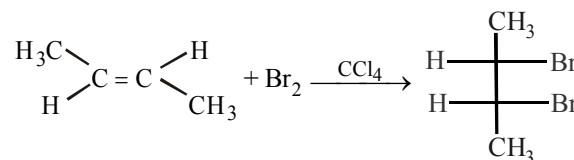
Hence, the correct order of nucleophilic substitution reactions



39. (b) The organic compounds which have chiral carbon atom (a carbon atom attached to four different group or atoms and do not have plane of symmetry rotate plane polarised light.
- $$\begin{array}{c} \text{CHO} \\ | \\ \text{HO}-\text{C}^*-\text{H} \\ | \\ \text{CH}_2\text{OH} \end{array} \quad (\text{C}^* \text{ is asymmetric carbon})$$
40. (b) The absolute configuration is (R, R) (using priority rules to get the absolute configuration) So the correct answer is (b)
41. (b) In option (b) the complex formed is with benzene whereas in other cases it is formed with nitrobenzene with $-NO_2$ group in different position (*o*-, *m*-, *p*-). The complex formed with nitrobenzene in any position of $-NO_2$ group is less stable than the complex formed with benzene so the correct answer is (b). The most stable complex has lowest energy.

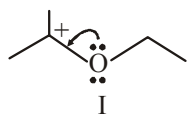
42. (b) $\begin{array}{c} \text{Cl} \\ | \\ \text{C}^--\text{Cl} \\ | \\ \text{Cl} \end{array} > \text{C}_6\text{H}_5\text{CH}_2^- > (\text{CH}_3)_2\text{CH}^- > (\text{CH}_3)_3\text{C}^-$
- $\begin{array}{ccc} \text{–ve charge} & \text{–M effect} & \text{+I effect of } \text{CH}_3 \text{ group} \\ \text{highly dispersed} & \text{delocalises} & \text{intensifies the –ve charge} \\ \text{due to –I effect} & \text{–ve charge} & \end{array}$

43. (d) The correct order of basicity is $\text{RCOO}^- < \text{CH} \equiv \text{C}^- < \text{NH}_2^- < \text{R}^-$
44. (a) Due to similar charges on adjacent atoms, the structure (a) is least stable.
45. (a) Anti addition of Br_2 on *trans* alkene provides meso compound.

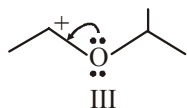


Therefore, no. of stereoisomers = 1

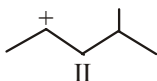
46. (d) The correct stability order is $\text{I} > \text{III} > \text{II} > \text{IV}$



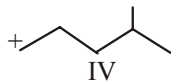
+ M effect, 6 hyperconjugative H's, 2 CH₃ groups (+ I effect)



+ M, 3 hyperconjugative H's, one CH₃ group

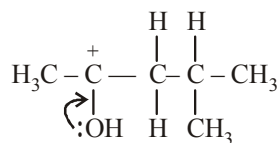
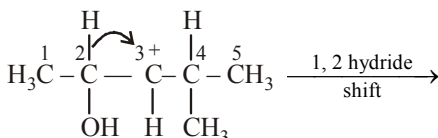


5 hyperconjugative H's 2 R groups



5 hyperconjugative H's one R group

47. (d) Migrating tendency of hydride is greater than that of alkyl group. Further migration of hydride from C-2 gives more stable carbocation (stabilized by +R effect of OH group and +I and hyperconjugative effects of methyl group).



More stable carbocation

48. (a) It is fact that aniline is better nucleophile than anilium ion. Anilium ion contain +ve charge, which reduces the tendency to donate lone pair of electron C₆H₅NH₃⁺.

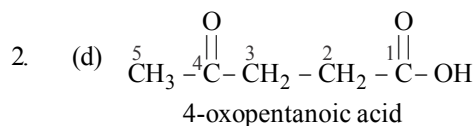
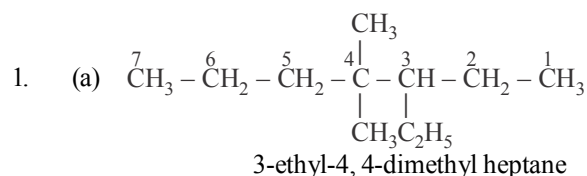
Anilium ion

Therefore, both assertion and reason are true.

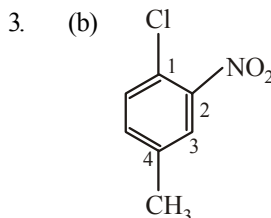
49. (c) The assertion that trans-2 butene reacts with Br₂ to product meso-2, 3-dibromobutane is correct but it does not involve syn-addition of Br₂.
50. (d) Resonance structures contain the same number of unpaired electrons. However, they differ in the way of distribution of electrons.

EXERCISE - 3

Exemplar Questions



Note : Carboxylic acid (—COOH) has more priority than ketone (>C=O).



1-chloro-4-methyl-2-nitrobenzene

For tri or higher substituted benzene derivatives, the compounds are named by identifying substituent positions on the ring by following the lowest locant rule.

4. (c) Electronegativity of carbon atom depends on its state of hybridisation. More the *s*-character more will be the electronegativity.

$$sp^3 < sp^2 < sp$$

s-character : 25% 33% 50%

Thus, *sp*-carbon (CH₃—CH₂—C≡CH) has the highest electronegativity.

5. (c) Two or more compounds having the same molecular formula but different functional groups are called functional isomers. Functional isomer of alcohol is ether, aldehyde is ketone and cyanide is isocyanide. But alkyl halides do not show functional isomerism.

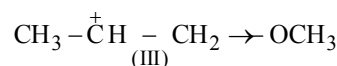
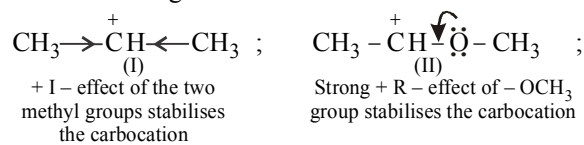
6. (d) Essential oils are insoluble in water and have high vapour pressure at 373K but are miscible with water vapour in vapour phase, it means these are steam volatile. Thus, steam distillation technique is a suitable method for the extraction of essential oils.

7. (d) Thin layer chromatography (TLC) involves separation of substances of a mixture over a thin layer of an adsorbent coated on a glass plate.

A thin layer of an adsorbent is spread over a glass plate and glass plate is placed in an eluant. As eluant rises, components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. Therefore, TLC technique will give the best results in identifying the different types of ink used at different places in the documents.

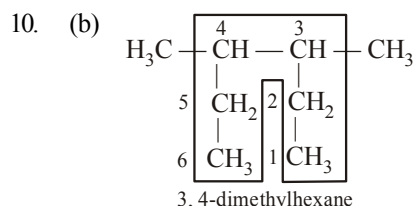
8. (b) Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

9. (a) Stability of the given cations can be understood by the following structures:



—I effect of —OCH₃ group destabilises the carbocation

Hence, the correct order of decreasing stability of carbocation will be : II > I > III

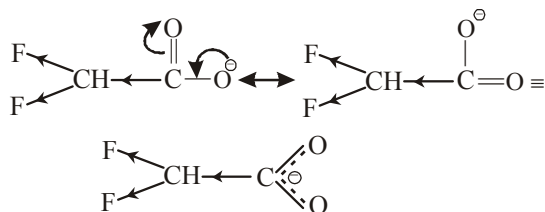


11. (a) Electronegativity of Cl, Br, C and Mg follows the order $\text{Cl} > \text{Br} > \text{C} > \text{Mg}$, thus chlorine has the greatest -I-effect and disperse the positive charge on 'C' atom most effectively.

Hence, $^*\text{CH}_3 - \text{CH}_2 - \text{Cl}$ has the greatest positive charge.

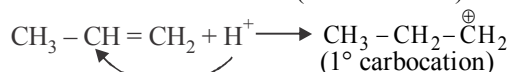
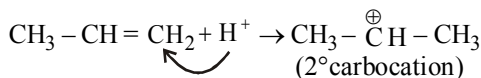
12. (d) In all the given ionic species, the negative charge is dispersed which stabilises them. Here, the negative charge is dispersed by two factors, i.e., +R-effect of the carboxylate ion (conjugation) and -I-effect of the halogens.

As it can be clearly seen in the given structures, that +R-effect is common in all the four species, therefore, overall dispersal of negative charge depends upon the number of halogen atoms and their electronegativity. Since, Fluorine has the highest electronegativity and two F-atoms are present in option (d), thus, dispersal of negative charge will be maximum in it, thus it is most stable.



Note : In structure (a), methyl group increases the density on C-atom.

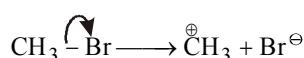
13. (c) When an electrophile attacks $\text{CH}_3 - \text{CH} = \text{CH}_2$, there are two possibilities of an intermediate formed:



As 2° carbocation is more stable than 1° carbocation thus first addition is more feasible.

Note : Stability of carbocations is the basis of Markownikoff's rule.

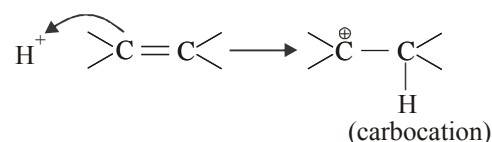
14. (b) Arrow denotes the direction of movement of electrons.



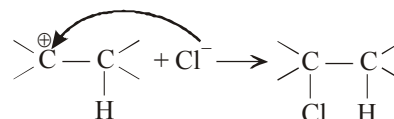
Since, Br is more electronegative than carbon, hence heterolytic fission occurs in such a way that CH_3 gets a positive charge and Br gets a negative charge.

15. (b) Addition of HCl to an alkene takes place in two steps as follows:

Step I : π -bonds creates an electron cloud, electrophile (H^+) from $\text{H} - \text{Cl}$ attacks the electron cloud and a carbocation is formed.



Step II : The chloride ion attacks the carbocation formed.

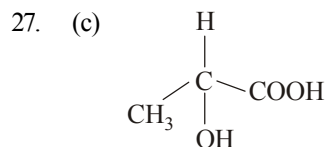


NEET/AIPMT (2013-2017) Questions

16. (a)
-
- IUPAC name of the structure is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid
17. (c) Decreasing order of deactivating effect of the given *m*-directing group is
 $\text{NO}_2 > -\text{CN} > -\text{SO}_3\text{H} > -\text{COOH}$
 $-\text{NO}_2$ group is most deactivating group due to strong -E, -I and -M effects.
18. (b) $-\text{NO}_2$ is a powerful electron withdrawing group. Its presence on ring makes the ring less active.
19. (d)
-
20. (b) Greater the number of e^- donating alkyl groups (+I effect), greater will be the stability of carbocations.
21. (c) Conformers are form of stereoisomers in which isomers can be interconverted by rotation about single bonds. I and II are staggered and eclipsed conformers respectively.
22. (c) Stability depends on number of hyperconjugative structure.
23. (b) In the carbonium ion the carbon atom carrying the positive charge is sp^2 hybridized.
24. (c) The prussian ferric ferrocyanide blue colour is of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
26. (N) Out of the given four compounds only (iv) compound is chiral and hence only this compound will undergo racemisation. Therefore none of the given option is correct.
26. (a) 10 ml, 1 M $\text{H}_2\text{SO}_4 = 20 \text{ ml}$, 1 M NH_3
 $\therefore$ wt of N in one mole $\text{NH}_3 = 14$
 $\therefore 20 \times 10^{-3} \text{ mol NH}_3 \longrightarrow 20 \times 10^{-3} \times 14 \text{ nitrogen}$

∴ 0.75 g of sample contains

$$= \frac{14 \times 20 \times 10^{-3}}{0.75} \times 100 = 37.33\%$$

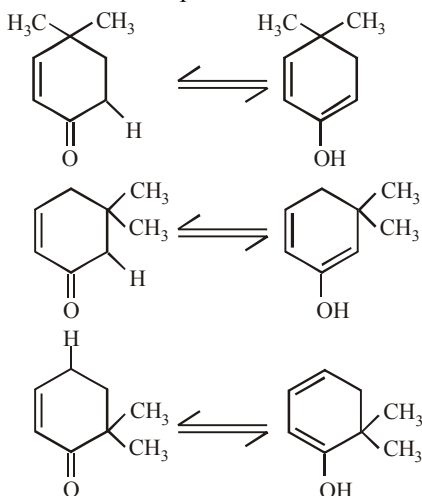


Four different Substituent, only one chiral centre.

Hence only enantiomers are possible.

28. (a) Nucleophile is a species that provide electron while species which are deficient of electrons termed as lewis acid, hence nucleophiles are usually lewis bases.

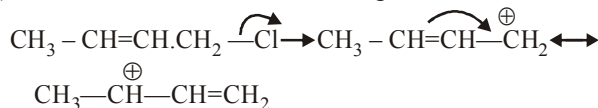
29. (c) All of these compounds show tautomerism



30. (b) Only structure (III) has hyperconjugation with free radical.

So, hyperconjugation is possible in III only.

31. (b) π bond is transferred after leaving Cl^-



32. (b) Wt. of organic substance = 0.25 g

$$V_1 = 40 \text{ mL}, T_1 = 300 \text{ K}$$

$$P_1 = 725 - 25 = 700 \text{ mm of Hg}$$

$$P_2 = 760 \text{ mm of Hg (at STP)}$$

$$T_2 = 273 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 (\text{Volume of nitrogen at STP})$$

$$= \frac{273 \times 700 \times 40}{300 \times 760} = 33.52 \text{ mL}$$

Percentage of nitrogen

$$= \frac{28 \times \text{volume of } \text{N}_2 \text{ at STP} \times 100}{22400 \times \text{wt. of organic substance}}$$

$$= \frac{28 \times 33.52 \times 100}{22400 \times 0.25} = 16.76\%$$

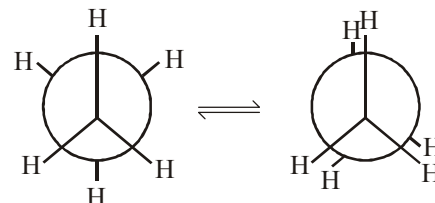
33. (d) $\text{CH}_3 - \text{C} \equiv \text{C}^\ominus$

$$\left[\begin{array}{l} \text{No. of } \sigma \text{ bp} - 1 \\ \ell_p - 1 \end{array} \right] 2 \text{ \& hybridisation is sp}$$

34. (b) is optically active

due to absence of plane of symmetry and center of symmetry.

35. (d) In staggered conformation any two hydrogen atoms on adjacent carbon atoms are as far apart as possible there by minimising repulsion between the electron clouds of σ -bonds of two non-bonded H-atomic (torsional strain)

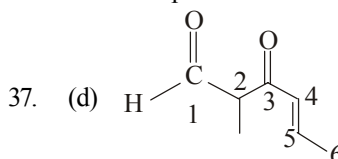


Staggered form

Eclipsed form

No torsional strain

36. (c) Steam distillation is the most suitable method of separation of 1 : 1 mixture of ortho and para nitrophenols as there is intramolecular hydrogen bonding in o-nitrophenol.



3-keto-2-methylhex-4-enal

Aldehydes get higher priority over ketone and alkene in numbering of principal carbon chain.

38. (c)

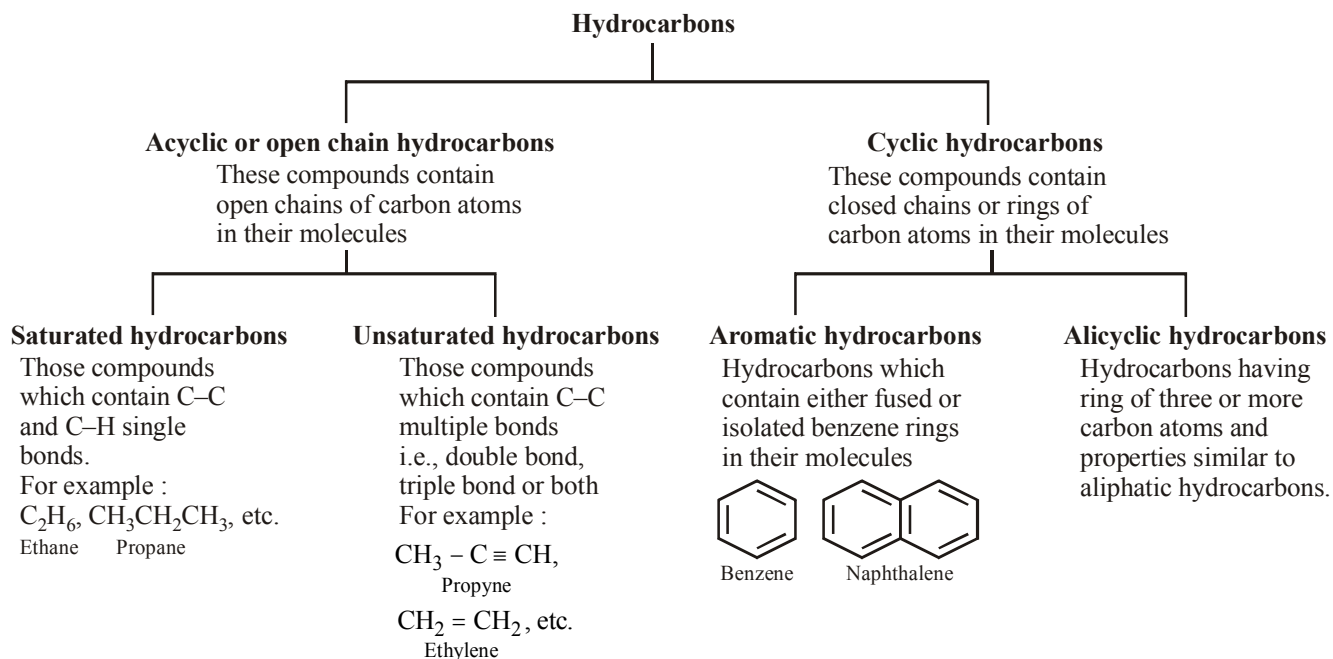
Chapter

13

Hydrocarbons

CLASSIFICATION OF HYDROCARBONS

Depending upon the types of carbon-carbon bonds present, hydrocarbons are classified as

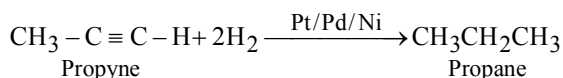
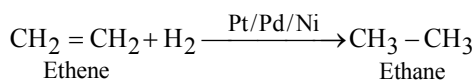
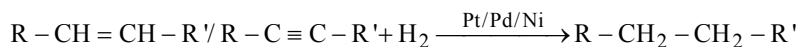


ALKANES

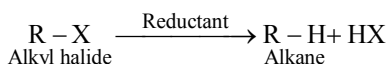
They have the general formula C_nH_{2n+2} . They exhibit structural and chain isomerism. All carbon atoms of alkanes are sp^3 hybridized.

Methods of Preparation

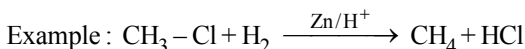
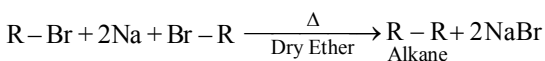
(i) From unsaturated hydrocarbons:



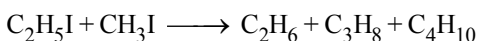
When the catalyst is Pt or Pd, the hydrogenation proceeds smoothly at ordinary temperature and pressure. With nickel as catalyst, higher temperature ($250^\circ - 300^\circ C$) and pressure are needed.

(ii) From alkyl halides:**(a) Reduction of Alkyl Halides :**

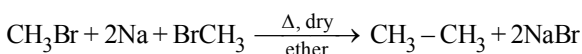
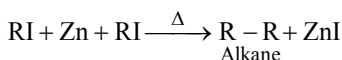
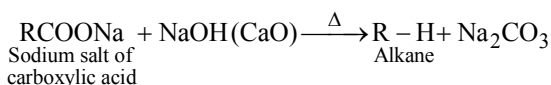
Reductants : Zn-Cu couple/EtOH, Na-EtOH, Zn-HCl, Pt or Pd or Ni/H₂, Al-Hg/EtOH, LiAlH₄ etc.

**(b) Wurtz Reaction :**

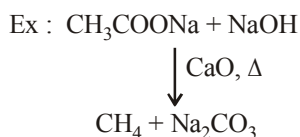
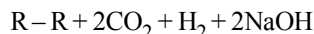
Methane cannot be prepared by this method. The alkane produced is higher and symmetrical. When the two reacting alkyl halides are different, a mixture of three different alkanes is obtained. The Wurtz reaction is not useful for preparing unsymmetrical alkanes.



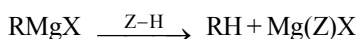
Example :

**(c) Frankland's reaction :****(iii) From carboxylic acids:****(a) Decarboxylation**

The reaction is employed for stepping down a homologous series.

**(b) Kolbe's electrolytic method**

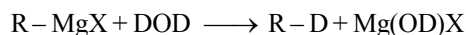
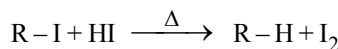
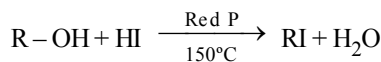
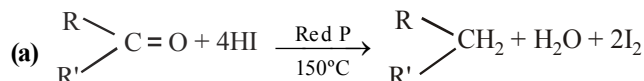
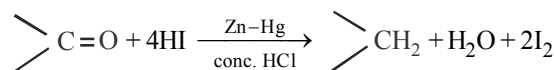
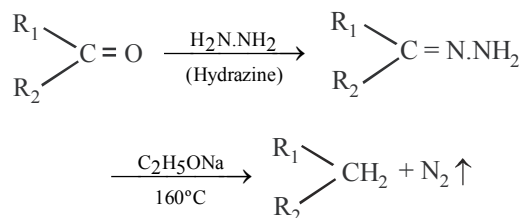
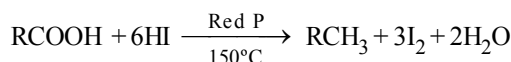
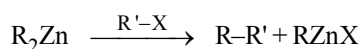
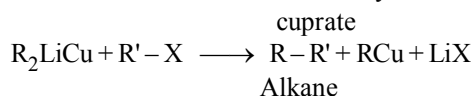
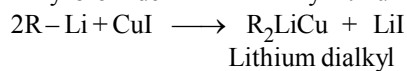
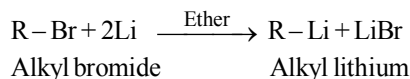
Methane cannot be prepared by this method. The side products are olefins, alcohols (particularly in alkaline solution) and esters. Presence of alkyl groups in α -position decreases the yield of alkane.

(iv) From Grignard reagent :

ZH [compound containing active hydrogen]. Ex :

HOH, NH₃, RC $\equiv$ CH, C₆H₅OH, CH₃COOH, RNH₂, R₂NH, Pyrrole, C₂H₅OH etc.

Note : If heavy water, D₂O, is used, then the product is deuterioalkane (R-D).

**(v) By the reduction of alcohols :****(vi) By the reduction of aldehydes and ketones :****(b) Clemmensen's reduction :****(c) Wolff-Kishner reduction :****(vii) By reduction of acids :****(viii) From dialkyl zinc :****(ix) Corey-House Synthesis :****Properties of Alkanes :****Physical properties :**

- (i) They are non-polar molecules.
- (ii) C₁ to C₄ - gases; C₅ to C₁₇ - liquids, C₁₈ and above solids.
- (iii) Being non-polar, they are soluble in non-polar solvents.
- (iv) **Boiling point :** The forces of attraction among the alkane molecules are the weakest van der Waal's forces of attraction as molecular mass increases, their van der Waal's forces of attraction also increases resulting in increases of B.Pt. Among isomeric alkanes, the boiling point decreases with increasing branching.

Ex. *n*-Pentane > iso-Pentane > neo-Pentane

(v) **Melting Point :**

Unbranched alkanes containing 2, 4, 6, 8 etc. carbon atoms have higher melting points than the unbranched alkanes containing 3, 5, 7, 9 etc. carbon atoms.

M.P. with even no. of carbon atoms >

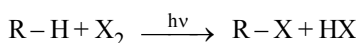
odd no. of carbon atoms

(vi) **Fuel Capacity :**

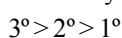
Decreasing order of fuel capacity is

more branched > less branched

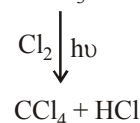
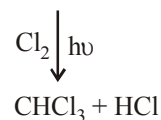
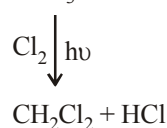
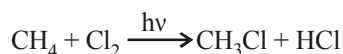
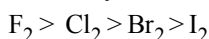
> unbranched and lower mol. wt. > higher mol. wt.

Chemical properties :(i) **Substitution reactions**(a) **Halogenation :**

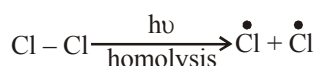
Reactivity order of hydrogen atoms in alkanes is



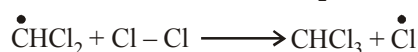
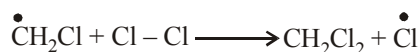
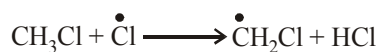
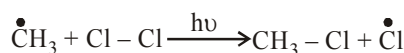
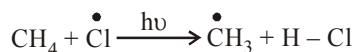
Reactivity order of halogens is

**Mechanism**

Step 1: Initiation :



Step 2: Propagation :



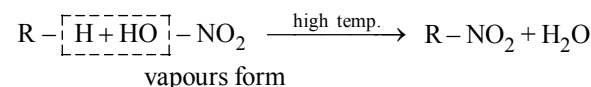
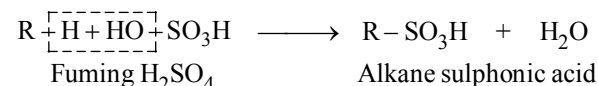
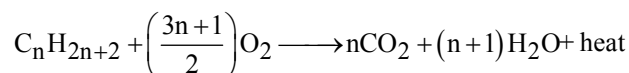
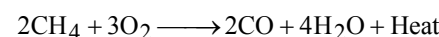
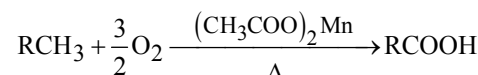
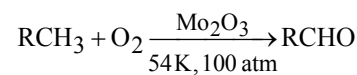
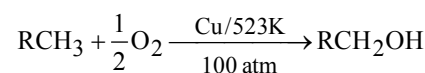
Step 3: Termination:



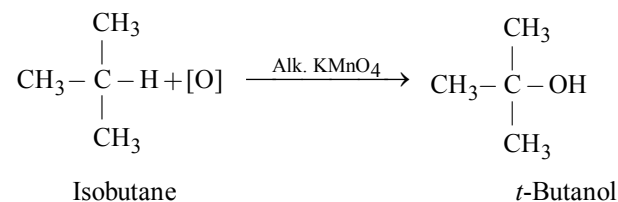
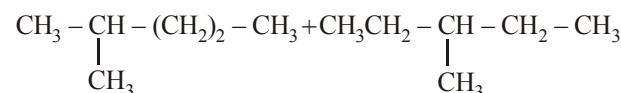
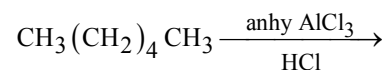
Note : Iodination of alkanes is reversible.



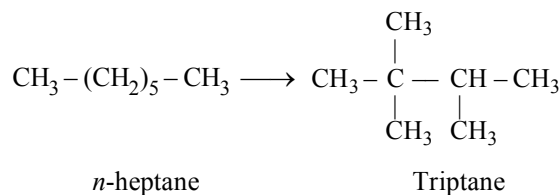
Iodination may be carried out in the presence of an oxidising agent such as HIO_3 , HNO_3 , HgO , etc. which destroys the HI as it is formed and so drives the reaction to the right.

(b) **Nitration :**(c) **Sulphonation :**(ii) **Combustion and oxidation**(a) **Complete combustion :**(b) **Incomplete combustion :**(c) **Controlled Oxidation**

Note : Strong oxidising agents such as $KMnO_4$ readily oxidise a $3^\circ H$ atom to a hydroxy group.

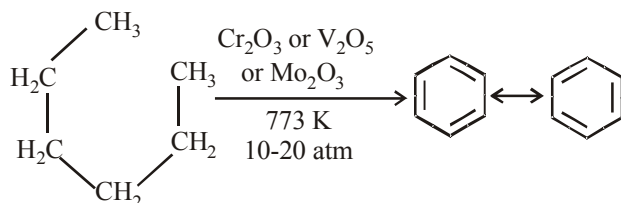
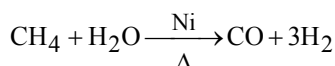
(iii) **Isomerisation**

For example : If we take *n*-heptane then it converts into more stable form triptane.

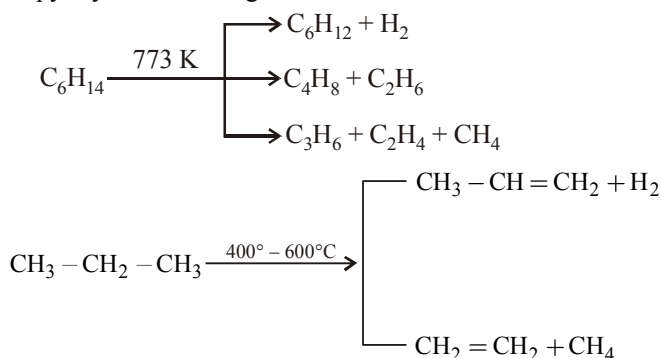


(iv) Aromatization

If an alkane having six or more carbon atoms is heated at 600°C in the presence of a catalyst such as Cr_2O_3 supported over alumina or Pt, an aromatic hydrocarbon results.

**(v) Reaction with steam****(vi) Pyrolysis :**

Decomposition of higher alkanes to lower alkanes is called pyrolysis or cracking.



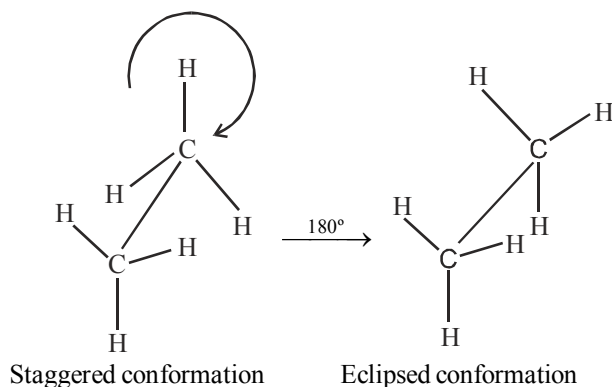
Cracking is used for manufacture of petrol, petrol gas, oil gas, etc.

Conformations

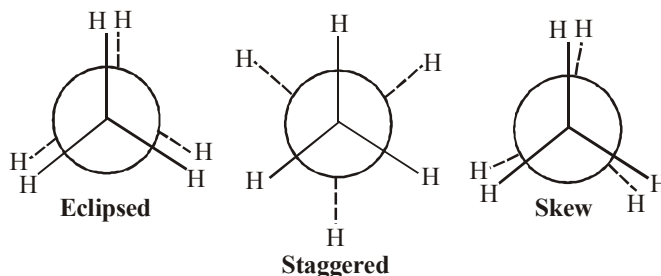
The spatial arrangement of atoms which can be converted into one another by rotation around a C–C single bond are called conformations or conformers or rotamers. If one CH_3 group of ethane is kept constant and other methyl group is rotated through C–C bond axis, an infinite no. of atomic arrangements are possible, which are called conformations.

The form in which H-atoms on the two carbons are as close as possible is called eclipsed. The form in which H-atoms on the two carbons are as far apart as possible is called staggered.

Example : Conformations of ethane ($\text{CH}_3 - \text{CH}_3$):

(i) Sawhorse projections:

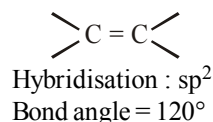
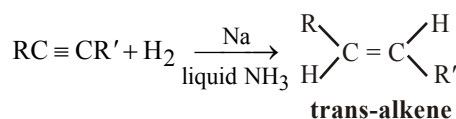
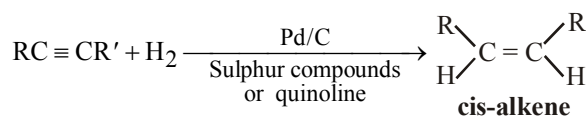
The infinite number of possible intermediate conformation between the two extreme conformation are referred to as skew conformations.

(ii) Newman Projections :

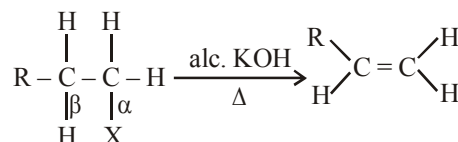
Relative stabilities of conformations: staggered form of ethane is more stable because the e^- clouds of C–H bonds are as far apart as possible and thus, the repulsions are minimum. In eclipsed form, e^- clouds come closer thus causing increase in repulsions. Thus, staggered form is more stable than eclipsed form.

ALKENES

They are unsaturated hydrocarbons containing at least one double bond. They have the general formula C_nH_{2n} . They exhibit chain and position isomerism (structural isomerism). Besides these, they also exhibit geometrical isomerism (stereoisomerism).

**Methods of Preparation****(i) From alkynes :****(ii) From alkyl halides: by β -elimination reaction**

Alkyl halides on reaction with alcoholic KOH or NaOH forms corresponding alkenes.



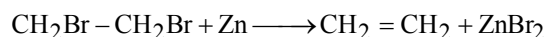
Reactivity of alkyl halides : $3^\circ > 2^\circ > 1^\circ$ halide

$\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$

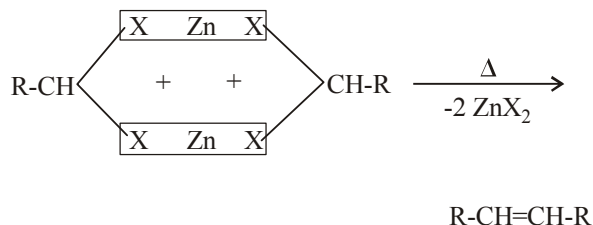
Saytzeff's rule : According to this rule, "the dehydrohalogenation of an alkyl halide results preferentially in the production of more alkylated alkene, i.e., more stable alkene."

(iii) from dihalides: by dehalogenation

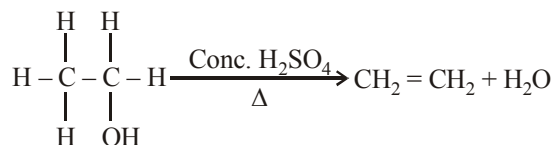
(a) From vicinal dihalides :



(b) From gem dihalides :



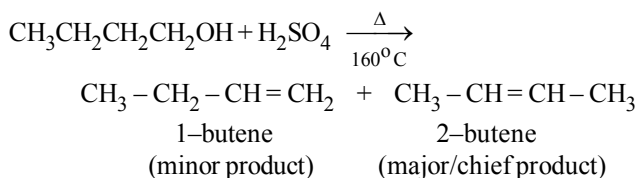
(iv) From alcohols by acidic dehydration:



Dehydrating agent :

conc. $\text{H}_2\text{SO}_4 \Rightarrow 170^\circ\text{C}$ temp. P_2O_5 or $\text{H}_3\text{PO}_4 \Rightarrow 200^\circ\text{C}$ $\text{Al}_2\text{O}_3 \Rightarrow 350^\circ\text{C}$

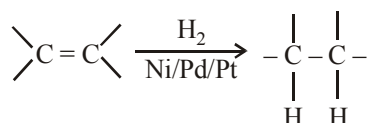
(vapour state)

Order of reactivity of alcohols : $= 3^\circ > 2^\circ > 1^\circ$ alcoholDehydration occurs according to Saytzeff's rule (β -elimination)**Properties of Alkenes****Physical properties :**

- The first three members are gases, next fourteen liquids and higher ones solids.
- They are insoluble in H_2O and soluble in organic solvents.
- Their boiling points, melting points and specific gravities rise with the increase of molecular weight. The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

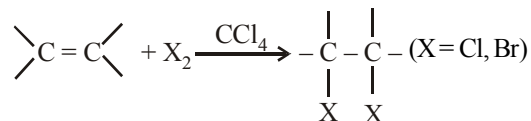
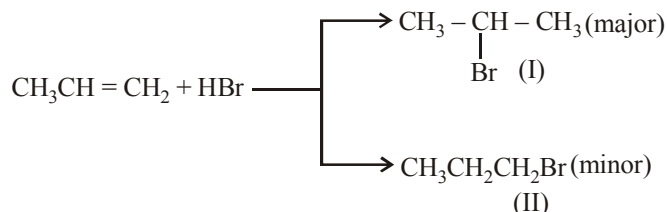
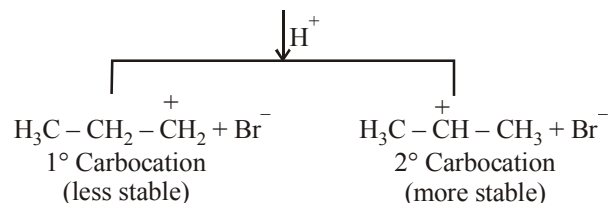
MP. and BP. $\propto$ mol. wt.

$$\propto \frac{1}{\text{branching in alkenes}}$$

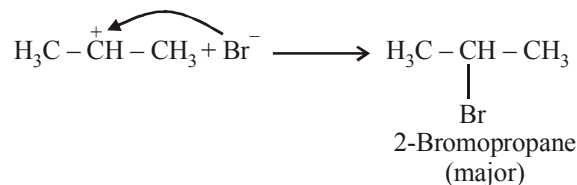
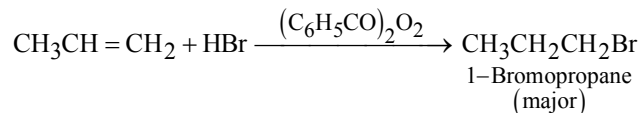
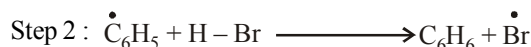
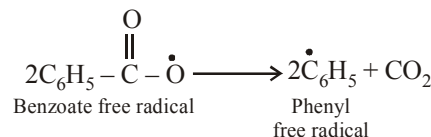
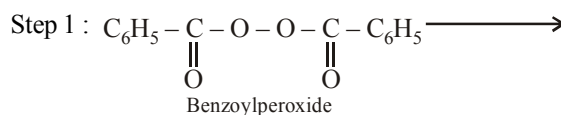
Chemical properties :(i) Addition of H_2 :**Heat of hydrogenation :** The amount of heat liberated in the hydrogenation of one mole of alkene is known as heat of hydrogenation.

$$\text{Stability of alkene} \propto \frac{1}{\text{Heat of hydrogenation}}$$

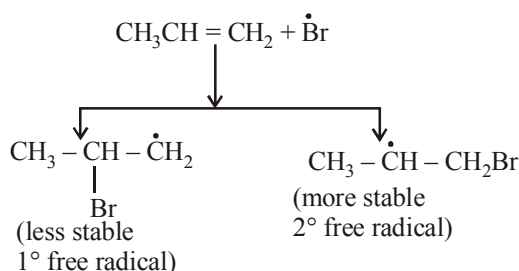
(ii) Addition of halogens:

Reactivity order of halogens is $\Rightarrow \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ **Note :** A 5% solution of Br_2 in CCl_4 solvent is used for the detection of $>\text{C}=\text{C}<$ bond since red brown colour of Br_2 is discharged due to the formation of a colourless compound.(iii) Addition of HX : ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)The addition of HX to an unsymmetrical alkene follows the Markovnikov's rule according to which: 'the negative part of the addendum gets attached to that C-atom which has lesser number of H-atoms'. Thus, (I) is the major product.**Mechanism:**Step 1: $\text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{HBr}$ 

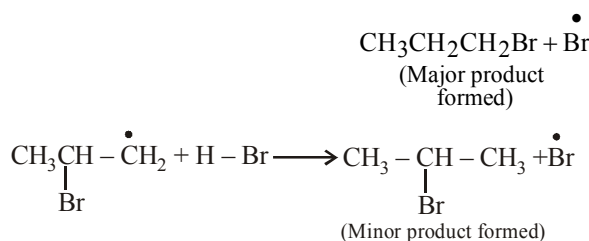
Step 2:

However, in the presence of sunlight, air or an organic peroxide, the addition of HBr to unsymmetrical alkene takes place contrary to the Markovnikov rule. Ex:**Mechanism:**

Step 3 : Attack of $\dot{\text{Br}}$ free radical on propylene gives two free radicals.



Step 4 : $\text{CH}_3-\text{CH}-\text{CH}_2\text{Br} + \text{H}-\text{Br} \longrightarrow$

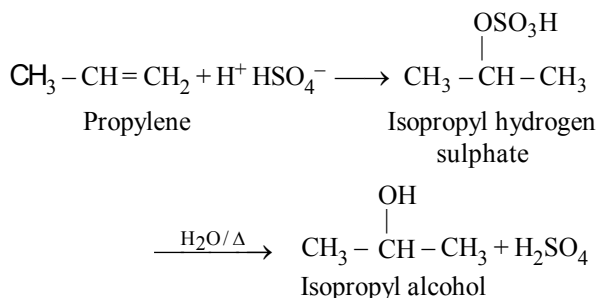


Note : Out of HF, HBr, HCl and HI, only HBr shows peroxide effect.

Symmetrical alkenes such as 2-butene, $(\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3)$, 3-Hexene, etc., do not show peroxide effect.

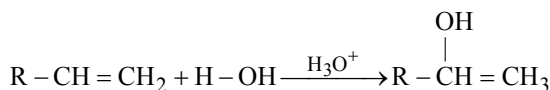
(iv) Addition of H_2SO_4

Addition of H_2SO_4 to unsymmetrical alkenes occur according to Markovnikov's rule.



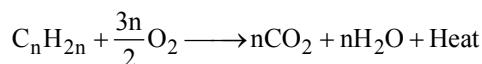
(v) Addition of water:

Addition of H_2O to unsymmetrical alkenes occurs according to Markonikov's rule



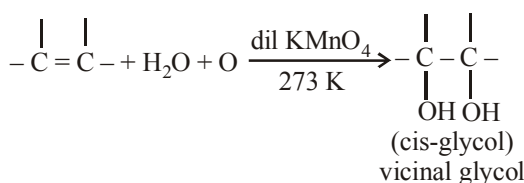
(vi) Combustion and oxidation:

(a) Combustion :

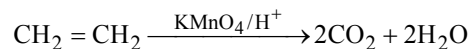
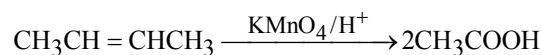
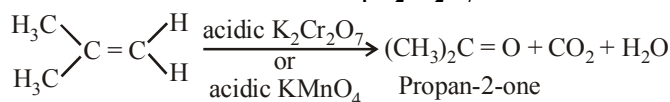


(b) Oxidation :

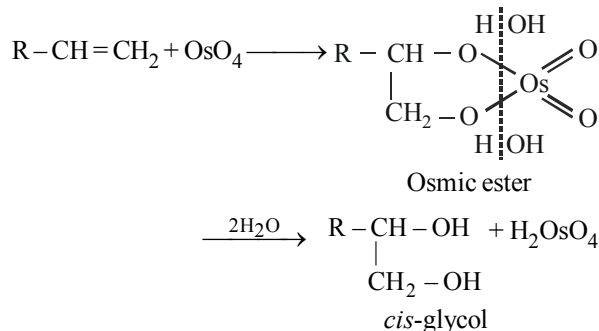
With 1% alkaline KMnO_4 (Baeyer's reagent)



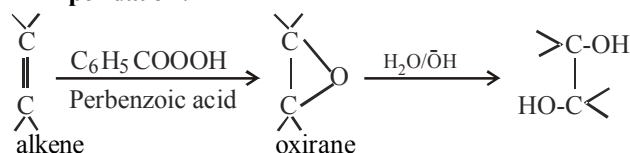
With acidic or hot $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$



With Osmium tetra oxide (OsO_4) :-

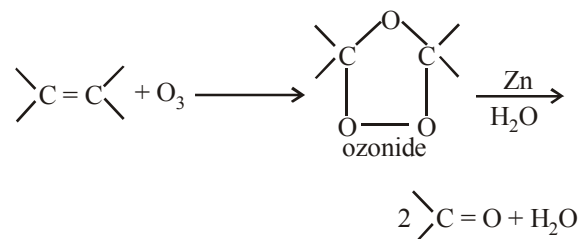


Epoxidation :



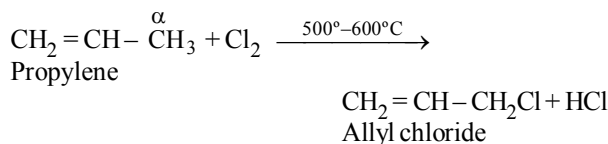
(vii) Ozonolysis:

The addition of ozone on the double bonds and subsequent hydrolysis of the ozonide formed is termed ozonolysis.

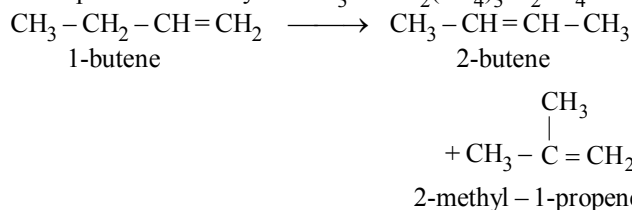


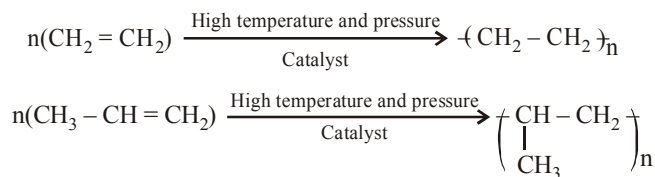
The hydrogen peroxide formed in the reaction is removed by adding zinc dust because it being an oxidising agent oxidises aldehydes into carboxylic acids. Ozonolysis of alkene offers a valuable method of detection and location of double bonds in complex organic molecules.

(viii) Substitution reaction :



(ix) Isomerisation : Alkenes isomerise when heated at high temperature ($500-700^\circ\text{C}$) or at lower temperatures ($200-300^\circ\text{C}$) in the presence of anhyd. AlCl_3 or $\text{Al}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$



(x) Polymerisation**ALKYNES**

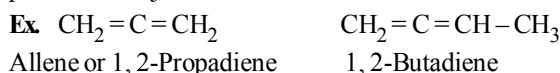
They are unsaturated HC's with at least one triple bond between two C-atoms. Their general formula is $\text{C}_n\text{H}_{2n-2}$.

Dienes or Alkadienes

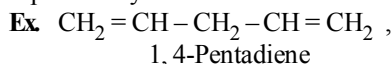
They contain two $>\text{C}=\text{C}<$ bonds. General formula $\text{C}_n\text{H}_{2n-2}$

Types of alkadienes :

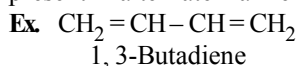
(i) **Cumulative diene** : In these dienes, the double bonds are present on adjacent carbon atoms.



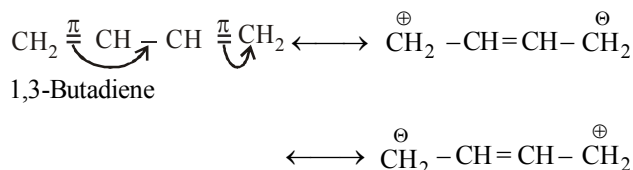
(ii) **Isolated dienes** : In these dienes, the double bonds are separated by two or more C - C bonds.



(iii) **Conjugated dienes** : The dienes in which double bonds are present in alternate manner are called conjugated dienes.

**Stability of alkadienes :**

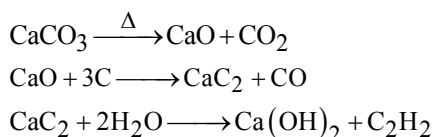
Conjugated dienes are more stable than non-conjugated dienes. This can be explained on the basis of hybridization and resonance. All the carbon atoms in a conjugated diene (1, 3-Butadiene) are sp^2 hybridized. The delocalization of π electrons gives rise to resonance in the molecule which as a result shows more stability than the corresponding nonconjugated dienes.



They exhibit position isomerism. Hybridization of both carbons is sp .

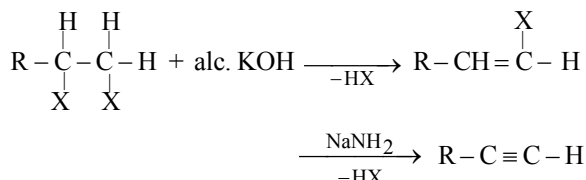
Methods of Preparation

(i) **From calcium carbide:**

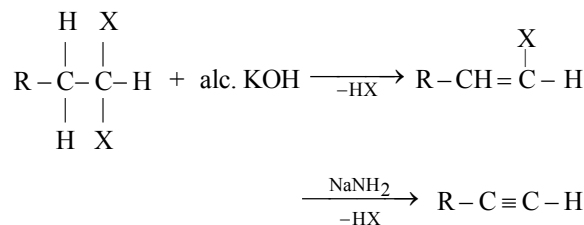


(ii) **From dihalide (Dehydrohalogenation) :**

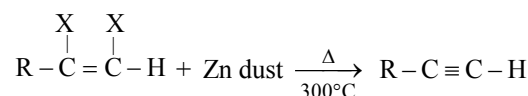
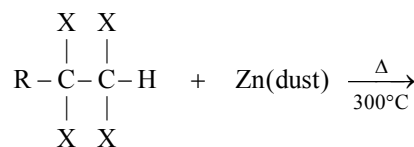
(a) Vicinal dihalides :



(b) Gem dihalides :



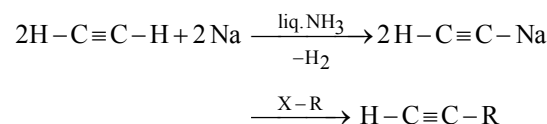
(iii) **From tetrahaloalkanes (Dehalogenation) :-**



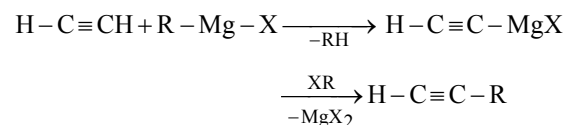
Note : In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends, then the product cyclo alkene is obtained.

(iv) **Synthesis of Higher Alkynes :**

With Na :



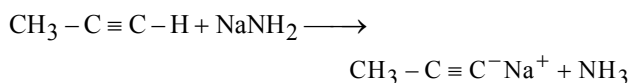
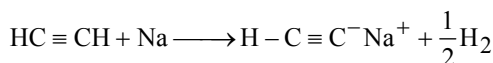
With Grignard Reagent :

**Properties of Alkynes****Physical properties**

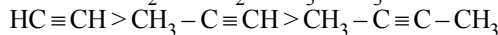
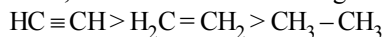
- The first three members are gases, $\text{C}_4 - \text{C}_8$ liquids and higher ones solids.
- They are insoluble in H_2O except few lower alkynes which are partially soluble in H_2O due to their polarizability.
- Their m.pt, b.pt and density increases with increase in molar mass. M. pt. and b. pt decreases with branching.

Chemical properties

- Acidic nature:** Alkynes are acidic as compared to alkenes and alkanes. This is because the H-atoms in alkynes (ex: ethyne) are attached to sp -hybridised C-atoms whereas they are attached to sp^2 hybridised carbons in ethene and sp^3 hybridised carbons in ethane. Due to maximum % of s-character in ethyne, the sp -hybridised orbitals of C-atoms in ethyne have highest electronegativity. Hence they attract the shared e-pair of C-H bond of ethyne to a greater extent than that of sp^2 hybridised orbitals of C in ethene and sp^3 hybridised orbitals of C in ethane. Thus, in ethyne, H-atoms can be liberated as protons easily and hence ethyne (in general alkynes) are acidic in nature.

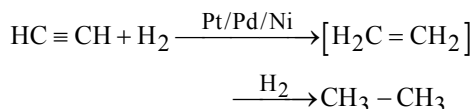


Thus, we have the acidic strength of:

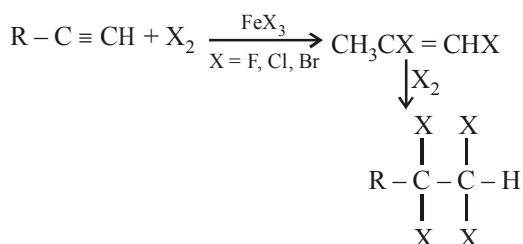


(ii) Addition reactions:

(a) Addition of dihydrogen:



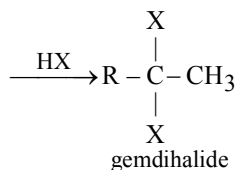
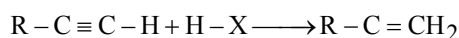
(b) Addition of halogens:



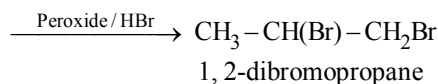
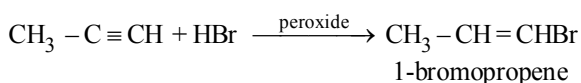
(c) Addition of HX (X = Cl, Br, I):

Alkynes form gem dihalide with HX because reaction follows Markownikoff's Ist and IInd rule both.

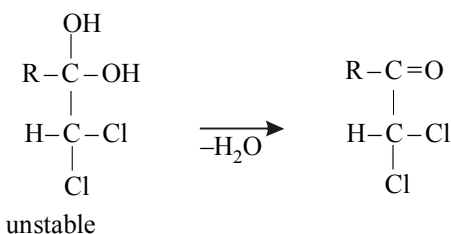
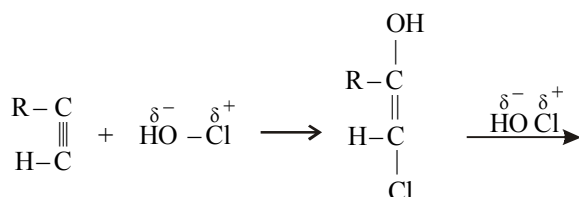
Reactivity order: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$



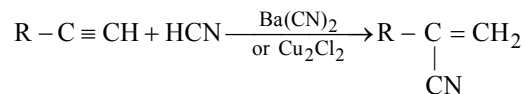
Peroxide effect (Addition of HBr):



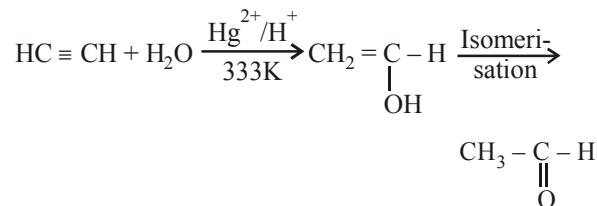
(d) Reaction with Hypochlorous acid or Chlorine water:



(e) Addition of HCN:



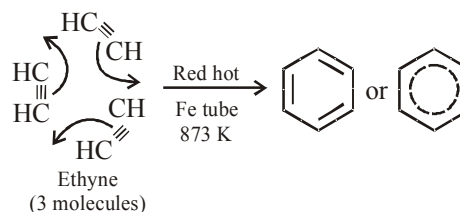
(f) Addition of water:



(iii) Polymerisation:

(a) **Linear polymerisation:** Under suitable conditions, polymerization of acetylene give polyacetylene or polyethyne which is a high molecular weight polyene with repeating units of $(\text{CH} = \text{CH} - \text{CH} = \text{CH})_n$ and is represented as $(\text{CH} = \text{CH} - \text{CH} = \text{CH})_n$. Thin films of polyacetylene can be used as electrodes in batteries.

(b) **Cyclic polymerisation:**



AROMATIC HYDROCARBONS

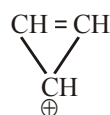
These hydrocarbons are also called 'arenes'. They possess pleasant odour and are thus called 'aromatic compounds'. The aromatic compounds undergo substitution reactions more readily than the addition reactions.

Aromatic compounds have the cyclic system and contain $(4n + 2)$ π electrons [Eric Huckel's rule]

when $n = 0, 1, 2, 3, 4, \dots$

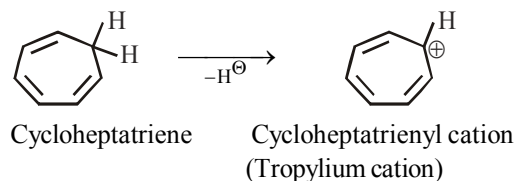
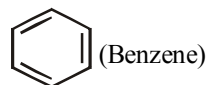
Hence delocalisation alone is not sufficient criterion for aromaticity.

Ex. (i) When $n = 0$, $\pi e^- = 2$



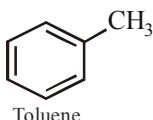
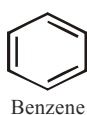
Cyclopropenyl cation (Planar)

Ex. (ii) When $n = 1$; $\pi e^- = 4(1) + 2 = 6$



Classification of Aromatic Compounds:**(i) Aromatic homocyclic :****(a) Aromatic hydrocarbons [Arenes] :**

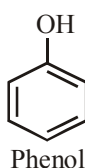
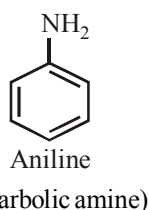
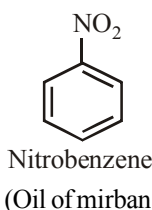
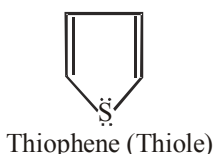
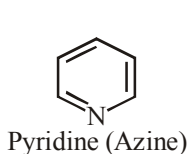
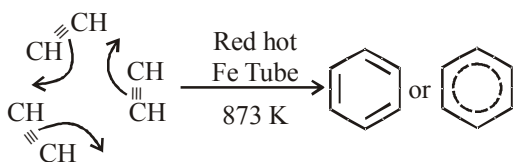
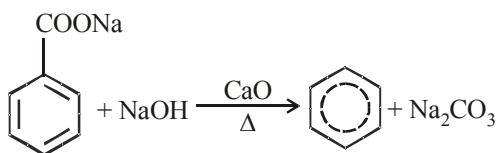
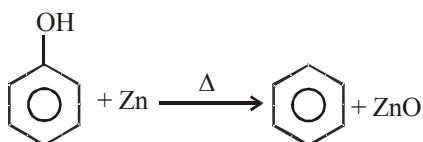
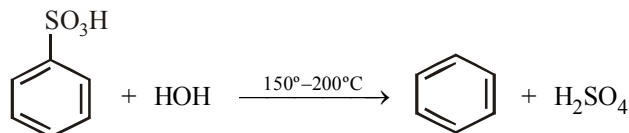
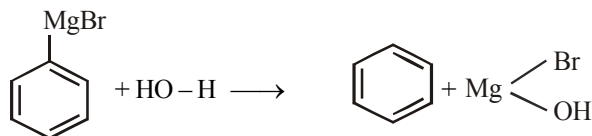
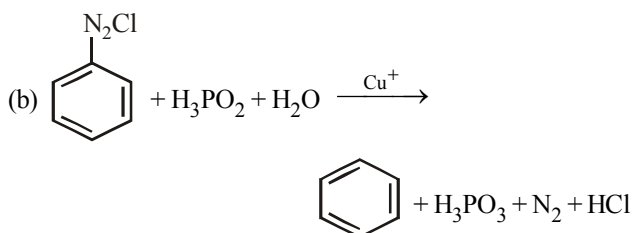
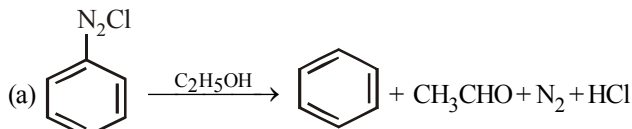
- (1) **Monocyclic arenes :** The Compounds having only one ring in the structural formula.



- (2) **Polycyclic arenes :** Aromatic hydrocarbons having more than one ring in their structural formula are called polycyclic arenes.

**(b) Aromatic hydrocarbon derivatives / Functional aromatic compounds :**

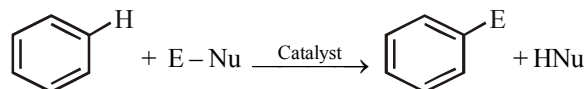
An aromatic compound with at least one functional group in the structural formula is known as F.A.C.

**(ii) Heterocyclic aromatic compounds :****Preparation of Benzene****(i) Cyclic polymerisation of ethyne:****(ii) Decarboxylation of sodium benzoate :****(iii) Reduction of phenol:****(iv) Hydrolysis of benzene sulphonic acid :****(v) From Grignard reagent :****(vi) Reduction of benzenediazonium chloride :****Properties of Benzene****Physical properties :**

- It is a colourless liquid with specific smell.
- It is highly inflammable and burn with a sooty flame.
- It is non-polar, immiscible with water and miscible with organic solvents.

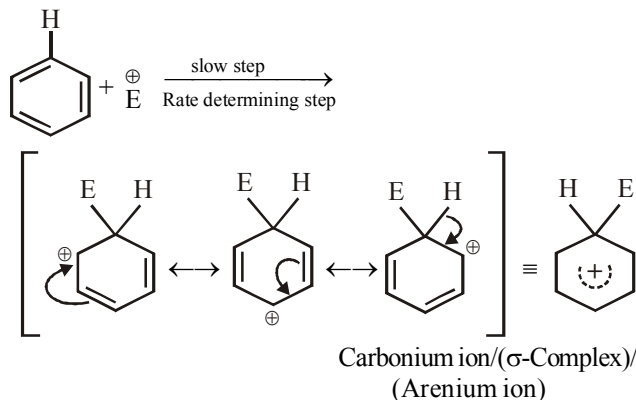
Chemical properties :

- (i) Electrophilic substitution reactions: The reaction can be represented by :

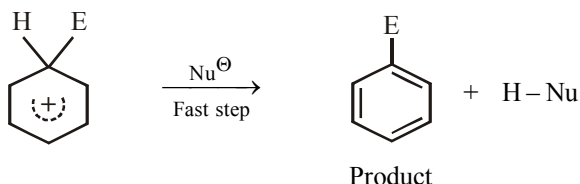
**Mechanism :**

- In first step, all electrophiles form E^+ by substitution reaction

$$E-Nu \longrightarrow E^+ + Nu^-$$
- In second step, electrophile attacks aromatic ring forming carbocation which is stabilised due to resonance.

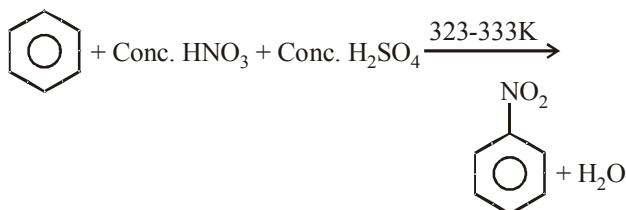


- (iii) In third step, elimination of proton from carbonium ion takes place to form substitution product.

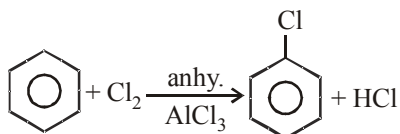


Benzene gives electrophilic substitution while alkenes undergo electrophilic addition.

(a) **Nitration:**

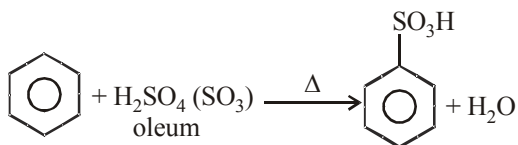


(b) **Halogenations:**

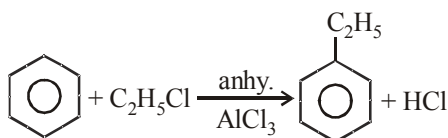
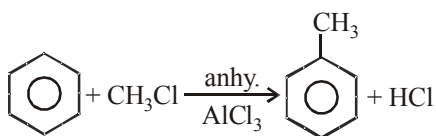


Similarly benzene undergoes bromination when it is treated with Br₂ in presence of FeBr₃.

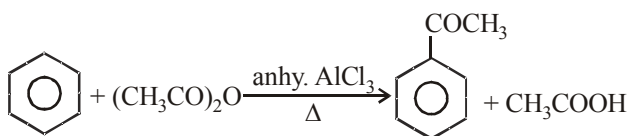
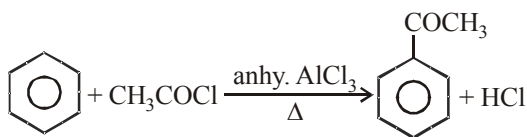
(c) **Sulphonation:**



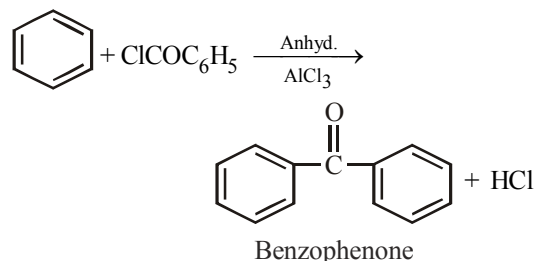
(d) **Friedel-Crafts alkylation reactions:**



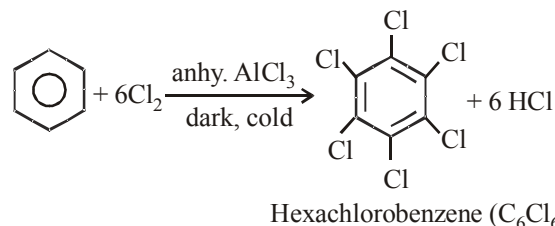
(e) **Friedel-Crafts acylation reaction:**



Benzoylation :

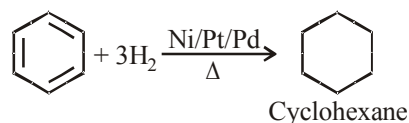


Note : The catalyst used may be AlCl₃, FeCl₃, SnCl₄, BF₃ or ZnCl₂ but anhydrous AlCl₃ is commonly used. When excess of electrophilic reagent is used for example treatment of benzene with excess of Cl₂ in presence of anhydrous AlCl₃ in dark.

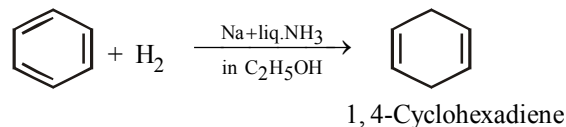


(ii) **Addition reactions:**

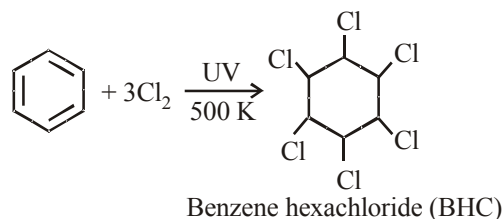
(a) **Hydrogenation :**



Partial (Birch reaction) :- Reduction by Na/liquid NH₃

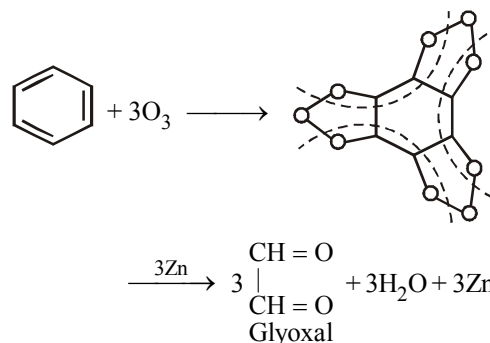


(b) **Halogenation :**

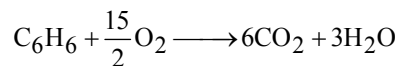


Similarly Br₂ is used to prepare hexabromides. I₂ cannot give this reaction.

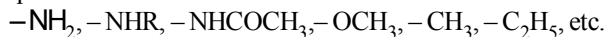
- (iii) **Ozonolysis / Addition of ozone :** When treated with ozone, benzene triozonide is produced which on hydrolysis yields glyoxal.



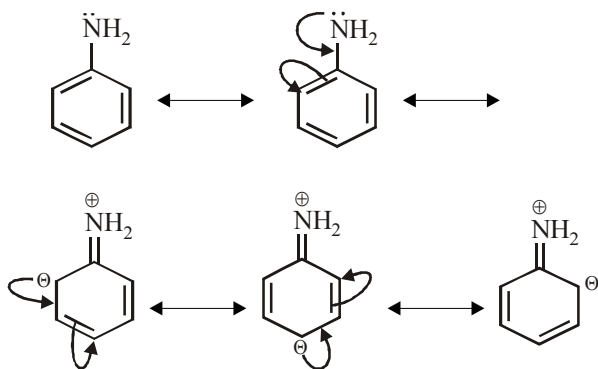
(iv) Combustion:

**Directive Influence of a Functional Group in Monosubstituted Benzene****Ortho and para directing groups:**

These groups direct the incoming group to *o*- and *p*- positions. Examples:



All *o*, *p*-directing groups except alkyl groups contain one or more lone pair of electrons which are involved in resonance or configuration with the π -electrons present in the ring. For example consider resonance in aniline.

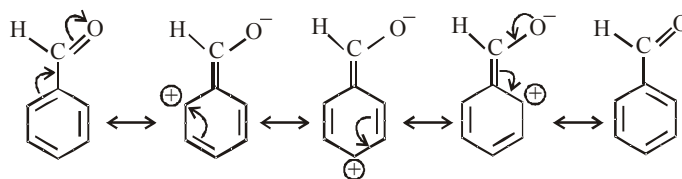


As a result, the ortho and para positions in the ring become the points of high electron density or negatively charged. The new entering group which is an electrophile will prefer to come to ortho and para positions rather than the meta position in the ring. These groups are also called activating groups.

Meta directing groups

These groups direct the incoming group to meta position.

Examples: $-\text{NO}_2, -\text{CN}, -\text{CHO}, -\text{COR}, -\text{COOH}, -\text{COOR}, -\text{SO}_3\text{H}$, etc. In all meta directing groups the atom of the group which is directly attached to the ring has more electronegative atom linked to it by multiple bonds. The resonating structures for benzaldehyde molecule are following.



Thus, overall e^- density on benzene ring decreases making further substitution difficult. The electron density at *o*- and

p- positions is less than at *m*-position. Thus, E^+ attacks the comparatively e^- rich *m*-position resulting in meta substitution. These groups are also called 'deactivating groups'.

Aromatic Hydrocarbons

- Contain at least one unsaturated ring
- Aromaticity :**
 - Aromatic compound must have planer structure
 - must contain $(4n+2)$ π electrons
 - must have cyclic clouds of delocalised π es
- PREPARATION**
 - $3\text{HC} \equiv \text{CH} \xrightarrow[\text{Fe tube}]{\text{Red hot}} \text{Benzene}$
 - phenol $\xrightarrow[\Delta]{\text{Zn dust}} \text{Benzene}$
 - $\text{C}_6\text{H}_5\text{COO}^- \text{Na}^+ + \text{NaOH} \xrightarrow[\Delta]{\text{CaO}} \text{Benzene}$
- PROPERTIES**
 - Electrophilic substitution**
 - $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{AlCl}_3} \text{Chlorobenzene} + \text{HCl}$
 - $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow{\text{AlCl}_3} \text{toluene}$
 - $\text{C}_6\text{H}_6 + \text{Conc. HNO}_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}} \text{Benzene ring} + \text{H}_2\text{O}$

Alkynes

- General formula : $\text{C}_n\text{H}_{2n-2}$
- C atom possesses sp^3 hybridised state.
- PREPARATION**
 - Hydrogenation**
 $\text{CH}_2 = \text{CH}_2 + \text{H}_2 \xrightarrow{\text{Pt/Pd/Ni}} \text{CH}_3 - \text{CH}_3$
 - Wurtz reaction**
 $\text{R}-\text{Br} + 2\text{Na} \xrightarrow[\text{ether}]{\text{dry}} \text{R}-\text{R} + 2\text{NaBr}$
 - Decarboxylation**
 $\text{CH}_3\text{COO}^- \text{Na}^+ + \text{NaOH} \xrightarrow[\Delta]{\text{CaO}} \text{CH}_4 + \text{Na}_2\text{CO}_3$
 - Kolbe's electrolytic method**
 $2\text{CH}_3\text{COO}^- \text{Na}^+ + 2\text{H}_2\text{O} \rightarrow \text{CH}_3 - \text{CH}_3 + 2\text{CO}_2 + \text{H}_2 + 2\text{NaOH}$
- PROPERTIES**
 - Boiling points decrease with increasing branching
 - Melting point with even no of C-atom > odd no. of C-atoms
 - Halogenation
 $\text{R}-\text{H} + \text{X}_2 \xrightarrow{h\nu} \text{R}-\text{X} + \text{HX}$
 Compound with even number of C-atom

Alkenes

- Aromatisation**
 $n\text{-Hexane} \xrightarrow{\text{Cr}_2\text{O}_3 \text{ or } \text{V}_2\text{O}_5} \text{Benzene}$
- Conformation**
 Stability order: staggered > skew > eclipsed

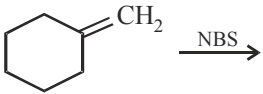
Alkynes

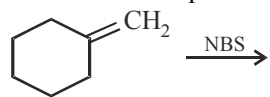
- General formula : $\text{C}_n\text{H}_{2n-2}$
- C atom is in sp^2 hybridised state.
- PREPARATIONS**
 - $\text{R}-\text{C} \equiv \text{C}-\text{R} \xrightarrow[\text{catalyst}]{\text{Lindlar's}} \text{RCH} = \text{CHR}$
 - Dehydrohalogenation**
 $\text{H}_3\text{C}-\text{CHBr}-\text{CH}_2\text{CH}_3 \rightarrow \text{H}_3\text{C}-\text{CH} = \text{CH}-\text{CH}_3$
 - Dehydration of alcohol**
 $\text{H}-\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{75\% \text{ H}_2\text{SO}_4} \text{CH}_3-\text{CH} = \text{CH}_2 + \text{H}_2\text{O}$
- PROPERTIES**
 - Addition reaction**
 $\text{R}-\text{CH} = \text{CH}_2 + \text{H}_2 \xrightarrow[\text{Ni}]{\text{Raney}} \text{RCH}_2-\text{CH}_3$
 Markovnikov reaction
 - $\text{R}-\text{CH} = \text{CH}_2 + \text{HCl} \rightarrow \text{RCH}_2-\text{CH}_3$
 Reactivity : $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
 - Antimarkovnikov reaction (Kharasch effect)**
 $\text{R}-\text{CH} = \text{CH}_2 + \text{HBr} \xrightarrow{\text{H}_2\text{O}_2} \text{RCH}_2-\text{CH}_2\text{Br}$
 - Ozonolysis**
 $\text{H}_3\text{C}-\text{CH} = \text{CH}_2 + \text{O}_3 \xrightarrow{\text{zn/H}_2\text{O}} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{H} + \text{H}-\text{C}(=\text{O})-\text{H}$

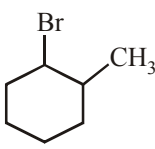
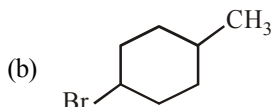
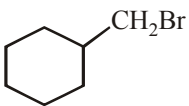
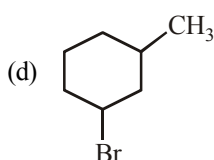
EXERCISE - 1

Conceptual Questions

- Which of the following react with KMnO_4 to produce pyruvic acid?
 - butyne
 - propyne
 - 2-Pentyne
 - ethyne
- In Wurtz reaction if we take CH_3Cl and $\text{C}_2\text{H}_5\text{Cl}$ then product, will be-
 - propane + ethane
 - propane
 - propane + ethane + butane
 - propane + butane
- Reactivity of hydrogen atoms attached to different carbon atoms in alkanes has the order
 - Tertiary > Primary > Secondary
 - Primary > Secondary > Tertiary
 - Tertiary > Secondary > Primary.
 - Both (a) and (b)
- When CH_3Cl and AlCl_3 are used in Friedel-Crafts reaction, the electrophile is
 - Cl^+
 - AlCl_4^-
 - CH_3^+
 - AlCl_2^+
- By which one of the following compounds both CH_4 and $\text{CH}_3 - \text{CH}_3$ can be prepared in one step?
 - CH_3I
 - CH_3OH
 - $\text{CH}_3\text{CH}_2\text{I}$
 - $\text{C}_2\text{H}_5\text{OH}$
- In the free radical chlorination of methane, the chain initiating step involves the formation of
 - chlorine free radical
 - hydrogen chloride
 - methyl radical
 - chloromethyl radical.
- Which one of the following reactions is expected to readily give a hydrocarbon product in good yields ?
 - $\text{RCOOK} \xrightarrow[\text{oxidation}]{\text{Electrolytic}}$
 - $\text{RCOO}^- \text{Ag}^+ \xrightarrow{\text{Br}_2}$
 - $\text{CH}_3\text{CH}_3 \xrightarrow[\text{h}\nu]{\text{Cl}_2}$
 - $(\text{CH}_3)_3\text{CCl} \xrightarrow{\text{C}_2\text{H}_5\text{OH}}$
- What will be the product in the following reaction?

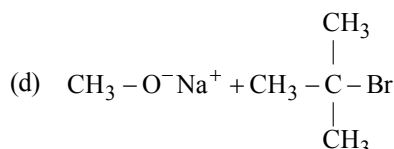
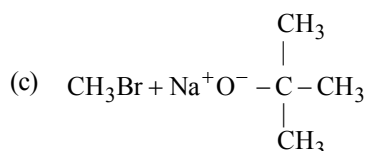
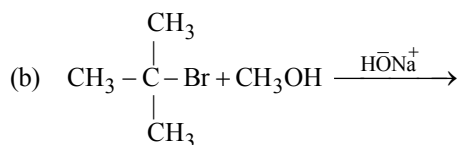
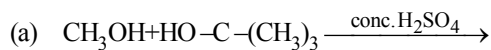

- The reaction of ethyl magnesium bromide with water would give
 - ethane
 - ethyl alcohol
 - ethyl bromide
 - ethyl ether
- On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be
 - pentane
 - isopentane
 - neopentane
 - propane
- 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly
 - 1-bromo-3-methylbutane
 - 2-bromo-3-methylbutane
 - 2-bromo-2-methylbutane
 - 1-bromo-2-methylbutane
- $\begin{array}{c} \text{CH} \\ ||| \\ \text{CH} \end{array}$ reacts with acetic acid in presence of Hg^{2+} to give :
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}(\text{CH}_3\text{COO})_2 \end{array}$
 - $\begin{array}{c} \text{CH}(\text{CH}_3\text{COO})_2 \\ | \\ \text{CH}(\text{CH}_3\text{COO})_2 \end{array}$
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2(\text{CH}_3\text{COO}) \end{array}$
 - None of these
- Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is
 - 2-methylpentane
 - 2, 2-dimethylbutane
 - 2, 3-dimethylbutane
 - n-hexane
- Which one of the following contain isopropyl group?
 - 2, 2, 3, 3-tetramethylpentane
 - 2-methylpentane
 - 2, 2, 3-trimethylpentane
 - 3, 3-dimethylpentane
- Which types of isomerism is shown by 2, 3-dichlorobutane?
 - Structural
 - Geometric
 - Optical
 - Diastereo
- In mixture of *iso*-octane and *n*-heptane the percentage of *n*-heptane is 11, the octane number of this fuel is :
 - 89
 - 10
 - 100
 - 80
- Which of the following isomers will have the highest octane number?
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
 - $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - (\text{CH}_2)_4 - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - (\text{CH}_2)_6 - \text{CH}_3 \end{array}$



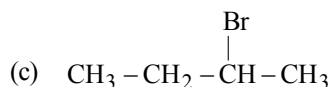
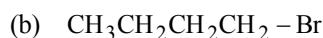
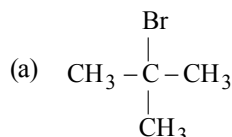
- 
- 
- 
- 

- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
- $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - (\text{CH}_2)_4 - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - (\text{CH}_2)_6 - \text{CH}_3 \end{array}$

18. Aromatisation of *n*-hexane gives :
 (a) cyclohexane (b) benzene
 (c) cycloheptane (d) toluene
19. For the preparation of *t*-butyl methyl ether which one of the following methods should be recommended?



20. At 130°C, normal butane reacts with bromine, the product will be :



(d) All of the above

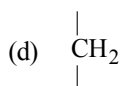
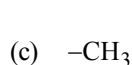
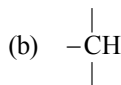
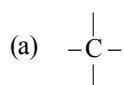
21. When C_2H_2 , CH_4 and C_2H_4 pass through a test tube which has ammonical Cu_2Cl_2 , find out which gas comes out unaffected from test tube?

- (a) C_2H_2 and CH_4 (b) C_2H_2 and C_2H_4
 (c) C_2H_4 and CH_4 (d) C_2H_2

22. A hydrocarbon contains 10.5 g carbon and 1 g hydrogen. Its 0.36 g has 1 L volume at 1 atm and 127°C, hydrocarbon is :

- (a) C_6H_7 (b) C_7H_8
 (c) C_5H_6 (d) None of these

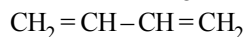
23. In cyclopropane, cyclobutane and cyclohexane, the common group is



24. The highest boiling point is expected for :

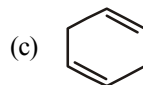
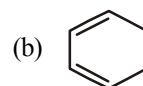
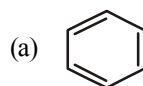
- (a) iso-octane
 (b) *n*-octane
 (c) 2, 2, 3, 3-tetramethylbutane
 (d) *n*-butane

25. The number of σ and π bonds in

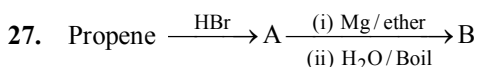


- (a) 8 σ and 2 π bonds (b) 9 σ and 1 π bonds
 (c) 9 σ and 3 π bonds (d) 9 σ and 2 π bonds

26. 1, 2-Dibromocyclohexane on dehydrobromination gives :



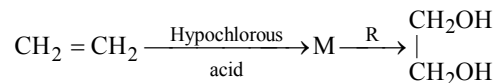
(d) None of these



In the above sequence of reactions, B is

- (a) propane (b) butane
 (c) propene (d) ethane

28. In reaction sequence



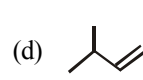
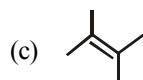
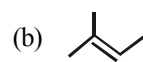
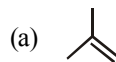
molecule 'M' and reagent 'R' respectively are

- (a) $\text{CH}_3\text{CH}_2\text{Cl}$ and NaOH
 (b) $\text{CH}_3\text{CH}_2\text{OH}$ and H_2SO_4
 (c) $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{OH}$ and aqueous NaHCO_3
 (d)  and heat

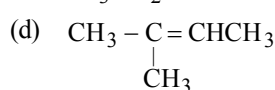
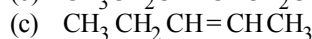
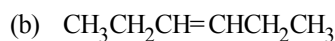
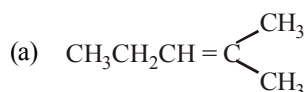
29. Which of the following reagents convert propene to 1-propanol?

- (a) H_2O , H_2SO_4 (b) Aqueous KOH
 (c) MgSO_4 , $\text{NaBH}_4/\text{H}_2\text{O}$ (d) B_2H_6 , H_2O_2 , OH^-

30. The alkene that will yield 2, 3-dimethyl-2 butanol on hydration is :



31. Which alkene on ozonolysis gives $\text{CH}_3\text{CH}_2\text{CHO}$ and $\text{CH}_3\text{C}(=\text{O})\text{CH}_3$?



32. Aromatisation of n-heptane by passing over ($\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$) catalyst at 773 K gives:
 (a) benzene (b) toluene
 (c) mixture of both (d) heptylene
33. The compound

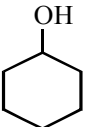
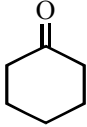
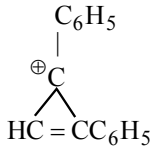
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3 \end{array}$$
 on reaction with NaIO_4 in the presence of KMnO_4 gives
 (a) $\text{CH}_3\text{CHO} + \text{CO}_2$
 (b) CH_3COCH_3
 (c) $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{COOH}$
 (d) $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{CHO}$
34. Butene-1 may be converted to butane by reaction with
 (a) $\text{Sn} - \text{HCl}$ (b) $\text{Zn} - \text{Hg}$
 (c) Pd/H_2 (d) $\text{Zn} - \text{HCl}$
35. $\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{CrO}_2\text{Cl}_2} \text{Z}$
 In the given sequence Z is:
 (a) benzaldehyde (b) toluic acid
 (c) phenyl acetic acid (d) benzoic acid
36. Acid catalyzed hydration of alkenes except ethene leads to the formation of
 (a) mixture of secondary and tertiary alcohols
 (b) mixture of primary and secondary alcohols
 (c) secondary or tertiary alcohol
 (d) primary alcohol
37. The compound most likely to decolourise a solution of alkaline KMnO_4 is:
 (a) $\text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_2\text{CH}_3$
 (b) $\text{C}_{10}\text{H}_{22}$
 (c) $\text{CH}_3 - \text{CH}_3$
 (d) $(\text{CH}_3)_4\text{C}$
38. The addition of HBr is easiest with:
 (a) $(\text{CH}_3)_2\text{C} = \text{CH}_2$ (b) $\text{CH}_3 - \text{CH} = \text{CH}_2$
 (c) $\text{ClCH} = \text{CHCl}$ (d) $\text{CH}_2 = \text{CH} - \text{Cl}$
39. Which of the production will be formed by the reaction?

$$\text{H}_2\text{C} = \text{CH}_2 \xrightarrow[\text{Cold}]{\text{Alkaline KMnO}_4} \text{X}$$

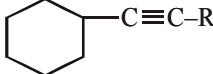
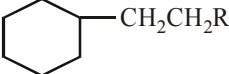
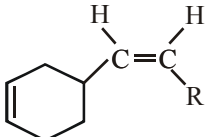
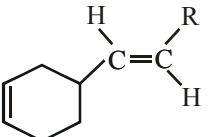
 (a) Ethanol (b) Ethanoic acid
 (c) Ethylene glycol (d) Oxalic acid
40. HOCl reacts on 3-methyl-2-pentene, the main product will be:
 (a)
$$\begin{array}{c} \text{CH}_3 - \text{CH} = \text{C} - \text{CHOH} - \text{CH}_3 \\ | \\ \text{Cl} \end{array}$$

 (b)
$$\begin{array}{c} \text{OH} \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3 - \text{CH} - \text{C} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{Cl} \end{array}$$

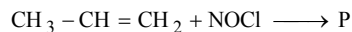
 (c)
$$\begin{array}{c} \text{Cl} \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3 - \text{CH} - \text{C} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{OH} \end{array}$$

 (d) None of these
41. Which compound is aromatic?
 (a)  (b) 
 (c)  (d) 
42. Cyclohexene on reaction with cold alkaline KMnO_4 forms
 (a) *trans*-hexanediol (b) hexadiketone
 (c) *cis*-hexanediol (d) None of these
43. Correct statement about 1,3-dibutene:
 (a) conjugated double bonds are present
 (b) reacts with HBr
 (c) forms polymer
 (d) All of these
44. The main product of the reaction is:

$$\text{Cyclohexene} - \text{C} \equiv \text{C} - \text{R} \xrightarrow[\text{R}'\text{OH}]{\text{Na, NH}_3(\ell)} \text{Product}$$

 (a)  (b) 
 (c)  (d) 
45. Which of the following has highest knocking?
 (a) Olefins (b) Branched chain olefins
 (c) Straight chain olefins (d) Aromatic hydrocarbons
46. Acetylene reacts with HCN in the presence of $\text{Ba}(\text{CN})_2$ to yield:
 (a) 1,1-dicyanoethane (b) 1,2-dicyanoethane
 (c) vinyl cyanide (d) None of these
47. Allene (C_3H_4) contains:
 (a) one double bond, one triple bond and one single bond
 (b) one triple and two double bonds
 (c) two triple and one double bonds
 (d) two double and four single bonds
48. Among the following, the aromatic compound is:
 (a)  (b) 
 (c)  (d) 
49. A compound (X) on ozonolysis followed by reduction gives an aldehyde, $\text{C}_2\text{H}_4\text{O}$ and 2-butanone, compound (X) is
 (a) 3-methylpentene-2 (b) 3-methylpentene-3
 (c) 3-methylhexene-3 (d) 3-ethylpentene-3

50. Identify the product, P in the following reaction :



- (a) $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{NO} \quad \text{Cl} \end{array}$ (b) $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{NO} \end{array}$
- (c) $\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\ | \quad | \\ \text{NO} \quad \text{Cl} \end{array}$ (d) $\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} \\ | \quad | \\ \text{Cl} \quad \text{NO} \end{array}$

51. Which of the following gives propyne on hydrolysis?

- (a) Al_4C_3 (b) Mg_2C_3
(c) B_4C (d) La_4C_3

52. The major product obtained on treatment of $\text{CH}_3\text{CH}_2\text{CH}(\text{F})\text{CH}_3$ with $\text{CH}_3\text{O}^-/\text{CH}_3\text{OH}$ is :

- (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_3$
(b) $\text{CH}_3\text{CH}=\text{CHCH}_3$
(c) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$
(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$

53. Which one of the following is the strongest bond?

- (a) $>\text{C}=\text{C}<$ (b) $-\text{C}\equiv\text{C}-$
(c) $\begin{array}{c} | \\ -\text{C}-\text{C}= \\ | \quad | \end{array}$ (d) $\begin{array}{c} | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \end{array}$

54. $\text{R}-\text{CH}_2-\text{CCl}_2-\text{R} \xrightarrow{\text{Reagent}} \text{R}-\text{C}\equiv\text{C}-\text{R}$

The reagent is

- (a) Na (b) HCl in H_2O
(c) KOH in $\text{C}_2\text{H}_5\text{OH}$ (d) Zn in alcohol.

55. Below, some catalysts and corresponding processes/reactions are matched. The mismatch is :

- (a) $[\text{RhCl}(\text{PPh}_3)_2]$: Hydrogenation
(b) $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$: Polymerization
(c) V_2O_5 : Haber-Bosch process
(d) Nickel-Hydrogenation

56. A compound is treated with NaNH_2 to give sodium salt. Identify the compound

- (a) C_2H_2 (b) C_6H_6
(c) C_2H_6 (d) C_2H_4

57. Which of these will not react with acetylene?

- (a) NaOH (b) Ammonical AgNO_3
(c) Na (d) HCl

58. What is the product when acetylene reacts with hypochlorous acid?

- (a) CH_3COCl (b) ClCH_2CHO
(c) Cl_2CHCHO (d) ClCHCOOH

59. Which of the following species participate in sulphonation of benzene ring ?

- (a) H_2SO_4 (b) SO_3
(c) HSO_3^- (d) SO_2^-

60. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene ?

- (a) $\text{H}_2/\text{Pd}/\text{BaSO}_4$ (b) H_2, PtO_2
(c) NaBH_4 (d) $\text{Liq-NH}_3/\text{C}_2\text{H}_5\text{OH}$

61. In the reaction



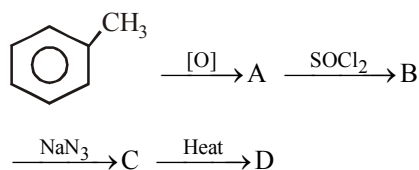
the product formed is :

- (a) propene (b) propyne
(c) propyne and propene (d) 4-methylpentyn-2

62. Ammonical silver nitrate forms a white precipitate easily with

- (a) $\text{CH}_3\text{C}\equiv\text{CH}$ (b) $\text{CH}_3\text{C}\equiv\text{CCH}_3$
(c) $\text{CH}_3\text{CH}=\text{CH}_2$ (d) $\text{CH}_2=\text{CH}_2$

63. In the following sequence of the reactions, what is D?



- (a) Primary amine
(b) An amide
(c) Phenyl isocyanate
(d) A chain lengthened hydrocarbon

64. When acetylene passed through dil. H_2SO_4 in presence of HgSO_4 , the compound formed is

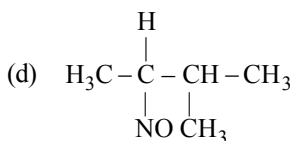
- (a) ether (b) acetaldehyde
(c) acetic acid (d) ketone

65. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne

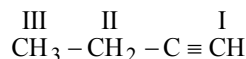
- (a) bromine, CCl_4
(b) H_2 , Lindlar catalyst
(c) dilute H_2SO_4 , HgSO_4
(d) ammonical Cu_2Cl_2 solution

66. $(\text{CH}_3)_2\text{C}=\text{CHCH}_3 + \text{NOBr} \longrightarrow$ product. The structure of the product is

- (a) $(\text{CH}_3)_2\text{C}(\text{NO})-\text{CH}(\text{Br})\text{CH}_3$
(b) $(\text{CH}_3)_2\text{C}(\text{Br})-\text{CH}(\text{NO})\text{CH}_3$
(c) $(\text{CH}_3)_2\text{CH}-\text{C}(\text{NO})(\text{Br})\text{CH}_3$

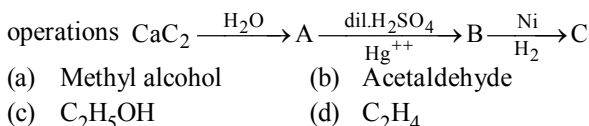


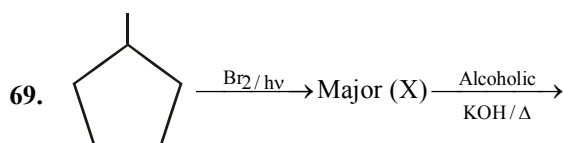
67. Which C-atom is the most electronegative in this structure?



- (a) I
(b) II
(c) III
(d) all are equal electronegative

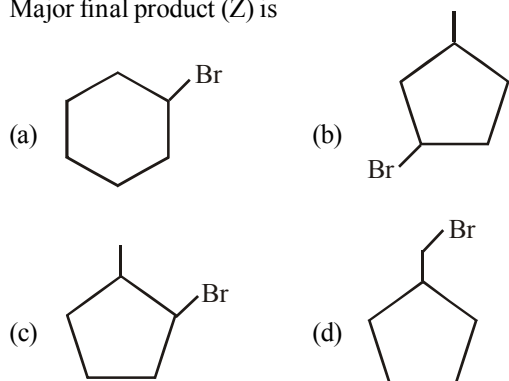
68. What is the end product of the following sequences of





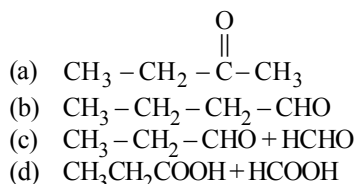
Major (Y) $\xrightarrow{\text{H-Br/Peroxide}}$ Major (Z)

Major final product (Z) is



70. The C - H bond length is minimum in the bond formed by
(a) $sp - s$ overlapping (as in alkynes)
(b) $sp^2 - s$ overlapping (as in alkenes)
(c) $sp^3 - s$ overlapping (as in alkanes)
(d) None of these

71. The product(s) obtained via oxymercuration ($\text{HgSO}_4 + \text{H}_2\text{SO}_4$) of 1-butyne would be



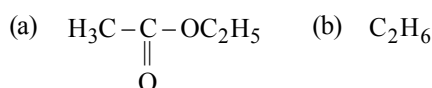
72. The ring structure of benzene was proposed by



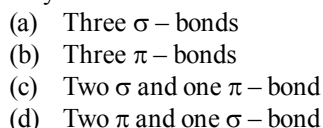
73. Propyne on polymerisation gives



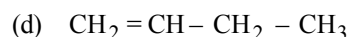
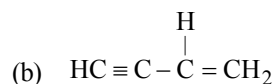
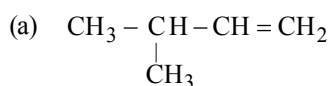
74. Ethyl alcohol is heated with conc. H_2SO_4 . The product formed is :



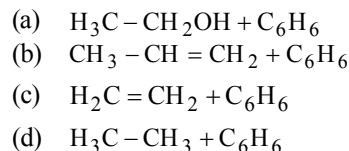
75. Triple bond of ethyne is made of or Cylindrical shape of an alkyne is due to



76. Which of the following organic compound will give a mixture of 1-chlorobutane and 2-chlorobutane on chlorination?



77. Using anhydrous AlCl_3 as catalyst, which one of the following reactions produces ethylbenzene (PhEt)?



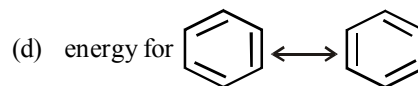
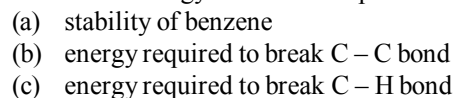
78. Nitration of toluene using fuming sulphuric and nitric acid gives :



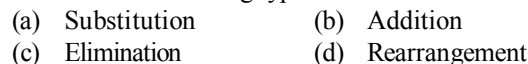
79. Which of the following compounds does not follow Markownikoff's law ?



80. Resonance energy of benzene represents :



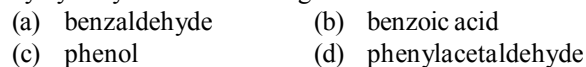
81. $\text{C}_3\text{H}_8 + \text{Cl}_2 \xrightarrow{\text{light}} \text{C}_3\text{H}_7\text{Cl} + \text{HCl}$ is an example of which of the following type of reactions?



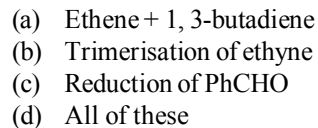
82. Benzene can react with :



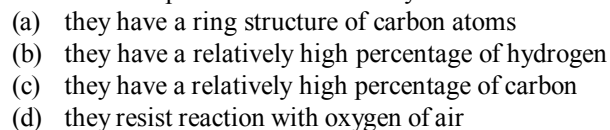
83. Toluene on treatment with CrO_3 and $(\text{CH}_3\text{CO})_2\text{O}$ followed by hydrolysis with dil HCl gives



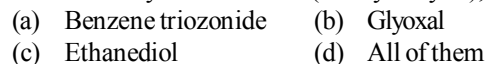
84. Benzene can be obtained in the reaction



85. Aromatic compounds burn with sooty flame because



86. After ozonolysis of benzene (not hydrolysis), the product is



87. The molecular formula of a compound in which double bond is present between C & C :



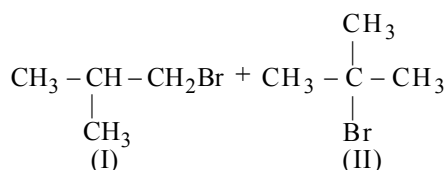
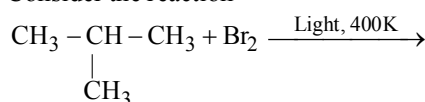
88. An organic compound 'X' - (molecular formula $C_6H_7O_2N$) has six atoms in a ring system, two double bonds and a nitro group as substituent; 'X' is:
 (a) heterocyclic
 (b) homocyclic and aromatic
 (c) aromatic but not homocyclic
 (d) homocyclic but not aromatic
89. The alkene $R-CH=CH_2$ reacts readily with B_2H_6 and formed the product B which on oxidation with alkaline hydrogen peroxide produces
 (a) $R-CH_2-CHO$ (b) $R-CH_2-CH_2-OH$
 (c) $R-\overset{\text{CH}_3}{\underset{|}{C}}=O$ (d) $R-\underset{\text{OH}}{\underset{|}{CH}}-\underset{\text{OH}}{\underset{|}{CH_2}}$
90. Compound X of molecular formula C_4H_6 takes up one equivalent of hydrogen in presence of Pt to form another compound Y which on ozonolysis gives only ethanoic acid. The compound X can be
 (a) $CH_2=CH-CH=CH_2$
 (b) $CH_2=C=CHCH_3$
 (c) $CH_3C\equiv CCH_3$
 (d) All the three
91. Predict the product C obtained in the following reaction of butyne-1.
 $CH_3CH_2-C\equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$
 (a) $CH_3-CH_2-CH_2-\overset{\text{I}}{\underset{\text{Cl}}{|C}}-H$
 (b) $CH_3-CH_2-\overset{\text{I}}{\underset{|}{CH}}-CH_2Cl$
 (c) $CH_3CH_2-\overset{\text{I}}{\underset{\text{Cl}}{|C}}-CH_3$
 (d) $CH_3-\overset{\text{Cl}}{\underset{|}{CH}}-CH_2CH_2I$
92. Which of the compounds with molecular formula C_5H_{10} yields acetone on ozonolysis?
 (a) 3-methyl-1-butene (b) cyclopentane
 (c) 2-methyl-1-butene (d) 2-methyl-2-butene.
93. The IUPAC name of the compound having the formula $CH\equiv C-CH=CH_2$ is:
 (a) 1-butyne-3-ene (b) but-1-yne-3-ene
 (c) 1-butene-3-yne (d) 3-butene-1-yne
94. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by :
 (a) oxidation
 (b) cracking
 (c) distillation under reduced pressure
 (d) hydrolysis
95. In the following reaction, $C_6H_5CH_2Br \xrightarrow[2.H_3O^+]{1.Mg, Ether} X$, the product 'X' is
 (a) $C_6H_5CH_2CH_2C_6H_5$ (b) $C_6H_5CH_2OCH_2C_6H_5$
 (c) $C_6H_5CH_2OH$ (d) $C_6H_5CH_3$
96. The IUPAC name of the compound $CH_3CH=CHC\equiv CH$ is
 (a) Pent-1-yn-3-ene (b) Pent-4-yn-2-ene
 (c) Pent-3-en-1-yne (d) Pent-2-en-4-yne
97. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is
 (a) benzyl alcohol (b) benzophenone
 (c) acetophenone (d) benzoic acid.
98. Which of the following reactions will yield 2,2-dibromopropane?
 (a) $CH_3-CH=CH_2 + HBr \rightarrow$
 (b) $CH_3-C\equiv CH + 2HBr \rightarrow$
 (c) $CH_3CH=CHBr + HBr \rightarrow$
 (d) $CH\equiv CH + 2HBr \rightarrow$
99. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly
 (a) *m*-chlorobenzene (b) benzoyl chloride
 (c) benzyl chloride (d) *o*- and *p*-chlorotoluene.
100. The hydrocarbon which can react with sodium in liquid ammonia is
 (a) $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$
 (b) $CH_3CH_2C\equiv CH$
 (c) $CH_3CH=CHCH_3$
 (d) $CH_3CH_2C\equiv CCH_2CH_3$

EXERCISE - 2

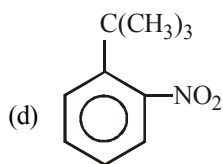
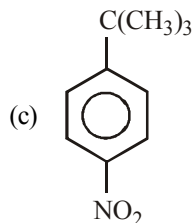
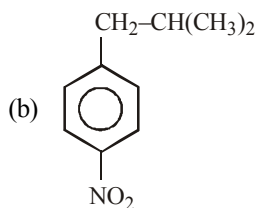
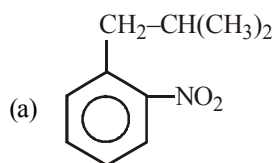
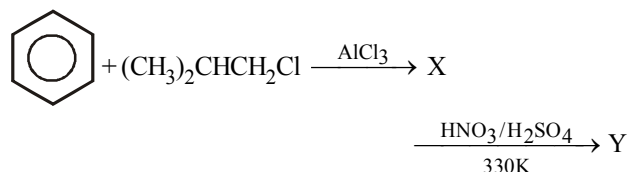
Applied Questions

1. The alkene C_6H_{10} producing $OHC(CH_2)_4CHO$ on ozonolysis is
 (a) Hexene-1 (b) Hexene-3
 (c) Cyclohexene (d) 1-Methylcyclohexene
2. Chlorination of benzene is not possible in the following reaction :
 (a) $C_6H_6 + Cl_2 \xrightarrow{FeCl_3}$
 (b) $C_6H_6 + HOCl \xrightarrow{H^+}$
 (c) $C_6H_6 + I-Cl \xrightarrow{ZnCl_2}$
 (d) $C_6H_6 + Cl_2 \xrightarrow{AlCl_3}$
3. The conversion of $ClCH=CHCl$ to $Cl_2CH-CHCl_2$ can be carried out with
 (a) Cl_2 (b) $Cl_2/h\nu$
 (c) $Cl_2/AlCl_3$ (d) $Cl_2/aq. NaOH$

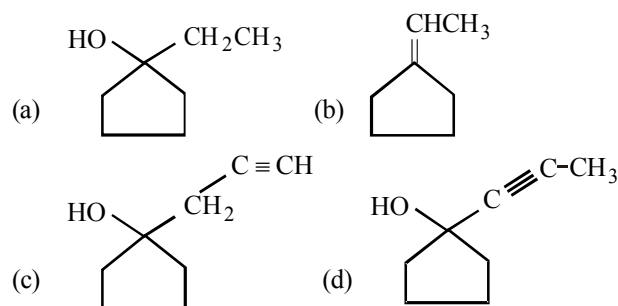
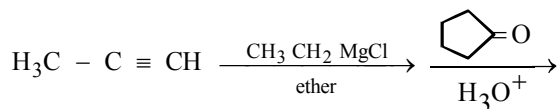
4. A compound (X) (C_5H_8) reacts with ammonical $AgNO_3$ to give a white precipitate, and on oxidation with hot alkaline $KMnO_4$ gives the acid, $(CH_3)_2CHCOOH$, therefore X is –
- (a) $CH_2=CH-CH=CH-CH_3$
(b) $CH_3-CH=CH-CH_2-CH_3$
(c) $(CH_3)_2CH-C\equiv CH$
(d) $(CH_3)_2C=C=CH_2$
5. Combustion of which of the following compound (in the presence of excess of oxygen) does not result in the change in hybrid state of C atom –
- (a) CH_4 (b) $CH_2=CH_2$
(c) CH_3-CH_3 (d) $HC\equiv CH$
6. The reaction of propene with $HOCl$ proceeds via the addition of
- (a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- in a single step
7. Consider the reaction



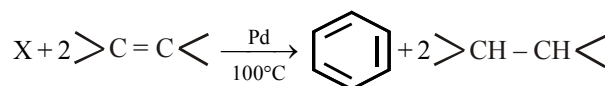
- Compounds I and II are formed in nearly equal amounts
 - Compound I is formed in larger proportions
 - Compound II is formed in larger proportions
 - Relative amount of II cannot be predicted
8. Identify the end product Y –



9. The major product of the following reaction



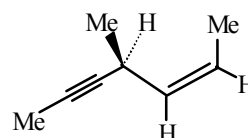
- 10.** In the following change,



The X may be

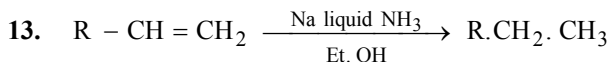
- (a) Cyclohexene (b) Cyclohexadiene
(c) Cyclogexatriene (d) None of these

- 11.**



Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives

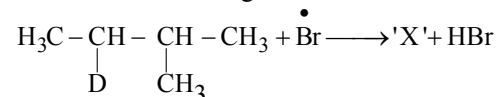
- (a) an optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture
12. The nodal plane in the π -bond of ethene is located in
(a) the molecular plane
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon - carbon σ -bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon - carbon σ -bond.



The reaction is called

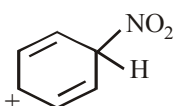
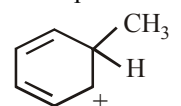
- (a) Birch's reduction (b) Clemensen's reduction
(c) Catalytic reduction (d) All of these

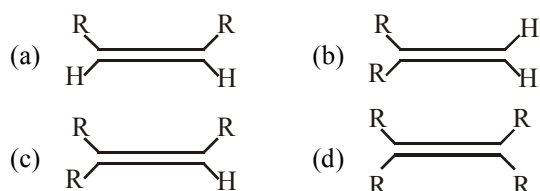
14. Consider the following reaction



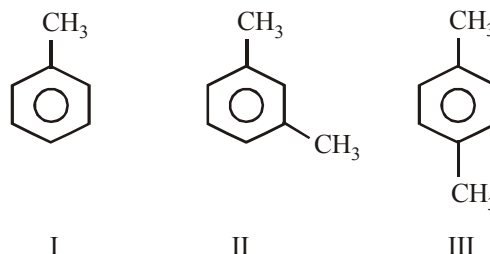
Identify the structure of the major product 'X'

- (a) $\text{H}_3\text{C}-\underset{\text{D}}{\text{CH}}-\overset{\bullet}{\text{CH}}-\overset{\bullet}{\text{CH}_2}$
- (b) $\text{H}_3\text{C}-\underset{\text{D}}{\text{CH}}-\overset{\bullet}{\text{C}}(\text{CH}_3)-\text{CH}_3$
- (c) $\text{H}_3\text{C}-\overset{\bullet}{\text{C}}(\text{D})(\text{CH}_3)-\text{CH}-\text{CH}_3$
- (d) $\text{H}_3\text{C}-\overset{\bullet}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

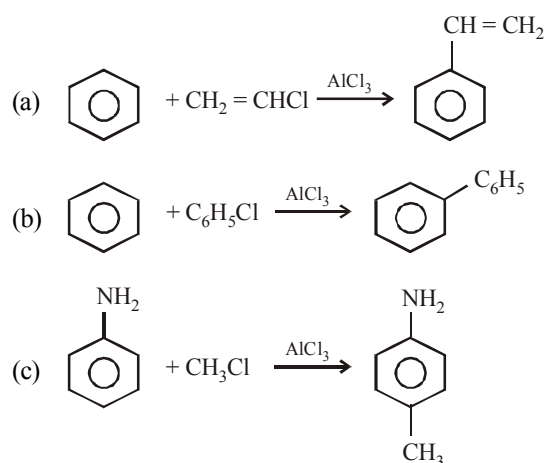
15. Acetylenic hydrogens are acidic because
 (a) Sigma electron density of C – H bond in acetylene is nearer to carbon, which has 50% s-character
 (b) Acetylene has only open hydrogen in each carbon
 (c) Acetylene contains least number of hydrogens among the possible hydrocarbons having two carbons
 (d) Acetylene belongs to the class of alkynes with molecular formula, C_nH_{2n-2} .
16. The probability factor for the replacement of hydrogen atom during chlorination/bromination is
 (a) more important in chlorination
 (b) more important in bromination
 (c) equally important in chlorination/bromination
 (d) not definite
17. Which is the most suitable reagent among the following to distinguish compound (3) from rest of the compounds ?
 1. $CH_3 - C \equiv C - CH_3$
 2. $CH_3 - CH_2 - CH_2 - CH_3$
 3. $CH_3 - CH_2C \equiv CH$
 4. $CH_3 - CH = CH_2$
 (a) Bromine in carbon tetrachloride
 (b) Bromine in acetic acid
 (c) Alk $KMnO_4$
 (d) Ammonical silver nitrate.
18. Which is least reactive towards addition of HCl ?
 (a) $CH_3CH_2CH=CH_2$ (b) $CH_2=CH-CH=CH_2$
 (c) $CH_3CH_2C \equiv CH$ (d) $CH_3CH=CHCHO$
19. In the presence of platinum catalyst, hydrocarbon A adds hydrogen to form n-hexane. When hydrogen bromide is added to A instead of hydrogen, only a single bromo compound is formed. Which of the following is A?
 (a) $CH_3 - CH_2 - CH = CH - CH_2 - CH_3$
 (b) $CH_3 - CH_2 - CH_2 - CH = CH - CH_3$
 (c) $CH_3 - CH = CH - CH_2 - CH_2 - CH_3$
 (d) $CH_2 = CH - CH_2 - CH_2 - CH_2 - CH_3$
20. A hydrocarbon A on chlorination gives B which on heating with alcoholic potassium hydroxide changes into another hydrocarbon C. The latter decolourises Baeyer's reagent and on ozonolysis forms formaldehyde only. A is
 (a) Ethane (b) Butane
 (c) Methane (d) Ethene
21. Which of the following is an aromatic species ?
 (a)  (b) 
 (c)  (d) All of the three
22. Which one of the following alkenes will react faster with H_2 under catalytic hydrogenation conditions? (R = Alkyl Substituent)



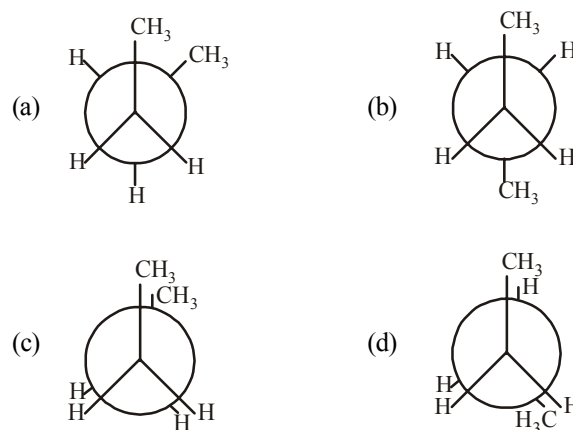
23. Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at $40^\circ C$ gives predominantly
 (a) 1-bromo-2-butene under kinetically controlled conditions
 (b) 3-bromobutene under thermodynamically controlled conditions
 (c) 1-bromo-2-butene under thermodynamically controlled conditions
 (d) 3-bromobutene under kinetically controlled conditions
24. The ease of nitration of the following three hydrocarbons follows the order



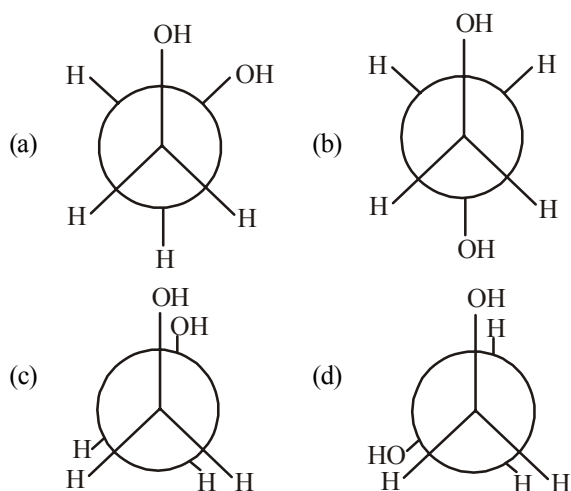
- (a) $II = III \approx I$ (b) $II > III > I$
 (c) $III > II > I$ (d) $I = III > I$
25. Which of the reaction is not possible ?



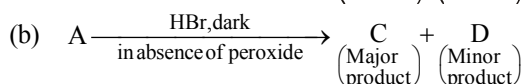
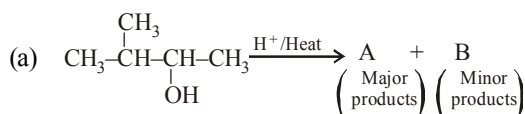
- (d) All the three
26. In the following the most stable conformation of n-butane is:



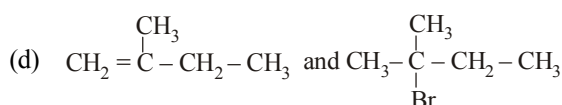
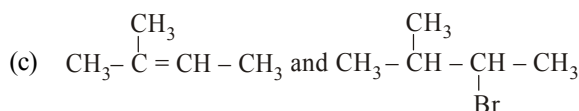
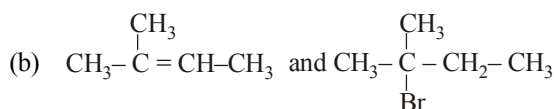
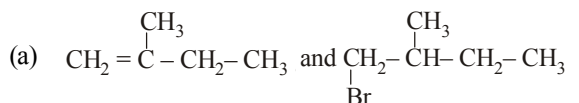
27. Which of the following conformers for ethylene glycol is most stable?



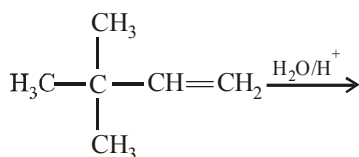
28. In the following reactions,



the major products (A) and (C) are respectively :

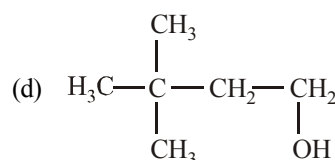
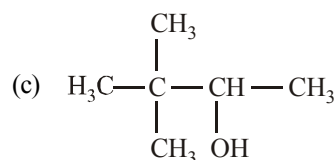
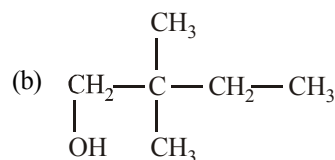
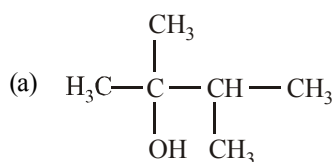


29. In the following reaction :



A B
Minor Product + Major Product

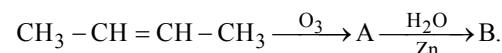
The major product is :



30. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains

- (a) mixture of *o*- and *p*-bromotoluenes
 (b) mixture of *o*- and *p*-dibromobenzenes
 (c) mixture of *o*- and *p*-bromoanilines
 (d) mixture of *o*- and *m*-bromotoluenes

31. In the following sequence of reactions, the alkene affords the compound 'B'

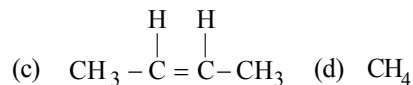


The compound B is

- (a) $\text{CH}_3\text{CH}_2\text{CHO}$ (b) CH_3COCH_3
 (c) $\text{CH}_3\text{CH}_2\text{COCH}_3$ (d) CH_3CHO

32. The treatment of CH_3MgX with $\text{CH}_3\text{C}\equiv\text{C}-\text{H}$ produces

- (a) $\text{CH}_3-\text{CH}=\text{CH}_2$ (b) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$



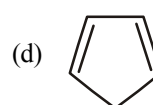
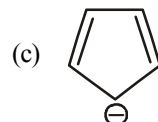
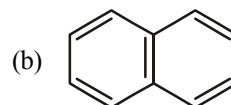
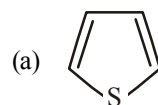
33. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is

- (a) propene (b) 1-butene
 (c) 2-butene (d) ethene

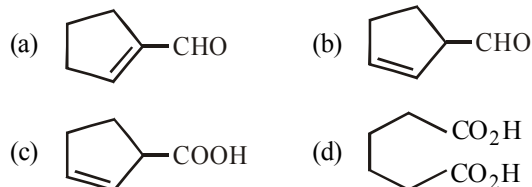
34. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds:

- (a) 1-Pentene
 (b) 2-Pentene
 (c) 2-Methyl-2-pentene
 (d) 2-Methyl-1-pentene

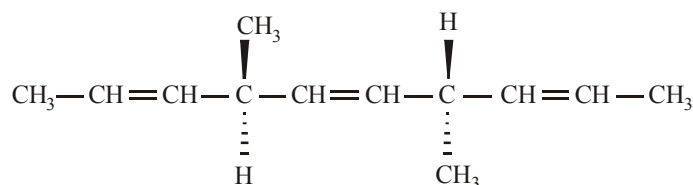
35. The non aromatic compound among the following is :



36. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is



37. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are
 (a) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
 (b) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
 (c) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C}\equiv\text{CH}$
 (d) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
38. The bond energy (in kcal mol^{-1}) of a C–C single bond is approximately
 (a) 1 (b) 10
 (c) 100 (d) 1000
39. The number of optically active products obtained from the complete ozonolysis of the given compound is :

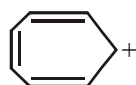


- (a) 0 (b) 1
 (c) 2 (d) 4
40. 2-Hexyne gives *trans*-2-Hexene on treatment with :
 (a) Pt/H_2 (b) Li/NH_3
 (c) Pd/BaSO_4 (d) LiAlH_4
41. The correct increasing order of acidity of the following alkynes
 (1) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$
 (2) $\text{CH}_3-\text{C}\equiv\text{CH}$
 (3) $\text{CH}\equiv\text{CH}$
 (a) $1 < 2 < 3$ (b) $2 < 3 < 1$
 (c) $3 < 2 < 1$ (d) $1 < 3 < 2$
42. Which one of the following has the least boiling point?
 (a) 2, 2-dimethylpropane (b) n-butane
 (c) 2-methylpropane (d) n-pentane

43. Hyperconjugation is more pronounced in
 (a) 2-methylpropene
 (b) but-2-ene
 (c) 2, 3-dimethylbut-2-ene
 (d) 2-methylbut-2-ene
44. Reaction of hydrogen bromide with propene in the absence of peroxide is a/an
 (a) free radical addition
 (b) nucleophilic addition
 (c) electrophilic substitution
 (d) electrophilic addition
45. Among the three conformations of ethane, the order of stability follows the sequence
 (a) eclipsed > gauche > staggered
 (b) eclipsed > staggered > gauche
 (c) staggered > gauche > eclipsed
 (d) gauche > staggered > eclipsed

DIRECTIONS for Qs. 46 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
46. **Statement-1** : 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.
Statement-2 : It involves the free radical mechanism.
47. **Statement-1** : CH_4 does not react with Cl_2 in dark.
Statement-2 : Chlorination of CH_4 takes place in sunlight.
48. **Statement-1** : Iodination of alkanes is reversible.
Statement-2 : Iodination is carried out in presence of iodic acid.
49. **Statement-1** : All the hydrogen atoms in $\text{CH}_2=\text{C}=\text{CH}_2$ lie in one plane.
Statement-2 : Carbon atoms are sp^2 and sp hybridized.
50. **Statement-1** : Tropylium cation is aromatic in nature



Statement-2 : The only property that determines its aromatic behaviour is its planar structure.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Arrange the following in decreasing order of their boiling points.
 - n*-butane
 - 2-methylbutane
 - n*-pentane
 - 2,2-dimethylpropane
 - $1 > 2 > 3 > 4$
 - $2 > 3 > 4 > 1$
 - $4 > 3 > 2 > 1$
 - $3 > 2 > 4 > 1$
- Arrange the halogens F_2 , Cl_2 , Br_2 , I_2 , in order of their increasing reactivity with alkanes.
 - $I_2 < Br_2 < Cl_2 < F_2$
 - $Br_2 < Cl_2 < F_2 < I_2$
 - $F_2 < Cl_2 < Br_2 < I_2$
 - $Br_2 < I_2 < Cl_2 < F_2$
- The increasing order of reduction of alkyl halides with zinc and dilute HCl is
 - $R-Cl < R-I < R-Br$
 - $R-Cl < R-Br < R-I$
 - $R-I < R-Br < R-Cl$
 - $R-Br < R-I < R-Cl$
- The correct IUPAC name of the following alkane is

$$\begin{array}{c}
 \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \\
 | \qquad \qquad \qquad | \\
 \text{CH} \qquad \qquad \qquad \text{CH}_2 \\
 | \qquad \qquad \qquad | \\
 \text{CH}_3 \quad \text{CH}_3 \qquad \text{CH}_3
 \end{array}$$
 - 3,6-diethyl-2-methyloctane
 - 5-isopropyl-3-ethyloctane
 - 3-ethyl-5-isopropyloctane
 - 3-isopropyl-6-ethyloctane
- The addition of HBr to 1-butene gives a mixture of products A, B and C.

$$\begin{array}{c}
 \text{Br} \\
 | \\
 \text{H}_3\text{C}_2-\text{C}-\text{CH}_3 \\
 | \\
 \text{H}
 \end{array}$$

(A)

$$\begin{array}{c}
 \text{C}_2\text{H}_5 \\
 | \\
 \text{H}-\text{C}-\text{CH}_3 \\
 | \\
 \text{Br}
 \end{array}$$

(B)

(C) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br}$

The mixture consists of

 - A and B as major and C as minor products
 - B as major, A and C as minor products
 - B as minor, A and C as major products
 - A and B as minor and C as major products
- Which of the following will not show geometrical isomerism?

$$\begin{array}{c}
 \text{F} \quad \text{H} \\
 \diagdown \quad \diagup \\
 \text{C} = \text{C} \\
 \diagup \quad \diagdown \\
 \text{Cl} \quad \text{D}
 \end{array}$$

(a)

$$\begin{array}{c}
 \text{F} \quad \text{F} \\
 \diagdown \quad \diagup \\
 \text{C} = \text{C} \\
 \diagup \quad \diagdown \\
 \text{Cl} \quad \text{Cl}
 \end{array}$$

(b)

$$\begin{array}{c}
 \text{H}_3\text{C} \quad \text{C}_2\text{H}_5 \\
 \diagdown \quad \diagup \\
 \text{C} = \text{C} \\
 \diagup \quad \diagdown \\
 \text{H}_5\text{C}_2 \quad \text{CH}_3
 \end{array}$$

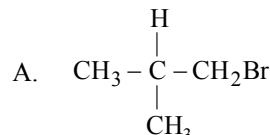
(c)

$$\begin{array}{c}
 \text{CH}_3 \quad \text{CH}_3 \\
 \diagdown \quad \diagup \\
 \text{C} = \text{C} \\
 \diagup \quad \diagdown \\
 \text{CH}_3 \quad \text{C}_2\text{H}_5
 \end{array}$$

(d)
- Arrange the following hydrogen halides in order of their decreasing reactivity with propene.
 - $\text{HCl} > \text{HBr} > \text{HI}$
 - $\text{HBr} > \text{HI} > \text{HCl}$
 - $\text{HI} > \text{HBr} > \text{HCl}$
 - $\text{HCl} > \text{HI} > \text{HBr}$
- Arrange the following carbanions in order of their decreasing stability.

- $\text{H}_3\text{C}-\text{C}\equiv\text{C}^-$
 - $\text{H}-\text{C}\equiv\text{C}^-$
 - $\text{H}_3\text{C}-\bar{\text{C}}\text{H}_2$
- $\text{A} > \text{B} > \text{C}$
 - $\text{B} > \text{A} > \text{C}$
 - $\text{C} > \text{B} > \text{A}$
 - $\text{C} > \text{A} > \text{B}$

- Arrange the following alkyl halides in decreasing order of the rate of β -elimination reaction with alcoholic KOH.



- $\text{CH}_3-\text{CH}_2-\text{Br}$
 - $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br}$
- $\text{A} > \text{B} > \text{C}$
 - $\text{C} > \text{B} > \text{A}$
 - $\text{B} > \text{C} > \text{A}$
 - $\text{A} > \text{C} > \text{B}$

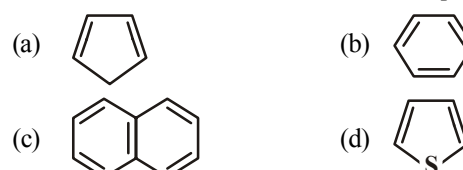
- Which of the following reactions of methane is incomplete combustion?

- $2\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Cu} / 523 \text{ K} / 100 \text{ atm}} 2\text{CH}_3\text{OH}$
- $\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Mo}_2\text{O}_3} \text{HCHO} + \text{H}_2\text{O}$
- $\text{CH}_4 + \text{O}_2 \longrightarrow \text{C}(s) + 2\text{H}_2\text{O}(l)$
- $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

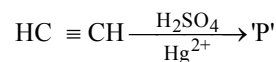
NEET/AIPMT (2013-2017) Questions

- Which of the following chemical system is non aromatic?

[NEET Kar. 2013]



- In the following reaction :



Product 'P' will not give

[NEET Kar. 2013]

- Iodoform test
- Tollen's reagent test
- Brady's reagent test
- Victor Meyer test

- The radical,  is aromatic because it has : [2013]

- 7 p-orbitals and 6 unpaired electrons
- 7 p-orbitals and 7 unpaired electrons
- 6 p-orbitals and 7 unpaired electrons
- 6 p-orbitals and 6 unpaired electrons

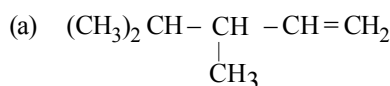
14. Which of the following organic compounds has same hybridization as its combustion product (CO_2)? [2014]

(a) Ethane (b) Ethyne
(c) Ethene (d) Ethanol

15. The oxidation of benzene by V_2O_5 in presence of air produces : [2015 RS]

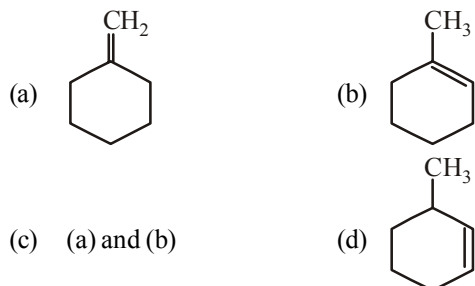
(a) benzoic anhydride (b) maleic anhydride
(c) benzoic acid (d) benzaldehyde

16. 2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid? [2015 RS]

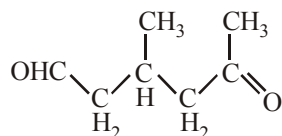


(b) $(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}_2$
(c) $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3$
(d) $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$

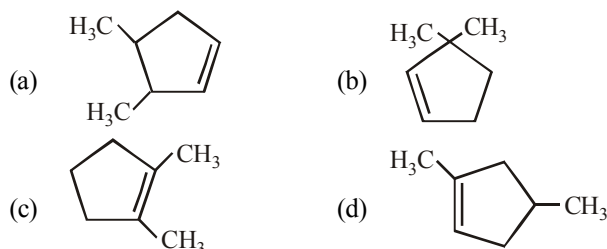
17. In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule, to give a product 1-chloro-1-methylcyclohexane. The possible alkene is : [2015 RS]



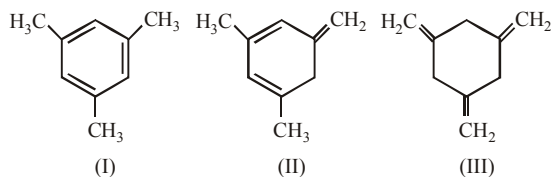
18. A single compound of the structure : [2015]



is obtainable from ozonolysis of which of the following cyclic compounds?



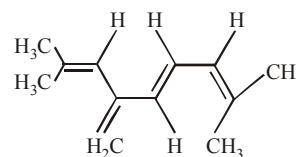
19. Given:



The enthalpy of the hydrogenation of these compounds will be in the order as : [2015]

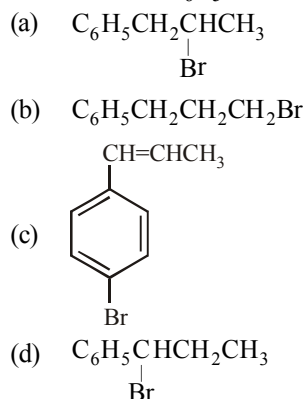
(a) $\text{III} > \text{II} > \text{I}$ (b) $\text{II} > \text{III} > \text{I}$
(c) $\text{II} > \text{I} > \text{III}$ (d) $\text{I} > \text{II} > \text{III}$

20. The total number of π -bond electrons in the following structure is : [2015]

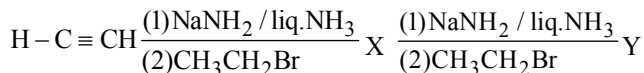


(a) 8 (b) 12
(c) 16 (d) 4

21. The reaction of $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ with HBr produces: [2015]



22. In the reaction



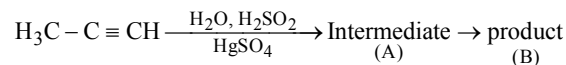
X and Y are

(a) X = 1-Butyne; Y = 3-Hexyne
(b) X = 2-Butyne; Y = 3-Hexyne
(c) X = 2-Butyne; Y = 2-Hexyne
(d) X = 1-Butyne; Y = 2-Hexyne

23. Which one is the correct order of acidity? [2017]

(a) $\text{CH}\equiv\text{CH} > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}_3$
(b) $\text{CH}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_3-\text{CH}_3$
(c) $\text{CH}_3-\text{CH}_3 > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}\equiv\text{CH}$
(d) $\text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}=\text{CH}_2 > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}\equiv\text{CH}$

24. Predict the correct intermediate and product in the following reaction : [2017]



(a) A : $\text{H}_3\text{C}-\underset{\text{OH}}{\text{C}}=\text{CH}$ B : $\text{H}_3\text{C}-\underset{\text{SO}_4}{\text{C}}=\text{CH}_2$
(b) A : $\text{H}_3\text{C}-\underset{\text{O}}{\text{C}}=\text{CH}_3$ B : $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$
(c) A : $\text{H}_3\text{C}-\underset{\text{OH}}{\text{C}}=\text{CH}_2$ B : $\text{H}_3\text{C}-\underset{\text{O}}{\text{C}}=\text{CH}_3$
(d) A : $\text{H}_3\text{C}-\underset{\text{SO}_4}{\text{C}}=\text{CH}_2$ B : $\text{H}_3\text{C}-\underset{\text{O}}{\text{C}}-\text{CH}_3$

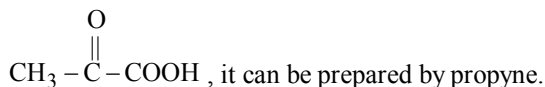
25. With respect to the conformers of ethane, which of the following statements is true? [2017]

(a) Bond angle changes but bond length remains same
(b) Both bond angle and bond length change
(c) Both bond angles and bond length remains same
(d) Bond angle remains same but bond length changes

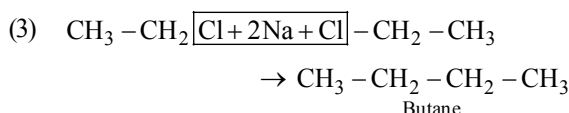
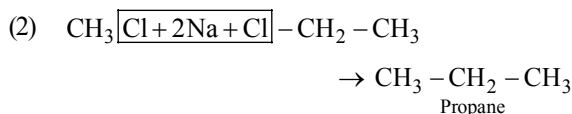
Hints & Solutions

EXERCISE - 1

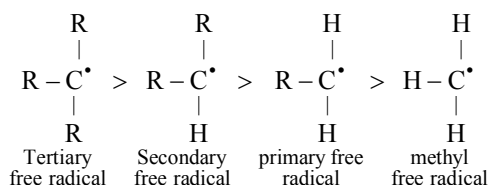
1. (b) Since Pyruvic acid has three carbons



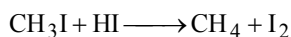
2. (c) (1) $\text{CH}_3 \boxed{\text{Cl} + 2\text{Na} + \text{Cl}} - \text{CH}_3 \rightarrow \text{CH}_3 - \text{CH}_3$
Ethane



3. (c) The reactivity of H-atoms depends upon the stability of free radicals follows the order :
Tertiary > secondary > primary, therefore, reactivity of H-atoms follows the same order, i.e., tertiary > secondary > primary.

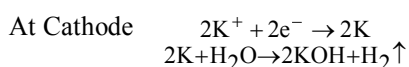
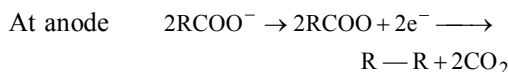
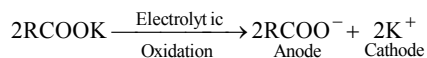


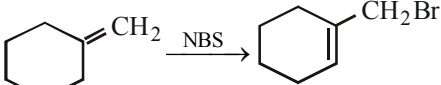
4. (c) $\text{CH}_3\text{Cl} + \text{AlCl}_3 \longrightarrow \text{CH}_3^+ + \text{AlCl}_4^-$
Electrophile
Here the electrophile is alkyl carbonium ion.
5. (a) CH_3I is the compound.



6. (a) $\text{Cl}_2 \xrightarrow{\text{Chain initiation}} 2\text{Cl}^\bullet$

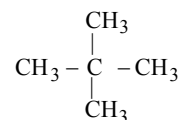
7. (a) Electrolysis of a concentrated aqueous solution of either sodium or potassium salts of saturated mono-carboxylic acids yields higher alkane at anode.



8. (c) 
(Kolbe's Method)

9. (a) $\text{C}_2\text{H}_5\text{MgBr} + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_6 + \text{Mg} \begin{array}{l} \text{Br} \\ \text{OH} \end{array}$

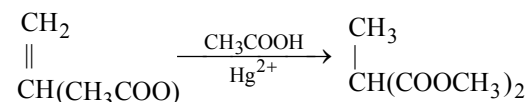
10. (c) In neopentane all the H atoms are same (1°).



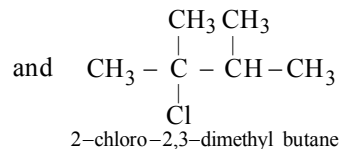
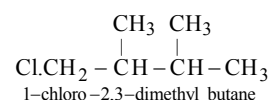
11. (c) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{CH}_3 \xrightarrow[\text{sunlight}]{\text{Br}_2} \text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{Br}}{|}{\text{C}}} - \text{CH}_2\text{CH}_3$
2-bromo-2-methyl butane

Ease of replacement of H-atom $3^\circ > 2^\circ > 1^\circ$.

12. (a) $\begin{array}{c} \text{CH} \\ ||| \\ \text{CH} \end{array} + \text{CH}_3\text{COOH} \xrightarrow{\text{Hg}^{2+}}$



13. (c) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3$. Since it contains only two types of H-atoms hence it will give only two mono chlorinated compounds viz.



14. (b) $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}^- \\ \diagup \\ \text{CH}_3 \end{array}, \text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{CH}_3$
(2-methyl pentane)
Isopropyl group

It contains isopropyl group.

15. (c) $\text{CH}_3 - \overset{\text{Cl}}{\overset{|}{\text{C}}} - \overset{\text{Cl}}{\overset{|}{\text{C}}} - \text{CH}_3$. 2,3-dichloro butane will exhibit optical

isomerism due to the presence of two asymmetric carbon atom.

16. (a) Octane number is the % of *iso*-octane in the mixture of *iso*-octane and *n*-heptane which produces same knocking effect as the fuel under observation.

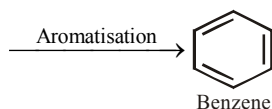
Given % of *n*-heptane = 11%

∴ % of *iso*-octane = 100 – 11 = 89%

∴ Octane number is 89.

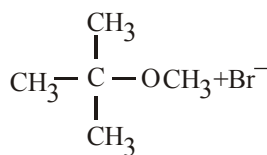
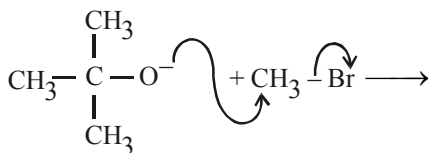
17. (a) More branched is the alkane, higher will be its octane number because more branched chains have higher antiknocking tendency than the corresponding straight chain hydrocarbons. Among the given options 2,2,4-trimethyl pentane, will have the highest octane number, 100.

18. (b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$



Aromatisation is a process in which aromatic compounds are formed from open chain compounds.

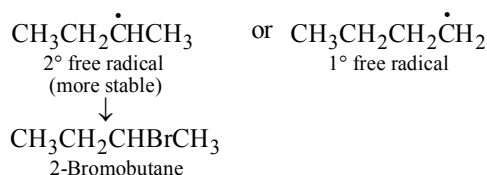
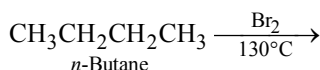
19. (c) For the preparation of *t*-butylmethyl ether, the method described in option (c) should be recommended. It is due to the reason that alkoxides are not only nucleophiles but also strong bases. So, they tend to react with alkyl halides by elimination to yield alkenes. Here the danger of competition between nucleophilic substitution and elimination reaction increases with the tendency of alkyl halides to undergo elimination which follows the order $3^\circ > 2^\circ > 1^\circ$. So, first of all we have to select 1° halide and obviously the second choice will be sodium *t*-butoxide.



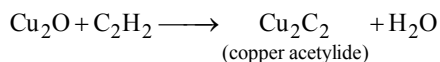
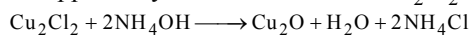
Also the method described in option (a) is not suitable as the ease of dehydration of alcohol follows the order $3^\circ > 2^\circ > 1^\circ$. So *t*-butanol will quickly give an alkene.

20. (c) The reaction of Br_2 on alkane proceeds via free radical mechanism; 2° free radical is more stable than 1° free radical.

Hence 2-bromobutane is major product.



21. (c) C_2H_4 and CH_4 will come out unaffected. C_2H_2 forms copper acetylide with ammoniacal Cu_2Cl_2



22. (b) Sum of masses of C and H = 10.5 + 1.0 = 11.5

$$\% \text{ of C} = \frac{10.5}{11.5} \times 100 = 91.3\%$$

$$\% \text{ of H} = \frac{1.0}{11.5} \times 100 = 8.7\%$$

Element	%	Ratio of atoms	Simplest ratio
C	91.3	91.3/12 = 7.61	7.61/7.61 = 1 × 7 = 7
H	8.7	8.7/1 = 8.7	8.7/7.61 = 1.14 × 7 = 8

∴ Empirical formula = C_7H_8

We know that $n = \frac{PV}{RT}$

$$\frac{\text{mass}}{\text{molar mass}} = \frac{PV}{RT}$$

$$\frac{2.81}{M} = \frac{1 \times 1}{0.082 \times 400}; M = 92.168 \approx 92$$

$$\therefore n = \frac{84 + 8}{92} = 1$$

$$\therefore \text{Molecular formula} = (\text{C}_7\text{H}_8) \times 1 = \text{C}_7\text{H}_8$$

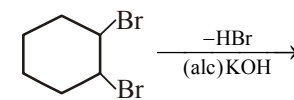
23. (d) 

In all these we find CH_2 group i.e. correct answer is (d).

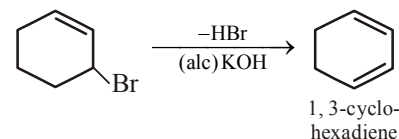
24. (b) For isomeric alkanes, the one having longest straight chain has highest b.p. because of larger surface area.

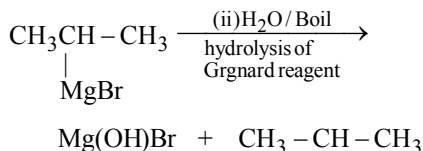
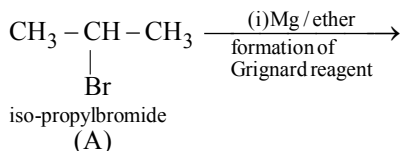
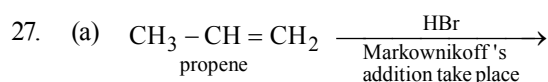
25. (d) $\text{H} \overset{\sigma}{\underset{\sigma}{|}} \text{C} \overset{\pi}{=} \text{C} \overset{\sigma}{\underset{\sigma}{|}} \text{C} \overset{\pi}{=} \text{C} \overset{\sigma}{\underset{\sigma}{|}} \text{H}$

As shown above, the given compound (1, 3-butadiene) contains 9σ and 2π bonds.

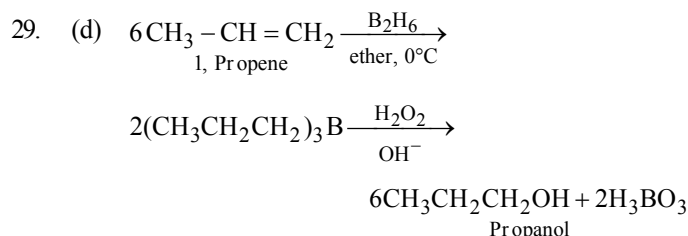
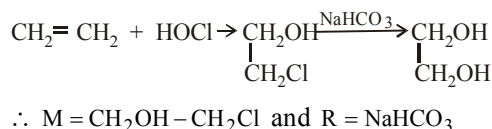
26. (b) 

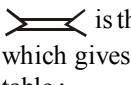
1, 2-dibromo-
cyclohexane

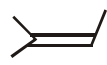
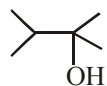
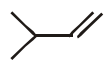
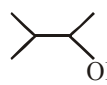




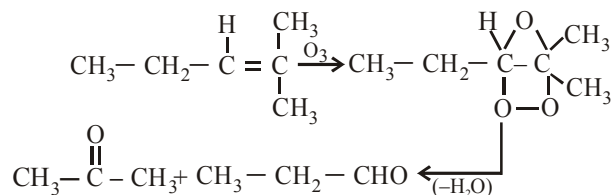
28. (c) We know that



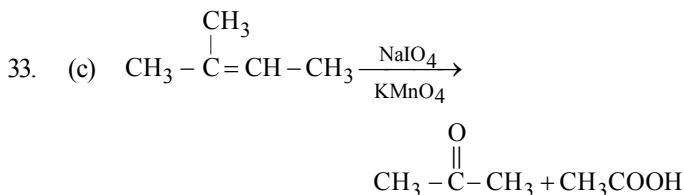
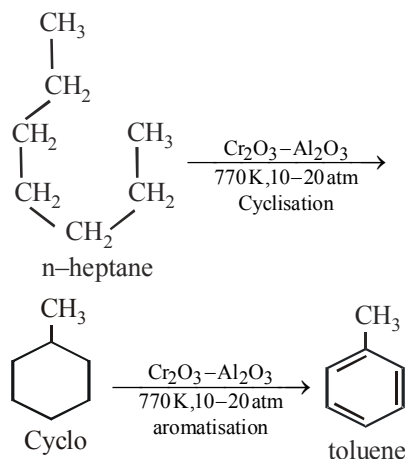
30. (c)  is the only compound among the given options which gives 2, 3-dimethyl-2-butanol as shown in the table :

Compound	Product obtained on hydration
	 2-methyl-2-propanol
	 2-methyl-2-butanol
	 2,3-dimethyl-2-butanol
	 3-methyl-2-butanol

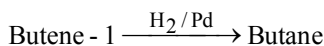
31. (a)



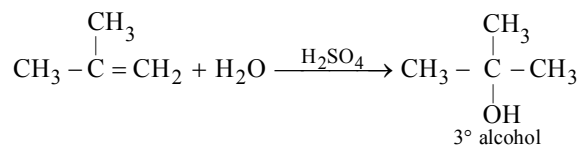
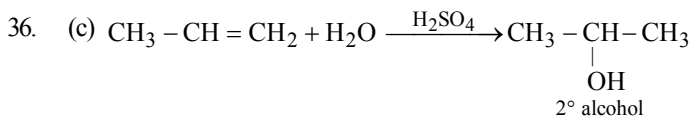
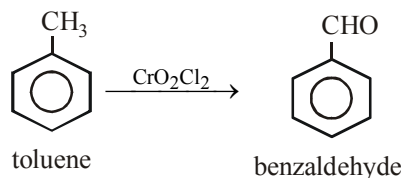
32. (b) n-heptane first undergo cyclisation by passing over $\text{Cr}_2\text{O}_3 - \text{Al}_2\text{O}_3$ at 770 K and 10 – 20 atm and gives methyl cyclohexane which on aromatization gives toluene.



34. (c) Alkenes combine with hydrogen under pressure and in presence of a catalyst (Ni, Pt or Pd) and form alkanes.



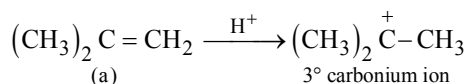
35. (a) Toluene on oxidation with mild oxidising agent like chromyl chloride (CrO_2Cl_2) gives benzaldehyde.



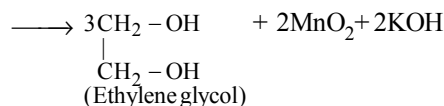
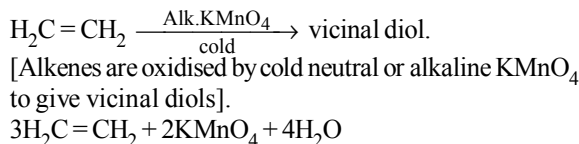
Addition follows Markownikoff's rule.

37. (a) Only alkenes and alkynes (or compounds having $\text{C} = \text{C}$ or $\text{C} \equiv \text{C}$) decolourise alkaline KMnO_4 solution. Only (a) is alkene, other three are alkanes.

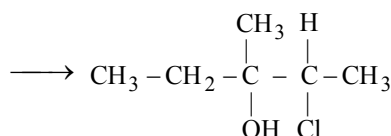
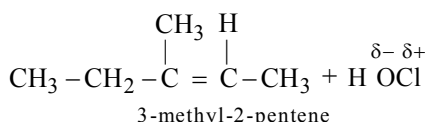
38. (a) Addition of HBr to alkene is an electrophilic addition reaction. The reaction proceeds via formation of carbonium ion. Since 3° carbonium ion is most stable, hence the reactant which involves formation of 3° carbonium ion will react most easily with HBr



39. (c) Completing the reaction



40. (c) The reaction follows Markownikoff rule i.e. negative part adds to carbon atom having lesser number of hydrogen atoms.



41. (d) is the answer because it contains two benzene rings.

42. (c) Cyclohexene +
- KMnO_4
- (cold & alkaline)

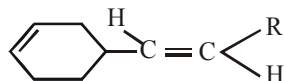
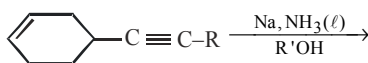


43. (d)
- $\text{CH}_2=\text{CH}=\text{CH}=\text{CH}_2$

1, 3-butadiene

It is a conjugated diene (having alternate $\text{C}=\text{C}$ and $\text{C}-\text{C}$). It reacts with HBr . It polymerises to form synthetic rubber.

44. (d) It is a stereoselective reaction and in it a trans product is formed.



[It is a reduction. Metal dissolved reduction $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ reaction is stereo selective].

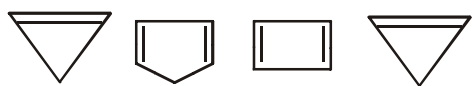
45. (c) Knocking depends upon the structure of the hydrocarbon and follows the order
- n
- Alkanes > branched alkanes > straight chain alkenes > branched alkenes > arenes

46. (c)
- $\text{CH}\equiv\text{CH} + \text{H}-\text{CN} \xrightarrow{\text{Ba(CN)}_2} \text{CH}_2=\text{CHCN}$

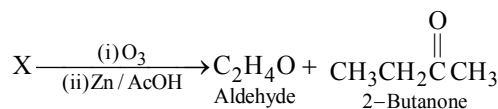
Vinyl cyanide

47. (d) Allene is
- $\text{H}_2\text{C}=\text{C}=\text{CH}_2$

48. (a) According to Huckel's rule, the cyclic planar conjugated system having
- $(4n+2)$
- π
- electrons show aromaticity.

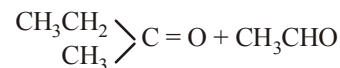
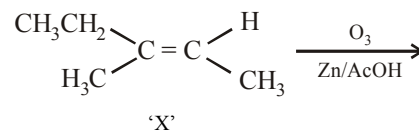
2 π electrons 4 π electrons 4 π electrons 4 π electrons

49. (a) Putting the given data in form of equation, we get

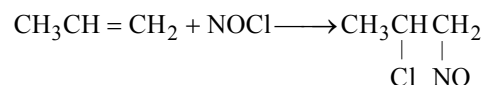


The formula of an aldehyde with molecular formula $\text{C}_2\text{H}_4\text{O}$ is CH_3CHO .

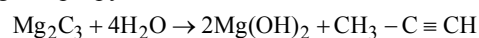
The compound X is



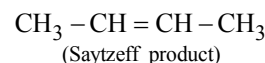
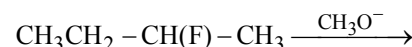
50. (b) Nitrosyl chloride adds on olefins according to Markownikov's rule, where
- NO^+
- constitutes the positive part of the addendum.



51. (b)
- Mg_2C_3
- gives propyne.

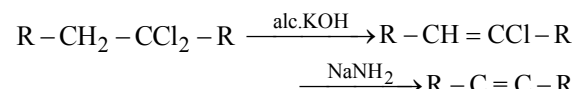


52. (b)
- $\text{CH}_3\text{CH}_2-\text{CH}(\text{F})-\text{CH}_3$
- is a secondary halide. So, it will undergo dehydro-halogenation to form alkene.



53. (b) Greater the
- s
- character of C, higher is its electronegativity, shorter and stronger will be the bond formed by it. Thus
- $-\text{C}\equiv\text{C}-$
- is the strongest bond.

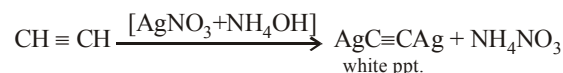
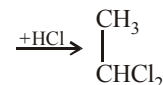
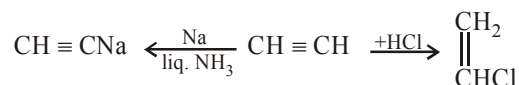
54. (c) On heating ethylene chloride (1, 1 dichloro ethane) with alcoholic potash followed by sodamide alkyne is obtained



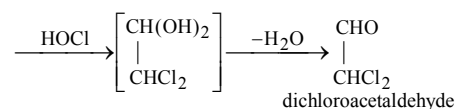
55. (c)
- V_2O_5
- is used as a catalyst in contact process for the manufacture of
- SO_3
- and hence
- H_2SO_4
- . In Haber-Bosch process for the manufacture of
- NH_3
- , finely divided Fe + molybdenum are used.

56. (a) Only
- C_2H_2
- (acetylene) has acidic H-atoms and hence reacts with
- NaNH_2
- to form sodium salt, i.e.,
- $\text{HC}\equiv\text{CH} + \text{NaNH}_2 \longrightarrow \text{HC}\equiv\text{CNa} + \text{NH}_3$
- .

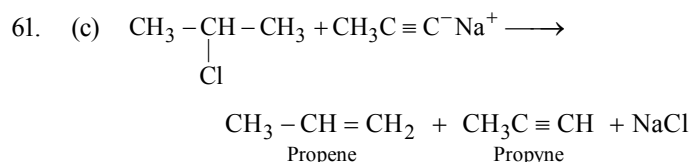
57. (a) Acetylene reacts with the other three as:



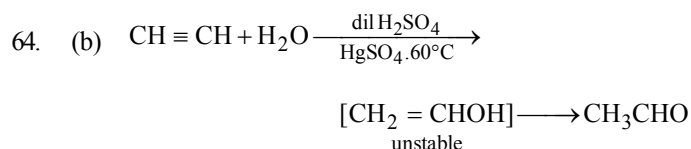
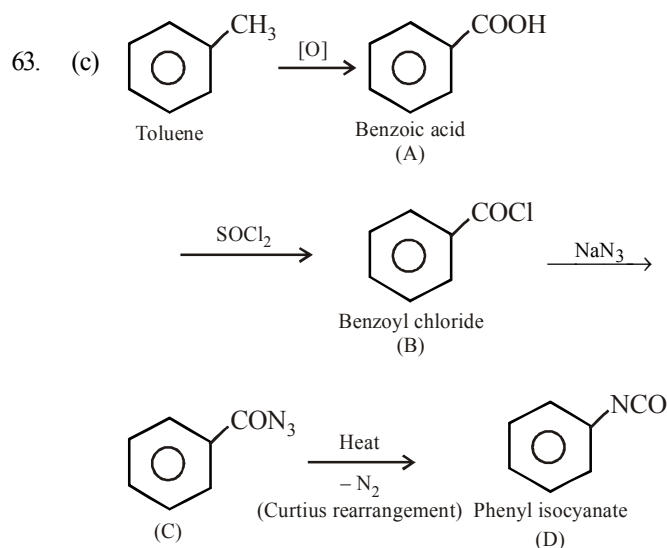
58. (c)
- $\text{CH}\equiv\text{CH} + \text{HOCl} \longrightarrow \begin{array}{c} \text{CHOH} \\ || \\ \text{CHCl} \end{array}$



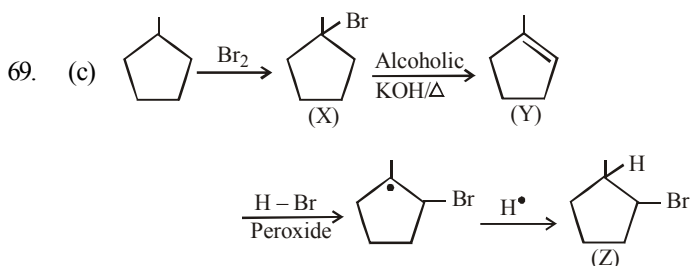
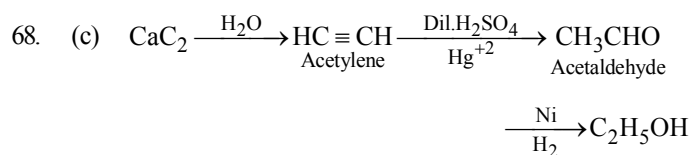
59. (b) SO_3 participates in sulphonation of benzene.
 60. (d) $\text{H}_2/\text{Pd}/\text{BaSO}_4$ reduces an alkyne to *cis*-alkene, H_2/Pt reduces it to alkane, NaBH_4 does not reduce an alkyne. Reduction of an alkyne by active metal in liq. NH_3 gives *trans*-alkene.



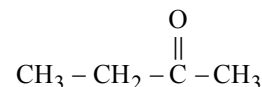
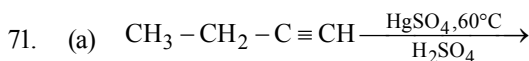
62. (a) Terminal alkynes give a white precipitate easily on reaction with ammonical silver nitrate solution.



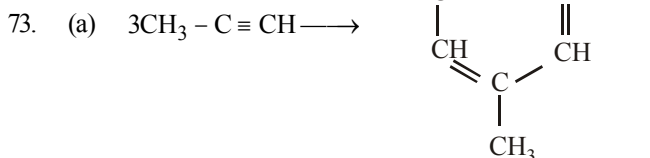
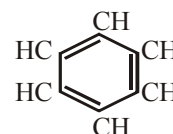
65. (d) In 1-butyne terminal hydrogen is acidic where as in 2-butyne there is no terminal hydrogen. Thus 2-butyne will not react with ammonical Cu_2Cl_2 . While 1-butyne, being terminal alkyne, will give red ppt. with ammonical cuprous chloride
 66. (b) The reaction follows Markownikoff rule, namely the bromide ion adds on to the carbon having the least number of hydrogen and the more positive part namely the $-\text{NO}$ group adds to the other carbon of the double bond.
 67. (a) As the number of bonds between carbon atoms increases, electronegativity of that carbon also increases due to increasing active power of electrons. Also sp hybrid is more e^- negative than sp^2 which is more electronegative than sp^3 ($\because$ s character decreases) Hence, option (a) is correct.



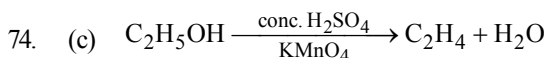
70. (a)



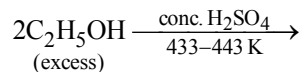
72. (c) Kekule in 1865 suggested a ring structure of benzene in which the ring was composed of six carbon atoms, each of which carries one atom of hydrogen. To satisfy the fourth valency of the carbon atom, he suggested three alternate double bonds.



Mesitylene or 1,3,5-trimethyl benzene

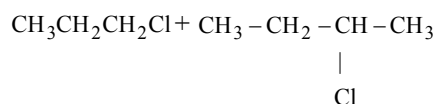
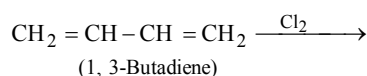


Note : If ethyl alcohol is taken in excess and the reaction is carried out at a temperature of 433-443 K diethyl ether is formed.

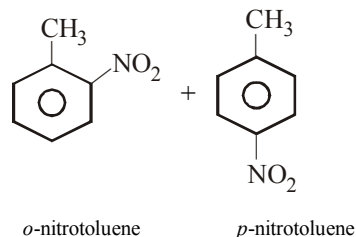
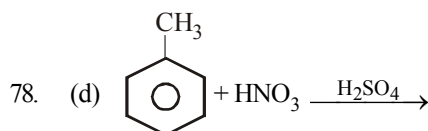
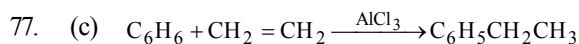


75. (d) In $\text{CH} \equiv \text{CH}$ triple bond consists of one σ and two π bonds.

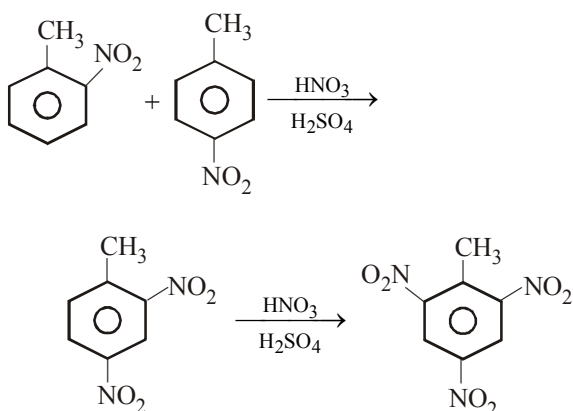
76. (c) When 1,3-butadiene is reacted with Cl_2 , then a mixture of 1-chlorobutane and 2-chlorobutane is formed.



(1-chlorobutane) (2-chlorobutane)
 Hence, option (b) is correct.



Under vigorous conditions, toluene produces TNT or trinitrotoluene.

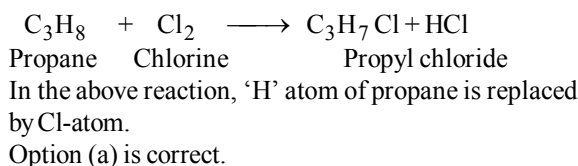


(TNT or Trinitrotoluene)

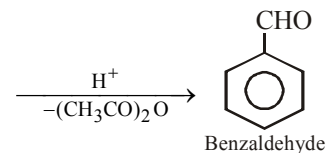
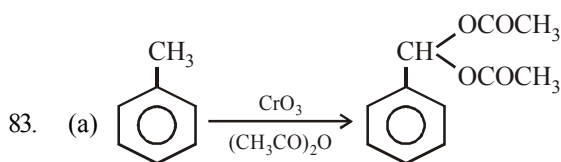
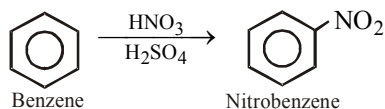
79. (c) As per Markovnikoff's law, the positive part (e.g. H of HX) or the less negative part of the reagent adds to that carbon atom of alkene which has more number of hydrogen atoms (the rich gets richer). So (c) is the correct option as the two carbons containing the double bond have one H atom each i.e. symmetric.

80. (a) Resonance energy is the difference in observed energy and calculated energy of resonance hybrid. Greater its value, more is its stability. So, resonance energy represents stability of benzene.

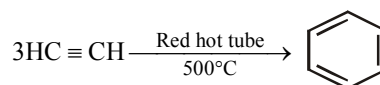
81. (a) That reaction in which an atom or a group of atoms attached to C-atom of the substrate molecule is replaced by another atom or group of atoms is called as substitution reaction.



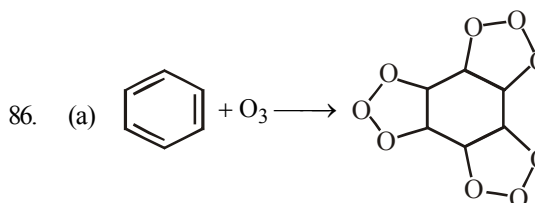
82. (b) Benzene undergoes electrophilic substitution with HNO_3/H_2SO_4 (Nitration).



84. (b) Benzene can be obtained by polymerisation of acetylene.

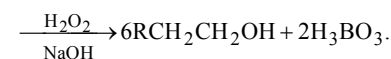
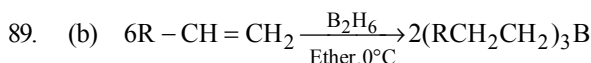


85. (c) They have a relatively high percentage of carbon.

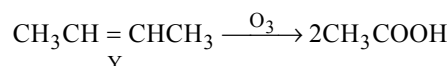
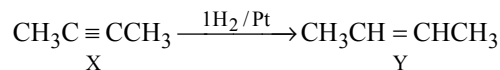
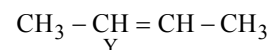
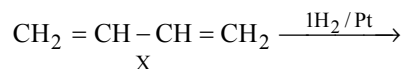


87. (c) Double bond in between carbon-carbon is present in alkenes whose general formula is C_nH_{2n} .

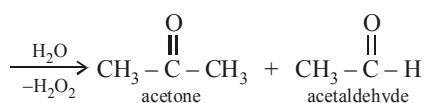
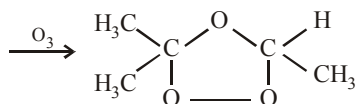
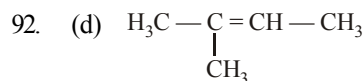
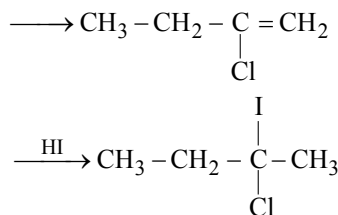
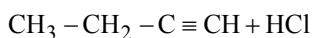
88. (d) The compound has $-NO_2$ group, so N is not present in ring and the six membered ring has C atoms only, so it should be homocyclic. Further the six-membered cyclic compound has only two double bonds, it is not aromatic (for aromaticity six membered cyclic compound should have three alternate double bonds)



90. (d) Formation of only CH_3COOH by ozonolysis indicates that the compound Y should be $CH_3CH=CHCH_3$ which can be formed by all of the three given compounds

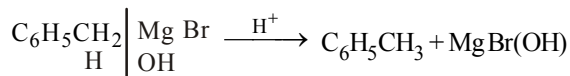
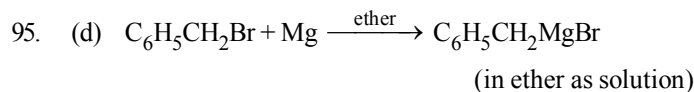


91. (c) This reaction occurs according to Markovnikoff's rule which states that when an unsymmetrical alkene undergo hydrohalogenation, the negative part goes to that C-atom which contain lesser no. of H-atom.

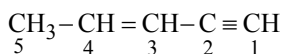


93. (c) If both the double and triple bonds are present, the compound is regarded as derivative of alkyne. Further if double and triple bonds are at equidistance from either side, the preference is given to double bond.

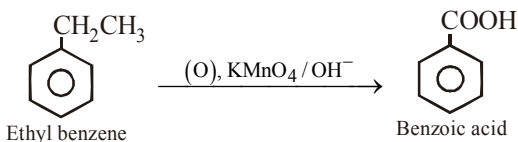
94. (b) During cracking higher hydrocarbons (liquid) are converted to lower gaseous hydrocarbons.



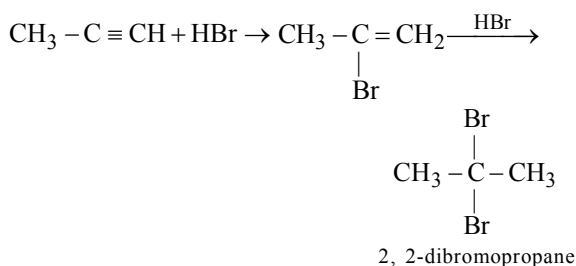
96. (c) When both double and triple bonds are present, then triple bond is considered as the principal group.



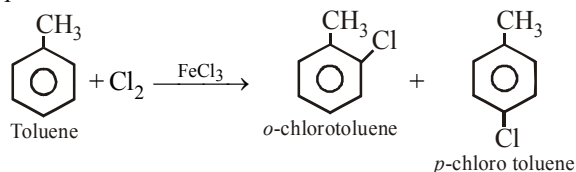
97. (d) When alkyl benzene are oxidised with alkaline KMnO_4 (strong oxidising agent) the entire alkyl group is oxidised to $-\text{COOH}$ group regardless of length of side chain.



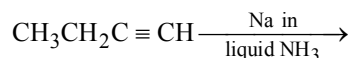
98. (b) The reaction follows Markownikov's rule which states that when unsymmetrical reagent adds across unsymmetrical double or triple bond the negative part adds to carbon atom having lesser number of hydrogen atoms.



99. (d) FeCl_3 is Lewis acid. In presence of FeCl_3 *o*- and *p*-chlorotoluene is formed.

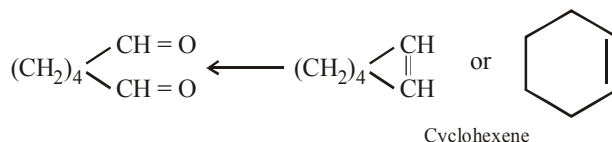


100. (b) Alkynes having terminal $-\text{C} \equiv \text{H}$ react with Na in liquid ammonia to yield H_2 gas. $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$ can react with Na in liquid NH_3 so the correct answer is (b).



EXERCISE - 2

1. (c) Since the alkene on ozonolysis gives a single compound, having two aldehydic groups, it must be cyclic

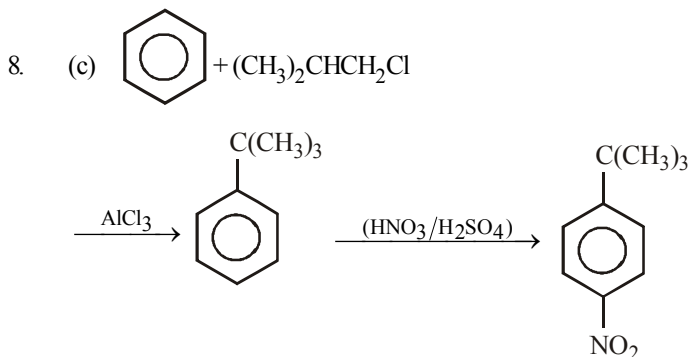


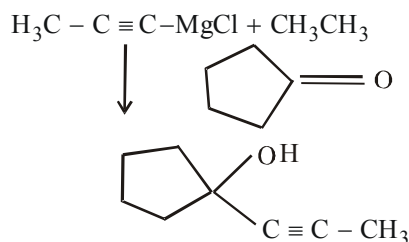
2. (b) Reaction (b) does not involve the formation of Cl^+ , the electrophile.

3. (a)
4. (c) Compound X reacts with ammoniacal AgNO_3 solution, so it must be a terminal alkyne. Formation of $(\text{CH}_3)_2\text{CHCOOH}$ on oxidation of X with hot alkaline KMnO_4 further confirms that X is $(\text{CH}_3)_2\text{CHC} \equiv \text{CH}$.

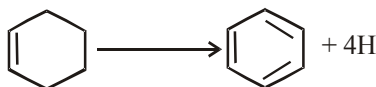
5. (d) Combustion of hydrocarbons change them to CO_2 gas in which C is sp -hybridised. Therefore, $\text{HC} \equiv \text{CH}$, in which carbon is in sp -hybrid state will not result in the change in hybrid state of C-atom

6. (b)
7. (c) Bromination of alkanes in presence of UV light takes place through free radical mechanism. Bromine substitutes that hydrogen, abstraction of which leads to formation of stablest free radical. (Reactivity Selectivity Principle). So in isobutane, bromine will come at second carbon, since after abstraction of hydrogen it will form 3° free radical giving II as the major product.





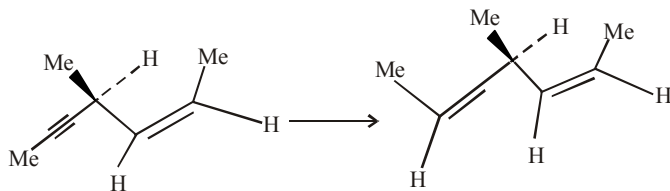
10. (a) Two moles of alkene is reduced X must be



which give 4H atoms needed for alkene.

11. (b) Addition on triple bond takes place by the *syn*-addition of hydrogen in presence of poisoned palladium catalyst.

Since the configuration of the double bond already present is *cis*, the compound formed will have a plane of symmetry and hence optically inactive.



12. (a) The π bond is formed by the sideways overlapping of two *p*-orbitals of the two carbon atoms.

The molecular plane does not have any π electron density as the *p*-orbitals are perpendicular to the plane containing the ethene molecule. The nodal plane in the π -bond of ethene is located in the molecular plane.

13. (a) The given reaction is Birch reduction.

14. (b) $\text{Br}^\bullet$ is less reactive and more selective and so the most stable free radical (3°) will be the major product.

15. (a) The acidity of acetylene or 1-alkyne can be explained on the basis of molecular orbital concept according to which formation of C—H bond in acetylene involves sp -hybridised carbon atom. Now since *s* electrons are closer to the nucleus than *p* electrons, the electrons present in a bond having more *s* character will be correspondingly more closer to the nucleus.

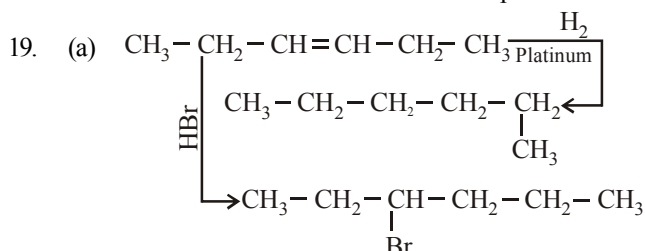
Thus owing to high *s* character of the C—H bond in alkynes (*s* = 50%), the electrons constituting this bond are more strongly held by the carbon nucleus i.e., the acetylenic carbon atom or the sp orbital acts as more electronegative species than the sp^2 and sp^3 with the result the hydrogen present on such a carbon atom ($\equiv\text{C}-\text{H}$) can be easily removed as a proton.

16. (a) More is the reactivity of a free radical, lesser is its selectivity for different type of H atoms (1° , 2° , or 3°) and hence the probability factor will be more in such reagent. Since $\text{Cl}^\bullet$ is more reactive, it is less selective

and hence it will be more influenced by the probability factor.

17. (d) Br_2 in CCl_4 (a), Br_2 in CH_3COOH (b) and alk. KMnO_4 (c) will react with all unsaturated compounds, i.e., 1, 3 and 4 while ammonical AgNO_3 (d) reacts only with terminal alkynes, i.e., 3 and hence 3 can be distinguished from 1, 2 and 4 by ammonical AgNO_3 (d).

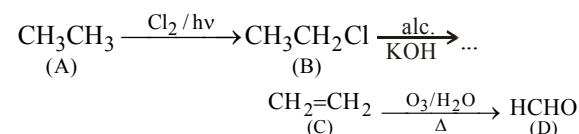
18. (d) Presence of electron-withdrawing substituent (e.g. $\text{C}=\text{O}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CN}$, etc.) deactivates the carbon-carbon double bond towards electrophilic addition.



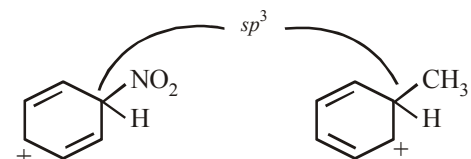
20. (a) Given $\text{A} \xrightarrow{\text{Cl}_2} \text{B} \xrightarrow{\text{alc./KOH}} \text{C} \xrightarrow{\text{O}_3/\text{H}_2\text{O}} \text{CH}_2\text{O}$

Hydrocarbon

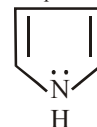
Since hydrocarbon C give only CH_2O , on ozonolysis, C should be $\text{CH}_2 = \text{CH}_2$ hence on going backward, A should be ethane. Thus the reactions are



21. (c) An aromatic compound have cyclic clouds of delocalised $(4n + 2)$ π electrons above and below the plane of the molecule. Among the given three compounds, only compound (c) satisfies these conditions.



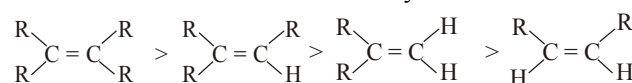
Carbon bearing $-\text{NO}_2$ (or $-\text{CH}_3$) group is sp^3 hybridised and does not have a *p* orbital with the result delocalisation of π electrons over the complete ring is interrupted.



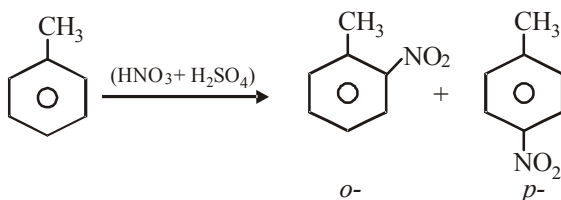
4π electrons and 2 non-bonding electrons (present in *p* orbital of N) form a cyclic cloud of 6π electrons

22. (a) Heat of hydrogenation of alkene $\propto \frac{1}{\text{Stability of alkene}}$

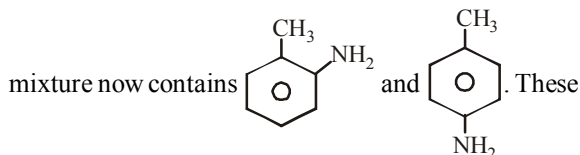
Hence the alkene which will react fastest with H_2 will be the least stable. Order of stability will be



Further the relative rates of hydrogenation decrease with increase of steric hindrance

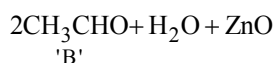
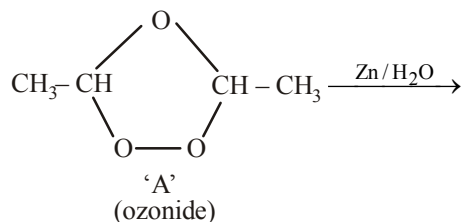


on reduction with Sn/HCl they will form corresponding anilines in which $-\text{NO}_2$ group changes to $-\text{NH}_2$. The



anilines when diazotized and then treated with CuBr forms *o*-, *p*- bromotoluenes.

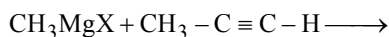
31. (d) Completing the sequence of given reactions,



Thus 'B' is CH_3CHO

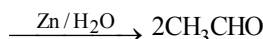
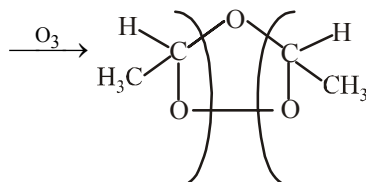
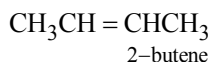
Hence (d) is correct answer.

32. (d) Writing the reaction we get

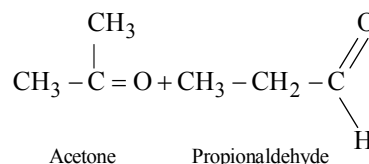
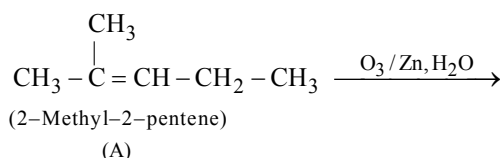


So we find that CH_4 is produced in this reaction.

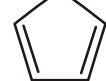
33. (c) The given molecular formula suggests that the aldehyde formed will be acetaldehyde hence the alkene will be



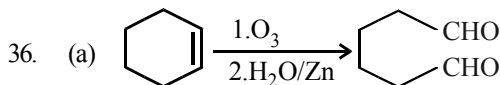
34. (c) From the products formed it is clear that the compound has 5 carbon atoms with a double bond and methyl group on 2nd carbon atom.



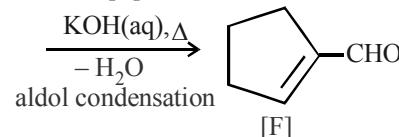
35. (d) sp^3 Carbon



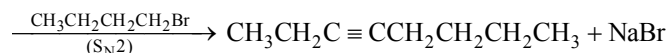
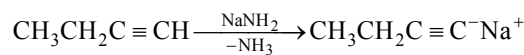
Cyclopentadiene is non aromatic, as it has sp^3 carbon in the ring.



[E]

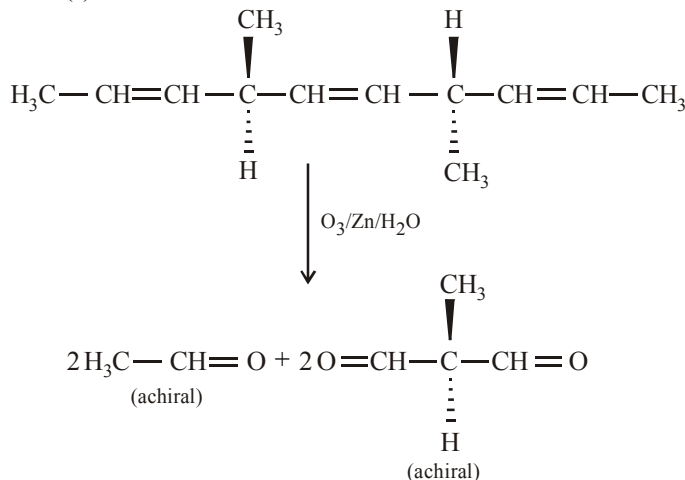


37. (d) Only (d) can form 3-Octyne



38. (c) $\text{C} - \text{C}$ bond energy = $348 \text{ kJ/mol} = \frac{348}{4.2} \text{ kcal/mol}$
 $= 82.85 \text{ kcal/mol} \approx 100 \text{ kcal/mol}$.

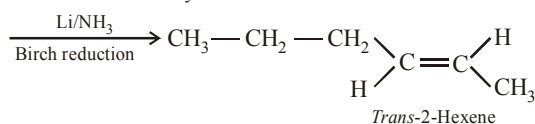
39. (a)



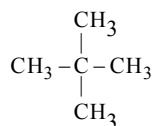
40. (b) Anti addition of hydrogen atoms to the triple bond occurs when alkynes are reduced with sodium (or lithium) metal in ammonia, ethylamine, or alcohol at low temperature. This reaction called, a dissolving metal reduction, produces an (E)- or *trans*-alkene. Sodium in liq. NH_3 is used as a source of electrons in the reduction of an alkyne to a *trans* alkene.



2-Hexyne



41. (a) Only terminal alkynes show acidic nature. Ethyne is more acidic than propyne. But-2-yne is not acidic as it does not contain any hydrogen attached to sp hybridised carbon.
42. (a) Higher is the branching lesser will be the boiling point further increase in molecular weight increases boiling point in alkane. Hence 2, 2-dimethyl propane will have least boiling point.



43. (c) The order of hyperconjugation is
 $-\text{CH}_3 > \text{CH}_3\text{CH}_2- > (\text{CH}_3)_2\text{CH}- > (\text{CH}_3)_3\text{C}-$
 $\text{CH}_3 - \text{C} = \text{CH}_2$
 $\quad |$
 $\quad \text{CH}_3$ (2-methylpropene)

$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ (but-2-ene)

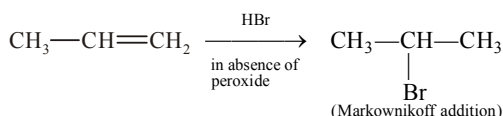
$\text{CH}_3 - \text{C} = \text{C} - \text{CH}_3$
 $\quad | \quad |$
 $\quad \text{CH}_3 \text{CH}_3$ (2, 3-dimethylbut-2-ene)

$\text{H}_3\text{C} - \text{HC} = \text{C} - \text{CH}_3$
 $\quad |$
 $\quad \text{CH}_3$ (2-methylbut-2-ene)

$\text{CH}_3 - \text{CH}_2 - \text{C} = \text{CH}_2$
 $\quad |$
 $\quad \text{CH}_3$ (2-methylbut-1-ene)

Larger the number of methyl groups linked to carbon-carbon double bond, more is the hyperconjugative C-H bonds and greater is the stability of alkenes hence (c) will be more pronounced for hyperconjugation.

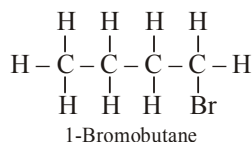
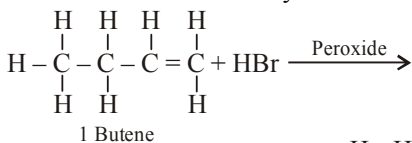
44. (d) Addition of hydrogen halide to alkene is an example of electrophilic addition involving carbocations as intermediates.



45. (c) Among the infinite number of conformations the *staggered conformation* in which hydrogen atoms are as far apart as possible is the *most stable* while the *eclipsed conformation* in which hydrogen atoms are perfectly eclipsed is the *least stable*.

Gauche conformation lie between these two in stability. Thus, order of stability is
 staggered > gauche > eclipsed

46. (a) This reaction is followed by anti Markownikoff rule



In this reaction anti Markownikoff's addition is explained on the basis of the fact that in the presence

peroxides, addition takes place via free radical mechanism rather than the ionic mechanism.

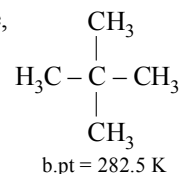
47. (b) Chlorination of CH_4 does not take place in dark is correct because it is a free radical reaction and free radicals are obtained in presence of sun light.
48. (b) Iodination is reversible since formed HI is a strong reducing agent and reduces the alkyl iodide back to alkane. $\text{CH}_4 + \text{I}_2 \rightleftharpoons \text{CH}_3\text{I} + \text{HI}$
 Iodination can be done only in presence of strong oxidising agents like iodic acid which destroys the hydriodic acid.
49. (d) The two hydrogen atoms on first carbon and the two H-atoms on the third carbon atom lie in perpendicular planes. The central carbon atom is sp -hybridized while terminal carbon atoms are sp^2 -hybridized
50. (c) $(4n + 2)\pi$ electrons and planar structure are the essential conditions for aromaticity.

EXERCISE - 3

Exemplar Questions

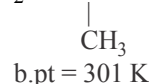
1. (d) We know that, as the number of carbon atom increases, boiling point increases while boiling point decreases with branching.

2, 2-dimethyl propane,



n-pentane, b.pt = 309.1 K

2-methyl butane, $\text{H}_3\text{C} - \text{H}_2\text{C} - \text{HC} - \text{CH}_3$

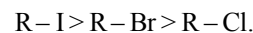


n-butane, b.pt = 273 K

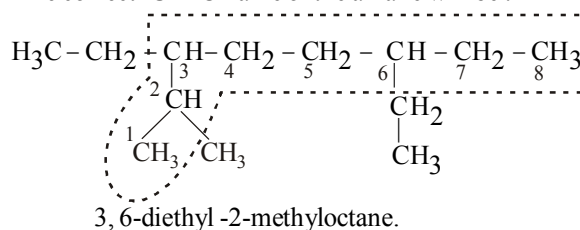
2. (a) Reactivity of halogens decreases with decrease in electronegativity which decreases down the group. Hence the order of reactivity of alkanes with halogens is
 $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

Also with I_2 , the reaction is too slow that it requires a catalyst.

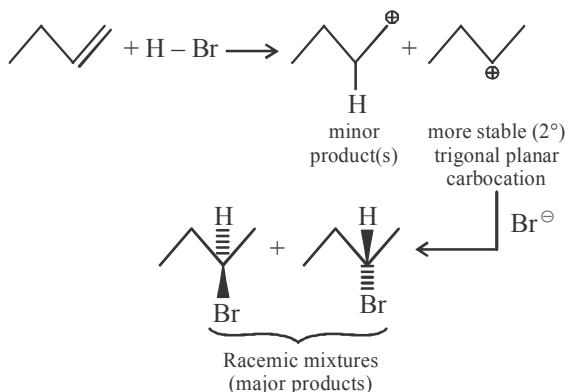
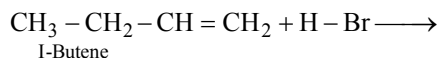
3. (b) The reactivity of halogens with alkanes follows the order : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. Further, the reactivity of reduction of alkyl halides with Zn & dilute HCl increases as the strength of C-X (X = F, Cl, Br, I) bond decreases. Hence, reduction of alkyl halide with Zn and dilute HCl follows the order :



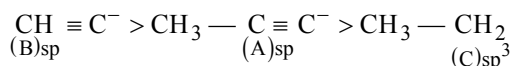
4. (a) The correct IUPAC name of the alkane will be :



5. (a) 1-butene is an unsymmetrical alkene and will follow Markownikoff's rule to give major product.

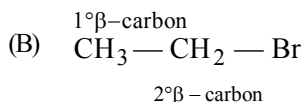
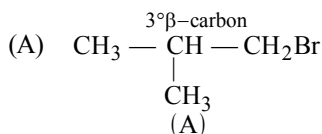


6. (d) In option (d), a carbon with double bond has two same functional groups (CH₃) attached to it. The rotation around carbon will not produce a new compound. Hence, geometrical isomerism is not possible.
7. (c) Lesser the bond energy of hydrogen halide more will be its reactivity. Hence, the order of reactivity of given compounds with propene will be HI > HBr > HCl.
8. (b) + I-effect decreases the stability of carbanion. Since, -CH₃ group shows + I-effect, therefore, it intensifies the negative charge and hence destabilises the carbanion (A) relative to (B). Also, sp hybridised carbanion is more stabilised than sp³.



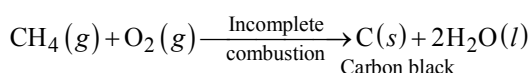
Hence, the order of decreasing stability will be: B > A > C

9. (d) Alkyl halides on heating with alcoholic KOH eliminates halogen from α-carbon atom and hydrogen is eliminated from β-carbon atom to form an alkene.



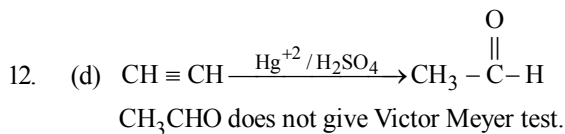
More the number of β-substituents (alkyl groups) more stable alkene will be formed on β-elimination, more will be the reactivity. Thus the correct order is A > C > B

10. (c) During incomplete combustion of alkanes with insufficient amount of air carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters.



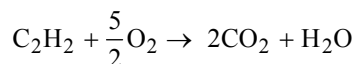
NEET/AIPMT (2013-2017) Questions

11. (a) Huckel rule is not obeyed. It has only four electrons. Further it does not have continuous conjugation.



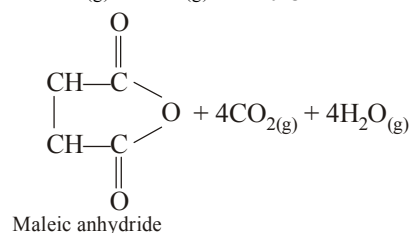
13. (d) Presence of 6p orbitals, each containing one unpaired electron, in a six membered cyclic structure is in accordance with Huckel rule of aromaticity.

14. (b) The combustion reaction of ethylene is



Both HC≡CH and CO₂ have sp hybridization.

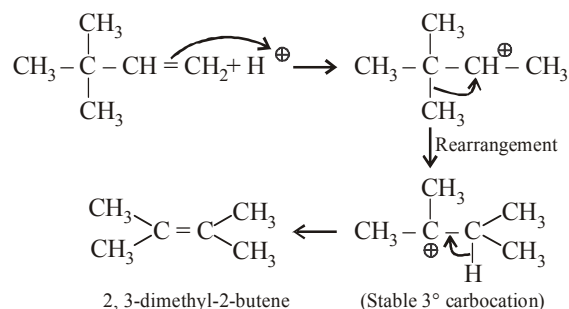
15. (b) $2\text{C}_6\text{H}_6(g) + 9\text{O}_2(g) \xrightarrow[410^\circ\text{C}]{\text{V}_2\text{O}_5}$



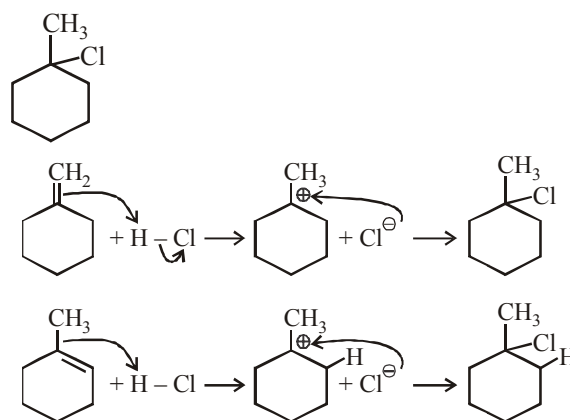
16. (b) $\text{CH}_3\text{C}(\text{CH}_3) = \text{C}(\text{CH}_3) - \text{CH}_3$

2,3-Dimethyl-2-butene

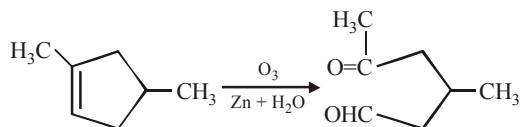
(CH₃)₂CH - CH(CH₃) - CH = CH₂ contain 7 carbon atoms



17. (c) 1-chloro-1-methylcyclohexane.



18. (d)



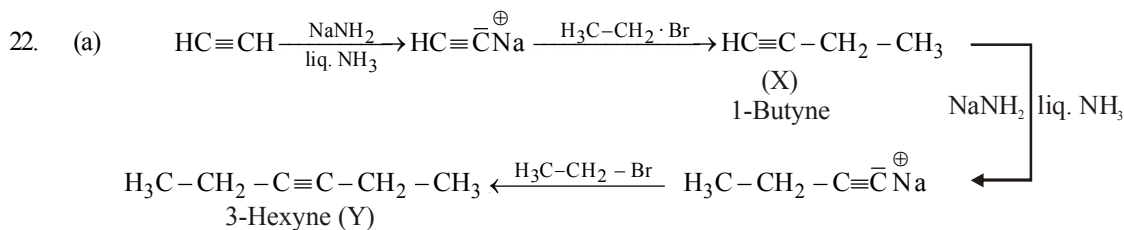
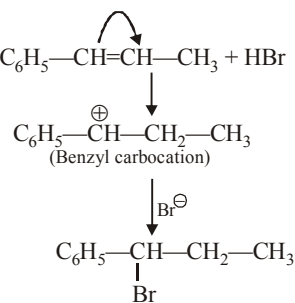
19. (a) Enthalpy of hydrogenation $\propto \frac{1}{\text{stability of alkene}}$

$\therefore \text{III} > \text{II} > \text{I}$

20. (a) No. of double bonds = 4
No. of π bond electrons

= $2 \times \text{no. of double bond}$

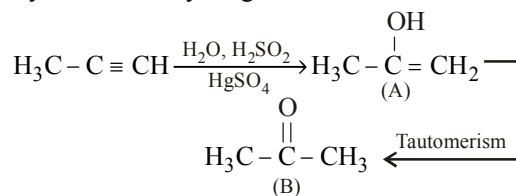
= $2 \times 4 = 8$

21. (d) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_3 + \text{HBr}$ 

23. (a) Correct order is $\text{H}-\text{C}\equiv\text{C}-\text{H} > \text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{H} > \text{H}_2\text{C}=\text{CH}_2 > \text{CH}_3-\text{CH}_3$

$\left(\begin{array}{c} \text{Two acidic} \\ \text{hydrogens} \end{array} \right)$
 $\left(\begin{array}{c} \text{One acidic} \\ \text{hydrogen} \end{array} \right)$

24. (c) Hydration of alkynes give ketones.



25. (c) There is no change in bond angles and bond lengths in the conformations of ethane.

Chapter 14

Environmental Chemistry

ENVIRONMENTAL POLLUTION

The addition of any undesirable material to air, water and soil by a natural source (or due to human activity) which affects the quality of environment is called an environmental pollution.

A substance which causes pollution is called pollutant. They can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings.

Types of Pollutants :

(i) Primary and Secondary Pollutants:

(a) **Primary pollutants:** Those which enter the environment after their formation and remain as such.

Ex. : NO, NO₂, SO₂

(b) **Secondary pollutants :** The harmful materials which are formed by chemical reaction between primary pollutants in the atmosphere.

Ex. Hydrocarbon + Oxide of nitrogen $\xrightarrow{h\nu}$ compound

(ii) Bio-degradable and Non Bio-degradable Pollutants :

(a) **Bio degradable pollutants :** They are thus not harmful, but if present in excess in environment, they do not undergo degradation completely and thus become pollutant.

(b) **Non bio degradable pollutants :** The materials (such as Hg, Al, DDT) which do not undergo degradation (or degrade very slowly) but their presence even in very small amount in the environment is very harmful.

ATMOSPHERIC POLLUTION

Atmosphere consists of concentric layers of air and each layer has a different density. The lowest region in which the human beings along with other organisms live is called troposphere. It extends upto a height of ~ 10 km from sea level. Above the troposphere, between 10-50 km above sea level, lies stratosphere. Atmospheric pollution is studied as tropospheric and stratospheric pollution.

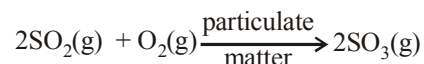
Tropospheric Pollution.

It occurs due to presence of undesirable solid or gaseous particles in air. The major pollutants are:

(I) Gaseous air pollutants

(i) Oxides of sulphur:

Produced when S containing fossil fuel (coal, petroleum etc.) is burnt in automobiles, industries, refineries, metallurgical operations etc. SO₂ is the more common. It causes respiratory diseases, eg. asthma, bronchitis. It causes irritation to eyes. SO₂ get oxidised to SO₃ by following reactions:

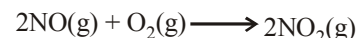
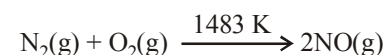


In presence of moisture SO₃ is converted into highly corrosive sulphuric acid.



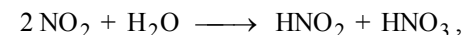
(ii) Oxides of nitrogen:

Source - combustion of coal, gasoline, natural gas, petroleum refining, chemical plants, manufacturing explosives and fertilizers, tobacco smoke.



High conc. of NO₂ damage the leaves of plants and retard the rate of photosynthesis. It can lead to acute respiratory disease in children and is toxic to living tissues.

NO₂ reacts with moisture to form acids.

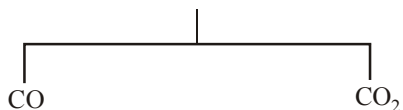


(iii) Hydrocarbons

They are formed by incomplete combustion of fuel used in automobiles. They are carcinogenic

They harm plants by causing ageing, breakdown of tissues, shedding of leaves, flowers and twigs.

(iv)

Oxides of carbon

- (a) It is formed as a result of incomplete combustion of hydrocarbons.
 (b) Mainly released from automobile exhaust.
 (c) It is poisonous because it binds with Hb in blood forming carboxyhaemoglobin,

$$\text{Hb} + \text{CO} \longrightarrow \text{HbCO}$$
 (Carboxy haemoglobin)

$$\text{Hb} + \text{O}_2 \longrightarrow \text{HbO}_2$$
 (oxyhaemoglobin)
 Thus as a result O_2 carrying capacity of blood is reduced. This oxygen deficiency results in headache, weak eyesight, nervousness and cardiovascular disorder.
- (a) CO_2 is discharged in to atmosphere by respiration, burning of fossil fuels, decomposition of limestone, during volcanic eruptions.
 (b) The increased amount of CO_2 in air is responsible for global warming.

Global Warming and Green House Effect

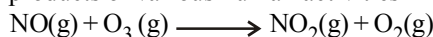
The atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called natural greenhouse effect as it maintains the temperature and makes the earth perfect for life. Some of the gases present in earth's atmosphere like CO_2 , CH_4 , O_3 , CFC's, water vapours etc. which are capable of trapping solar energy are called green house gases. However, if the conc. of these gases increase beyond sustainable limit, the average global temperature will increase thereby causing global warming

Consequences of global warming :

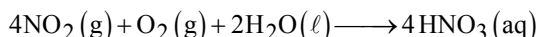
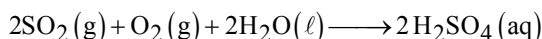
- Global warming would result in rise in sea level due to increased rate of melting of glaciers and floods.
- Increase in infectious diseases like malaria, dengue, etc.

Acid Rain

Normal pH of rain water is 5.6 if pH of rain water drops below 5.6, it is called acid rain. H_2SO_4 , HNO_3 (and small amount of HCl) which are formed from the oxide of S and N_2 present in the air is causes acid rain. These oxides are discharged into atmosphere as a by products of various human activities



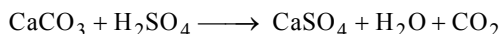
SO_2 and NO_2 then undergo oxidation and react with water to form H_2SO_4 and HNO_3 which are major contributors of acid rain.



Ammonium salts are also formed and can be seen as an atmospheric haze. Aerosol particles of oxides or ammonium salts in rain drops result in wet deposition.

Harmful effects of acid-rain:

- It damages buildings and statues which contain marble, lime stone, mortar etc.



- It damage irons and steel structure.
- It corrodes water pipes. As a result, heavy metals (like Fe, Pb, Cu) are mixed with water which have toxic effect.
- Acid rain increases the acidity of the lake, which is harmful to fishes.
- It damages trees, plants and retards the growth of the plants.

(II) Particulate pollutants

Particulates are the minute solid particles or liquid droplets in air. These particles are usually individually invisible to the naked eye. Collectively, however, small particles often form a haze that restricts visibility. The viable particulates are the minute living organisms that are dispersed in atmosphere. These include bacteria, fungi, moulds, algae etc. Non-viable particulates are formed either by the breakdown of larger materials or by the condensation of minute particles and droplets. There are four types of non-viable particulates in the atmosphere : mists, smoke, fumes and dust.

- Mist** is produced by particles of spray liquids and the condensation of vapours in air.
 - Smoke** denotes very small soot particles produced by burning and combustion of organic matter.
 - Fumes are condensed vapours** Fumes of metals are well-known particulates of this type.
 - Dust** consists of the particles produced during crushing, grinding and attribution of solid materials.
- Particulates are present in vehicle emissions, smoke particles, dust and ash.

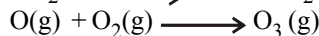
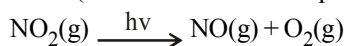
SOME EFFECTS OF AIR POLLUTION**Smog**

It is a mixture of smoke and fog in suspended droplet form. It is of two types:

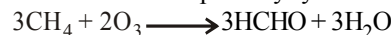
- Classical smog:** It occurs in cool, humid climate. It consists of a mixture of smoke fog and SO_2 . Classical smog is of reducing nature and have high concentrations of SO_2
- Photochemical Smog :** It occurs in warm, dry, sunny climate. It is formed as a result of action of sunlight on unsaturated hydrocarbons and nitrogen-oxide. Photochemical smog is of oxidising nature and have high concentration of oxidising agents.

Formation of photochemical smog

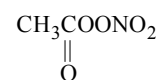
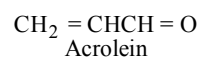
The chemistry of formation of photochemical smog centres around NO, which is emitted into air with the exhaust gases. This NO oxidises in air to NO_2 which in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom. (Photochemical decomposition)



Both NO and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN) that cause the eyes to water and burn and are harmful to the respiratory system.



Acrolein and peroxyacetyl nitrate (PAN) are particularly noxious.



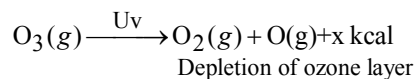
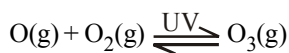
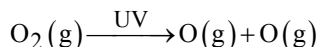
Peroxyacetyl nitrate (PAN)

Control of photochemical smog :

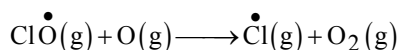
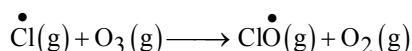
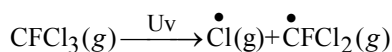
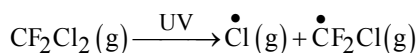
Catalytic converters are used in automobiles which prevent the release of NO and hydrocarbons to atmosphere.

Stratospheric Pollution**Formation of ozone layer**

O₃ in stratosphere (11 -50 km) is a product of UV radiations acting on O₂ molecules.



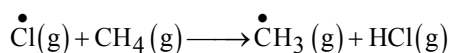
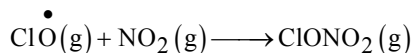
The presence of chemicals like CFC's and NO in stratosphere result in depletion of ozone layer. This is shown below:



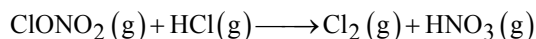
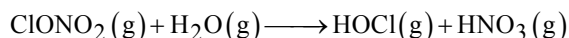
The $\dot{\text{Cl}}$ radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFC's are transporting agents for continuously generating $\dot{\text{Cl}}$ radicals into stratosphere and damaging the ozone layer.

Ozone hole

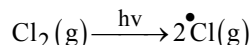
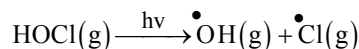
In summers, NO₂ and CH₄ react with $\text{Cl}\dot{\text{O}}$ and $\dot{\text{Cl}}$ forming chlorine sinks preventing ozone depletion.



In winters, polar stratospheric clouds are formed which provide surface on which chlorine nitrate formed gets hydrolysed to form hypochlorous acid. It also reacts with the HCl produced to give Cl₂.



When sunlight returns in spring, sun's warmth breaks up the clouds and HOCl and Cl₂ are photolysed by sunlight as:



These $\dot{\text{Cl}}$ radicals thus formed initiate the chain reaction for O₃ depletion as discussed above.

Effects of O₃ layer depletion

Due to depletion of O₃ layer, U.V. radiations fall on the earth.

- (i) The U.V. radiations, damage the cornea and lens of the eyes.
- (ii) The U.V. radiations affect the plant proteins and thus reduce the chlorophyll.
- (iii) The U.V. radiations, disturb the heat balance of the earth.

WATER POLLUTION

The contamination of water by foreign substances which would constitute a health hazard and make it harmful for all purposes (domestic, industrial or agriculture etc.) is known as water pollution. The polluted water may have offensive odour, bad taste, unpleasant colour, murky oily, etc.

Sources of Water Pollution

Easily identified source or place of pollution is called point source, ex: municipal and industrial discharge pipes. Non point sources of pollution are those where a source of pollution cannot be easily identified, ex: agricultural run-off, acid rain, storm water drainage etc. The major water pollution and their sources :

Pollutant	Source
Microorganisms	Domestic sewage
Organic wastes	Domestic sewage, animal waste, decaying animals and plants and discharge from food processing factories
Plant nutrients	Chemical fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining.
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Cooling water used by industrial plants (which is discharged as hot water)

Important Causes of Water Pollution

- (i) **Pathogens:** They are disease causing agents and include bacteria and other organisms that enter water from domestic sewage and animal excreta.
- (ii) **Organic wastes:** It includes organic matter such as leaves, grass, trash, etc. Excessive phytoplankton growth is also a cause of water pollution. These wastes are biodegradable.

They consume oxygen dissolved in water. If excess of organic matter is added to water, all the available O_2 is used up. This causes the death of aquatic life.

It is defined as the amount of free oxygen required for biological oxidation of the organic matter by aerobic conditions at 20°C for a period of five days. Its unit is mg/l or ppm .

The amount of BOD in water is a measure of the amount of organic material in water, in terms of how much O_2 will be required to break it down biologically. Clean water would have a BOD value of less than 5 ppm whereas highly polluted river water could have a BOD value of 17 ppm or more.

A large number of organic and inorganic compounds, however, are resistant to microbial oxidation. They, therefore, don't contribute to the BOD, though their presence makes water unfit for consumption.

Note : Estimation of BOD requires 5 days so another parameter called chemical oxygen demand (COD) can also be used. It is a measure of all types of oxidisable impurities present in the sewage. COD values are higher than BOD values. Oxidising agent used in COD determination is acidified $K_2Cr_2O_7$.

(iii) Chemical pollutants:

- Heavy metals water soluble inorganic chemicals that include heavy metals like Cd, Hg, Ni, etc. constitute an important class of pollutants. These metals are not excreted by the body and can damage kidneys, central nervous system, liver, etc.
- Acid-polluted water ($\text{pH} < 3$) :** This is deadly to most forms of aquatic life. Acid mine water principally contain sulphuric acid produced by the oxidation of iron pyrites (FeS_2). Industrial wastes and acid rain may also contribute to the acidity of natural waters.
- Organic chemicals like petroleum products, pesticides, industrial chemicals like polychlorinated biphenyl (PCB's) are also a source of water pollution. PCB's are carcinogenic.
- Detergents and Fertilizers:** These may contain phosphates as additives. The addition of phosphates to water, in the form of the phosphate anion PO_4^{3-} , encourages the formation of algae, which reduces the dissolved oxygen concentration of water. The process, known as eutrophication, impedes the development of higher life forms, such as fish.

International Standards for Drinking Water

- Fluoride:** Soluble F^- is added to drinking water to bring its conc upto 1 ppm or 1 mg dm^{-3} . F^- ions makes the teeth enamel much harder. However, F^- ion conc above 2 ppm causes brown motting of teeth. Above 10 ppm , it causes harmful effect to bones and teeth.
- Lead:** Drinking water gets contaminated with lead if water is relatively acidic and lead pipes are used for water

transportation. The accepted limit is 50 ppb . It can damage kidney, liver, reproductive system, etc.

- Sulphate:** Sulphate is harmless at moderate levels, but excess

SO_4^{2-} ($> 500 \text{ ppm}$) in drinking water causes laxative effect.

- Nitrate:** Maximum limit is 50 ppm . Excess level can cause disease called methemoglobinemia (blue baby syndrome)

- Other Metals :** The maximum recommended levels of common metals in drinking water are :

Metal	Max. concentration (ppm or mg dm^{-3})
Zn	5
Fe	0.2
Mn	0.05
Cu	3
Cd	0.005
Al	0.2

SOIL POLLUTION

Causes of Soil Pollution

Pesticides: Pesticides are substances that are used to kill or block the reproductive processes of unwanted organisms. The repeated use of same or similar pesticides make the pests resistant to them. Being water insoluble, non-biodegradable and high persistent toxins are transferred from lower trophic level to higher trophic level through food chain, resulting in serious metabolic and physiological disorders in higher animals.

Insecticides: Control of insects by insecticides helps to cure diseases (for example malaria and yellow fever) and protect crops. They are organophosphates and carbamates which are less persistent and more biodegradable than pesticides. However, they are severe nerve toxins and are harmful to humans. Insects have become resistant to them also.

Herbicides: Herbicides are used to kill weeds. Ex: Sodium Chlorate (NaClO_3), sodium arsenite (Na_3AsO_3) etc. They are not persistent and decompose in a few months. They are toxic to mammals, cause birth defects.

Organic herbicides are, therefore, now used. They are much more toxic to certain types of plants than to others.

Fungicides: Fungicides are used to check the growth of fungi. (Fungi are the plants without chlorophyll). Organic compounds of mercury have been used as fungicides.

Industrial Waste

- They are biodegradable and non-biodegradable.
- Biodegradable wastes are generated by cotton mills, food processing units, paper mills and textile factories.
- Non-biodegradable wastes are generated by thermal power plants which produce fly ash, integrated iron and steel plants, fertilizer industries, industries manufacturing Al, Zn, Cu, chemical, drugs, pharmaceuticals, dyes, pesticides, rubber goods, etc.

STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTION

- Waste management i.e., reduction of waste and proper disposal, also recycling of materials and energy.

- (ii) Adopting methods in day-to-day life which result in reduction of the pollution, i.e., proper collection and disposal.

GREEN CHEMISTRY

Green Chemistry focuses on processes and products that reduce or eliminate the use and generation of hazardous substances. The use of starting materials-reagents and solvents that pose less hazard to man and his environment, is one aspect. Using raw materials more efficiently and generating less waste is another.

Use of Green Chemistry in Day-to-Day Life:

(i) **Dry cleaning of clothes:**

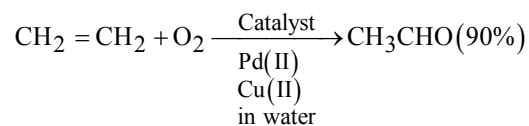
Earlier, tetrachloroethene was used as a solvent for dry cleaning but it contaminates ground water and is a carcinogen. It is being replaced by liquified CO_2 with a suitable detergent which causes less harm to ground water.

Now, H_2O_2 is used for bleaching clothes which makes less use of water.

(ii) **Bleaching of paper:**

Earlier, Cl_2 gas was used but now H_2O_2 with a suitable catalyst is being used for bleaching paper.

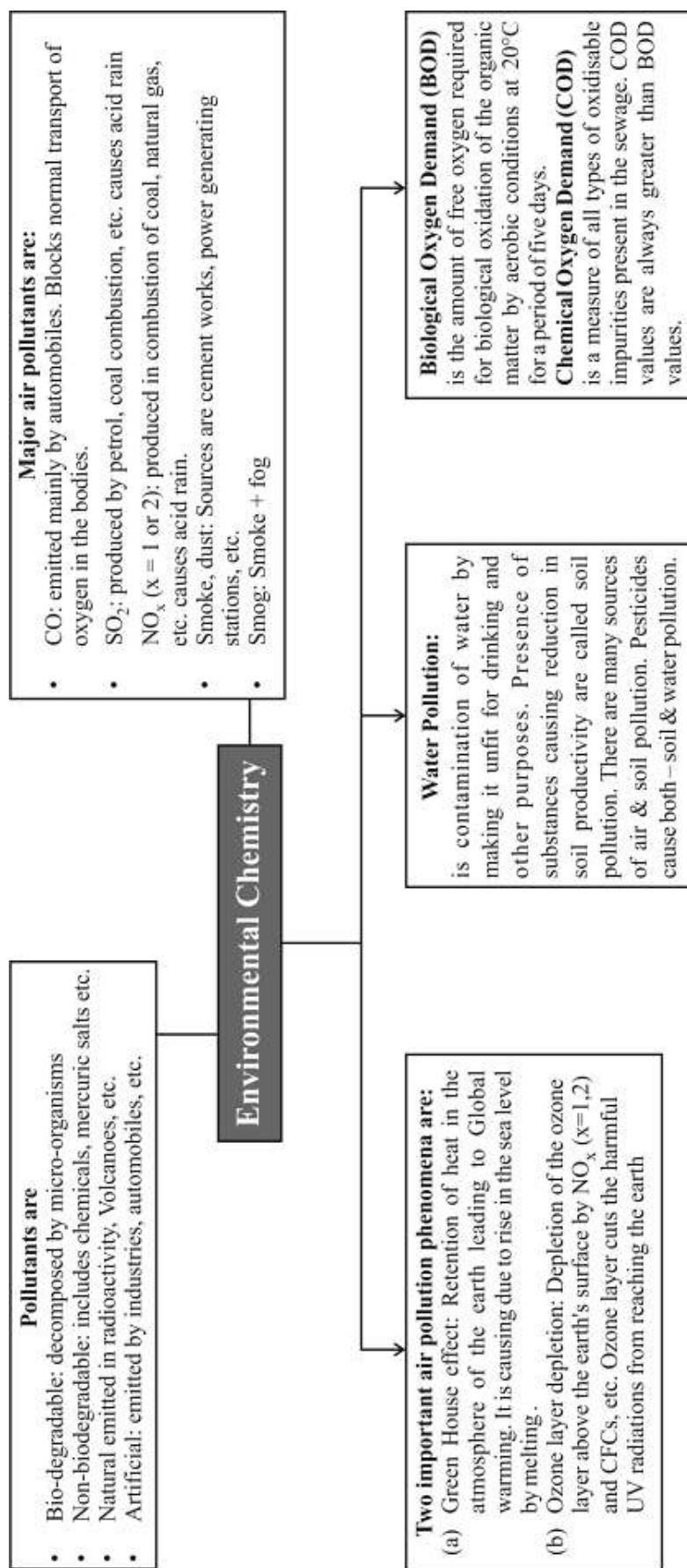
(iii) **Synthesis of Chemicals:**



- (iv) Development of a method for catalytic dehydrogenation of diethanolamine in which a new technique allows the production of an environmentally friendly herbicide in a less dangerous way.
- (v) Development of processes using carbon dioxide as the blowing agent, for manufacture of polystyrene foam sheet packaging material.

Note : Thus, green chemistry is a cost effective approach which involves reduction in material, energy consumption and waste generation.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- The pollutants which came directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?
(a) CO (b) Hydrocarbon
(c) Peroxyacetyl nitrate (d) NO
- The green house effect is caused by
(a) CO₂ (b) NO₂
(c) NO (d) CO
- The gas responsible for ozone depletion :
(a) NO and freons (b) SO₂
(c) CO₂ (d) CO
- Sewage mostly constitutes
(a) Non-biodegradable pollutants
(b) Biodegradable pollutants
(c) Effluents
(d) Air pollutants
- In Antarctica ozone depletion is due to the formation of following compound
(a) acrolein (b) peroxyacetyl nitrate
(c) SO₂ and SO₃ (d) chlorine nitrate
- The main element of smog is
(a) O₃ and PAN (b) O₃
(c) PAN (d) PPN and PBN
- Classical smog occurs in places of
(a) excess SO₂ (b) low temperature
(c) high temperature (d) excess NH₃
- CFC which is a main reason behind air pollution, is produced by
(a) sewage pollutant (b) aerosols
(c) industrial remains (d) Above all
- Which is related to 'Green House Effect'?
(a) Farming of Green plants
(b) Farming of Vegetables in Houses
(c) Global Warming
(d) Biodegradable pollutant
- Phosphate pollution is caused by
(a) sewage and agricultural fertilizers
(b) weathering of phosphate rocks only
(c) agricultural fertilizers only
(d) phosphate rocks and sewage
- The uppermost region of the atmosphere is called
(a) Ionosphere (b) Stratosphere
(c) Troposphere (d) Exosphere
- Which of the following is the coldest region of atmosphere
(a) Thermosphere (b) Mesosphere
(c) Troposphere (d) Stratosphere
- Acid rain is due to
(a) CH₃ (b) N₂O₅
(c) SO₂ and NO₂ (d) C₂H₅OH
- The region which is greatly affected by air pollution is
(a) Thermosphere (b) Stratosphere
(c) Troposphere (d) Mesosphere
- The substance which is a primary pollutant?
(a) H₂SO₄ (b) CO
(c) PAN (d) Aldehydes
- Formation of London smog takes place in
(a) winter during day time
(b) summer during day time
(c) summer during morning time
(d) winter during morning time
- Green house gases –
(a) allow shorter wavelength to enter earth's atmosphere while doesn't allow longer wavelength to leave the earth's atmosphere.
(b) allow longer wavelength to enter earth atmosphere while doesn't allow shorter wavelength to leave the surface
(c) don't have wavelength specific character.
(d) show wavelength specific behaviour near the earth while far from earth these have wavelength independent behaviour.
- Which of the following is/are the hazardous pollutant(s) present in automobile exhaust gases?
(i) N₂ (ii) CO
(iii) CH₄ (iv) Oxides of nitrogen
(a) (ii) and (iii) (b) (i) and (ii)
(c) (ii) and (iv) (d) (i) and (iii)
- Carbon monoxide (CO) is harmful to man because
(a) it forms carbolic acid
(b) it generates excess CO₂
(c) it is carcinogenic
(d) it competes with O₂ for haemoglobin
- Today the concentration of green house gases is very high because of
(a) use of refrigerator
(b) increased combustion of oils and coal
(c) deforestation
(d) All of the above
- The non-viable particulate among the following is
(a) Dust (b) Bacteria
(c) Moulds (d) Fungi
- BOD of pond is connected with
(a) microbes & organic matter
(b) organic matter
(c) microbes
(d) None of these
- Lead is
(a) Radiological pollutant (b) Sound pollutant
(c) Soil pollutant (d) Air pollutant

24. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value
(a) slightly lower than that of rain water without thunderstorm
(b) slightly higher than that when the thunderstorm is not there
(c) uninfluenced by occurrence of thunderstorm
(d) which depends upon the amount of dust in air
25. Minamata disease of Japan is due to pollution of
(a) Aresenic (b) Lead
(c) Cynide (d) Mercury
26. Select the process that does not add particulate materials to air.
(a) Use of air conditioner
(b) Burning of fosssil fuels
(c) Paper industry
(d) Incomplete combustion of coal
27. Which causes death of fish in water bodies polluted by sewage?
(a) Foul smell (b) Pathogens
(c) Herbicides (d) Decrease in D.O.
28. Sewage water is purified by
(a) aquatic plants (b) microoganisms
(c) light (d) fishes
29. Which pollutant is harmful for 'Tajmahal'?
(a) Hydrogen (b) O₂
(c) SO₂ (d) Chlorine
30. The biggest particulate matter is
(a) HNO₃ droplets (b) Soot
(c) H₂SO₄ droplets (d) Fly ash
31. Negative soil pollution is
(a) reduction in soil productivity due to erosion and over use
(b) reduction in soil productivity due to addition of pesticides and industrial wastes
(c) converting fertile land into barren land by dumping ash, sludge and garbage
(d) None of the above
32. The quantity of DDT in food chain
(a) decreases (b) remains same
(c) increases (d) changes
33. Which is known as 'Third poison of environment' and also creates 'Blue baby syndrome'
(a) Nitrate present in water
(b) Phosphate and detergents found in water
(c) Cynide
(d) Pesticides
34. The aromatic compounds present as particulates are
(a) Polycyclic aromatic hydrocarbons
(b) Benzene
(c) Toluene
(d) Nitrobenzene
35. Water is often treated with chlorine to
(a) remove hardness
(b) increase oxygen content
(c) kill germs
(d) remove suspended particles
36. Thermal pollution affects mainly—
(a) vegetation (b) aquatic creature
(c) rocks (d) air
37. B.O.D. test or biochemical oxygen demand test is made for measuring
(a) air pollution (b) water pollution
(c) noise pollution (d) soil pollution
38. A dental disease characterised by mottling of teeth is due to presence of a certain chemical element in drinking water. Which is that element?
(a) Boron (b) Chlorine
(c) Fluorine (d) Mercury
39. The viable particulate among the following is
(a) Fumes (b) Algae
(c) Smoke (d) Mist
40. The high amount of E. coli in water is the indicator of
(a) hardness of water
(b) industrial pollution
(c) sewage pollution
(d) presence of chlorine in water
41. A lake with an inflow of domestic sewage rich in organic waste may result in
(a) drying of the lake very soon due to algal bloom
(b) an increase production of fish due to lot of nutrients
(c) death of fish due to lack of oxygen
(d) increased population of aquatic food web organisms
42. Which of the following is the major cause of global warming?
(a) re-radiation of U.V. rays by CO₂ and H₂O
(b) re-radiation of I.R. rays by CO₂ and H₂O
(c) re-radiation of I.R. rays by O₂ and N₂
(d) re-radiation of U.V. rays by O₂ and N₂
43. Select the one that is an oxygen demanding waste.
(a) Grease (b) Oil
(c) Pesticides (d) Domestic sewage
44. The greenhouse effect is because of the
(a) presence of gases, which in general are strong infrared absorbers, in the atmosphere
(b) presence of CO₂ only in the atmosphere
(c) pressure of O₃ and CH₄ in the atmosphere
(d) N₂O and chlorofluorohydrocarbons in the atmosphere
45. Which one of the following statement is **not** true ?
(a) pH of drinking water should be between 5.5 – 9.5.
(b) Concentration of DO below 6 ppm is good for the growth of fish.
(c) Clean water would have a BOD value of less than 5 ppm.
(d) Oxides of sulphur, nitrogen and carbon are the most widespread air pollutant.
46. Identify the wrong statement in the following:
(a) Chlorofluorocarbons are responsible for ozone layer depletion
(b) Greenhouse effect is responsible for global warming
(c) Ozone layer does not permit infrared radiation from the sun to reach the earth
(d) Acid rain is mostly because of oxides of nitrogen and sulphur

47. Identify the incorrect statement from the following :
- Ozone absorbs the intense ultraviolet radiation of the sun.
 - Depletion of ozone layer is because of its chemical reactions with chlorofluoro alkanes.
 - Ozone absorbs infrared radiation.
 - Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer.
48. The smog is essentially caused by the presence of
- Oxides of sulphur and nitrogen
 - O_2 and N_2
 - O_2 and O_3
 - O_3 and N_2
49. What is DDT among the following ?
- Greenhouse gas
 - A fertilizer
 - Biodegradable pollutant
 - Non-biodegradable pollutant
50. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was :
- Methyl isocyanate
 - Methylamine
 - Ammonia
 - Phosgene

EXERCISE - 2

Applied Questions

- The statement which is not true
 - NO_2 does not play any role in photochemical smog
 - SO_3 is more harmful air pollutant than SO_2
 - SO_2 does not affect larynx (voice box)
 - NO is more toxic to living tissues than NO_2
- Black-foot disease is caused due to groundwater contaminated with excess of
 - Nitrate
 - Fluoride
 - Arsenic
 - Sulphur
- The false statement among the followings :
 - The average residence time of NO is one month
 - Limestone acts as a sink for SO_x
 - SO_x can be removed from flue gases by passing through a solution of citrate ions
 - Ammonia acts as a sink for NO_x
- Exposure of an organism to UV system causes
 - photodynamic action
 - formation of thymidine
 - splitting of H-bonds of DNA
 - splitting of phosphodiester bonds
- Under column-I, a list of gases that are known to have a 'greenhouse effect' is given. Relate them to their main source selecting from the list given under Column - II
- Air pollution causing photochemical oxidants production include
 - Carbon monoxide, sulphur dioxide
 - Nitrous oxide, nitric acid fumes, nitric oxide
 - Ozone, peroxyacetyl nitrate, aldehydes
 - Oxygen, chlorine, fuming nitric acid
- Photochemical smog formed in congested metropolitan cities mainly consists of
 - ozone, peroxyacetyl nitrate and NO_x
 - smoke, peroxyacetyl nitrate and SO_2
 - hydrocarbons, SO_2 and CO_2
 - hydrocarbons, ozone and SO_x
- Which of the following statements about polar stratosphere clouds (PSCs) is not correct?
 - PSCs do not react with chlorine nitrate and HCl
 - Type I clouds are formed at about $-77^\circ C$ and contain solid $HNO_3 \cdot 3H_2O$
 - Type II clouds are formed at about $-85^\circ C$ and contain some ice
 - A tight whirlpool of wind called Polar Vortex is formed which surrounds Antarctica
- Which one of the following statements is correct ?
 - Extensive use of chemical fertilizers may lead to eutrophication of nearby water bodies
 - Both Azotobacter and Rhizobium fix atmospheric nitrogen in root nodules of plants
 - Cyanobacteria such as Anabaena and Nostoc are important mobilizers of phosphates and potassium for plant nutrition in soil
 - At present it is not possible to grow maize without chemical fertilizers
- Which of the following metal is a water pollutant and causes sterility in human being
 - As
 - Mn
 - Mg
 - Hg
- Eutrophication causes reduction in
 - Dissolved oxygen
 - Nutrients
 - Dissolved salts
 - All the above

	Column-I		Column-II
A.	Nitrous oxide	1.	Secondary pollutant from car exhausts
B.	Chlorofluorocarbon (CFCs)	2.	Combustion of fossil fuels, wood, etc
C.	Methane	3.	Denitrification
D.	Ozone (O_3)	4.	Refrigerators, aerosol, sprays
E.	Carbon dioxide	5.	Cattle, rice fields, toilets.

- A-3, B-4, C-5, D-1, E-2
- A-5, B-1, C-3, D-4, E-2
- A-4, B-5, C-1, D-2, E-3
- A-1, B-3, C-4, D-5, E-2

12. Lichens do not like to grow in cities
 (a) because of absence of the right type of algae and fungi
 (b) because of lack of moisture
 (c) because of SO_2 pollution
 (d) because natural habitat is missing
13. Which one of the following pairs is mismatched
 (a) Fossil fuel burning – release of CO_2
 (b) Nuclear power – radioactive wastes
 (c) Solar energy – Greenhouse effect
 (d) Biomass burning – release of CO_2
14. In a coal fired power plant electrostatic precipitators are installed to control emission of
 (a) SO_2 (b) NO_x
 (c) SPM (d) CO
15. Presence of which fuel gas in the exhaust fumes shows incomplete combustion of fuel.
 (a) Sulphur dioxide
 (b) Carbon monoxide and water vapour
 (c) Carbon monoxide
 (d) Nitrogen dioxide
16. The term “Bio-magnification” refers to the
 (a) growth of organism due to food consumption
 (b) increase in population size
 (c) blowing up of environmental issues by man
 (d) increase in the concentration of non-degradable pollutants as they pass through food chain
17. The statement which is not correct about control of particulate pollution
 (a) In electrostatic precipitator, the particulates are made to acquire positive charge which are then attracted by the negative electrode and removed
 (b) Gravity settling chamber removes larger particles from the air
 (c) Cyclone collector removes fine particles in the diameter range 5-20 microns
 (d) Wet scrubbers are used to wash away all types of particulates
18. Which of the following is/are the hazardous pollutant(s) present in automobile exhaust gases?
 (i) N_2 (ii) CO
 (iii) CH_4 (iv) Oxides of nitrogen
 (a) (ii) and (iii) (b) (i) and (ii)
 (c) (ii) and (iv) (d) (i) and (iii)
19. Green chemistry means such reactions which :
 (a) produce colour during reactions
 (b) reduce the use and production of hazardous chemicals
 (c) are related to the depletion of ozone layer
 (d) study the reactions in plants
20. Which one of the following statements regarding photochemical smog is not correct?
 (a) Carbon monoxide does not play any role in photochemical smog formation.
 (b) Photochemical smog is an oxidising agent in character.
 (c) Photochemical smog is formed through photochemical reaction involving solar energy.
 (d) Photochemical smog does not cause irritation in eyes and throat.

DIRECTIONS for Qs. 21 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement- 1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
 (b) Statement -1 is True, Statement -2 is True ; Statement-2 is NOT a correct explanation for Statement - 1
 (c) Statement - 1 is True, Statement- 2 is False
 (d) Statement -1 is False, Statement -2 is True
21. **Statement-1** : Inhabitants close to very busy airports are likely to experience health hazards.
Statement-2 : Sound level of jet aeroplanes usually exceeds 160 dB.
22. **Statement-1** : Suspended particulate matter (SPM) is an important pollutant released by diesel vehicles.
Statement-2 : Catalytic converters greatly reduce pollution caused by automobiles.
23. **Statement-1** : Eutrophication shows increase in productivity in water.
Statement-2 : With increasing eutrophication, the diversity of the phytoplankton increases.
24. **Statement-1** : The main cause of Bhopal gas tragedy was phosgene.
Statement-2 : Phosgene is a volatile liquid.
25. **Statement-1** : CO_2 causes green house effect.
Statement-2 : Other gases do not show such effect.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Which of the following gases is not a green house gas?
 (a) CO (b) O_3
 (c) CH_4 (d) H_2O vapour
2. Photochemical smog occurs in warm, dry and sunny climate. One of the following is not amongst the components of photochemical smog, identify it.
- (a) NO_2
 (b) O_3
 (c) SO_2
 (d) Unsaturated hydrocarbon
3. Which of the following statements is not true about classical smog?
 (a) Its main components are produced by the action of sunlight on emissions of automobiles and factories

- (b) Produced in cold and humid climate
 (c) It contains compounds of reducing nature
 (d) It contains smoke, fog and sulphur dioxide
4. Biochemical Oxygen Demand, (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be
 (a) rich in dissolved oxygen
 (b) poor in dissolved oxygen
 (c) highly polluted
 (d) not suitable for aquatic life
5. Which of the following statement(s) is/are wrong?
 (a) Ozone is not responsible for green house effect
 (b) Ozone can oxidise sulphur dioxide present in the atmosphere to sulphur trioxide
 (c) Ozone hole is thinning of ozone layer present in stratosphere
 (d) Ozone is produced in upper stratosphere by the action of UV rays on oxygen
6. Sewage containing organic waste should not be disposed in water bodies because it causes major water pollution. Fishes in such a polluted water die because of
 (a) large number of mosquitoes
 (b) increase in the amount of dissolved oxygen
 (c) decrease in the amount of dissolved oxygen in water
 (d) clogging of gills by mud
7. Which of the following statements about photochemical smog is wrong?
 (a) It has high concentration of oxidising agents
 (b) It has low concentration of oxidising agent
 (c) It can be controlled by controlling the release of NO_2 , hydrocarbons, ozone etc
 (d) Plantation of some plants like pinus helps in controlling photochemical smog
8. The gaseous envelope around the earth is known as atmosphere. The lowest layer of this is extended upto 10 km from sea level, this layer is
 (a) stratosphere (b) troposphere
 (c) mesosphere (d) hydrosphere
9. Dinitrogen and dioxygen are main constituents of air but these do not react with each other to form oxides of nitrogen because
 (a) the reaction is endothermic and requires very high temperature
 (b) the reaction can be initiated only in presence of a catalyst
 (c) oxides of nitrogen are unstable
 (d) N_2 and O_2 are unreactive
10. The pollutants which come directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?
 (a) CO (b) Hydrocarbon
 (c) Peroxyacetyl nitrate (d) NO
11. Which of the following statements is correct?
 (a) Ozone hole is a hole formed in stratosphere from which ozone oozes out
 (b) Ozone hole is a hole formed in troposphere from which ozone oozes out
 (c) Ozone hole is thinning of ozone layer of stratosphere at some places
 (d) Ozone hole means vanishing of ozone layer around the earth completely
12. Which of the following practices will not come under green chemistry?
 (a) If possible, making use of soap made of vegetable oils instead of using synthetic detergents.
 (b) Using H_2O_2 for bleaching purpose instead of using chlorine based bleaching agents
 (c) Using bicycles for travelling small distances instead of using petrol/ diesel based vehicles
 (d) Using plastic cans for neatly storing substances

NEET/AIPMT (2013-2017) Questions

13. Roasting of sulphides give the gas X as a by product. This is colorless gas with choking smell of burnt sulphur and caused great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas X is : [2013]
 (a) SO_2 (b) CO_2
 (c) SO_3 (d) H_2S
14. Which one of the following statements is not true? [NEET Kar. 2013]
 (a) Dissolved oxygen (DO) in cold water can reach a concentration upto 10 ppm.
 (b) Clean water would have a BOD value of 5 ppm.
 (c) Fluoride deficiency in drinking water is harmful. Soluble fluoride is often used to bring its concentration upto 1 ppm.
 (d) When the pH of rain water is higher than 6.5, it is called acid rain.
15. Which of the following is not a common component of Photochemical Smog? [2014]
 (a) Ozone
 (b) Acrolein
 (c) Peroxyacetyl nitrate
 (d) Chlorofluorocarbons
16. Which of the following is a sink for CO ? [2017]
 (a) Microorganism present in the soil
 (b) Oceans
 (c) Plants
 (d) Haemoglobin

Hints & Solutions

EXERCISE - 1

1. (c)
2. (a) CO_2 causes Green House Effect.
3. (a) NO and freons are responsible for ozone depletion.
4. (b) Domestic sewage constitute biodegradable pollutants.
5. (a) In antarctica ozone depletion is due to formation of acrolein.
6. (a) 7. (b) 8. (b) 9. (c)
10. (a) Phosphate pollution is caused by sewage and agricultural fertilizers.
11. (d) The uppermost region of atmosphere is exosphere.
12. (b) The coldest region is mesosphere (temp. -27°C to -92°C)
13. (c) Acid rain is rain or any other form of precipitation that is unusually acidic. It has harmful effects on plants, aquatic animals, and infrastructure. Acid rain is mostly caused by human emissions of sulfur and nitrogen compounds which react in the atmosphere to produce acids. In recent years, many governments have introduced laws to reduce these emissions.
14. (c) Air pollution greatly affect the troposphere.
15. (b) CO is primary pollutant.
16. (d) London smog is formed in morning during winter.
17. (a) Radiation coming from sun or outerspace have high energy or short wavelength, which are allowed to enter by green house gases. However, radiation emitted by earth is in infrared region, having long wavelength, are reflected back by the envelope of green house gases.
18. (c) CO and oxides of Nitrogen are poisonous gases present in automobile exhaust gases.
19. (d) CO is highly toxic and impairs respiration. CO combine with haemoglobin of blood and reduces its O_2 carry capacity.
20. (d)
21. (a) Dust
22. (a) BOD of pond is connected with microbes and organic matter.
23. (c)
24. (a) Normal rain water has pH 5.6. Thunderstorm results in the formation of NO and HNO_3 which lowers the pH.
25. (d) Minamata is caused by Hg poisoning.
26. (a)
27. (d) Decrease in D.O causes death of fish
28. (b) Sewage water is purified by micro-organisms.
29. (c)
30. (d) Fly ash.
31. (a) 32. (c) 33. (b)
34. (a) PAH (Poly Aromatic Hydrocarbon)
35. (c) Water is often treated with Cl_2 to kill germs.
36. (b) Thermal pollution is caused by power plants. Power plant requires a larger quantity of water for cooling. The water after cooling is left in the water body. The temperature of left water is generally very high and affects aquatic life.
37. (b) Strength of sewage or degree of water pollution is measured in terms of BOD (Biochemical oxygen demand) value.
38. (c) The excess of fluorine in water causes fluorosis. The symptoms of fluorosis are mottling of teeth (yellowish streaks) and abnormal bones liable to fracture etc. It is an example of endemic disease.
39. (b) Algae
40. (c) 41. (c) 42. (b)
43. (d) [Many organic substances break up into simpler substances by taking up dissolved oxygen in presence of some bacteria. As they continue, dissolved oxygen, runs short for aquatic life, which is then badly affected. Moreover many harmful products are formed]
44. (a) Green house gases such as CO_2 , ozone, methane, the chlorofluorocarbon compounds and water vapour form a thick cover around the earth which prevents the IR rays emitted by the earth to escape. It gradually leads to increase in temperature of atmosphere.

45. (b) The ideal value of D.O for growth of fishes is $8 \text{ mg}/\ell$. $7 \text{ mg}/\ell$ is desirable range, below this value fishes get susceptible to disease. A value of $2 \text{ mg}/\ell$ or below is lethal for fishes.
46. (c) Ozone layer acts as a shield and does not allow ultraviolet radiation from sun to reach earth. It does not prevent infra-red radiation from sun to reach earth. Thus option (c) is wrong statement and so it is the correct answer.
47. (c) The ozone layer, existing between 20 to 35 km above the earth's surface, shield the earth from the harmful U. V. radiations from the sun.
Depletion of ozone is caused by oxides of nitrogen
- $$\text{N}_2\text{O} + h\nu \longrightarrow \text{NO} + \text{N}$$
- reactive nitric oxide
- $$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$$
- $$\text{O}_3 + h\nu \longrightarrow \text{O}_2 + \text{O}$$
- $$\text{NO}_2 + \text{O} \longrightarrow \text{NO} + \text{O}_2$$
- $$2 \text{O}_3 + h\nu \longrightarrow 3 \text{O}_2 \text{ (Net reaction)}$$
- The presence of oxides of nitrogen increase the decomposition of O_3 .
48. (a) Smog is caused by oxides of sulphur and nitrogen.
49. (d) DDT is a non-biodegradable pollutant.
50. (a) Methyl isocyanate, $\text{CH}_3 - \text{N} = \text{C} = \text{O}$
13. (c) Solar energy is not responsible for green house effect instead it is a source of energy for the plants and animals.
14. (c) SPM $\rightarrow$ Suspended Particulates matter.
15. (c) Presence of CO in the exhaust fumes shows incomplete combustion.
16. (d)
17. (a) Particulates acquire negative charge and are attracted by the positive electrode.
18. (c) CO and oxides of Nitrogen are poisonous gases present in automobile exhaust gases.
19. (b) Green chemistry may be defined as the programme of developing new chemical products and chemical processes or making improvements in the already existing compounds and processes so as to make less harmful to human health and environment. This means the same as to reduce the use and production of hazardous chemicals.
i.e. correct answer is option (b).
20. (d) The oxidised hydrocarbons and ozone in presence of humidity cause photochemical smog.
Hydrocarbons + O_2 , NO_2 , NO, O, $\text{O}_3 \rightarrow$ Peroxides, formaldehyde, peroxyacetylnitrate (PAN), acrolein etc.
It is oxidising in nature and causes irritation to eyes, lungs, nose, asthmatic attack and damage plants.
21. (a) Noise level upto 64 dB (decibel) is well tolerated. Prolonged exposure to noise level to 80 dB or more leads to loss of hearing ability, fatigue, nervousness, fever, hypertension, gastric disorder, increase in cholesterol level and dilation of pupil of the eye. As the jet aeroplanes have the noise upto 150-160 dB, the inhabitants in the vicinity of busy airports are likely to experience above health hazards. Maximum noise level is recorded in rockets, i.e., 180 dB.
22. (b) SPM (Suspended Particulate Matter) is defined as particles floating in the air with a diameter below $10 \mu\text{m}$. Studies have shown that high SPM concentrations in the air can have a detrimental impact on respiratory organs. SPM is generated from natural sources (e.g., volcanoes or dust storms) and human activities (vehicles, incinerators and industrial plants).

EXERCISE - 2

- (b) SO_3 is more harmful pollutant than SO_2 .
- (c)
- (a) The average residence time of NO is 4 days.
- (c) 5. (a) 6. (c) 7. (a)
- (a) PSCs react with chlorine nitrate and HCl to give HOCl and Cl_2 .
- (a) 10. (b)
- (a) Eutrophication causes reduction in D.O.
- (c) Because they are very sensitive to sulphur dioxide and in cities the amount of SO_2 is high so lichen do not grow in cities.

SPM	Other aerosols
Less than 10 μm Tend to float longer in air due to small size	Less than 100 μm Tend to settle fairly quickly due to comparative heaviness

Catalytic converters is a device designed to reduce the amount of emissions from automobiles. The current (so-called three-way) systems use a heated metal catalyst to reduce the emissions of carbon monoxide (CO), hydrocarbons, and nitric oxide (NO), all of which contribute to the formation of photochemical smog. In an automobile's exhaust system, a catalytic converter provides an environment for a chemical reaction where unburned hydrocarbons completely combust.

23. (b) Eutrophication is a natural process which literally means well nourished or enriched. It is a natural state in many lakes and ponds which have a rich supply of nutrients. Eutrophication become excessive, however when abnormally high amount of nutrient from sewage, fertilizers, animal wastage and detergent, enter streams and lakes causes excessive growth or blooms of microorganisms. With increasing eutrophication, the diversity of the phytoplankton community of a lake increases and the lake finally becomes dominated by blue - green algae.
24. (d) Phosgene (COCl_2) is a poisonous and suffocating volatile liquid. Release of methyl isocyanate in industrial accident of Bhopal was the main reason of Bhopal gas tragedy.
25. (c) Other gases like CFCs, Ozone, water vapour and nitrous oxide also show green house effect.

EXERCISE - 3

Exemplar Questions

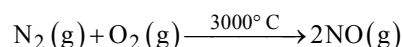
1. (a) Those gases which absorb sunlight near the earth's surface and then radiates back to the earth are called green house gases.

Carbon dioxide, water vapour, methane, ozone, oxides of nitrogen, chlorofluoro carbons (CFCs) etc; are green house gases. CO is not a green house gas.
2. (c) The smog which is formed in presence of sunlight is called photochemical smog. The main components of the photochemical smog results from the action of

sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories.

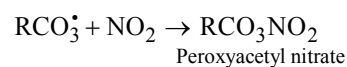
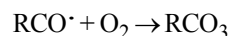
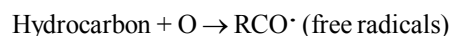
3. (a) Classical smog occurs in cold humid climate. It is a mixture of smoke, fog and sulphur dioxide.
4. (a) Water considered to be clean if it has BOD less than 5 ppm whereas highly polluted water has BOD more than 17 ppm.

Therefore, water having BOD less than 5 ppm is rich in dissolved oxygen.
5. (a) O_3 is responsible for greenhouse effect. Its contribution is about 8%.
6. (c) The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. Hence, oxygen from water decreases. It is harmful for aquatic life.
7. (b) Photochemical smog has high concentration of oxidants such as O_3 , organic oxidant and is therefore called as oxidising agent.
8. (b) The lowest region of the atmosphere in which human beings along with other organisms live is called troposphere. It extends upto the height of ~ 10 km from sea level. Troposphere is a turbulent, dusty zone containing air, much water vapour and clouds.
9. (a) Nitrogen and oxygen do not react with each other at normal temperature. At high altitude when lightning strikes, they combine to form oxides of nitrogen.



10. (c) Hydrocarbons present in atmosphere combine with oxygen atom produced by the photolysis of NO_2 to form highly reactive intermediate called free radical. Free radical initiates a series of reaction.

Peroxyacetyl nitrates are formed, which can be said as secondary pollutants.



11. (c) Ozone hole is thinning of ozone layer of stratosphere at some place. NO and chlorofluorocarbon have been found to be the most responsible for depleting the ozone layer.
12. (d) Using plastic cans for neatly storing substances will not come under green chemistry. The plastic materials are non-biodegradable.
13. (a) Based on the features given gas must be SO_2 .
14. (d) Acid rain is the rain water containing sulphuric acid and nitric acid which are formed from the oxides of sulphur and nitrogen present in the air as pollutants and rain water has a pH range of 4-5.
15. (d) The oxidised hydrocarbons and ozone in presence of humidity cause photochemical smog.
Hydrocarbons + O_2 , NO_2 , NO, O, $\text{O}_3 \rightarrow$ Peroxides, formaldehyde, peroxyacetyl-nitrate (PAN), acrolein etc. Hence chlorofluoro carbons are not common component of photochemical smog.
16. (a) Microorganisms present in the soil is a sink for CO.

NEET/AIPMT (2013-2017) Questions

Chapter 15

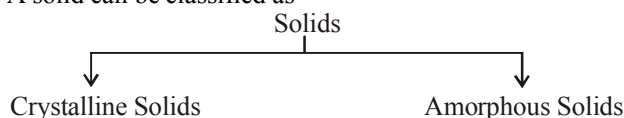
The Solid State

SOLIDS

Solids are characterised by the state of matter in which particles are closely packed and held together by strong intermolecular attractive forces.

Types of Solids :

A solid can be classified as



Crystalline solids :

A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape.

Amorphous solids :

Amorphous solids have no precise melting point but when heated, become increasingly pliable until they assume the properties usually associated with liquids.

Difference Between Crystalline and Amorphous Solids :

Property	Crystalline Solids	Amorphous Solids
Shape	Definite, Characteristic geometrical shape	Irregular shape
Melting Point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	Give plain and smooth surfaces on cutting with a sharp edged tool	Give irregular surfaces when cut with a sharp edged tool
Heat of fusion	Definite and characteristic	Not definite
Nature	True solids	Pseudo solids or supercooled liquids
Order in arrangement of particles	Long range order	Only short range order
Anisotropy and Isotropy	Anisotropic in nature, crystalline solids show different values of physical properties along different directions and hence they are anisotropic in nature.	Isotropic in nature, Amorphous solids are isotropic in nature because some of their properties like electrical resistance, refractive index, thermal expansion, etc., are same in all the directions.
Examples	Crystalline solids:- All solids elements (metals and non-metals) and compounds exist in this form.	Amorphous solids:- rubber, glass, fused silica, plastics, etc.

Note :

- (a) Glass is considered a super cooled liquid because glass is a amorphous solid and hence, it shows the property to flow, though slowly. This is supported by the fact that glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top.
- (b) Any material can be made amorphous or glassy either by rapidly cooling its melt or freezing its vapours. For example : Silica (SiO_2) which crystallises as quartz can be converted into amorphous silica (i.e. silica glass) by melting and rapid

cooling.

- (c) Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

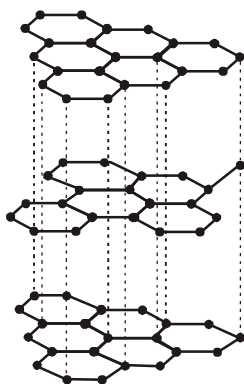
CLASSIFICATION OF CRYSTALLINE SOLIDS

Crystalline solids are classified on the basis of nature of intermolecular forces operating in them into four categories, viz. molecular, ionic, metallic and covalent solids. The different properties of the four types of solids are given in the table below:

Type of Solid	Constituent Particles	Nature of Binding Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular Solids (i) Non-Polar	Atoms of noble gas or non-polar molecules	Dispersion or London forces	Ar, H_2 , I_2 , CH_4 , Solid CO_2	Soft	Insulator	Very low
(ii) Polar	Polar molecules	Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded	Molecules containing H linked to F, O or N	Hydrogen bonding	H_2O (ice), NH_3	Hard	Insulator	Low
(2) Ionic Solids	Ions	Coulombic or electrostatic forces	NaCl, LiF, ZnS, CaF_2 , MgBr_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solution state	High
(3) Metallic Solids	Positive ions in a sea of delocalised electrons	Metallic bonding	All metals and alloys	Hard but malleable and ductile	Conductors in solid as well as in molten state	Fairly High
(4) Covalent or Network Solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C(diamond), AlN, C(graphite)	Hard Soft	Insulators Conductor (exception)	Very High

Note :

- (a) Ionic solids are insulators in the solid state because ions are not free to move. However, in the molten state, when dissolved in water, the ions become free to move about and they conduct electricity.
- (b) **Exceptional behaviour of graphite :** Graphite is soft, conductor of electricity and a good solid lubricant because of its typical structure. Carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between the layers and is free to move. This imparts graphite the above mentioned properties.



Structure of graphite

CRYSTAL LATTICES AND UNIT CELLS**Crystal :**

A crystal is a homogeneous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.

Space Lattice :

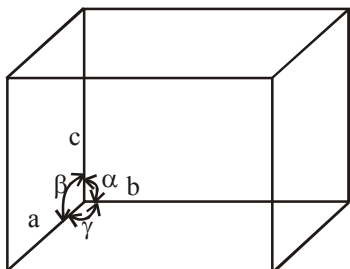
The arrangement of constituents particles like atoms, ions or molecules in different sites in three dimensional space is called space lattice.

There are only 14 possible three dimensional lattices and these are called **Bravais Lattices**. The characteristics of a crystal lattice are:

- Each point in a lattice is called lattice point or lattice site.
- Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule or an ion.
- Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit Cell :

It is the smallest portion of the crystal lattice which when repeated in different directions, generates the entire lattice. A unit cell is characterised by six parameters, i.e., a , b , c , α , β and γ ; where a , b and c are its dimensions along the edges while α , β and γ are the angles between the edges. These are depicted in the figure given below:



Unit cells can be broadly divided into two categories:

Primitive unit cells :

Unit cell in which constituent particles are present only on the corner positions of a unit cell.

Centred or non-primitive unit cells :

Unit cell in which constituent particles are present at positions other than corners in addition to those at corners

Types of Non-Primitive Unit Cells :**(i) Body-centred unit cells (*bcc*) :**

Unit cell in which besides corners, one constituent particle is present at the body-centre.

(ii) Face-centred unit cells (*fcc*) :

Unit cell in which besides corners, one constituent particle is present at the centre of each face.

(iii) End-centred unit cells :

Unit cell in which besides corners, one constituent particle is present at the centre of any two opposite faces.

Contribution of Atoms Present at Different Lattice Sites :

In a crystal, atoms located at the corners and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell

- A point that lies at the corner of unit cell is shared among eight unit cells and thus, it contributes for $1/8$ of each such point to unit cell.
- A point along an edge is shared by four unit cells and thus contribute for $1/4$ of each such point to unit cell.
- A face-centred point is shared by two unit cells and thus contributes for $1/2$ of each such point to unit.
- A body-centred point lies entirely within the unit cell and thus contributes for one each such point to unit cell.

Calculation Number of Atoms in a Unit Cell**Primitive cubic/simple cubic unit cell :**

Total number of atoms in one unit cell is $8 \times \frac{1}{8} = (1)$

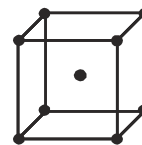
(8 corners $\times$ each corner is shared by 8 particles)

bcc unit cell :

Total number of atoms per unit cell

- Eight Corner atoms contribute one atom per unit cell.
- Centre atom contribute one atom per unit cell.
- So, total $1 + 1 = 2$ atoms per unit cell.

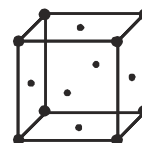
$$Z = 8 \times \frac{1}{8} + 1 = 2$$

**fcc unit cell :**

Total number of atoms per unit cells

- The eight corners atoms contribute for $\frac{1}{8}$ of an atom and thus one atom per unit cell.
- Each of six face centered atoms is shared by two adjacent unit cells and therefore one face centred atom contribute half of its share. Means

$$6 \times \frac{1}{2} = 3 \text{ atom per unit cell.}$$



- So, total $Z = 3 + 1 = 4$ atoms per unit cell.

CLOSE PACKING IN CRYSTALS :

Close-packing of particles results in two highly efficient lattices, hexagonal close packed (*hcp*) and cubic close packed (*ccp*). The latter is also called face centered cubic (*fcc*) lattice.

Hexagonal Close Packing :

In *hcp*, the pattern of spheres is repeated in alternate layers and is often written as ABAB _ _ _ pattern.

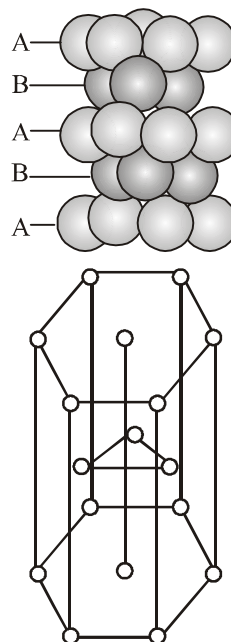


Fig. Hexagonal close-packed structure showing set of parallel planes
Here each atom is surrounded by 12 others and is said to have co-ordination number of 12.

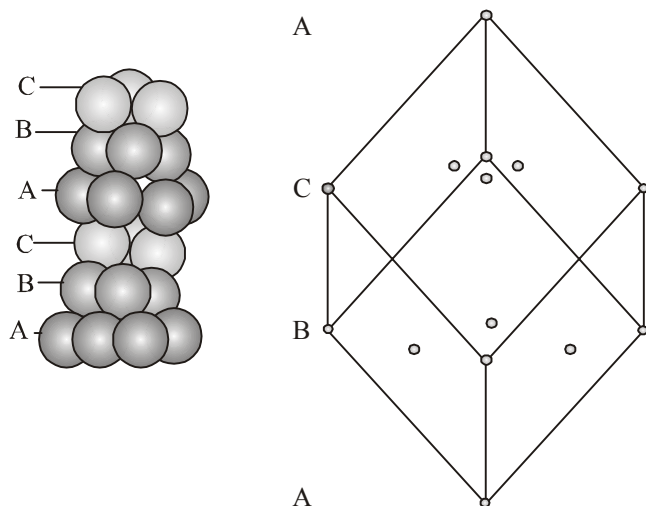
The *hcp* arrangement of atoms occupies 74% of the available space and thus has 26% vacant space.

It has only one set of parallel close packed layers.

Hexagonal close packed structure is found in Be, Cd, Li, Ca, Cr, Mo, V, Mg, Zn, Ce, Zr, Os, Ru, He, etc.

Cubic Close Packing :

In *ccp*, the pattern of layers is often written as ABCABC _ _



As in *hcp*, each atom in *ccp* arrangement has 12 nearest neighbours. In other words, the co-ordination number of the atom is 12.

The *ccp* arrangement of atoms occupy 74% of the available space and thus has 26% vacant space.

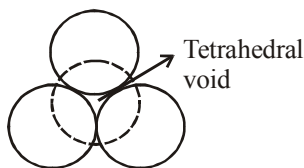
It has four sets of parallel close packed layers. Hence the chances for slipping of one layer over the other are more in the *ccp* arrangement than in the *hcp* arrangement. Hence metals having *ccp* structure (e.g. Cu, Ag, Au and Pt) are highly malleable and ductile.

Cubic close-packed structure is found in Al, Cr, Co, Cu, Au, Ag, Fe, Pb, Mn, Ni, Ca, Sr, Pt, all noble gases except He.

Type and Number of Voids

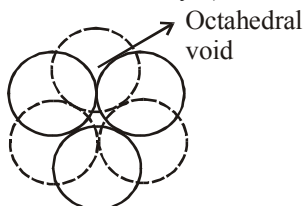
Close-packing of particles in *hcp* or *ccp* results in two types of voids : octahedral and tetrahedral.

- (i) **Tetrahedral void** : Tetrahedral voids are formed when centres of four spheres are joined, i.e.,



If the number of close packed spheres is N , then the number of tetrahedral voids generated = $2N$

- (ii) **Octahedral void** : A void surrounded by six spheres (i.e. when triangular voids in the second layer are above the triangular voids in the first layer) is called octahedral void, i.e.,



If the number of close packed spheres is N , then the number of octahedral voids generated = N and, the number of tetrahedral voids generated = $2N$

Note : In ionic compounds anions are present in the packing whereas cations occupy the voids if the cations are small, they may occupy tetrahedral voids while if cations are large they occupy octahedral voids. Further, it is not necessary that all voids must be occupied. The formula of the compound can be calculated by knowing the fraction of voids occupied.

COORDINATION NUMBER :

In every ionic compound, positive ions are surrounded by negative ions and *vice versa*. Normally each ion is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ion is termed its **coordination number**. The coordination number of positive and negative ions of a compound are same when the two types of ions are equal in number (e.g., NaCl, ZnS, etc.). On the other hand, when an ionic compound contains different number of positive and negative ions (as in CaCl_2 , Na_2S etc.), the coordination numbers of positive and negative ions are different. For example, in CaCl_2 since Cl^- ions are twice the number of Ca^{2+} ions, the coordination number of calcium ion is twice the coordination number of chloride ion.

RADIUS RATIO RULES :

The ratio of the radii of the cation to the anion in crystal lattice is called **radius ratio**.

$$\text{Radius ratio} = \frac{r}{R} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}}$$

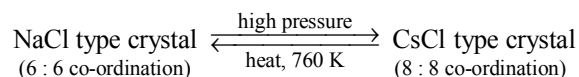
Table shows the relationship of radius ratio, co-ordination number and the geometrical shapes of some ionic crystals.

Limiting radius ratio (r^+) / (r^-)	C.N.	Shape
<0.155	2	Linear
0.155–0.225	3	Planar triangle
0.225–0.414	4	Tetrahedral
0.414–0.732	4	Square planar
0.414–0.732	6	Octahedral
0.732–0.999	8	Body-centred cubic

EFFECT OF PRESSURE AND TEMPERATURE ON CRYSTAL STRUCTURE

Effect of Pressure

Increase of pressure increases the co-ordination number during crystallization e.g., by applying high pressure, the NaCl crystal structure having 6 : 6 co-ordination number changes to CsCl crystal structure having co-ordination number 8 : 8.



Effect of Temperature

Increase of temperature, however, decreases the co-ordination number e.g., upon heating to 760 K, the CsCl crystal structure having co-ordination of 8 : 8 changes to NaCl crystal structures having co-ordination 6 : 6.

PACKING EFFICIENCY

It is the percentage of total space filled by the particles.

Type of structure	Relation between 'a' and 'r' a : edge length r : radius of sphere	Packing Efficiency
hcp and ccp (fcc)	$r = \frac{a}{2\sqrt{2}}$	74%
bcc	$r = \frac{\sqrt{3}}{4}a$	68%
Simple cubic lattice	$r = \frac{a}{2}$	52.4%

Relationships between the nearest neighbour distance (d) and the edge (a) of unit cell of a cubic crystal.

Simple	Face-centred	Body-centred
$d = a$	$d = \frac{a}{\sqrt{2}}$ $= 0.707 a$	$d = \frac{\sqrt{3}}{2}a$ $= 0.866 a$

DENSITY OF A UNIT CELL

For cubic crystals of elements

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} \text{ g/cm}^3$$

For cubic crystals of ionic compounds

$$\rho = \frac{ZM}{a^3 N_A} \text{ g/cm}^3 \text{ or kg m}^{-3}$$

where $\rho \rightarrow$ density of the unit cell
 $Z \rightarrow$ no. of atoms present in one unit cell
 $M \rightarrow$ molar mass
 $a \rightarrow$ edge length of the unit cell
 $N_A \rightarrow$ Avogadro's number

BRAGG EQUATION :

According to Bragg, a crystal (composed of series of equally spaced atomic planes) could be employed not only as a **transmission grating** (as suggested by Laue) but also as a reflection grating. When X-rays are incident on a crystal face, these penetrate into the crystal and strike the atoms in successive planes. From each of these planes the X-rays are reflected like the reflection of a beam of light from a bundle of glass plates of equal thickness. Based on this model, Bragg derived a simple relation between the wavelength (λ) of the X-rays used, the distance (d) between the successive atomic planes and the angle of incident X-rays or the angle of reflection (θ).

$$n\lambda = 2d \sin \theta \quad (\text{where } n = 1, 2, 3, \dots)$$

The equation is known as **Bragg's equation or Bragg's law**. The reflection corresponding to $n = 1$ (for a given family of planes) is called *first order reflection*; the reflection corresponding to $n = 2$ is the *second order reflection* and so on.

IMPERFECTIONS IN SOLIDS**Point Defects and Line Defects :**

Broadly the defects in crystals are of two types point and line defects. Point defects are irregularities from ideal arrangement around a point or an atom in lattice. However, when the deviation from the ideal arrangement exist in the entire row of lattice points, the defect is called line defect.

Point defect is of 3 types :

(i) Stoichiometric Defects :

Those point defects that do not disturb the stoichiometry of the solid.

(a) **Vacancy defect** : This defect arises when some lattice sites are vacant. Thus generally arises due to absorption of heat from the surroundings. It decreases the density of a substance.

(b) **Interstitial defect** : This defect arises when some constituent particles occupy an interstitial site. It increases the density of the substance.

The above two types of defects are generally shown by **non-ionic solids**. Ionic solids do not show simple vacancy and interstitial defects. Instead, they show these defects as Schottky and Frenkel defects, as explained below:

(c) **Frenkel defect** : This defect arises when an ion is missing from its lattice site and it occupies the interstitial site. It does not change the density of the crystal.

Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions.

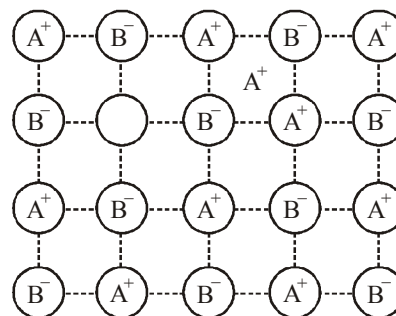


Fig. Frenkel defect

Eg. ZnS, AgCl, AgBr, AgI etc.

(d) **Schottky defect** : This defect arises when equal number of cations and anions are missing from their lattice sites. It decreases the density of substance.

Schottky defect is more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal.

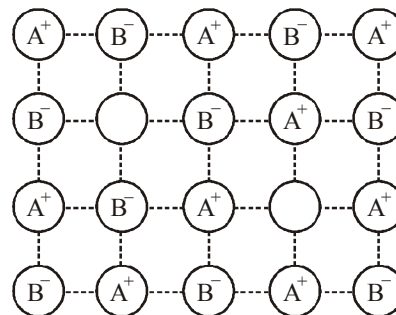


Fig. Schottky defect

Eg. NaCl, KCl, CsCl, KBr etc.

Note : AgBr shows both i.e., Frenkel and Schottky defect.

(ii) Impurity defects :

These defects arise when foreign atoms are present at lattice site (in place of host atoms) or at vacant interstitial sites.

(iii) Non-stoichiometric defects :

As a result of these defects, the ratio of cations to anions becomes different from that indicated by ideal chemical formula.

Example : VO_x (where x can vary between 0.6 to 1.3)

Two types of non-stoichiometric defects are :

(a) **Metal excess defect :**

Metal excess defects due to anion vacancies

It occurs due to *anionic vacancies* i.e. anions diffuse to the surface of the crystal resulting in anionic sites which are occupied by unpaired electrons. These sites are called F-centres. The e^{-1} s absorb energy from the visible light and impart colour to crystal

Examples :

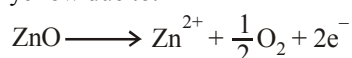
- (1) The excess sodium in NaCl makes the crystal appears yellow.
- (2) Excess potassium in KCl makes it violet.
- (3) Excess lithium in LiCl makes it pink.

Note : Greater the number of F-centres, greater is the intensity of colour.

Metal excess defects due to interstitial cations :

It may occur if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site.

Example : When ZnO is heated, it loses oxygen and turns yellow due to:



The excess of Zn^{2+} ions get trapped into vacant interstitial sites.

(b) **Metal Deficiency defect :**

It occurs due to missing of cation from its lattice site and presence of higher charge cation in adjacent site. It occurs when metals show variable valency, Example : FeO, FeS and NiO.

ELECTRICAL PROPERTIES OF SOLIDS

On the basis of conductivity, solids are classified as:

- (i) **Conductors :** The solids having conductivities ranging between 10^4 to $10^7 \Omega^{-1} \text{m}^{-1}$. Metals are good conductors.
- (ii) **Insulators :** The solids having very low conductivities ranging between 10^{-20} to $10^{-10} \Omega^{-1} \text{m}^{-1}$. Example : plastic, rubber, non-metals etc.
- (iii) **Semiconductors:** The solids having conductivities in the intermediate range from 10^{-6} to $10^4 \Omega^{-1} \text{m}^{-1}$.

Band Theory :

The behaviour of conductors, insulators and semiconductors are explained on the basis of band theory. The atomic orbitals of metals overlap to form a large number of molecular orbitals and this set is called **a band**. Two bands are formed:

Valence band (lower energy) and conduction band (higher energy)

If valence band is partially filled or overlaps with higher energy conduction band, e^{-1} s can easily flow under the influence of electric field. Thus, metals conduct electricity.

If gap between filled valence band and unoccupied conduction band is large, e^{-1} s cannot jump from valence band to conduction band. Hence, the substance has extremely low conductivity and it behaves as an insulator.

If the gap between valence band and conduction band is small, some e^{-1} s may jump from valence band to conduction band. Hence, the substance shows some conductivity and it acts as a semiconductor. Electrical conductivity of semiconductor increases with temperature as more electrons can jump to conduction band. Pure substances like Si and Ge show this type of behaviour and are called **intrinsic semiconductor**.

Extrinsic semiconductors are obtained by adding impurity to a semiconductor so as to increase its conductivity.

The process of adding impurities to a crystalline substance so as to change its properties is called doping.

Thus, the impurities added may be electron rich or electron deficit. Each of these is briefly described below :

(i) **Doping with electron rich impurities :** Group 14 element like silicon or germanium has 4 electrons in the valence shell. When it is doped with Group 15 element like P or As, the silicon or germanium atoms at some lattice sites are substituted by atoms of P or As. Now, as these atoms have 5 electrons in the valence shell, after forming normal four covalent bonds with the neighbouring silicon atoms, the fifth extra electron is free and gets delocalized. These delocalized electrons increase the conductivity of silicon or germanium, the silicon or germanium crystals doped with electron rich impurities are called **n-type semiconductors**.

(ii) **Doping with electron deficit impurities :** When Group 14 element like Si or Ge is doped with Group 13 element like B, Al or Ga, the Si or Ge atom at some lattice sites are substituted by those of B, Al or Ga. Now, as Group 13 elements have only three valence electrons, they can form three covalent bonds with the neighbouring silicon atoms. Thus, a hole is created at the site where fourth electron is missing. This is called electron hole or electron vacancy. Electron deficit doped silicon or germanium are called **p-type semiconductors**.

MAGNETIC PROPERTIES OF SOLIDS

Magnetic properties of materials are studied in terms of magnetic moments which arise due to orbital motion and spinning motion of electrons.

Based on their behaviour in the external magnetic field, substances are classified as below :

Diamagnetic Substances :

Those substances which are weakly repelled by external magnetic field. It is shown by substances which contain fully-filled orbitals. For ex: TiO_2 , H_2O , NaCl, benzene, etc.

Paramagnetic Substances :

Which are weakly attracted by external magnetic field. It is shown by substances which contain unpaired e^{-1} s. Example : O_2 , Cu^{2+} , Fe^{3+} , Cr^{3+} . However, they lose their magnetism in the absence of magnetic field.

Ferromagnetic Substances:

The substances which are strongly attracted by magnetic field are termed as ferromagnetic substances. This type of substance has alignment of all the unpaired electrons in the same direction (orientation) These substances are permanently magnetised i.e. these substances show magnetism even in the absence of magnetic field. Examples are Ni, Fe, Co and CrO_2 .

Anti-Ferromagnetic Substances :

Substances which possess zero net magnetic moment. It is due to presence of equal number of electrons in opposite directions. For ex: MnO , Mn_2O_3 . Their magnetic moment will compensate each others magnetic moment.

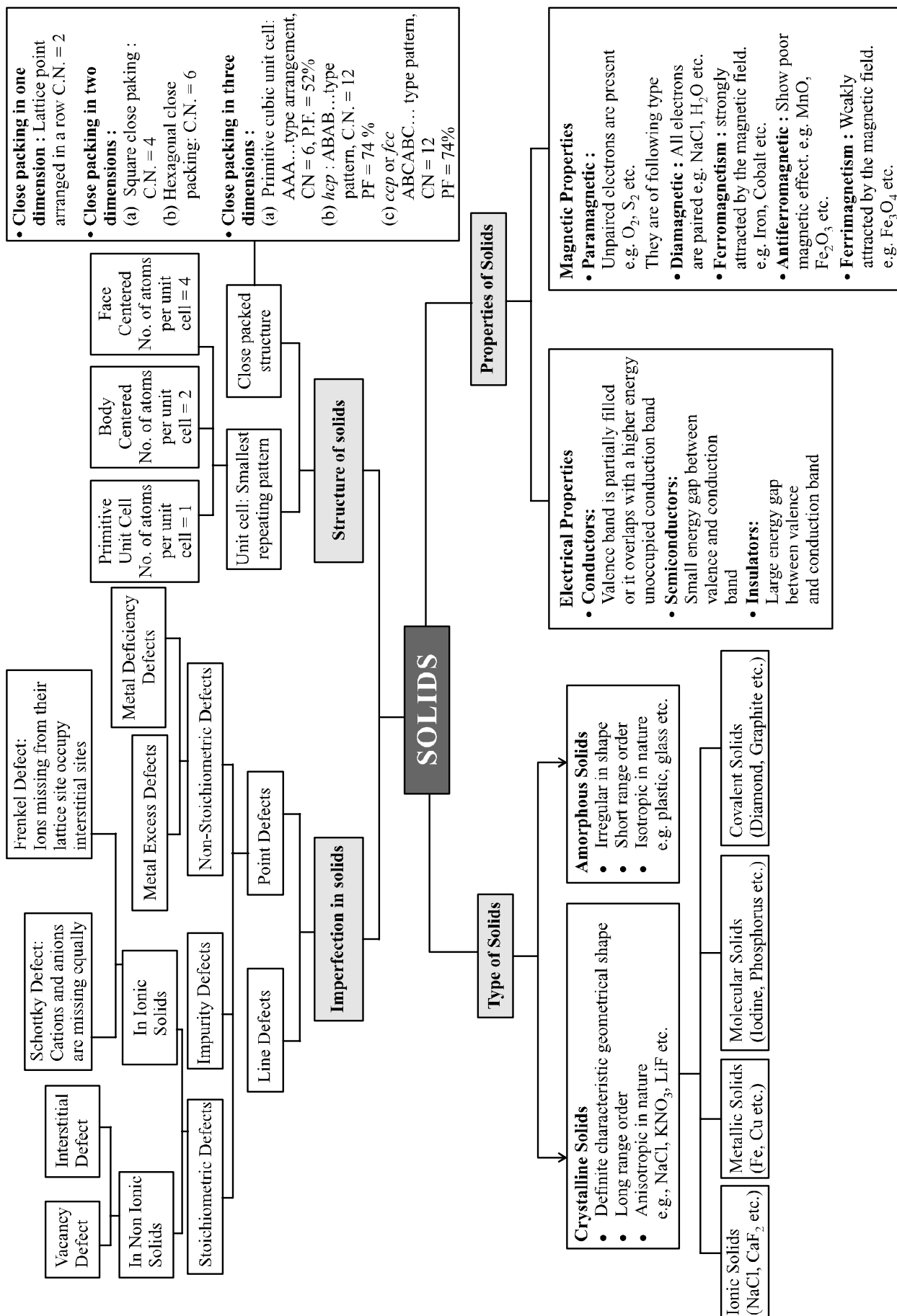
Ferrimagnetic Substances :

When unequal number of unpaired electrons are aligned in opposite directions, the net magnetic moment is not zero. Such substances are termed as ferrimagnetic substances e.g., ferrite Fe_2O_3 .

Note :

- (i) All magnetically ordered substances, i.e., ferromagnetic and anti-ferromagnetic solids change into paramagnetic at high temperature. This is due to randomisation of domains (spins) on heating. For ex: ferrimagnetic substance, Fe_3O_4 , becomes paramagnetic at 850 K.
- (ii) Each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie temperature**.

CONCEPT MAP



EXERCISE - 1

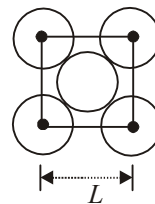
Conceptual Questions

- Frenkel and Schottky defects are :
 - nucleus defects
 - non-crystal defects
 - crystal defects
 - nuclear defects
- Which of the following compounds is a good conductor of electricity in solution state ?
 - Covalent
 - Molecular
 - Metallic
 - Ionic
- Most crystals show good cleavage because their atoms, ions or molecules are
 - weakly bonded together
 - strongly bonded together
 - spherically symmetrical
 - arranged in planes
- Certain crystals produce electric signals on application of pressure. This phenomenon is called :
 - pyroelectricity
 - ferroelectricity
 - piezoelectricity
 - ferrielectricity
- A solid with high electrical and thermal conductivity is
 - Si
 - Li
 - NaCl
 - Ice
- Solid CH_4 is
 - ionic solid
 - covalent solid
 - molecular solid
 - does not exist
- An example of a covalent crystalline solid is:
 - Si
 - Al
 - NaF
 - Ar
- The pure crystalline substance on being heated gradually first forms a turbid liquid at constant temperature and still at higher temperature turbidity completely disappears. The behaviour is a characteristic of substance forming
 - Allotropic
 - Liquid
 - Isomeric
 - Isomorphous
- Na and Mg crystallize in the bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is :
 - 4 and 2
 - 9 and 14
 - 14 and 9
 - 2 and 4
- For fcc if AB is just like the rock salt like structure then, A^+ and B^- are located at –
 - A^+ - Tetrahedral voids ; B^- - Corner
 - A^+ - Corner and faces ; B^- - Octahedral voids
 - A^+ - Octahedral voids ; B^- - Corner and faces
 - A^+ - Corner and faces ; B^- - Octahedral and tetrahedral voids
- The ionic radii of X^+ and Y^- ions are 146 and 216 pm respectively. The probable type of structure shown by it is
 - CsCl type
 - Rock salt type
 - Zinc blend type
 - CaF_2 type
- The element which is used as semiconductor is
 - Al
 - Bi
 - Cr
 - Si
- A solid has a structure in which 'W' atoms are located at the corners of a cubic lattice 'O' atoms at the centre of edges and Na atoms at the centre of the cube. The formula for the compound is
 - Na_2WO_3
 - Na_2WO_2
 - NaWO_2
 - NaWO_3
- A solid is made of two elements X and Z. The atoms Z are in ccp arrangement while the atoms X occupy all the tetrahedral sites. What is the formula of the compound?
 - XZ
 - XZ_2
 - X_2Z
 - X_2Z_3
- The radius ratio in CsCl is 0.93. The expected lattice structure is
 - tetrahedral
 - square planar
 - octahedral
 - body-centred cubic
- In NaCl crystal each Cl^- ion is surrounded by
 - 4 Na^+ ions
 - 6 Na^+ ions
 - 1 Na^+ ions
 - 2 Na^+ ions
- Edge length of a cube is 400 pm, its body diagonal would be
 - 566 pm
 - 600 pm
 - 500 pm
 - 693 pm
- In stoichiometric defects, the types of compound exhibit Frenkel defects have/has
 - Low co-ordination nos.
 - High co-ordination.
 - Small difference in the size of cations and anions
 - None of these.
- For orthorhombic system axial ratios are $a \neq b \neq c$ and the axial angles are
 - $\alpha = \beta = \gamma \neq 90^\circ$
 - $\alpha = \beta = \gamma = 90^\circ$
 - $\alpha = \beta = \gamma = 90^\circ, \beta = 90^\circ$
 - $\alpha \neq \beta \neq \gamma = 90^\circ$
- In the fluorite structure, the coordination number of Ca^{2+} ion is :
 - 4
 - 6
 - 8
 - 3
- Na and Mg crystallize in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is
 - 4 and 2
 - 9 and 14
 - 14 and 9
 - 2 and 4
- In the solid state, MgO has the same structure as that of sodium chloride. The number of oxygens surrounding each magnesium in MgO is
 - 6
 - 1
 - 2
 - 4

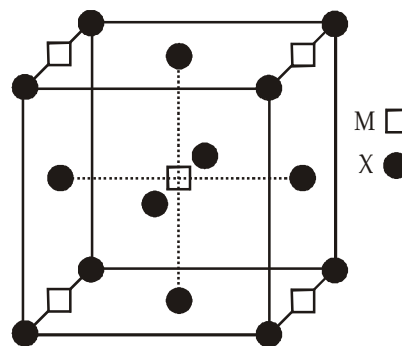
23. Equal number of atoms or ion missing from normal lattice point creating a vacancy due to
 (a) Frenkel defect (b) Mass defect
 (c) Schottky defect (d) Interstitial defect
24. When molten zinc is converted into solid state, it acquires *hcp* structure. The number of nearest neighbours of Zn will be
 (a) 6 (b) 12
 (c) 8 (d) 4
25. Hexagonal close packed arrangement of ions is described as
 (a) ABC ABA (b) ABC ABC
 (c) ABABA (d) ABBAB
26. CsBr has *bcc* structure with edge length 4.3. The shortest interionic distance in between Cs^+ and Br^- is
 (a) 3.72 (b) 1.86
 (c) 7.44 (d) 4.3
27. Schottky defect generally appears in :
 (a) NaCl (b) KCl
 (c) CsCl (d) all of these
28. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g ?
 [Atomic masses : Na = 23, Cl = 35.5]
 (a) 5.14×10^{21} unit cells (b) 1.28×10^{21} unit cells
 (c) 1.71×10^{21} unit cells (d) 2.57×10^{21} unit cells
29. In a solid '*AB*' having the *NaCl* structure, '*A*' atoms occupy the corners of the cubic unit cell. If all the face-centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
 (a) AB_2 (b) A_2B
 (c) A_4B_3 (d) A_3B_4
30. A solid AB crystallises as *NaCl* structure and the radius of the cation is 0.100 nm. The maximum radius of the anion can be:
 (a) 0.137 nm (b) 0.241 nm
 (c) 0.274 nm (d) 0.482 nm
31. Edge length of a cube is 400 pm. Its body diagonal would be
 (a) 500 pm (b) 566 pm
 (c) 600 pm (d) 693 pm
32. In the calcium fluoride structure, the coordination number of the cation and anion are respectively
 (a) 6, 6 (b) 8, 4
 (c) 4, 4 (d) 4, 8
33. The limiting radius ratio for tetrahedral shape is:
 (a) 0 to 0.155 (b) 0.225 to 0.414
 (c) 0.155 to 0.225 (d) 0.414 to 0.732
34. The second order Bragg diffraction of X-rays with $\lambda = 1.00 \text{ \AA}$ from a set of parallel planes in a metal occurs at an angle 60° . The distance between the scattering planes in the crystal is
 (a) $0.575 \text{ \AA}$ (b) $1.00 \text{ \AA}$
 (c) $2.00 \text{ \AA}$ (d) $1.15 \text{ \AA}$
35. For a cubic geometry the limiting $\frac{r^+}{r^-}$ is :
 (a) 0.414 (b) 0.155
 (c) > 0.731 (d) 0.731
36. CsBr crystallises in a body centered cubic lattice. The unit cell length is 436.6 pm. Given that the atomic mass of Cs = 133 and that of Br = 80 amu and Avogadro number being $6.02 \times 10^{23} \text{ mol}^{-1}$, the density of CsBr is
 (a) 0.425 g/cm^3 (b) 8.5 g/cm^3
 (c) 4.25 g/cm^3 (d) 82.5 g/cm^3
37. The pyknometric density of sodium chloride crystal is $2.165 \times 10^3 \text{ kg m}^{-3}$ while its X-ray density is $2.178 \times 10^3 \text{ kg m}^{-3}$. The fraction of unoccupied sites in sodium chloride crystal is
 (a) 5.96×10^{-3} (b) 5.96×10^4
 (c) 5.96×10^{-2} (d) 5.96×10^{-1}
38. Potassium fluoride has *NaCl* type structure. What is the distance between K^+ and F^- ions if cell edge is '*a*' cm.
 (a) $2a \text{ cm}$ (b) $a/2 \text{ cm}$
 (c) $4a \text{ cm}$ (d) $a/4 \text{ cm}$
39. In the Bragg's equation for diffraction of X-rays, *n* represents for
 (a) quantum number (b) an integer
 (c) Avogadro's numbers (d) moles
40. The edge length of unit cell of a metal having molecular weight 75 g/mol is $5 \text{ \AA}$ which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm.
 (a) 217 pm (b) 210 pm
 (c) 220 pm (d) 205 pm
41. An element occurring in the *bcc* structure has 12.08×10^{23} unit cells. The total number of atoms of the element in these cells will be
 (a) 24.16×10^{23} (b) 36.18×10^{23}
 (c) 6.04×10^{23} (d) 12.08×10^{23}
42. The number of atoms in 100 g of an *fcc* crystal with density, $d = 10 \text{ g/cm}^3$ and cell edge equal to 100 pm, is equal to
 (a) 1×10^{25} (b) 2×10^{25}
 (c) 3×10^{25} (d) 4×10^{25}
43. Potassium has a *bcc* structure with nearest neighbour distance 4.52 Å. Its atomic weight is 39. Its density (in kg m^{-3}) will be
 (a) 454 (b) 804
 (c) 852 (d) 910
44. The radii of Na^+ and Cl^- ions are 95 pm and 181 pm respectively. The edge length of *NaCl* unit cell is
 (a) 276 pm (b) 138 pm
 (c) 552 pm (d) 415 pm
45. The cubic unit cell of a metal (molar mass = 63.55 g mol^{-1}) has an edge length of 362 pm. Its density is 8.92 g cm^{-3} . The type of unit cell is
 (a) primitive (b) face centered
 (c) body centered (d) end centered

46. Coordination numbers of Zn^{2+} and S^{2-} in the crystal structure of wurtzite are
 (a) 4, 4 (b) 6, 6
 (c) 8, 4 (d) 8, 8
47. Each of the following solids show, the Frenkel defect except
 (a) ZnS (b) AgBr
 (c) AgI (d) KCl
48. Doping of silicon (Si) with boron (B) leads to :
 (a) *n*-type semiconductor (b) *p*-type semiconductor
 (c) metal (d) insulator
49. Schottky defect defines imperfection in the lattice structure of
 (a) solid (b) gas
 (c) liquid (d) plasma
50. On doping Ge metal with a little of In or Ga, one gets
 (a) *p*-type semi conductor (b) *n*-type semi conductor
 (c) insulator (d) rectifier
51. If *Z* is the number of atoms in the unit cell that represents the closest packing sequence ABC ABC, the number of tetrahedral voids in the unit cell is equal to :
 (a) *Z* (b) $2Z$
 (c) $Z/2$ (d) $Z/4$
52. Schottky defect in crystals is observed when
 (a) an ion leaves its normal site and occupies an interstitial site
 (b) unequal number of cations and anions are missing from the lattice
 (c) density of the crystal increases
 (d) equal number of cations and anions are missing from the lattice
53. The appearance of colour in solid alkali metal halides is generally due to
 (a) Schottky defect (b) Frenkel defect
 (c) Interstitial positions (d) F-centre
54. The crystal system of a compound with unit cell dimensions " $a = 0.387$, $b = 0.387$ and $c = 0.504$ nm and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ " is
 (a) cubic (b) hexagonal
 (c) orthorhombic (d) rhombohedral
55. Crystal defect indicated in the diagram below is
 $\text{Na}^+ \text{Cl}^- \text{Na}^+ \text{Cl}^- \text{Na}^+ \text{Cl}^- \quad \text{Cl}^- \square \text{Cl}^- \text{Na}^+ \square \text{Na}^+$
 $\text{Na}^+ \text{Cl}^- \square \text{Cl}^- \text{Na}^+ \text{Cl}^- \quad \text{Cl}^- \text{Na}^+ \text{Cl}^- \text{Na}^+ \square \text{Na}^+$
 (a) Interstitial defect
 (b) Schottky defect
 (c) Frenkel defect
 (d) Frenkel and Schottky defects
56. Schottky defect generally appears in :
 (a) NaCl (b) KCl
 (c) CsCl (d) all of these
57. Which defect causes decrease in the density of crystal
 (a) Frenkel (b) Schottky
 (c) Interstitial (d) F-centre
58. What is the coordination number of sodium in Na_2O ?
 (a) 6 (b) 4
 (c) 8 (d) 2
59. If NaCl is doped with 10^{-4} mol % of SrCl_2 , the concentration of cation vacancies will be ($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)
 (a) $6.02 \times 10^{16} \text{ mol}^{-1}$ (b) $6.02 \times 10^{17} \text{ mol}^{-1}$
 (c) $6.02 \times 10^{14} \text{ mol}^{-1}$ (d) $6.02 \times 10^{15} \text{ mol}^{-1}$
60. The fraction of total volume occupied by the atoms present in a simple cube is
 (a) $\frac{\pi}{3\sqrt{2}}$ (b) $\frac{\pi}{4\sqrt{2}}$
 (c) $\frac{\pi}{4}$ (d) $\frac{\pi}{6}$
61. If '*a*' stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively,
 (a) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (b) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$
 (c) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{3}}{2}a$ (d) $1a : \sqrt{3}a : \sqrt{2}a$
62. With which one of the following elements silicon should be doped so as to give *p*-type of semiconductor ?
 (a) Germanium (b) Arsenic
 (c) Selenium (d) Boron
63. AB; crystallizes in a body centred cubic lattice with edge length '*a*' equal to 387 pm. The distance between two oppositely charged ions in the lattice is :
 (a) 335 pm (b) 250 pm
 (c) 200 pm (d) 300 pm
64. Among the following which one has the highest cation to anion size ratio?
 (a) NaF (b) CsI
 (c) CsF (d) LiF
65. A solid compound XY has NaCl structure. If the radius of the cation is 100 pm, the radius of the anion (Y^-) will be :
 (a) 275.1 pm (b) 322.5 pm
 (c) 241.5 pm (d) 165.7 pm
66. A metal crystallizes with a face-centered cubic lattice. The edge length of the unit cell is 408 pm. The diameter of the metal atom is :
 (a) 288 pm (b) 408 pm
 (c) 144 pm (d) 204 pm
67. In a compound, atoms of element Y form *ccp* lattice and those of element X occupy $2/3^{\text{rd}}$ of tetrahedral voids. The formula of the compound will be
 (a) X_4Y_3 (b) X_2Y_3
 (c) X_2Y (d) X_3Y_4
68. Copper crystallises in *fcc* with a unit cell length of 361 pm. What is the radius of copper atom?
 (a) 127 pm (b) 157 pm
 (c) 181 pm (d) 108 pm

69. The edge length of a face centered cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is
 (a) 288 pm (b) 398 pm
 (c) 618 pm (d) 144 pm
70. The Ca^{2+} and F^- are located in CaF_2 crystal, respectively at face centred cubic lattice points and in
 (a) tetrahedral voids (b) half of tetrahedral voids
 (c) octahedral voids (d) half of octahedral voids
71. KCl crystallises in the same type of lattice as does NaCl. Given that $r_{\text{Na}^+}/r_{\text{Cl}^-} = 0.55$ and $r_{\text{K}^+}/r_{\text{Cl}^-} = 0.74$. Calculate the ratio of the edge length of the unit cell for KCl to that of NaCl.
 (a) 1.123 (b) 0.891
 (c) 1.414 (d) 0.414
72. Percentages of free space in cubic close packed structure and in body centered packed structure are respectively
 (a) 30% and 26% (b) 26% and 32%
 (c) 32% and 48% (d) 48% and 26%
73. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be :
 (a) 75 pm (b) 300 pm
 (c) 240 pm (d) 152 pm
74. The packing efficiency of the two-dimensional square unit cell shown below is :



- (a) 39.27% (b) 68.02%
 (c) 74.05% (d) 78.54%
75. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is



- (a) MX (b) MX_2
 (c) M_2X (d) M_5X_{14}

EXERCISE - 2

Applied Questions

- The correct statement regarding F-centre is
 (a) electron are held in the voids of crystals
 (b) F-centre produces colour to the crystals
 (c) conductivity of the crystal increases due to F-centre
 (d) All of these
- The anions (A) form hexagonal closest packing and the cations (C) occupy only 2/3 of octahedral holes. The simplest formula of the ionic compound is :
 (a) CA (b) C_3A_2
 (c) C_4A_3 (d) C_2A_3
- Certain crystals produce electric signals on application of pressure. This phenomenon is called
 (a) Pyroelectricity (b) Ferroelectricity
 (c) Piezoelectricity (d) Ferrielectricity
- For a cubic geometry the limiting $\frac{r^+}{r^-}$ is :
 (a) 0.414 (b) 0.155
 (c) >0.731 (d) 0.731
- Which of the following has maximum value of cation/anion ratio?
 (a) KCl (b) NaCl
 (c) CaF_2 (d) MgCl_2
- What is the number of tetrahedral voids per atom in a crystal?
 (a) 1 (b) 2
 (c) 6 (d) 8
- Fe_3O_4 contains the magnetic dipoles of cations oriented as
 (a) $\uparrow\downarrow\uparrow\downarrow$ (b) $\uparrow\uparrow\uparrow\downarrow\downarrow$
 (c) $\uparrow\uparrow\uparrow\uparrow$ (d) $\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow$
- The intermetallic compound LiAg crystallizes in a cubic lattice in which both lithium and silver atoms have coordination number of eight. To what crystal class does the unit cell belong
 (a) Simple cubic (b) Face-centred cubic
 (c) Body-centred cubic (d) None of these
- A compound is formed by elements A and B. The crystalline cubic structure has the A atoms at the corners of the cube and B atoms at the body centre. The simplest formula of the compound is
 (a) AB (b) A_6B
 (c) AB_6 (d) A_8B_4
- A compound formed by elements X and Y crystallizes in a cubic structure in which the X atoms are at the corners of a cube and the Y atoms are at the face centres. The formula of the compound is

- (a) XY_3 (b) X_3Y
(c) XY (d) XY_2
11. Na and Mg crystallize in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is
(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4
12. A match box exhibits
(a) Cubic geometry
(b) Monoclinic geometry
(c) Orthorhombic geometry
(d) Tetragonal geometry
13. Olive oil when allowed to cool slowly gets solidified and forms a solid over a wide range of temperature. Best description of the solid based on above observation is
(a) Ionic solid (b) covalent network solid
(c) metallic solid (d) molecular solid
14. A crystalline solid
(a) changes abruptly from solid to liquid when heated
(b) has no definite melting point
(c) undergoes deformation of its geometry easily
(d) has an irregular 3-dimensional arrangements
15. Which of the following statements about amorphous solids is incorrect?
(a) They melt over a range of temperature
(b) They are anisotropic
(c) There is no orderly arrangement of particles
(d) They are rigid and incompressible
16. To get a n-type semiconductor, the impurity to be added to silicon should have which of the following number of valence electrons
(a) 1 (b) 2
(c) 3 (d) 5
17. Which set of following characteristics for ZnS crystal is correct?
(a) Coordination number (4 : 4); *ccp*; Zn^{++} ion in the alternate tetrahedral voids
(b) Coordination number (6 : 6); *hcp*; Zn^{++} ion in all tetrahedral voids.
(c) Coordination number (6 : 4); *hcp*; Zn^{++} ion in all octahedral voids
(d) Coordination number (4 : 4); *ccp*; Zn^{++} ion in all tetrahedral voids.
18. In p-type semiconductor, the added impurity to silicon is --- and conduction of electric current is due to the movement of ----
(a) As, electrons (b) P, holes
(c) Ga, holes (d) Ga, electrons & holes
- DIRECTIONS for Qs. 19 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation of Statement-1
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation of Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True
19. **Statement-1** : In crystal lattice, the size of the tetrahedral hole is larger than an octahedral hole.
Statement-2 : The cations occupy less space than anions in crystal packing.
20. **Statement-1** : In any ionic solid (MX) with Schottky defects, the number of positive and negative ions are same.
Statement-2 : Equal number of cation and anion vacancies are present.
21. **Statement-1** : Space or crystal lattice differ in symmetry of the arrangement of points.
Statement-2 : $n\lambda = 2d \sin \theta$, is known as Bragg's equation.
22. **Statement-1** : Crystalline solids have long range order.
Statement-2 : Amorphous solids have short range order.
23. **Statement-1** : In close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres.
Statement-2 : A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape.
24. **Statement-1** : Electrical conductivity of semiconductors increases with increasing temperature.
Statement-2 : With increase in temperature, large number of electrons from the valence band can jump to the conduction band.
25. **Statement-1** : On heating ferromagnetic or ferrimagnetic substances, they become paramagnetic.
Statement-2 : The electrons change their spin on heating.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Which of the following conditions favours the existence of a substance in the solid state?
(a) High temperature (b) Low temperature
(c) High thermal energy (d) Weak cohesive forces
2. Which of the following is not a characteristic of a crystalline solid?
(a) Definite and characteristic heat of fusion
(b) Isotropic nature
(c) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal
(d) A true solid
3. Which of the following is an amorphous solid?
(a) Graphite (C) (b) Quartz glass (SiO_2)
(c) Chrome alum (d) Silicon carbide (SiC)
4. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances?
(a) $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$
(b) $\downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$
(c) $\uparrow \uparrow \downarrow \uparrow \uparrow \downarrow$
(d) $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$

5. Which of the following is true about the value of refractive index of quartz glass?
 - (a) Same in all directions
 - (b) Different in different directions
 - (c) Cannot be measured
 - (d) Always zero
6. Which of the following statement is not true about amorphous solids?
 - (a) On heating they may become crystalline at certain temperature
 - (b) They may become crystalline on keeping for long time
 - (c) Amorphous solids can be moulded by heating
 - (d) They are anisotropic in nature
7. The sharp melting point of crystalline solids is due to
 - (a) a regular arrangement of constituent particles observed over a short distance in the crystal lattice
 - (b) a regular arrangement of constituent particles observed over a long distance in the crystal lattice
 - (c) same arrangement of constituent particles in different directions
 - (d) different arrangement of constituent particles in different directions.
8. Iodine molecules are held in the crystals lattice by.....
 - (a) London forces
 - (b) dipole – dipole interactions
 - (c) covalent bonds
 - (d) coulombic forces
9. Which of the following is a network solid?
 - (a) SO_2 (solid)
 - (b) I_2
 - (c) Diamond
 - (d) H_2O (ice)
10. Which of the following solids is not an electrical conductor?
 1. Mg(s)
 2. TiO(s)
 3. $\text{I}_2(\text{s})$
 4. $\text{H}_2\text{O(s)}$
 - (a) Only 1
 - (b) Only 2
 - (c) 3 and 4
 - (d) 2, 3 and 4
11. Which of the following is not the characteristic of ionic solids?
 - (a) Very low value of electrical conductivity in the molten state
 - (b) Brittle nature
 - (c) Very strong forces of interactions
 - (d) Anisotropic nature
12. Graphite is a good conductor of electricity due to the presence of.....
 - (a) lone pair of electrons
 - (b) free valence electrons
 - (c) cations
 - (d) anions
13. Which of the following oxides behaves as conductor or insulator depending upon temperature?
 - (a) TiO
 - (b) SiO_2
 - (c) TiO_3
 - (d) MgO
14. Which of the following oxides shows electrical properties like metals?
 - (a) SiO_2
 - (b) MgO
 - (c) $\text{SO}_2(\text{s})$
 - (d) CrO_2
15. The lattice site in a pure crystal cannot be occupied by
 - (a) molecule
 - (b) ion
 - (c) electron
 - (d) atom
16. Graphite cannot be classified as
 - (a) conducting solid
 - (b) network solid
 - (c) covalent solid
 - (d) ionic solid
17. Cations are present in the interstitial sites in
 - (a) Frenkel defect
 - (b) Schottky defect
 - (c) vacancy defect
 - (d) metal deficiency defect
18. Schottky defect is observed in crystals when
 - (a) some cations move from their lattice site to interstitial sites
 - (b) equal number of cations and anions are missing from the lattice
 - (c) some lattice sites are occupied by electrons
 - (d) some impurity is present in the lattice
19. Which of the following is true about the charge acquired by p – type semiconductors?
 - (a) Positive
 - (b) Neutral
 - (c) Negative
 - (d) Depends on concentrations of p impurity
20. To get a n -type semiconductor from silicon, it should be doped with a substance with valency
 - (a) 2
 - (b) 1
 - (c) 3
 - (d) 5
21. The total number of tetrahedral voids in the face-centred unit cell is
 - (a) 6
 - (b) 8
 - (c) 10
 - (d) 12
22. Which of the following point defects are shown by AgBr(s) crystals?
 1. Schottky defect
 2. Frenkel defect
 3. Metal excess defect
 4. Metal deficiency defect
 - (a) 1 and 2
 - (b) 3 and 4
 - (c) 1 and 3
 - (d) 2 and 4
23. In which of the following pair, most efficient packing is present?
 - (a) hcp and bcc
 - (b) hcp and ccp
 - (c) bcc and ccp
 - (d) bcc and simple cubic cell
24. The percentage of empty space in a body centred cubic arrangement is
 - (a) 74
 - (b) 68
 - (c) 32
 - (d) 26
25. Which of the following statement is not true about the hexagonal close packing?
 - (a) The coordination number is 12
 - (b) It has 74% packing efficiency
 - (c) Tetrahedral voids of the second layer are covered by the spheres of the third layer
 - (d) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer
26. In which of the following structures coordination number for cations and anions in the packed structure will be same?
 - (a) Cl^- ions form fcc lattice and Na^+ ions occupy all octahedral voids of the unit cell

- (b) Ca^{2+} ions form fcc lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell
 (c) O^{2-} ions form fcc lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell
 (d) S^{2-} ions form fcc lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell
27. What is the coordination number in a square close packed structure in two dimensions?
 (a) 2 (b) 3
 (c) 4 (d) 6
28. Which kind of defects are introduced by doping?
 (a) Dislocation defect (b) Schottky defect
 (c) Frenkel defect (d) Electronic defect
29. Silicon doped with electron rich impurity forms.....
 (a) p - type semiconductor
 (b) n - type semiconductor
 (c) intrinsic semiconductor
 (d) insulator
30. Which of the following statements is not true?
 (a) Paramagnetic substances are weakly attracted by magnetic field.
 (b) Ferromagnetic substances cannot be magnetised permanently.
 (c) The domains in antiferromagnetic substances are oppositely oriented with respect to each other.
 (d) Pairing of electrons cancels their magnetic moment in the diamagnetic substances.
31. Which of the following is not true about the ionic solids?
 (a) Bigger ions form the close packed structure
 (b) Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size
 (c) Occupation of all the voids is not necessary
 (d) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids
32. A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field because.....
 (a) all the domains get oriented in the direction of magnetic field
 (b) all the domains get oriented in the direction opposite to the direction of magnetic field
 (c) domains get oriented randomly
 (d) domains are not affected by magnetic field
33. The correct order of the packing efficiency in different types of unit cells is
 (a) $\text{fcc} < \text{bcc} < \text{simple cubic}$
 (b) $\text{fcc} > \text{bcc} > \text{simple cubic}$
 (c) $\text{fcc} < \text{bcc} > \text{simple cubic}$
 (d) $\text{bcc} < \text{fcc} > \text{simple cubic}$
34. Which of the following defects is also known as dislocation defect?
 (a) Frenkel defect
 (b) Schottky defect
 (c) Non - stoichiometric defect
 (d) Simple interstitial defect
35. In the cubic close packing, the unit cell has
 (a) 4 tetrahedral voids each of which is shared by four adjacent unit cells
 (b) 4 tetrahedral voids within the unit cell
 (c) 8 tetrahedral voids each of which is shared by four adjacent unit cells
 (d) 8 tetrahedral voids within the unit cells
36. The edge lengths of the unit cells in terms of the radius of spheres constituting fcc, bcc and simple cubic unit cells are respectively
 (a) $2\sqrt{2}r, \frac{4r}{\sqrt{3}}, 2r$ (b) $\frac{4r}{\sqrt{3}}, 2\sqrt{2}r, 2r$
 (c) $2r, 2\sqrt{2}r, \frac{4r}{\sqrt{3}}$ (d) $2r, \frac{4r}{\sqrt{3}}, 2\sqrt{2}r$
37. Which of the following represents correct order of conductivity in solids?
 (a) $\kappa_{\text{metals}} \gg \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
 (b) $\kappa_{\text{metals}} \ll \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
 (c) $\kappa_{\text{metals}} > \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} = \text{zero}$
 (d) $\kappa_{\text{metals}} < \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} \neq \text{zero}$

NEET/AIPMT (2013-2017) Questions

38. Which of the following statements about the interstitial compounds is incorrect ? [NEET 2013]
 (a) They are chemically reactive.
 (b) They are much harder than the pure metal.
 (c) They have higher melting points than the pure metal.
 (d) They retain metallic conductivity.
39. The number of carbon atoms per unit cell of diamond unit cell is : [NEET 2013]
 (a) 8 (b) 6
 (c) 1 (d) 4
40. A metal has a fcc lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-3} . The molar mass of the metal is : (N_A , Avogadro's constant = $6.02 \times 10^{23} \text{ mol}^{-1}$) [NEET 2013]
 (a) 30 g mol^{-1} (b) 27 g mol^{-1}
 (c) 20 g mol^{-1} (d) 40 g mol^{-1}

Hints & Solutions

EXERCISE - 1

- (c) Frenkel and Schottky defects are crystal defects. It arises due to dislodgement of cation or anion from their places in the crystal lattice.
- (d) Ionic compounds are dissociated in solution state and form ions. Ions are good carrier of charge which make solution conducting.
- (d) Crystals show good cleavage because their constituent particles are arranged in planes.
- (c) The phenomenon is called piezoelectricity.
- (b) Out of the given substances, only Li has high electrical and thermal conductivity as Li is a metallic solid.
- (c) Solid CH_4 is a molecular solid. In this, the constituent molecules are held together by van der Waal's forces.
- (a) Si is an example of covalent crystalline solid among the given choices. Si atoms are covalently linked in tetrahedral manner.
- (b) Liquid crystals on heating first become turbid and then clear.
- (d) In a bcc cell eight atoms are located at the corners whereas one lies at the centre.

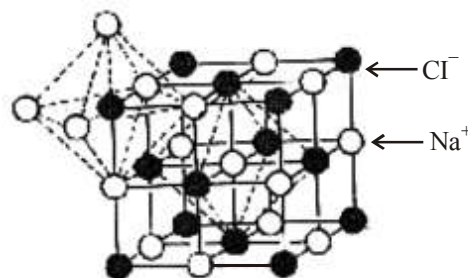
$$\therefore n = \left(8 \times \frac{1}{8} \right) + 1 = 2$$

whereas in an fcc cell eight atoms are at the corners and one atom is located at each of the six faces which is shared by two unit of cell.

$$\therefore n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2} \right) = 4$$

- (c) AB is just like NaCl. Thus twelve A^+ are at edges and 1 within body of fcc i.e. in octahedral voids and six B^- at faces and 8 at corner.
- (b) The radius ratio $\frac{r_+}{r_-} = \frac{146}{216} = 0.675$
It lies between 0.414 – 0.732. Hence, it exhibits rock salt type structure.
- (d) Semiconductors are those solids which are good conductors of electricity at room temperature but behave as insulators at room temperature, e.g., silicon and germanium.
- (d) In a unit cell, W atoms at the corner = $\frac{1}{8} \times 8 = 1$
O-atoms at the centre of edges = $\frac{1}{4} \times 12 = 3$
Na-atoms at the centre of the cube = 1
W : O : Na = 1 : 3 : 1
Hence, formula = NaWO_3
- (c) Let the number of Z atoms in the ccp arrangement = 100
Thus the number of tetrahedral sites = 200
Since all the tetrahedral sites are occupied by X atoms, the number of X atoms = 200
Hence ratio of X : Z = 2 : 1
Thus the formula is X_2Z

- (d) Since the radius ratio of CsCl is 0.93, it is expected to have a body centred cubic structure.
- (b) In NaCl crystal, each Cl^- ion is surrounded by 6 Na^+ ions. Similarly, each Na^+ is surrounded by 6 Cl^- ions.



- (d) For a simple cube, the relation can be obtained as under.
For a cube, body diagonal = $4r$

(r = radius of sphere)

For such a cube, we have a (edge length) = $\frac{4}{\sqrt{3}}r$ or

$$r = \frac{\sqrt{3}}{4}a$$

Thus, body diagonal

$$= 4r = 4 \times \frac{\sqrt{3}}{4} \times a$$

$$= \sqrt{3}a = \sqrt{3} \times 400 \text{ pm}$$

$$= 1.73 \times 400 \text{ pm} \approx 693 \text{ pm}.$$

- (a) In stoichiometric Frenkel defects occurs in those compound which have
 - Low C.N.
 - Large difference in size of cations and anions
- (b) For orthorhombic system $\alpha = \beta = \gamma = 90^\circ$
- (c) In fluorite structure each F^- ion is surrounded by four Ca^{++} ions whereas each Ca^{++} is surrounded by eight F^- ions, giving a body centred cubic arrangement. Thus the co-ordination number of Ca^{++} and F^- are 8 and 4 respectively.
- (d) The bcc cell consists of 8 atoms at the corners and one atom at centre. Contribution of each atom at each corner is equal to $\frac{1}{8}$.
 $\therefore n = \left(8 \times \frac{1}{8} \right) + 1 = 2$
The fcc cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.
 $\therefore n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2} \right) = 4$
- (a) Since MgO has a rock salt structure. In this structure each cation is surrounded by six anions and vice versa.

23. (c) The vacancy created due to missing of equal no. of atoms or ions from normal lattice point is called Schottky defect. In this type of defect electrical neutrality of ionic crystal is maintained.
24. (b) *hcp* is a closed packed arrangement in which the unit cell is hexagonal and coordination number is 12.
25. (c) ABAB..... is hexagonal close packing.
26. (a) For bcc structure, atomic radius, $r = \frac{\sqrt{3}}{4} a$

$$= \frac{\sqrt{3}}{4} \times 4.3 = 1.86$$

 Since, r = half the distance between two nearest neighbouring atoms.
 Shortest interionic distance = $2 \times 1.86 = 3.72$
27. (d) Schottky defect occurs in ionic crystals of type $A^+ B^-$, when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This defect generally appears in highly ionic compounds which have high coordination number. NaCl, KCl and CsCl all have high coordination numbers i.e., 6, 6 and 8 respectively. So, Schottky defect appear in all of the given compounds.
28. (d) Since in NaCl type of structure 4 formula units form a cell.
 58.5 gm. of NaCl = 6.023×10^{23} atoms

$$1 \text{ gm of NaCl} = \frac{6.023 \times 10^{23}}{58.5} \text{ atoms}$$

 4 atoms constitute 1 unit cell

$$\therefore \frac{6.023 \times 10^{23}}{58.5} \text{ atoms constitute}$$

$$= \frac{6.023 \times 10^{23}}{58.5 \times 4}$$

$$= 2.57 \times 10^{21} \text{ unit cells.}$$
29. (d) Effective number of 'A' atoms = $\left(8 \times \frac{1}{8}\right) + \left(4 \times \frac{1}{2}\right) = 3$
 Effective number of 'B' atoms = $\left(12 \times \frac{1}{4}\right) + 1 = 4$
 $\therefore$ Formula of the solid = A_3B_4 .
30. (b) Solid AB crystallizes as NaCl structure, so it has coordination number 6 and its r^+/r^- ranges from 0.414–0.732.
 For maximum radius of anion, we have to take the lower limit of the range 0.414–0.732. So, $\frac{r^+}{r^-} = 0.414$

$$\Rightarrow r^- = \frac{0.100}{0.414} \text{ nm} = 0.241 \text{ nm}$$
31. (d) Body diagonal (d) of a cubic crystal of edge length (a) is given by,
 $d = a\sqrt{3}$
 putting $a = 400 \text{ pm}$, we get
 $d = \sqrt{3} \times 400 \text{ pm} = 692.8 \text{ pm} \approx 693 \text{ pm}.$
32. (b) In CaF_2 , Ca^{2+} ions have ccp arrangement and F^- ions occupy the tetrahedral voids.
 In ccp arrangement total no. of Ca^{2+} ions is 4 and no. of tetrahedral voids is always $2n$ i.e. 8. Hence for every Ca^{2+} there are 8F^- ions as C.N., for F^- there are 4 Ca^{2+} ions.
33. (b) For tetrahedral shape radius ratio is 0.225–0.414.
34. (d) Order of Bragg diffraction (n) = 2; Wavelength (λ) = $1 \text{ \AA}$ and angle (θ) = 60° .
 We know from the Bragg's equation
 $n\lambda = 2d \sin \theta$
 or $2 \times 1 = 2d \sin 60^\circ$

$$\Rightarrow 2 \times 1 = 2d \cdot \frac{\sqrt{3}}{2} \Rightarrow d = \frac{2}{\sqrt{3}} = 1.15 \text{ \AA}$$

 (where d = Distance between the scattering planes)
35. (c) For cubic geometry the limiting ratio is

$$\frac{r^+}{r^-} > 0.731 \text{ i.e. (c)}$$
36. (b) For body centred cubic lattice $Z = 2$
 Atomic mass of unit cell = $133 + 80 = 213 \text{ a.m.u}$
 Volume of cell = $(436.6 \times 10^{-10})^3 \text{ cm}^3$

$$\text{Density, } \rho = \frac{ZM}{a^3 N_A} = \frac{2 \times 213}{(436.6 \times 10^{-10})^3 \times 6.02 \times 10^{23}}$$

$$= 8.50 \text{ g/cm}^3$$
37. (a) Fraction of unoccupied sites in NaCl crystal

$$= 1 - \frac{2.165 \times 10^3}{2.178 \times 10^3}$$

$$= \frac{2.178 \times 10^3 - 2.165 \times 10^3}{2.178 \times 10^3} = \frac{0.13 \times 10^3}{2.178}$$

$$= \frac{130}{2178} = 5.96 \times 10^{-3}$$
38. (b) Distance between K^+ and $\text{F}^- = \frac{1}{2} \times \text{length of the edge}$
39. (b) Bragg's equation is $n\lambda = 2d \sin \theta$
 where n is a positive integer i.e., 1, 2, 3, 4 etc. which stands for serial order of diffracted beams
40. (a) $\rho = \frac{ZM}{N_A V}$

$$Z = \frac{\rho N_A V}{M} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75}$$

 $Z = 2$, which represents *bcc* structure

$$\therefore r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 5 = 2.165 \text{ \AA} = 216.5 \text{ pm}$$

$$\approx 217 \text{ pm}$$
41. (a) There are two atoms in a *bcc* unit cell.
 So, number of atoms in 12.08×10^{23} unit cells

$$= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23} \text{ atoms.}$$
42. (d) $M = \frac{\rho \times a^3 \times N_A \times 10^{-30}}{Z}$

$$= \frac{10 \times (100)^3 \times 6.02 \times 10^{23} \times 10^{-30}}{4} = 15.05$$

- $\therefore$ Number of atoms in 100 g = $\frac{6.02 \times 10^{23}}{15.05} \times 100$
 $= 4 \times 10^{25}$
43. (d) For *bcc*, $d = \frac{\sqrt{3}}{2}a$ or $a = \frac{2d}{\sqrt{3}} = \frac{2 \times 4.52}{1.732} = 5.219 \text{ \AA}$
 $= 522 \text{ pm}$
- $$\rho = \frac{z \times M}{a^3 \times N_A \times 10^{-30}}$$

$$= \frac{2 \times 39}{(522)^3 \times (6.023 \times 10^{23}) \times 10^{-30}}$$

$$= 0.91 \text{ g/cm}^3 = 910 \text{ kg m}^{-3}$$
44. (c) In a *fcc* lattice, the distance between the cation and anion is equal to the sum of their radii, which is equal to half of the edge length of unit cell,
 i.e. $r^+ + r^- = \frac{a}{2}$ (where a = edge length)
 $r^+ = 95 \text{ pm}$, $r^- = 181 \text{ pm}$
 Edge length $= 2r^+ + 2r^- = (2 \times 95 + 2 \times 181) \text{ pm}$
 $= (190 + 362) \text{ pm} = 552 \text{ pm}$.
45. (b) $\rho = \frac{ZM}{N_A V}$
 $Z = \frac{\rho N_A V}{M} = \frac{8.92 \times 6.02 \times 10^{23} \times (362)^3 \times 10^{-30}}{63.55}$
 $= 4$
 $\therefore$ It has *fcc* unit cell
46. (a) Wurtzite has *face centred cubic* structure in which each Zn^{2+} ion is attached to four S^{2-} ions and each S^{2-} ion remains in contact with four Zn^{2+} ions. Hence coordination number of each ion is 4.
47. (d) In KCl, co-ordination number of cation and anion is 6 and 6 respectively. KCl is highly ionic so Schottky defect is common.
 Note : Schottky defect is common in compounds having high coordination number while Frenkel defect is common in compounds with low coordination number.
48. (b)
49. (a) Schottky defects are found in solid.
50. (a) *p*-type of semiconductors are produced
 (i) due to metal deficiency defects
 (ii) by adding impurity containing less electrons (i.e., atoms of group 13)
 Ge belongs to Group 14 and In to Group 13. Hence on doping, *p*-type semiconductor is obtained.
51. (b) In cubic closed pack system (CCP system) ABC ABC..... type of arrangement of layers is found. In this system, there are atoms at the corners as well as centre of the unit cell.
 $\therefore$ No. of atoms per unit cell $= 8 \times \frac{1}{8} + 1 = 2$
 Hence, the no. of tetrahedral voids in a unit cell $= 2Z$
52. (d) If in an ionic crystal of the type A^+ , B^- , equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. The defect is called Schottky defect.
53. (d) The appearance of colour in solid alkali metal halide is due to presence of F-centre found as defect in the crystal structure.
54. (b) $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
 These are the characteristics of a hexagonal system.
55. (b) When equal number of cations (Na^+) and anions (Cl^-) are missing from their regular lattice positions, we have Schottky defect.
56. (d) Schottky defect occurs in ionic crystals of type $\text{A}^+ \text{B}^-$, when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This defect generally appears in highly ionic compounds which have high coordination number. NaCl, KCl and CsCl all have high coordination numbers i.e., 6, 6 and 8 respectively. So, Schottky defect appear in all of the given compounds.
57. (b) More is the Schottky defect in crystal more is the decrease in density.
58. (b) In Na_2O there is antifluorite structure. Here negative ions form the ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion is surrounded by 8 positive ions. So coordination no. of Na^+ is 4.
59. (b) Since each Sr^{++} ion provides one cation vacancy, hence Concentration of cation vacancies = mole % of SrCl_2 added
 $= 10^{-4} \text{ mole \%}$
 $= \frac{10^{-4}}{100} \times 6.023 \times 10^{23} = 6.023 \times 10^{17} \text{ mol}^{-1}$
60. (d) Number of atoms per unit cell = 1
 Atoms touch each other along edges. Hence $r = \frac{a}{2}$
 (r = radius of atom and a = edge length)

$$\text{Therefore \% fraction} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$
61. (a) Following generalization can be easily derived for various types of lattice arrangements in cubic cells between the edge length (a) of the cell and r the radius of the sphere.
 For simple cubic : $a = 2r$ or $r = \frac{a}{2}$
 For body centred cubic :
 $a = \frac{4}{\sqrt{3}}r$ or $r = \frac{\sqrt{3}}{4}a$
 For face centred cubic :
 $a = 2\sqrt{2}r$ or $r = \frac{1}{2\sqrt{2}}a$
 Thus the ratio of radii of spheres for these will be simple : *bcc* : *fcc*
 $= \frac{a}{2} : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$
 i.e. option (a) is correct answer.
62. (d) The semiconductors formed by the introduction of impurity atoms containing one electron less than the parent atoms of insulators are termed as *p*-type semiconductors. Therefore silicon containing 14 electrons is to be doped with boron containing 13 electrons to give a *p*-type semi-conductor.

63. (a) For *bcc* lattice body diagonal = $a\sqrt{3}$.
The distance between the two oppositely charged ions

$$= \frac{a}{2}\sqrt{3}$$

$$= \frac{387 \times 1.732}{2} = 335 \text{ pm}$$
64. (c) $\frac{M^+}{X^-}$ is highest in CsF
 $\therefore$ correct choice : (c)
65. (c) Radius ratio of NaCl like crystal

$$= \frac{r^+}{r^-} = 0.414$$

$$r^- = \frac{100}{0.414} = 241.5 \text{ pm}$$
66. (a) For *ccp* $\sqrt{2}a = 4r$

$$\frac{\sqrt{2} \times 408}{2} = 2r \quad (2r = \text{Diameter})$$
Diameter = 288.5
67. (a) From the given data, we have
Number of Y atoms in a unit cell = 4
Number of X atoms in a unit cell = $8 \times \frac{2}{3} = \frac{16}{3}$
From the above we get the formula of the compound as $X_{16/3}Y_4$ or X_4Y_3
68. (a) For *fcc* unit cell, $4r = \sqrt{2}a$

$$r = \frac{\sqrt{2} \times 361}{4} = 127 \text{ pm}$$
69. (d) For an *fcc* crystal

$$r_{\text{cation}} + r_{\text{anion}} = \frac{\text{edge length}}{2}$$

$$110 + r_{\text{anion}} = \frac{508}{2}$$

$$r_{\text{anion}} = 254 - 110 = 144 \text{ pm}$$
70. (a)
71. (a) $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55$ and $\frac{r_{K^+}}{r_{Cl^-}} = 0.74$

$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 0.55 + 1 \text{ and } \frac{r_{K^+}}{r_{Cl^-}} + 1 = 0.74 + 1$$

$$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.55 \text{ and } \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = 1.74$$
Now edge length ratio of KCl and NaCl is

$$\frac{1.74}{1.55} = \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.123.$$
72. (b) Packing fraction is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the total volume of the unit cell.
P.F. for *ccp* and *bcc* are 0.74 and 0.68 respectively.
So, the free space in *ccp* and *bcc* are 26% & 32% respectively.

73. (d) For *bcc* structure $\sqrt{3}a = 4r$

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 351 = 152 \text{ pm.}$$
74. (d) Packing efficiency

$$= \frac{\text{Area occupied by circles within the square}}{\text{Area of square}}$$

$$= \frac{2\pi r^2}{L^2} \times 100 = \frac{2\pi r^2}{2(\sqrt{2}r)^2} \times 100 = \frac{\pi}{4} \times 100 = 78.54\%$$
75. (b) No. of M atoms = $\frac{1}{4} \times 4 + 1 = 1 + 1 = 2$
No. of X atoms = $\frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 3 + 1 = 4$
So, formula = $M_2X_4 = MX_2$

EXERCISE - 2

1. (d) All the given statements are correct about *F*-centres.
2. (d) The number of *A* ions per unit cell = $\frac{1}{6} \times 12$ (corners)
 $+ \frac{1}{2} \times 2$ (end centres) + 3 (in the body)
Number of octahedral voids per unit cell = $1 \times 6 = 6$.
Number of cations (*C*) per unit cell = $\frac{2}{3} \times 6 = 4$
Formula : C_4A_6 or C_2A_3
3. (c) When polar crystal is subjected to a mechanical stress, electricity is produced – a case of piezoelectricity. Reversely, if electric field is applied, mechanical stress is developed. Piezoelectric crystal acts as a mechanical electrical transducer.
4. (c) For cubic geometry the limiting ratio is

$$\frac{r^+}{r^-} > 0.731 \text{ i.e., (c)}$$
5. (c) Among the three options KCl, NaCl and $MgCl_2$, the size of anion is same. So larger the cation, larger will be the cation/anion ratio i.e., KCl will have larger cation/anion ratio among the three. So, we left with two options KCl and CaF_2 . Among these two CaF_2 will have maximum value of cation/anion ratio because decrease in ionic radii of anion from Cl^- to F^- does not overcome the effect of decrease in ionic radii of cation from K^+ to Ca^{2+} .
6. (b) Number of tetrahedral voids (V_T) in a crystal is twice the number of atoms (*n*) in a crystal i.e.,

$$V_T = 2n$$
So, number of tetrahedral voids per atom is given by

$$V_T / n = 2$$
7. (b)
8. (c) A body-centred cubic system consists of all eight corners plus one atom at the centre of cube.
9. (a) Atoms are present in the corners of cube = *A* and atom present at body centre = *B*.
We know that a cubic unit cell has 8 corners. Therefore

- contribution of each atom A at the corner = $\frac{1}{8}$. Since number of atoms per unit cell is 8, therefore total contribution = $8 \times \frac{1}{8} = 1$. We also know that atoms in the body centre, therefore number of atoms of B per unit cell = 1. Thus formula of the compound is AB.
10. (a) For a face centred cubic structure,
 No. of X atoms = $8 \times \frac{1}{8} = 1$
 No. of Y atoms = $6 \times \frac{1}{2} = 3$
 $\therefore$ Formula of the compound = XY_3
11. (d) In *bcc* - 8 atoms are at corners and one in the centre of the unit cell.
 Number of atoms per unit cell, $n = 8 \times \frac{1}{8} + 1 = 2$.
 In *fcc* - 8 atoms are at the corners and also centre of the six faces of each cell.
 Number of atoms per unit cell, $n = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$.
12. (c) Match box exhibits orthorhombic geometry i.e., $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$
13. (d) It can best be described as molecular solid.
14. (a) In crystalline solid there is perfect arrangement of the constituent particles only at 0 K. As the temperature increases the chance that a lattice site may be unoccupied by an ion increases. As the number of defects increases with temperature solid changes into liquid.
15. (b) Amorphous solids are isotropic, because these substances show same properties in all directions.
16. (d) For n-type, impurity added to silicon should have more than 4 valence electrons.
17. (a) ZnS has cubic close packed (ccp) structure. The S^{2-} ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, S^{2-} ion is surrounded by four Zn^{2+} ions.
18. (c)
19. (d) Tetrahedral holes are smaller in size than octahedral holes. Cations usually occupy less space than anions.
20. (a) Schottky defect is due to missing of equal number of cations and anions.
21. (b) Space or crystal lattice is a regular repeating arrangement of points in space and forms the basis of classification of all structures.
22. (b) In crystalline solids constituents are arranged in definite orderly arrangement. This regular arrangement of constituents extends throughout the three dimensional network of crystal. Thus crystalline substances said to have long range order. Whereas amorphous solids have no regular arrangement.
23. (c) Tetrahedral void is so called because it is surrounded

by four spheres tetrahedrally while octahedral void is so called because it is surrounded by six spheres octahedrally.

24. (a) In case of semiconductors, the gap between valence band and the conduction band is small and therefore some of the electrons may jump from valence band to conduction band and thus on increasing temperature conductivity is also increased.
25. (a) All magnetically ordered solids (ferromagnetic, ferrimagnetic and antiferromagnetic solids) transform to the paramagnetic state at high temperature due to the randomisation of spins.

EXERCISE - 3

Exemplar Questions

1. (b) At low temperature existence of a substance in the solid state is due to slow molecular motion and strong cohesive forces.
2. (b) Crystalline solid is anisotropic in nature as it shows different physical properties such as electrical resistance, refractive index in different directions.
3. (b) Quartz glass (SiO_2) is an amorphous solid due to its short range order of constituent particles.
4. (d) Substances which have domain structure are oppositely oriented and cancel each other's magnetic field are known as antiferromagnetic substances.

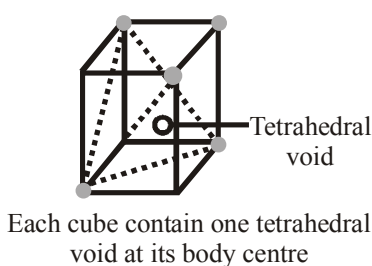
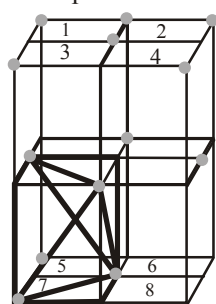


Schematic arrangement of antiferromagnetic substance

5. (a) Since, quartz glass is an amorphous solid having short range order of constituents. Hence, value of refractive index is same in all directions, measurable and not to be equal to zero always.
6. (d) Amorphous solids are isotropic in nature and any of its physical property will be same in all direction.
7. (b) Crystalline solids has a regular arrangement of constituent particles observed over a long distance in the crystal lattice due to which they exhibit sharp melting point.
8. (a) Iodine molecules belongs to a class of non – polar molecular solids in which constituents molecule are held together by London or dispersion forces.
9. (c) Diamond is a giant molecule in which constituent atoms are held together by covalent bonds.
10. (c) Iodine is a non–polar molecular solid and a non–conductor of electricity. Water is a hydrogen bonded molecular solid in which H and O are held together by polar covalent bond and each water molecule is held together by hydrogen bonding. Also, due to its non-ionic nature, it also behaves as a non-conductor of electricity.
11. (a) Ionic solids get easily dissociated into its ions in molten state and show high electrical conductivity.
12. (b) In graphite, each carbon is sp^2 hybridised having one free electron and due to the presence of free electrons graphite behaves as a good conductor of electricity.

13. (c) Certain metal oxides like VO_2 , VO_3 and TiO_3 etc. show metallic or insulating property depending upon temperature which is due to variation in energy gap between conduction band and valence band.
14. (d) Metal oxides like CrO_2 , TiO and ReO_3 show electrical conductivity similar to metals while SiO_2 , MgO and SO_2 do not show electrical properties.
15. (c) Each lattice point in a pure crystal is either an atom or molecule or ion which are joined together by a straight line to bring out geometry of lattice in pure crystal constituents which are arranged in fixed stoichiometric ratio.
16. (d) Graphite is a covalent solid which is made up of carbon atoms covalently bonded to three carbon atoms. As, the formation of covalent bond occurs throughout the crystal hence, it is a type of network solid. Also due to the presence of free electrons graphite is a conducting solid.
17. (a) When smaller ion (usually a cation) is dislocated from its normal site in crystal and move to interstitial site, it is known as Frenkel defect.
18. (b) Schottky defect is observed in crystal when equal number of cations and anions are missing from the lattice.
When lattice site is occupied by electron, this type of defect is known as metal excess defect.
19. (b) For the formation of *p*-type semiconductors, group 13 elements are doped with group 14 elements, which creates a hole in a molecule but the molecule as a whole remain neutral.
20. (d) To get a *n*-type semiconductor from silicon, it should be doped with a substance with valency 5.
e.g., silicon is doped with phosphorus to form a *n*-type semiconductor.
21. (b) In a fcc unit cell 8 tetrahedral voids are present at the centre of each 8 smaller cube of the unit cell.

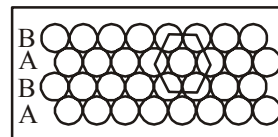
Eight tetrahedral voids
per fcc unit cell



Number of octahedral voids present = 4
Number of tetrahedral voids present = 8

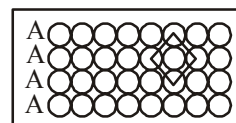
22. (a) In AgBr , both Ag^+ and Br^- ions are absent from the lattice causing Schottky defect. Also, Ag^+ ions are mobile so they have a tendency to move from their lattice site to interstitial site which causes Frenkel defect.
23. (b) As, packing efficiency for hcp or ccp is calculated to be 74%, it is maximum among all type of crystals.

24. (c) Packing efficiency for bcc arrangement is 68% which represents total filled space in the unit cell. Hence empty space in a bcc arrangement will be $100 - 68 = 32\%$.
25. (d) Hexagonal close packing can be diagrammatically represented as :



We can see that 1st layer (A) and 4th layer (B) are not exactly aligned.

26. (a) In NaCl crystal Cl^- ions are present at fcc lattice points and face centre and Na^+ occupies all the octahedral voids of the unit cell.
Thus, coordination number of Na^+ and Cl^- is 6.
27. (c) Coordination number in a square closed packed structure in 2-D must be equal to 4 as shown :



Square closed packed structure

28. (d) When electron rich or electron deficient impurity is added to a perfect crystal it introduces electronic defect in it.
29. (b) Silicon doped with electron rich impurity to form a *n*-type semiconductor.
30. (b) Ferromagnetic substances can be permanently magnetised by applying magnetic field and they will exhibit the magnetic properties even after the removal of magnetic field.
31. (d) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions present at the lattice points. As we know the radii of octahedral or tetrahedral void is related to radii of atoms (*r*) as
Radius of octahedral void (R_o) = $0.414 r$
Radius of tetrahedral void (R_t) = $0.225 r$
Where, *r* = radius of bigger atom involved
32. (a) When a ferromagnetic substance is placed in a magnetic field it becomes a permanent magnet because all the domains get oriented in the direction of magnetic field even after the removal of applied magnetic field.
33. (b) Packing efficiency in different types of unit cells is as follows :

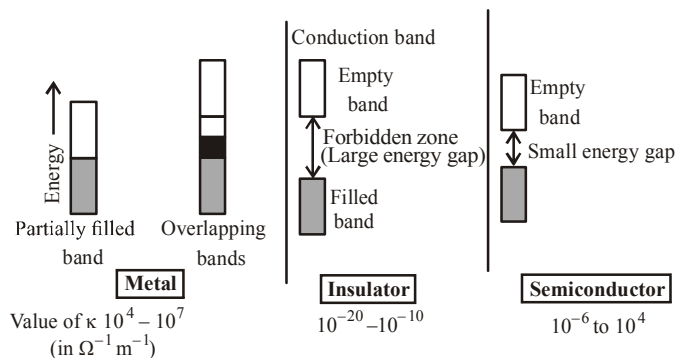
Unit cell	Packing efficiency
fcc	74%
bcc	68%
Simple cubic	52%

Thus, the correct order of packing efficiency is: fcc (74%) > bcc (68%) > simple cubic (52%).

34. (a) Frenkel defect is also known as dislocation defect because in this defect atoms present in crystal lattice are dislocated to interstitial site.
35. (d) In the cubic close packing the unit cell has 8 tetrahedral voids are located at each eight smaller cube of an unit cell.
36. (a) Edge lengths for different types of unit cells are given as :

Types of unit cell	Edge length
fcc	$2\sqrt{2}r$
bcc	$\frac{4}{\sqrt{3}}r$
Simple cubic	$2r$

37. (a) Conductivity of metal, insulator and semiconductors can be represented in the terms of κ (Kappa) which depends upon energy gap between valence band and conduction band.



Hence, correct order of conductivity in solids is :

$$\kappa_{\text{metals}} \gg \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$$

NEET/AIPMT (2013-2017) Questions

38. (a) In interstitial compounds small atoms like H, B & C enter into the void sites between the packed atoms of crystalline metal. They retain metallic conductivity and are chemically inert.
39. (a) Diamond is like ZnS. In diamond cubic unit cell, there are eight corner atoms, six face centered atoms and four more atoms inside the structure (tetrahedral voids).
Total no. of atoms present per unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 = 8$$

(corners) (face (inside
centered) body)

40. (b) Density is given by

$$d = \frac{Z \times M}{N_A a^3}; \text{ where } Z = \text{number of formula units present}$$

in unit cell, which is 4 for fcc

a = edge length of unit cell. M = Molecular mass

$$2.72 = \frac{4 \times M}{6.02 \times 10^{23} \times (404 \times 10^{-10})^3}$$

$$(\because 1 \text{ pm} = 10^{-10} \text{ cm})$$

$$M = \frac{2.72 \times 6.02 \times (404)^3}{4 \times 10^7} = 26.99$$

$$= 27 \text{ g mol}^{-1}$$

Chapter 16

Solutions

COMPONENTS OF SOLUTION

A solution is a homogenous mixture of two or more components called solute and solvent.

- (i) **Solute** : The component present in lesser amount than other component in solution is called solute.
- (ii) **Solvent** : The component present in greater amount than any or all other components is called the solvent.
A solution consisting of two components, i.e., one solute and one solvent is called a **binary solution**.

TYPES OF SOLUTIONS

On the basis of physical state of solute and solvent : There may be the following nine types of binary solutions :

S.No.	Solute	Solvent	Example
1.	Gas	Gas	Air
2.	Gas	Liquid	CO ₂ in soda water
3.	Gas	Solid	Hydrogen in Pd/Pt.
4.	Liquid	Gas	Fog
5.	Liquid	Liquid	Alcohol in water, benzene in toluene
6.	Liquid	Solid	Mercury in zinc amalgam
7.	Solid	Gas	Smog
8.	Solid	Liquid	Sugar in water
9.	Solid	Solid	Alloys

CONCENTRATION OF SOLUTIONS

Composition of a solution can be described by expressing its concentration. There are several ways of expressing the concentration of the solution quantitatively.

(i) Mass Percentage (w/W)

It is given by

$$\text{mass\% of a component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

(ii) Volume Percentage (v/V)

It is given by

$$\text{volume\% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100$$

(iii) Weight – Volume Percentage (w/V)

$$\text{Weight – volume percentage} = \frac{\text{Weight of solute (gm)}}{\text{Volume of solution (ml)}} \times 100$$

(iv) Parts per Million

It is defined as:

$$\text{Parts per million} = \frac{\text{Number of parts of component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

(v) Normality

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (lit)}}$$

$$\text{As Gram equivalents of solute} = \frac{\text{Weight of solute (gm)}}{\text{Equivalent weight of solute}}$$

(vi) Mole fraction

It is defined as:

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

(vii) Molarity (M)

It is defined as:

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$$

(viii) Molality (m)

It is defined as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{mass of solvent in kg}}$$

(ix) Formality

$$\text{Formality} = \frac{\text{weight of solute (gm)}}{\text{Formula weight of solute}} \times \frac{1}{\text{Volume of solution (lit.)}}$$

Note:

- (i) Mass %, ppm, mole fraction and molality are independent of temperature, whereas molarity is a function of temperature. It is because volume depends on temperature and mass does not.
- (ii) The molarity equation is $M_1 V_1 = M_2 V_2$
(for dilution from volume V_1 to V_2)

For a reaction between two reactants,

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

where n_1 and n_2 are their stoichiometric coefficients in the balanced equation.

SOLUBILITY

Solubility of a substance, is its maximum amount that can be dissolved in a specified amount of solvent. It depends on nature of solute and solvent, temperature and pressure.

Solubility of a Solid in a Liquid

When a solid solute is added to the solvent, some solute dissolves (dissolution) while some solute particles get separated (crystallization). A stage is reached when the two processes occur at the same rate and a state of dynamic equilibrium is reached. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. The concentration of solute in such a solution is its solubility.

Thus, the solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid in grams which can be dissolved in 100g of the liquid to form the saturated solution.

Effect of temperature: If dissolution process is endothermic ($\Delta H > 0$), solubility increases with increase in temperature and if it is exothermic ($\Delta H < 0$), solubility decreases.

Nature of the solute and solvent: Ionic compound dissolves in polar solvents due to strong electrostatic forces of attraction between ions and polar solvent molecules. Non-polar compound dissolve in non polar solvents due to similar solute-solute, solute-solvent and solvent-solvent interactions.

Effect of pressure: Solids and liquids are incompressible and practically remain unaffected by changes in pressure.

Solubility of a Gas in a Liquid

It is generally expressed in terms of absorption coefficient which is defined as the volume of gas (reduced to NTP) dissolved by unit volume of solvent at particular temperature and 1 atm. pressure of gas.

Nature of the gas: Easily liquifiable gases are more soluble. Example: CO_2 is more soluble than O_2 and H_2 .

Nature of the solvent: Gases capable of forming ions in aqueous solution are more soluble in water than in other solvent.

Example: HCl , NH_3 etc.

Effect of temperature: Solubility of a gas in a liquid decreases with increase in temperature. It is an exothermic process i.e., $\text{Gas} + \text{Solvent} \rightleftharpoons \text{Solution} + \text{Heat}$

Applying Le Chatelier, principle, increase in temperature would shift the equilibrium in backward direction, i.e., solubility will decrease.

Effect of pressure: The solubility of a gas increases with increase in pressure. Henry's law states that at a constant temperature, solubility of a gas in a liquid is directly proportional to the pressure of the gas, i.e. Expressing solubility in terms of mole fraction of gas in the solution Henry's law can be written as,

$$p = K_H x$$

$p \rightarrow$ partial pressure of the gas in vapour phase

$x \rightarrow$ mole fraction of the gas in solution

$K_H \rightarrow$ Henry's law constant

- Henry's constant, K_H is a junction of the nature of the gas.
- Greater the value of K_H , lower is the solubility of the gas at the same partial pressure.
- The value of K_H increases with increase in temperature.

$$K_H \propto \frac{1}{x} \text{ and } K_H \propto T \therefore x \propto \frac{1}{T}$$

It is due to this reason that aquatic species are more comfortable in cold water than in hot water.

Applications of Henry's Law

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- To avoid bends as well as toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium, nitrogen and oxygen.
- At high altitudes, the partial pressure of oxygen is less which leads to low concentration of oxygen in blood, causing climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

VAPOUR PRESSURE OF LIQUID SOLUTIONS AND RAOULT'S LAW**Vapour Pressure of Liquid-liquid Solutions**

When two volatile liquids are taken in a closed vessel, a stage is reached when an equilibrium is established between vapour phase and liquid phase. The relationship between them is given by Raoult's law i.e.,

It states that at a given temperature, the partial vapour pressure of any component of the solution is equal to the product of the vapour pressure of the pure component and its mole fraction in the solution.

$$p_1 \propto x_1 \text{ and } p_1 = p_1^\circ x_1$$

$$p_2 \propto x_2 \text{ and } p_2 = p_2^\circ x_2$$

where p_1 and p_2 are partial pressures of components 1 and 2

p_1° and p_2° are their partial pressures in pure state

x_1 and x_2 are mole fractions of component 1 and 2.

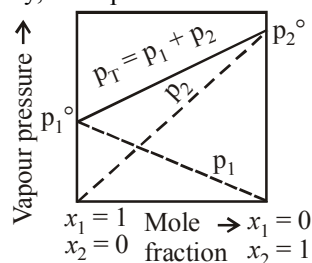
According to Dalton's law of partial pressure,

$$p_{\text{Total}} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ$$

$$= (1 - x_2) p_1^\circ + x_2 p_2^\circ$$

$$= p_1^\circ + (p_2^\circ - p_1^\circ) x_2$$

Diagrammatically, it is represented as:



The composition of the vapour phase is given by:

$$p_1 = y_1 p_{\text{Total}}$$

$$p_2 = y_2 p_{\text{Total}}$$

where y_1 and y_2 are the mole fractions of components 1 and 2 in the vapour phase.

Vapour Pressure of Solutions of Solids in Liquids

If a non-volatile solute is added to a solvent to give a solution, the vapour pressure of the solution will be from solvent alone and it is lower than the vapour pressure of the pure solvent at the same temperature.

Then, the total vapour pressure will be given by

$$p_T = p_1 + p_2$$

$$\text{as } p_2 = 0 \text{ (non-volatile solute)}$$

$$\therefore p_T = p_1 = p_1^\circ x_1$$

i.e., vapour pressure of solution $\propto$ mole fraction of the solvent in solution.

Mole fraction of the solvent in solution,

$$x_1 = \frac{n_1}{n_1 + n_2}$$

where n_1 = moles of solvent and n_2 = moles of solute

$$p_T = p_1^\circ x_1$$

$$\text{i.e., } \frac{p_1^\circ}{p_1} = \frac{n_1}{n_1 + n_2}$$

$$\frac{p_1^\circ - p_T}{p_1^\circ} = \frac{n_2}{n_1 + n_2}$$

where $\frac{p_1^\circ - p_T}{p_1^\circ}$ is called relative lowering of vapour pressure and

$$\frac{n_2}{n_1 + n_2} = \text{mole fraction of the solute in the solution.}$$

Limitations of Raoult's Law

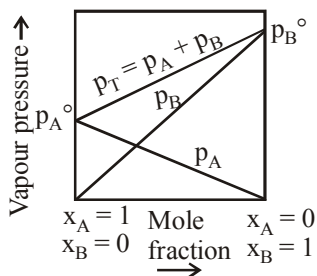
- Raoult's law is applicable only to very dilute solutions.
- Raoult's law is applicable to solutions containing non-volatile solute only.
- Raoult's law is not applicable to solutes which dissociates or associate in solution.

IDEAL AND NON-IDEAL SOLUTIONS

An Ideal solution possesses the following characteristics.

- The interactions between components are similar to those in pure components.
- There is no volume change and enthalpy change on mixing the components. ($\Delta V = 0$, $\Delta H = 0$)
- Each component obeys Raoult's law at all temperatures and concentrations i.e., $P_A = x_A P_A^\circ$ and $P_B = x_B P_B^\circ$
- They do not form azeotropes

Their graphical behaviour is shown as:



Examples:

- Benzene and toluene
- n-Hexane and n-Heptane
- Ethyl iodide and ethyl bromide
- Chlorobenzene and bromobenzene

Non Ideal: Solution possesses the following characteristics:

- The interactions between components are different from those in pure components.
- $\Delta V \neq 0$, $\Delta H \neq 0$ on mixing the components.
- They do not obey Raoult's law. They show positive or negative deviations from Raoult's law, i.e., $P_A \neq x_A P_A^\circ$ and $P_B \neq x_B P_B^\circ$
- They form azeotropes

Azeotropic Mixtures

They are binary mixtures of two liquids having same composition in liquid and vapour phase and boil at a constant temperature and can be distilled without any change in their composition. They are formed by non-ideal solutions. They are of two type.

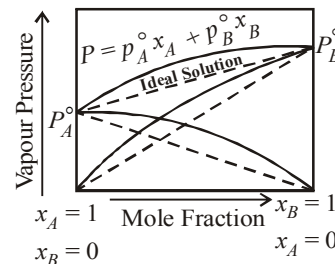
Minimum boiling azeotropes : it is formed by liquids showing positive deviation. Such azeotropes have boiling point lower than either any of the pure component.

Maximum boiling azeotropes : It is formed by liquids showing negative deviation such azeotropes have boiling point higher than either of the pure component.

Non-Ideal Solutions are divided into two types:

Non-ideal solutions showing positive deviations

- The interactions between components are less than in pure components, i.e., $A-B < A-A/B-B$
- $\Delta V_{\text{mixing}} = +ve$
- $\Delta H_{\text{mixing}} = -ve$
- $P_A > x_A P_A^\circ$, $P_B > x_B P_B^\circ$

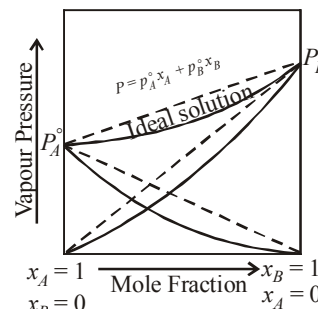


Examples:

- Acetone + ethyl alcohol
- Water + Ethylalcohol
- Acetone + Benzene

Non-ideal solutions showing negative deviations

- The interactions between components are more than in pure components, i.e., $A-B > A-A/B-B$
- $\Delta V_{\text{mixing}} = -ve$
- $\Delta H_{\text{mixing}} = -ve$
- $P_A < x_A P_A^\circ$, $P_B < x_B P_B^\circ$



Examples:

- $H_2O + HCl$
- $CH_3OH + CH_3COOH$
- $H_2O + HNO_3$
- Chloroform + Benzene

COLLIGATIVE PROPERTIES

Those properties of ideal solutions which depend only on the number of particles of solute dissolved in a definite amount of the solvent and do not depend on the nature of the solute are called colligative properties.

The important colligative properties are :

(i) Relative Lowering of Vapour Pressure

It is given by:

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1 + n_2} = \frac{w_2 / M_2}{w_1 / M_1 + w_2 / M_2}$$

for very dilute solution, $\frac{p^\circ - p_s}{p^\circ} \approx \frac{n_2}{n_1} = \frac{w_2 / M_2}{w_1 / M_1}$

for all solutions, $\frac{p^\circ - p_s}{p_s} = \frac{n_2}{n_1} = \frac{w_2 / M_2}{w_1 / M_1}$

(dilute or concentrated)

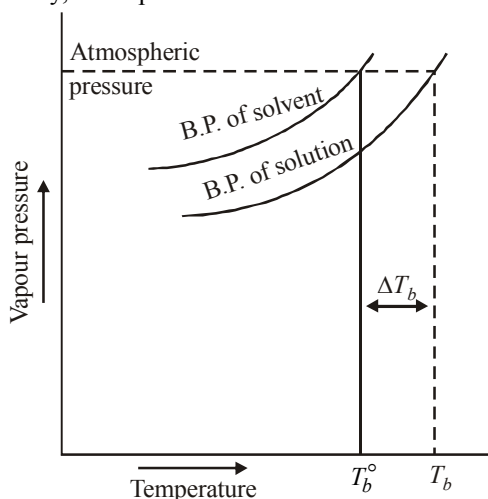
Where $n_1, w_1, M_1 \rightarrow$ number of moles, mass in g, mol. mass of solvent.

$n_2, w_2, M_2 \rightarrow$ number of moles, mass in g, mol. mass of solute.

(ii) Elevation of Boiling Point

The boiling point of the solution is always higher than that of the pure solvent. This is because vapour pressure of solution is lower than that of pure solvent and hence, the solution has to be heated more to make the vapour pressure equal to the atmospheric pressure.

Graphically, it is represented as



If T_b° is vapour pressure of solvent and T_b is vapour pressure of the solution then

$$T_b > T_b^\circ$$

The difference ΔT_b is called elevation in boiling point

$$\Delta T_b = T_b - T_b^\circ$$

Quantitatively, it is given by

$$\Delta T_b = K_b \times m, \text{ where } m = \text{molality}$$

$$T_b - T_b^\circ = K_b \times m = K_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$M_2 = \frac{1000 \times K_b \times w_2}{\Delta T_b \times w_1} \quad (K_b = \text{molal elevation constant or ebullioscopic constant})$$

Molal elevation constant is also given as

$$K_b = \frac{R M_1 T_b^2}{1000 \Delta H_v}$$

where, $T_b =$ b. pt. of pure solvent

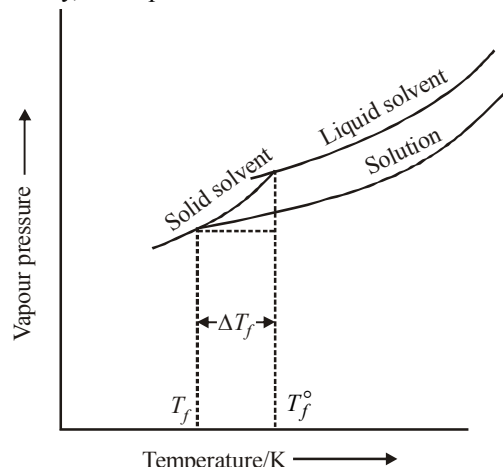
$\Delta H_v =$ Enthalpy of fusion of solvent

$M_1 =$ Molar mass of solvent

(iii) Depression in Freezing Point

Vapour pressure of the solution is less than that of pure solvent. As freezing point is the temperature at which the vapour pressure of the liquid and solid phase are equal, therefore, for the solution, this will occur at a lower temperature ($\therefore$ lower the temperature lower is the vapour pressure)

Graphically, it is represented as:



If T_f° is freezing point of pure solvent and T_f freezing point of the solution, then $T_f < T_f^\circ$. The depression in freezing point ΔT_f is given by

$$\Delta T_f = T_f^\circ - T_f$$

Quantitatively, it is given by

$$\Delta T_f = K_f \times m$$

$$T_f^\circ - T_f = K_f \times m \quad (m \rightarrow \text{molality})$$

$$= K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$M_2 = \frac{1000 \times K_f \times w_2}{\Delta T_f \times w_1} \quad (K_f = \text{molal depression constant or cryoscopic constant})$$

Relation for molal depression constant :

$$K_f = \frac{M_1 R T_f^2}{1000 \Delta H_f}$$

where, $T_f =$ Freezing point of pure solvent

$\Delta H_f =$ Enthalpy of fusion of solvent

Note:

Depression in freezing point is used in:

- making antifreeze solutions
- melting of ice on the roads

(iv) Osmotic Pressure

The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semipermeable membrane is called osmosis.

The minimum excess pressure that has to be applied on the solution to prevent the entry of the solvent into the solution through the semi-permeable membrane is called osmotic pressure.

Quantitatively, it is given by

$$\pi \propto C \quad \text{where } \pi \rightarrow \text{osmotic pressure}$$

$$\pi \propto T \quad C \rightarrow \text{conc. of solution}$$

$$\therefore \pi \propto CT \quad T \rightarrow \text{temperature}$$

$$\pi = CRT$$

R → gas constant

$$C = \frac{n}{V}$$

where, n = number of moles of the solute
V = volume of solution

$$\pi = \frac{n}{V} RT$$

$$\pi V = nRT$$

Note:

- When the semi-permeable membrane permits solvent molecules to come out through the membrane, it is called exo-osmosis and when the membrane permits solvent molecules to enter inside, it is called endo-osmosis.
- If pressure higher than osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semi-permeable membrane. This process is called reverse osmosis and it is used in the **desalination of water** i.e., removal of salts from sea water.
- Such solutions which have the same osmotic pressure at the same temperature are called isotonic solutions. If one solution is of lower osmotic pressure, it is called hypotonic with respect to more concentrated solution. The more concentrated solution is said to be hypertonic with respect to dilute solution.
- When an animal cell is placed in a hypotonic solution, the cell swells and bursts (hemolysis). When a cell is placed in hypertonic solution, the cell contracts in size (plasmolysis). When excess of fertilizers (like urea) are applied, plasmolysis takes place and plants dry up (wilt).

ABNORMAL MOLECULAR MASSES

In case of aqueous solutions of electrolytes, inorganic bases and salts, which dissociate completely or partially in the solution, or if association takes place in the solution as in the case of acetic acid and benzoic acid, the number of particles in the solution changes (increases in case of dissociation and decreases for association). As a result, value of colligative property also changes and as

$$\text{molecular mass} \propto \frac{1}{\text{colligative properties}}$$

∴ observed molecular mass comes out to be different from theoretical value. This observed molecular mass is called **abnormal molecular mass**.

Van't Hoff Factor

The extent of association or dissociation can be determined with the help of van't Hoff factor (*i*). It is defined as the ratio of normal mass to the observed molecular mass of solute i.e.,

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$\text{or } i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$\text{or } i = \frac{\text{Total number of moles of particles after association / dissociation}}{\text{Number of moles of particles before association / dissociation}}$$

Thus, the modified colligative properties are:

- (a) Relative lowering of vapour pressure

$$\frac{p^\circ - p_s}{p^\circ} = ix_2$$

- (b) Elevation in boiling point

$$\Delta T_b = T_b - T_b^\circ = ik_b m$$

- (c) Depression in freezing point

$$\Delta T_f = T_f^\circ - T_f = ik_f m$$

- (d) Osmotic pressure

$$\pi = iCRT = i \frac{n}{V} RT$$

Note:

- $i > 1$ if there is dissociation of the solute in solution and $i < 1$ if there is association of the solute in solution.
- For 100% dissociation of the solute, i = number of ions produced from one molecule of the solute.
- Degree of dissociation is defined as the fraction of the total substance that undergoes dissociation i.e.,

$$\text{Degree of dissociation } (\alpha) = \frac{\text{Number of moles dissociated}}{\text{Total number of moles taken}}$$

$$\begin{array}{lcl} & (A)_n & \rightleftharpoons nA \\ \text{Initial mole} & 1 & 0 \\ \text{Dissociation mole} & \alpha & n\alpha \\ \text{Equilibrium mole} & (1 - \alpha) & n\alpha \\ \therefore \text{Total number of moles} & = [(1 - \alpha) + n\alpha] \text{ mole} & \\ & = 1 + \alpha(n - 1) \text{ mole} & \end{array}$$

$$\therefore i = \frac{1 + \alpha(n - 1)}{1} = 1 + n\alpha - \alpha$$

$$\alpha = \frac{i - 1}{n - 1} \quad (n \rightarrow \text{number of ions produced on dissociation})$$

$$\text{or, } \alpha = \frac{M_c - M_o}{M_o(n - 1)} \quad \left[\begin{array}{l} M_c \rightarrow \text{normal molecular mass} \\ M_o \rightarrow \text{observed molecular mass} \end{array} \right]$$

- (iv) Degree of association is defined as the fraction of the total substance which exists in the form of associated molecules i.e.,

$$\begin{array}{lcl} & nA & \rightleftharpoons (A)_n \\ \text{Equilibrium} & (1 - \alpha) & \frac{\alpha}{n} \text{ mole} \\ \text{moles} & \text{mole} & \end{array}$$

$$\therefore \text{Total no. of moles} = 1 - \alpha + \frac{\alpha}{n}$$

$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$$

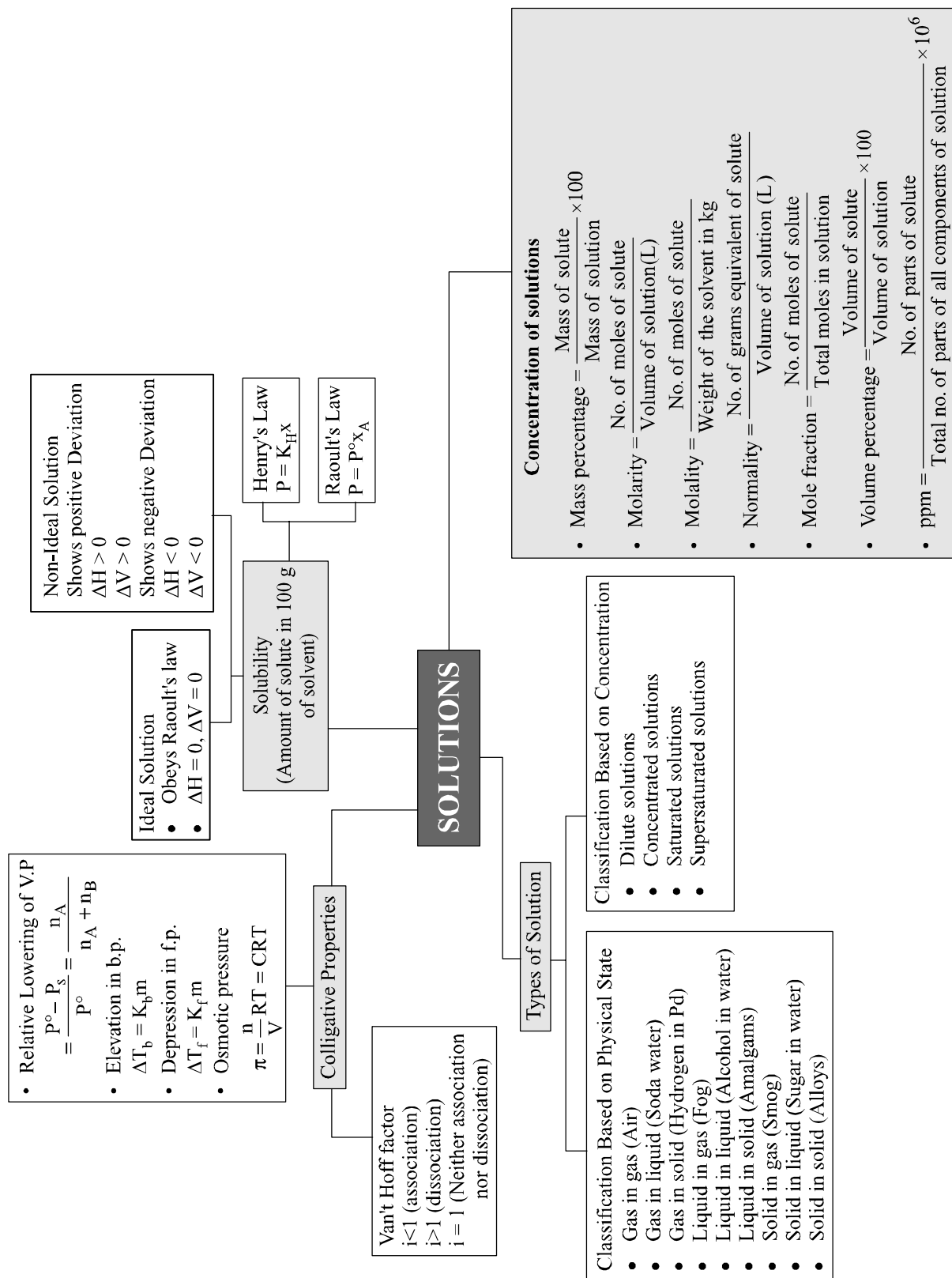
$$\text{Degree of association } (\alpha) = \frac{\text{Number of moles associated}}{\text{Total number of moles taken}}$$

$$\therefore \alpha = (1 - i) \frac{n}{n - 1}$$

n = number of molecules of the solute associated

$$\text{or, } \alpha = \frac{M_o - M_c}{M_o} \frac{n}{(n - 1)}$$

CONCEPT MAP

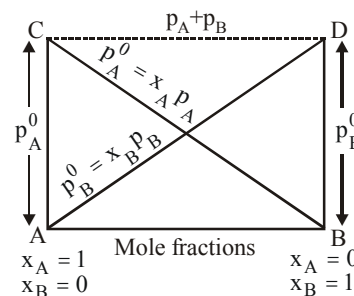


EXERCISE - 1

Conceptual Questions

- Lowering in vapour pressure is the highest for :
(a) 0.1 M glucose (b) 0.1 M BaCl_2
(c) 0.2 M urea (d) 0.1 M MgSO_4
- Formation of a solution from two components can be considered as
(i) Pure solvent $\rightarrow$ separated solvent molecules, ΔH_1
(ii) Pure solute $\rightarrow$ separated solute molecules, ΔH_2
(iii) Separated solvent & solute molecules $\rightarrow$ Solution, ΔH_3
Solution so formed will be ideal if
(a) $\Delta H_{\text{soln}} = \Delta H_3 - \Delta H_1 - \Delta H_2$
(b) $\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$
(c) $\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 - \Delta H_3$
(d) $\Delta H_{\text{soln}} = \Delta H_1 - \Delta H_2 - \Delta H_3$
- An aqueous solution containing 1 gm of urea boils at 100.25°C . The aqueous solution containing 3 g of glucose in the same volume will boil at (mol. wt. of urea = 60 and of glucose = 180) :
(a) 100.25°C (b) 100°C
(c) 100.15°C (d) 100.50°C
- The statement "If 0.003 moles of a gas are dissolved in 900 g of water under a pressure of 1 atmosphere, 0.006 moles will be dissolved under a pressure of 2 atmospheres", illustrates
(a) Dalton's law of partial pressure
(b) Graham's law
(c) Raoult's law
(d) Henry's law
- Which of the following modes of expressing concentration is independent of temperature ?
(a) Molarity (b) Molality
(c) Formality (d) Normality
- Molarity of liquid HCl will be, if density of solution is 1.17 gm/cc
(a) 36.5 (b) 32.05 (c) 18.25 (d) 42.10
- The molarity of a solution containing 5 gm of NaOH in 250 ml solution :
(a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0
- Concentrated hydrochloric acid contains 37% HCl (by mass). The density of this solution is 1.18 gm/ml . The molarity of the solution is :
(a) 10 M (b) 12 M (c) 13 M (d) 14 M
- An X molal solution of a compound in benzene has mole fraction of solute equal to 0.2. The value of X is
(a) 14 (b) 3.2 (c) 1.4 (d) 2
- The molarity of the solution containing 7.1 g of Na_2SO_4 in 100 ml of aqueous solution is
(a) 2 M (b) 0.5 M (c) 1 M (d) 0.05 M
- The vapour pressure of pure benzene at 25°C is 640 mm Hg and that of solution of solute A is 630 mm Hg. The molality of solution is –
(a) 0.2 m (b) 0.4 m (c) 0.5 m (d) 0.1 m
- The molarity of pure water is :
(a) 50 M (b) 18 M (c) 55.6 M (d) 100 M
- The osmotic pressure at 17°C of an aq. solution containing 1.75 gm of sucrose per 150 ml solution is :
(a) 0.08 atm (b) 8.1 atm (c) 0.8 atm (d) 9.1 atm
- An aqueous solution of glucose is 10% in strength. The volume in which 1 g mole of it is dissolved, will be :
(a) 9 litre (b) 1.8 litre (c) 8 litre (d) 0.9 litre
- 10 g of NaCl is dissolved in 10^6 g of the solution. Its concentration is :
(a) 100 ppm (b) 0.1 ppm (c) 1 ppm (d) 10 ppm
- On adding a solute to a solvent having vapour pressure 0.80 atm, vapour pressure reduces to 0.60 atm. Mole fraction of solute is :
(a) 0.25 (b) 0.75 (c) 0.50 (d) 0.33
- If 0.44 gm of substance dissolved in 22.2 gm of benzene lowers the freezing point of benzene by 0.567°C , then the molecular mass of substance is, the molal depression constant = $5.12^\circ\text{C mol}^{-1}$.
(a) 128.4 (b) 156.6 (c) 178.9 (d) 232.4
- 2.5 litres of NaCl solution contain 5 moles of the solute. What is the molarity?
(a) 5 molar (b) 2 molar (c) 2.5 molar (d) 12.5 molar
- Which of the following statements, regarding the mole fraction (x) of a component in solution, is incorrect?
(a) $0 \leq x \leq 1$ (b) $x \leq 1$
(c) x is always non-negative (d) None of these
- When 10 g of a non-volatile solute is dissolved in 100 g of benzene, it raises boiling point by 1°C then molecular mass of the solute is (K_b for benzene = 2.53 km^{-1})
(a) 223 g (b) 243 g (c) 233 g (d) 253 g
- The mole fraction of the solute in one molal aqueous solution is:
(a) 0.009 (b) 0.018 (c) 0.027 (d) 0.036
- When a solute is present in trace quantities the following expression is used
(a) Gram per million (b) Milligram percent
(c) Microgram percent (d) Parts per million
- 5 ml of N HCl, 20 ml of N/2 H_2SO_4 and 30 ml of N/3 HNO_3 are mixed together and volume made to one litre. The normality of the resulting solution is
(a) $\frac{N}{5}$ (b) $\frac{N}{10}$ (c) $\frac{N}{20}$ (d) $\frac{N}{40}$
- The molal freezing point constant for water is 1.86°C . Therefore, the change in freezing point of 0.1 molal of NaCl solution in water is expected to be
(a) 0.372°C (b) -1.86°C (c) -0.186°C (d) -0.372°C
- Vapour pressure of benzene at 30°C is 121.8 mm Hg. When 15 g of a non volatile solute is dissolved in 250 g of benzene its vapour pressure decreased to 120.2 mm Hg. The molecular weight of the solute (Mo. wt. of solvent = 78)
(a) 356.2 (b) 456.8 (c) 530.1 (d) 656.7
- If 20 g of a solute was dissolved in 500 ml. of water and osmotic pressure of the solution was found to be 600 mm of Hg at 15°C , then molecular weight of the solute is :
(a) 1000 (b) 1200 (c) 1400 (d) 1800

27. A solution containing components A and B follows Raoult's law when
 (a) A – B attraction force is greater than A – A and B – B
 (b) A – B attraction force is less than A – A and B – B
 (c) A – B attraction force remains same as A – A and B – B
 (d) volume of solution is different from sum of volume of solute and solvent
28. The vapour pressure of two liquids 'P' and 'Q' are 80 and 60 torr, respectively. The total vapour pressure of solution obtained by mixing 3 mole of P and 2 mole of Q would be
 (a) 72 torr (b) 140 torr
 (c) 68 torr (d) 20 torr
29. A mixture of components A and B will show –ve deviation when
 (a) $\Delta V_{\text{mix}} > 0$ (b) $\Delta H_{\text{mix}} < 0$
 (c) A – B interaction is weaker than A – A and B – B interactions
 (d) A – B interaction is stronger than A – A and B – B interactions.
30. A non-ideal solution was prepared by mixing 30 mL chloroform and 50 mL acetone. The volume of mixture will be
 (a) $> 80 \text{ mL}$ (b) $< 80 \text{ mL}$ (c) $= 80 \text{ mL}$ (d) $\geq 80 \text{ mL}$
31. The volume of gas decreases from 500 cc to 300 cc when a sample of gas is compressed by an average pressure of 0.6 atm. During this process 10 J of heat is liberated. The change in internal energy is.
 (a) -2.16 J (b) 12.15 J (c) 2.16 J (d) 101.3 J
32. Which of the following liquid pairs shows a positive deviation from Raoult's law?
 (a) Water - Nitric acid
 (b) Benzene - Methanol
 (c) Water - Hydrochloric acid
 (d) Acetone - Chloroform
33. 18 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution is
 (a) 76.00 torr (b) 752.40 torr
 (c) 759.00 torr (d) 7.60 torr
34. If all the four following compounds were sold at the same price, which would be cheapest for preparing an antifreeze solution for a car radiator?
 (a) $\text{C}_3\text{H}_5(\text{OH})_3$ (b) $\text{C}_2\text{H}_4(\text{OH})_2$
 (c) $\text{C}_2\text{H}_5\text{OH}$ (d) CH_3OH
35. The value of P° for benzene is 640 mm of Hg. The vapour pressure of solution containing 2.5 gm substance in 39 gm. benzene is 600 mm of Hg the molecular mass of X is –
 (a) 65.25 (b) 130 (c) 40 (d) 75
36. An ideal solution is formed when its components
 (a) have no volume change on mixing
 (b) have no enthalpy change on mixing
 (c) Both (a) and (b) are correct
 (d) Neither (a) nor (b) is correct
37. All form ideal solution except
 (a) C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$ (b) C_2H_6 and $\text{C}_2\text{H}_5\text{I}$
 (c) $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{H}_5\text{Br}$ (d) $\text{C}_2\text{H}_5\text{I}$ and $\text{C}_2\text{H}_5\text{OH}$.
38. For which of the following parameters the structural isomers $\text{C}_2\text{H}_5\text{OH}$ and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour)
 (a) Boiling points
 (b) Vapour pressure at the same temperature
 (c) Heat of vaporization
 (d) Gaseous densities at the same temperature and pressure
39. In the accompanied diagram, the ideal behaviour of a solution is shown by the line/s



- (a) AD (b) CB
 (c) CD (d) AD, CB and CD
40. Which one of the following is non-ideal solution
 (a) Benzene + toluene
 (b) *n*-hexane + *n*-heptane
 (c) Ethyl bromide + ethyl iodide
 (d) $\text{CCl}_4 + \text{CHCl}_3$
41. The molal elevation constant is the ratio of elevation in boiling point to:
 (a) molality (b) mole fraction
 (c) molarity (d) none
42. The azeotropic mixture of water (b.p. 100°C) and HCl (b.p. 85°C) boils at 108.5°C . When this mixture is distilled it is possible to obtain
 (a) pure HCl
 (b) pure water
 (c) pure water as well as pure HCl
 (d) neither HCl nor H_2O in their pure states
43. The molar freezing point constant for water is 1.86°C/mol . If 342 g of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is dissolved in 1000 g of water, the solution will freeze at:
 (a) -1.86°C (b) 1.86°C
 (c) -3.92°C (d) 2.42°C
44. Which will form maximum boiling point azeotrope
 (a) $\text{HNO}_3 + \text{H}_2\text{O}$ solution
 (b) $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ solution
 (c) $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{CH}_3$ solution
 (d) None of these
45. The vapour pressure at a given temperature of an ideal solution containing 0.2 mol of a non-volatile solute and 0.8 mol of solvent is 60 mm of Hg. The vapour pressure of the pure solvent at the same temperature is
 (a) 150 mm of Hg (b) 60 mm of Hg
 (c) 75 mm of Hg (d) 120 mm of Hg
46. When a hard boiled egg after shelling is immersed in saturated brine:
 (a) it shrinks
 (b) it grows in size
 (c) its size remains unchanged
 (d) it initially grows in size and then shrinks
47. The vapour pressure of a solvent decreases by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent if the decrease in the vapour pressure is to be 20 mm of Hg?
 (a) 0.8 (b) 0.6 (c) 0.4 (d) 0.2

48. A solution of acetone in ethanol
 (a) shows a positive deviation from Raoult's law
 (b) behaves like a non ideal solution
 (c) obeys Raoult's law
 (d) shows a negative deviation from Raoult's law
49. Azeotropic mixture of water and HCl has the percentage of HCl.
 (a) 20.2% (b) 26.4% (c) 48% (d) 68%
50. Which of the following aqueous solution has minimum freezing point ?
 (a) 0.01 m NaCl (b) 0.005 m C_2H_5OH
 (c) 0.005 m MgI_2 (d) 0.005 m $MgSO_4$
51. On adding 0.750 gm of compound in 25 gm of solvent, the freezing point is depressed by $0.502^\circ C$. The molecular wt. of the substance is [The molecular depression constant = $50.2^\circ C$ per 100 gm of solvent]
 (a) 100 (b) 200 (c) 300 (d) 400
52. 5 gm of CH_3COOH is dissolved in one litre of ethanol. Suppose there is no reaction between them. If the density of ethanol is 0.789 gm/ml then the molality of resulting solution is
 (a) 0.0256 (b) 0.1056 (c) 0.1288 (d) 0.1476
53. Which one of the following is a colligative property ?
 (a) Boiling point (b) Vapour pressure
 (c) Osmotic pressure (d) Freezing point
54. If 0.1 M solution of glucose and 0.1 M solution of urea are placed on two sides of the semipermeable membrane to equal heights, then it will be correct to say that
 (a) there will be no net movement across the membrane
 (b) glucose will flow towards urea solution
 (c) urea will flow towards glucose solution
 (d) water will flow from urea solution to glucose
55. When 800 gm of a 40% solution by weight was cooled, 100 gm of solute precipitated. The percentage composition of remaining solution is
 (a) 31.43% (b) 5.56% (c) 6.78% (d) 6.96%
56. At $25^\circ C$, the highest osmotic pressure is exhibited by 0.1 M solution of
 (a) $CaCl_2$ (b) KCl (c) glucose (d) urea
57. Which one of the following salts will have the same value of van't Hoff factor (i) as that of $K_4[Fe(CN)_6]$.
 (a) $Al_2(SO_4)_3$ (b) NaCl (c) $Al(NO_3)_3$ (d) Na_2SO_4
58. Which of the following 0.10 m aqueous solutions will have the lowest freezing point ?
 (a) $Al_2(SO_4)_3$ (b) $C_6H_{12}O_6$
 (c) KCl (d) $C_{12}H_{22}O_{11}$
59. Which of the following colligative property can provide molar mass of proteins (or polymers or colloids) with greatest precision ?
 (a) Osmotic pressure
 (b) Elevation of boiling point
 (c) Depression of freezing point
 (d) Relative lowering of vapour pressure
60. Camphor is often used in molecular mass determination because
 (a) it is readily available
 (b) it has a very high cryoscopic constant
 (c) it is volatile
 (d) it is solvent for organic substances
61. The freezing point of a 3% aq. solution of A is equal to the freezing point of 9% aq. solution of B. If the molecular weight of 'A' is 60, then the molecular wt. of B is
 (a) 45 (b) 90 (c) 180 (d) 360
62. 1.00 g of a non-electrolyte solute (molar mass 250 g mol^{-1}) was dissolved in 51.2 g of benzene. If the freezing point depression constant, K_f of benzene is $5.12 \text{ K kg mol}^{-1}$, the freezing point of benzene will be lowered by
 (a) 0.3 K (b) 0.5 K (c) 0.4 K (d) 0.2
63. The normality of mixture obtained by mixing 100 ml of 0.4 M H_2SO_4 and 200 ml of 0.2 M HCl is
 (a) 0.0267 (b) 0.2670 (c) 1.0267 (d) 1.1670
64. Brownian movement is found in
 (a) unsaturated solution (b) saturated solution
 (c) colloidal solution (d) suspension solution
65. A solution is formed by diluting 250 ml. of 0.400 N NH_2SO_4 with one litre of water. The normality of above formed solution is :
 (a) 0.400 N (b) 0.899 N (c) 0.040 N (d) 0.080 N
66. In a 0.2 molal aqueous solution of a weak acid HX the degree of ionization is 0.3. Taking k_f for water as 1.85, the freezing point of the solution will be nearest to
 (a) $-0.360^\circ C$ (b) $-0.260^\circ C$
 (c) $+0.481^\circ C$ (d) $-0.481^\circ C$
67. Which one of the following aqueous solutions will exhibit highest boiling point ?
 (a) 0.015 M urea (b) 0.01 M KNO_3
 (c) 0.01 M Na_2SO_4 (d) 0.015 M glucose
68. The amount of dibasic acid present in 100 ml of the aq. solution to give solution of [mol. wt. = 200] normality of 0.1 N is
 (a) 0.5 gm (b) 1 gm (c) 1.5 gm (d) 2 gm
69. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (Molecular weight of $CuCl_2$ = 134.4 g and K_b = $0.52 \text{ K kg mol}^{-1}$)
 (a) 0.16 (b) 0.05 (c) 0.1 (d) 0.2
70. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to :
 (a) ionization of benzoic acid.
 (b) dimerization of benzoic acid.
 (c) trimerization of benzoic acid.
 (d) solvation of benzoic acid.
71. A 0.5 molal solution of ethylene glycol in water is used as coolant in a car. If the freezing point constant of water be $1.86^\circ C$ per mole, the mixture shall freeze at
 (a) $0.93^\circ C$ (b) $-0.93^\circ C$ (c) $1.86^\circ C$ (d) $-1.86^\circ C$
72. The rise in the boiling point of a solution containing 1.8 g of glucose in 100 g of solvent is $0.1^\circ C$. The molal elevation constant of the liquid is
 (a) 0.01 K/m (b) 0.1 K/m (c) 1 K/m (d) 10 K/m
73. The solutions which have same osmotic concentrations are known as
 (a) Normal (b) Isotonic
 (c) Hypotonic (d) Hypertonic
74. The normal boiling point of the solution is the temperature at which the vapour pressure of the solution is –
 (a) equal to 1 torr (b) equal to 76 mm Hg
 (c) equal to 2.0 atm (d) equal to 1 atm

75. The temperature at which 10% aqueous solution (w/v) of glucose will exhibit the osmotic pressure of 14 bar is –
 (a) 307.3°C (b) 307.3 K (c) 34 K (d) –34°C
76. 4 gm castic soda is dissolved in 100 cc of solution. The normality of solution is
 (a) 0 (b) 0.5 (c) 1 (d) 1.5
77. If A contains 2% NaCl and is separated by a semipermeable membrane from B which contains 10% NaCl, then which event will occur?
 (a) NaCl will flow from A to B
 (b) NaCl will flow from B to A
 (c) Water will flow from A to B
 (d) Water will flow from B to A
78. KBr is 80% ionized in solution. The freezing point of 0.4 molal solution of KBr is :

$$K_f(\text{H}_2\text{O}) = 1.86 \frac{\text{K kg}}{\text{mole}}$$

 (a) 274.339 K (b) –1.339 K
 (c) 257.3 K (d) –1.339°C
79. Which of the following pairs of solution are isotonic at the same temperature?
 (a) 0.1 M $\text{Ca}(\text{NO}_3)_2$ and 0.1 M Na_2SO_4
 (b) 0.1 M NaCl and 0.1 M Na_2SO_4
 (c) 0.1 M urea and 0.1 M MgCl_2
 (d) 0.2 M urea and 0.1 M NaCl
80. The relationship between the values of osmotic pressure of 0.1 M solutions of $\text{KNO}_3(P_1)$ and $\text{CH}_3\text{COOH}(P_2)$ is :
 (a) $\frac{P_1}{P_1 + P_2} = \frac{P_2}{P_1 + P_2}$ (b) $P_1 > P_2$
 (c) $P_2 > P_1$ (d) $P_1 = P_2$
81. Which of the following solutions will exhibit highest boiling point?
 (a) 0.01 M Na_2SO_4 (aq) (b) 0.01 M KNO_3 (aq)
 (c) 0.015 M urea (aq) (d) 0.015 M glucose (aq)
82. What is the freezing point of a solution containing 8.1 g HBr in 100 g water assuming the acid to be 90% ionised?
 $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1})$:
 (a) 0.85K (b) –3.53K (c) 0K (d) –0.35K
83. Osmotic pressure of 0.4% urea solution is 1.64 atm and that of 3.42% cane sugar is 2.46 atm. When the above two solutions are mixed, the osmotic pressure of the resulting solution is :
 (a) 0.82 atm (b) 2.46 atm
 (c) 1.64 atm (d) 4.10 atm
84. The freezing point of 1% solution of lead nitrate in water will be :
 (a) 2°C (b) 1°C (c) 0°C (d) below 0°C
85. A solution of urea (mol. mass 56 g mol^{-1}) boils at 100.18°C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol^{-1} respectively, the above solution will freeze at
 (a) 0.654°C (b) –0.654°C
 (c) 6.54°C (d) –6.54°C
86. If $\frac{N}{10}$ 50 ml H_2SO_4 , $\frac{N}{3}$ 30 ml HNO_3 , $\frac{N}{2}$ 10 ml HCl is mixed and solution is made to 1L. Then normality of resultant solution is
 (a) $\frac{N}{20}$ (b) $\frac{N}{40}$ (c) $\frac{N}{50}$ (d) N
87. The molal elevation constant for water is 0.52. What will be the boiling point of 2 molar sucrose solution at 1 atm. pressure? (Assume B.P. of pure water as 100°C)
 (a) 101.04°C (b) 100.26°C
 (c) 100.52°C (d) 99.74°C
88. A 0.0020 m aqueous solution of an ionic compound $\text{Co}(\text{NH}_3)_5(\text{NO}_2)\text{Cl}$ freezes at –0.00732 °C. Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be ($K_f = -1.86^\circ\text{C/m}$)
 (a) 3 (b) 4 (c) 1 (d) 2
89. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase?
 (a) Addition of NaCl
 (b) Addition of Na_2SO_4
 (c) Addition of 1.00 molal KI
 (d) Addition of water
90. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be (K_f for water = 1.86 K kg mol^{-1}).
 (a) –0.372°C (b) –0.520°C
 (c) +0.372°C (d) –0.570°C
91. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of sodium ions, Na^+ and carbonate ions, CO_3^{2-} are respectively (Molar mass of $\text{Na}_2\text{CO}_3 = 106 \text{ g mol}^{-1}$)
 (a) 0.955 M and 1.910 M (b) 1.910 M and 0.955 M
 (c) 1.90 M and 1.910 M (d) 0.477 M and 0.477 M
92. The freezing point depression constant for water is –1.86°C m^{-1} . If 5.00 g Na_2SO_4 is dissolved in 45.0 g H_2O , the freezing point is changed by –3.82°C. Calculate the van't Hoff factor for Na_2SO_4
 (a) 2.05 (b) 2.62 (c) 3.11 (d) 0.381
93. The van't Hoff factor i for a compound which undergoes dissociation in one solvent and association in other solvent is respectively :
 (a) less than one and greater than one.
 (b) less than one and less than one.
 (c) greater than one and less than one.
 (d) greater than one and greater than one.
94. Mole fraction of the solute in a 1.00 molal aqueous solution is
 (a) 0.1770 (b) 0.0177 (c) 0.0344 (d) 1.7700
95. A 0.1 molal aqueous solution of a weak acid is 30% ionized. If K_f for water is 1.86°C/m, the freezing point of the solution will be :
 (a) –0.18°C (b) –0.54°C (c) –0.36°C (d) –0.24°C
96. 200 mL of an aqueous solution of a protein contains its 1.26 g. The osmotic pressure of this solution at 300 K is found to be 2.57×10^{-3} bar. The molar mass of protein will be ($R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$)
 (a) 51022 g mol^{-1} (b) 122044 g mol^{-1}
 (c) 31011 g mol^{-1} (d) 61038 g mol^{-1}
97. P_A and P_B are the vapour pressure of pure liquid components, A and B, respectively of an ideal binary solution. If X_A represents the mole fraction of component A, the total pressure of the solution will be.
 (a) $P_A + X_A(P_B - P_A)$ (b) $P_A + X_A(P_A - P_B)$
 (c) $P_B + X_A(P_B - P_A)$ (d) $P_B + X_A(P_A - P_B)$

98. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm Hg at 300 K. The vapour pressure of propyl alcohol is 200 mm Hg. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm Hg) at the same temperature will be
(a) 360 (b) 350 (c) 300 (d) 700
99. A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution?
(a) The solution is non-ideal, showing – ve deviation from Raoult's Law.
(b) The solution is non-ideal, showing + ve deviation from Raoult's Law.
(c) *n*-heptane shows + ve deviation while ethanol shows – ve deviation from Raoult's Law.
(d) The solution formed is an ideal solution.
100. The molarity of a solution obtained by mixing 750 mL of 0.5(M) HCl with 250 mL of 2(M) HCl will be:
(a) 0.875 M (b) 1.00 M (c) 1.75 M (d) 0.975 M

EXERCISE - 2

Applied Questions

1. π_1, π_2, π_3 and π_4 atm are the osmotic pressures of 5% (mass/volume) solutions of urea, fructose, sucrose and KCl respectively at certain temperature. The correct order of their magnitudes is :
(a) $\pi_1 > \pi_4 > \pi_2 > \pi_3$ (b) $\pi_1 < \pi_4 < \pi_2 < \pi_3$
(c) $\pi_4 > \pi_1 > \pi_2 > \pi_3$ (d) $\pi_4 > \pi_1 > \pi_3 > \pi_2$
2. The osmotic pressure (at 27° C) of an aqueous solution (200mL) containing 6 g of a protein is 2×10^{-3} atm. If $R = 0.080 \text{ L atm mol}^{-1} \text{K}^{-1}$, the molecular weight of protein is
(a) 7.2×10^5 (b) 3.6×10^5
(c) 1.8×10^5 (d) 1.0×10^5
3. The freezing point of equimolal aqueous solutions will be highest for :
(a) $\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$ (aniline hydrochloride)
(b) $\text{Ca}(\text{NO}_3)_2$
(c) $\text{La}(\text{NO}_3)_3$
(d) $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose)
4. Which of the following has been arranged in the increasing order of freezing point?
(a) $0.025\text{M KNO}_3 < 0.1\text{M NH}_2\text{CSNH}_2 < 0.05\text{M BaCl}_2 < 0.1\text{M NaCl}$
(b) $0.1\text{M NaCl} < 0.05\text{M BaCl}_2 < 0.1\text{M NH}_2\text{CSNH}_2 < 0.025\text{M KNO}_3$
(c) $0.1\text{M NH}_2\text{CSNH}_2 < 0.1\text{M NaCl} < 0.05\text{M BaCl}_2 < 0.025\text{M KNO}_3$
(d) $0.025\text{M KNO}_3 < 0.05\text{M BaCl}_2 < 0.1\text{M NaCl} < 0.1\text{M NH}_2\text{CSNH}_2$
5. The volume of 4 N HCl and 10 N HCl required to make 1 litre of 6 N HCl are
(a) 0.75 litre of 10 N HCl and 0.25 litre of 4 N HCl
(b) 0.50 litre of 4 N HCl and 0.50 litre of 10 N HCl
(c) 0.67 litre of 4 N HCl and 0.33 litre of 10 N HCl
(d) 0.80 litre of 4 N HCl and 0.20 litre of 10 N HCl
6. A solution of $\text{Al}_2(\text{SO}_4)_3$ {d=1.253 gm / ml} contain 22% salt by weight. The molarity, normality and molality of the solution is
(a) 0.805 M, 4.83 N, 0.825 m
(b) 0.825 M, 48.3 N, 0.805 m
(c) 4.83 M, 4.83 N, 4.83 m
(d) None of these
7. The mole fraction of water in 20% aqueous solution (By weight) of H_2O_2 is
(a) $\frac{77}{68}$ (b) $\frac{68}{77}$ (c) $\frac{20}{80}$ (d) $\frac{80}{20}$
8. Molarity of H_2SO_4 is 18 M. Its density is 1.8 g/ml. Hence molality is
(a) 36 (b) 200 (c) 500 (d) 18
9. The solution containing 4.0 gm of a polyvinyl chloride polymer in 1 litre of dioxane was found to have an osmotic pressure 6.0×10^{-4} atmosphere at 300K, the value of R used is 0.082 litre atmosphere mole $^{-1}$ K $^{-1}$. The molecular mass of the polymer was found to be
(a) 3.0×10^2 (b) 1.6×10^5 (c) 5.6×10^4 (d) 6.4×10^2
10. At temperature 327°C and concentration C osmotic pressure of a solution is P, the same solution at concentration C/2 and at temperature 427°C shows osmotic pressure of 2 atm, value of P will be
(a) $\frac{12}{7}$ (b) $\frac{24}{7}$ (c) $\frac{6}{5}$ (d) $\frac{5}{6}$
11. In countries nearer to polar region, the roads are sprinkled with CaCl_2 . This is
(a) to minimise the snow fall
(b) to minimise pollution
(c) to minimise the accumulation of dust on the road
(d) to minimise the wear and tear of the roads
12. If α is the degree of dissociation of Na_2SO_4 , the Vant Hoff's factor (*i*) used for calculating the molecular mass is
(a) $1 + \alpha$ (b) $1 - \alpha$ (c) $1 + 2\alpha$ (d) $1 - 2\alpha$
13. The correct relationship between the boiling points of very dilute solutions of AlCl_3 (t_1) and CaCl_2 (t_2), having the same molar concentration is
(a) $t_1 = t_2$ (b) $t_1 > t_2$ (c) $t_2 > t_1$ (d) $t_2 \geq t_1$
14. If the various terms in the given below expressions have usual meanings, the van't Hoff factor (*i*) cannot be calculated by which one of the following expressions
(a) $\pi V = \sqrt{i} n R T$
(b) $\Delta T_f = i K_f \cdot m$
(c) $\Delta T_b = i K_b \cdot m$
(d) $\frac{P_{\text{solvent}}^\circ - P_{\text{solution}}}{P_{\text{solvent}}^\circ} = i \left(\frac{n}{N + n} \right)$

15. A 0.001 molal solution of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_4]$ in water had a freezing point depression of 0.0054°C . If K_f for water is 1.80, the correct formulation for the above molecule is
 (a) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_3]\text{Cl}$ (b) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$
 (c) $[\text{Pt}(\text{NH}_3)_4\text{Cl}]\text{Cl}_3$ (d) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_4]$
16. The amount of urea to be dissolved in 500 c.c. of water ($K_f = 1.86^\circ\text{C mol}^{-1}$) to produce a depression of 0.186°C in the freezing point is :
 (a) 9 g (b) 6 g (c) 3 g (d) 0.3 g
17. Which has the minimum freezing point ?
 (a) One molal NaCl aq. solution
 (b) One molal CaCl_2 aq. solution
 (c) One molal KCl aq. solution
 (d) One molal urea aq. solution
18. On mixing 3 g of non-volatile solute in 200 mL of water, its boiling point (100°) becomes 100.52°C . If K_b for water is 0.6°C/m then molecular wt. of solute is :
 (a) 10.5 g mol^{-1} (b) 12.6 g mol^{-1}
 (c) 15.7 g mol^{-1} (d) 17.3 g mol^{-1}
19. 1 mol each of the following compounds is dissolved in 1 L of solution. Which will have the largest ΔT_b value?
 (a) HF (b) HCl (c) HBr (d) HI.
20. Equal masses of methane and oxygen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by oxygen is
 (a) $1/2$ (b) $2/3$ (c) $\frac{1}{3} \times \frac{273}{298}$ (d) $1/3$.
21. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3} , molar mass of the substance will be
 (a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}
 (c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1} .
22. At 80°C , the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg)
 (a) 52 mol percent (b) 34 mol percent
 (c) 48 mol percent (d) 50 mol percent
23. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is added to 178.2 g of water at 20°C , the vapour pressure of the resulting solution will be
 (a) 17.325 mm Hg (b) 15.750 mm Hg
 (c) 16.500 mm Hg (d) 17.500 mm Hg
24. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively:
 (a) 300 and 400 (b) 400 and 600
 (c) 500 and 600 (d) 200 and 300
25. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1})
 (a) 72.0 kPa (b) 36.1 kPa (c) 96.2 kPa (d) 144.5 kPa
26. A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g/mol is :
 (a) 171.2 (b) 68.4 (c) 34.2 (d) 136.2
27. K_f for water is $1.86^\circ\text{C kg mol}^{-1}$. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) must you add to get the freezing point of the solution lowered to -2.8°C ?
 (a) 72 g (b) 93 g (c) 39 g (d) 27 g
28. When 20 g of naphthoic acid ($\text{C}_{11}\text{H}_8\text{O}_2$) is dissolved in 50 g of benzene ($K_f = 1.72^\circ\text{C kg mol}^{-1}$), a freezing point depression of 2 K is observed. The Van't Hoff factor (i) is
 (a) 0.5 (b) 1 (c) 2 (d) 3
29. The Henry's law constant for the solubility of N_2 gas in water at 298 K is $1.0 \times 10^5 \text{ atm}$. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is
 (a) 4.0×10^{-4} (b) 4.0×10^{-5}
 (c) 5.0×10^{-4} (d) 4.0×10^{-6}
30. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL . The molarity of the solution is
 (a) 1.78 M (b) 2.00 M (c) 2.05 M (d) 2.22 M
31. The freezing point (in $^\circ\text{C}$) of a solution containing 0.1 g of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Mol. wt. 329) in 100 g of water ($K_f = 1.86^\circ\text{C kg mol}^{-1}$) is
 (a) -2.3×10^{-2} (b) -5.7×10^{-2}
 (c) -5.7×10^{-3} (d) -1.2×10^{-2}
32. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C . Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76^\circ\text{C kg mol}^{-1}$)
 (a) 724 (b) 740 (c) 736 (d) 718
33. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is ($K_f = 1.86^\circ\text{C kg mol}^{-1}$)
 (a) 0.372 K (b) 0.0558 K
 (c) 0.0744 K (d) 0.0186 K
34. Which observation(s) reflect(s) colligative properties?
 (i) a 0.5 m NaBr solution has a higher vapour pressure than a 0.5 m BaCl_2 solution at the same temperature
 (ii) pure water freezes at the higher temperature than pure methanol
 (iii) a 0.1 m NaOH solution freezes at a lower temperature than pure water

Choose the correct answer from the codes given below

- (a) (i), (ii) and (iii) (b) (i) and (ii)
 (c) (ii) and (iii) (d) (i) and (iii)

35. When a gas is bubbled through water at 298 K, a very dilute solution of the gas is obtained. Henry's law constant for the gas at 298 K is 100 kbar. If the gas exerts a partial pressure of 1 bar, the number of millimoles of the gas dissolved in one litre of water is
 (a) 0.555 (b) 5.55
 (c) 0.0555 (d) 55.5
36. 1.5 g of a non-volatile, non-electrolyte is dissolved in 50 g benzene ($K_b = 2.5 \text{ K kg mol}^{-1}$). The elevation of the boiling point of the solution is 0.75 K. The molecular weight of the solute in g mol^{-1} is
 (a) 200 (b) 50
 (c) 75 (d) 100
37. Which one of the following statements is false?
 (a) Raoult's law states that the vapour pressure of a component over a binary solution of volatile liquids is directly proportional to its mole fraction
 (b) Two sucrose solutions of the same molality prepared in different solvents will have the same depression of freezing point
 (c) The correct order of osmotic pressures of 0.01 M solution of each compound is $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{glucose}$
 (d) In the equation osmotic pressure $\pi = MRT$, M is the molarity of the solution
38. At 300 K the vapour pressure of an ideal solution containing 1 mole of liquid A and 2 moles of liquid B is 500 mm of Hg. The vapour pressure of the solution increases by 25 mm of Hg, if one more mole of B is added to the above ideal solution at 300 K. Then the vapour pressure of A in its pure state is
 (a) 300 mm of Hg (b) 400 mm of Hg
 (c) 500 mm of Hg (d) 600 mm of Hg
39. Henry's law constant of oxygen is $1.4 \times 10^{-3} \text{ mol. lit}^{-1} \cdot \text{atm}^{-1}$ at 298 K. How much of oxygen is dissolved in 100 ml at 298 K when the partial pressure of oxygen is 0.5 atm?
 (a) 1.4 g (b) 3.2 g
 (c) 22.4 mg (d) 2.24 mg
40. 1 g of a non-volatile, non-electrolyte solute of molar mass 250 g/mol was dissolved in 51.2 g of benzene. If the freezing point depression constant K_f of benzene is $5.12 \text{ kg K mol}^{-1}$. The freezing point of benzene is lowered by
 (a) 0.3 K (b) 0.5 K
 (c) 0.2 K (d) 0.4 K
41. Negative deviation from Raoult's law is observed in which one of the following binary liquid mixtures?
 (a) Ethanol and acetone
 (b) Benzene and toluene
 (c) Acetone and chloroform
 (d) Chloroethane and bromoethane
42. The system that forms maximum boiling azeotrope is
 (a) carbondisulphide – acetone
 (b) benzene – toluene
 (c) acetone – chloroform
 (d) *n*-hexane – *n*-heptane
43. Which one of the following gases has the lowest value of Henry's law constant?
 (a) N_2 (b) He
 (c) H_2 (d) CO_2
44. A solution is prepared by dissolving 10 g NaOH in 1250 mL of a solvent of density 0.8 mL/g. The molality of the solution in mol kg^{-1} is
 (a) 0.25 (b) 0.2
 (c) 0.008 (d) 0.0064
45. The freezing point of equimolal aqueous solution will be highest for
 (a) $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$ (b) $\text{Ca}(\text{NO}_3)_2$
 (c) $\text{La}(\text{NO}_3)_2$ (d) $\text{C}_6\text{H}_{12}\text{O}_6$

DIRECTIONS for Qs. 46 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
46. **Statement-1** : If one component of a solution obeys Raoult's law over a certain range of composition, the other component will not obey Henry's law in that range.
Statement-2 : Raoult's law is a special case of Henry's law.
47. **Statement-1** : Lowering of vapour pressure is directly proportional to osmotic pressure of the solution.
Statement-2 : Osmotic pressure is a colligative property.
48. **Statement-1** : If a liquid solute more volatile than the solvent is added to the solvent, the vapour pressure of the solution may increase i.e., $p_s > p^0$.
Statement-2 : In the presence of a more volatile liquid solute, only the solute will form the vapours and solvent will not.
49. **Statement-1** : Azeotropic mixtures are formed only by non-ideal solutions and they may have boiling points either greater than both the components or less than both the components.
Statement-2 : The composition of the vapour phase is same as that of the liquid phase of an azeotropic mixture.
50. **Statement-1** : Camphor is used as solvent in the determination of molecular masses of naphthalene, anthracene etc.
Statement-2 : Camphor has high molal elevation constant.

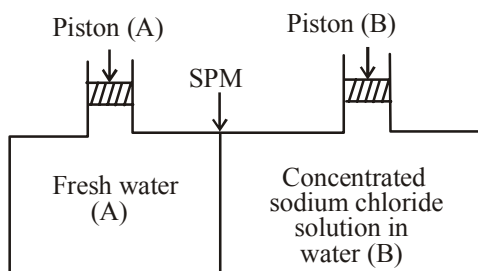
EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Which of the following units is useful in relating concentration of solution with its vapour pressure?
(a) Mole fraction (b) Parts per million
(c) Mass percentage (d) Molality
- On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?
(a) Sugar crystals in cold water
(b) Sugar crystals in hot water
(c) Powdered sugar in cold water
(d) Powdered sugar in hot water
- At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is
(a) less than the rate of crystallisation
(b) greater than the rate of crystallisation
(c) equal to the rate of crystallisation
(d) zero
- A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is
(a) saturated (b) supersaturated
(c) unsaturated (d) concentrated
- Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depends upon
(a) temperature (b) nature of solute
(c) pressure (d) nature of solvent
- Low concentration of oxygen in the blood and tissues of people living at high altitude is due to
(a) low temperature
(b) low atmospheric pressure
(c) high atmospheric pressure
(d) both low temperature and high atmospheric pressure
- Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?
(a) Methanol and acetone
(b) Chloroform and acetone
(c) Nitric acid and water
(d) Phenol and aniline
- Colligative properties depend on
(a) the nature of the solute particles dissolved in solution
(b) the number of solute particles in solution
(c) the physical properties of the solution particles dissolved in solution
(d) the nature of solvent particles
- Which of the following aqueous solutions should have the highest boiling point?
(a) 1.0 M NaOH (b) 1.0 M Na₂SO₄
(c) 1.0 M NH₄NO₃ (d) 1.0 M KNO₃
- The unit of ebullioscopic constant is
(a) K kg mol⁻¹ or K (molality)⁻¹
(b) mol kg K⁻¹ or K⁻¹ (molality)
(c) kg mol⁻¹ K⁻¹ or K⁻¹ (molality)⁻¹
(d) K mol kg⁻¹ or K (molality)
- In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M MgCl₂ solution is
(a) the same (b) about twice
(c) about three time (d) about six times
- An unripe mango placed in a concentrated salt solution to prepare pickle shrivels because
(a) it gains water due to osmosis
(b) it loses water due to reverse osmosis
(c) it gains water due to reverse osmosis
(d) it loses water due to osmosis
- At a given temperature, osmotic pressure of a concentrated solution of a substance
(a) is higher than that of a dilute solution
(b) is lower than that of a dilute solution
(c) it gains water due to reverse osmosis
(d) it loses water due to osmosis
- Which of the following statements is false?
(a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.
(b) The osmotic pressure of a solution is given by the equation $\pi = CRT$ (where, C is the molarity of the solution)
(c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is
 $BaCl_2 > KCl > CH_3COOH > \text{sucrose}$
(d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution
- The value of van't Hoff factors for KCl, NaCl and K₂SO₄ respectively are
(a) 2, 2 and 2 (b) 2, 2 and 3
(c) 1, 1 and 2 (d) 1, 1 and 1
- Which of the following statement is false?
(a) Units of atmospheric pressure and osmotic pressure are same
(b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration
(c) The value of molal depression constant depends on nature of solvent
(d) Relative lowering of vapour pressure, is a dimensionless quantity

17. Value of Henry's constant K_H
 (a) increases with increase in temperature
 (b) decreases with increase in temperature
 (c) remains constant
 (d) first increases then decreases
18. The value of Henry's constant, K_H is
 (a) greater for gases with higher solubility
 (b) greater for gases with lower solubility
 (c) constant for all gases
 (d) not related to the solubility of gases
19. Consider the figure and mark the correct option.

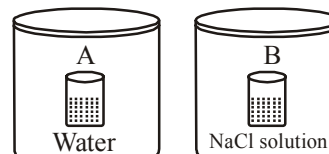


- (a) Water will move from side (A) to side (B) if a pressure lower than osmotic pressure is applied on piston (B)
 (b) Water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B)
 (c) Water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B)
 (d) Water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A)
20. We have three, aqueous solutions of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solutions will be in the order
 (a) $i_A < i_B < i_C$ (b) $i_A > i_B > i_C$
 (c) $i_A = i_B = i_C$ (d) $i_A < i_B > i_C$
21. On the basis of information given below mark the correct option.

Information

- (i) In bromoethane and chloroethane mixture intermolecular interactions of A — A and B — B type are nearly same as A — B type interactions.
 (ii) In ethanol and acetone mixture A — A or B — B type intermolecular interactions are stronger than A — B type interactions.
 (iii) In chloroform and acetone mixture A — A or B — B type intermolecular interactions are weaker than A — B type interactions.
- (a) Solution (ii) and (iii) will follow Raoult's law
 (b) Solution (i) will follow Raoult's law
 (c) Solution (ii) will show negative deviation from Raoult's law
 (d) Solution (iii) will show positive deviation from Raoult's law

22. Two beakers of capacity 500 mL were taken. One of these beakers labelled as "A" was filled with 400 mL water whereas the beaker labelled "B" was filled with 400 mL of 2M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in figure.



At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution?

- (a) Vapour pressure in container (A) is more than that in container (B)
 (b) Vapour pressure in container (A) is less than that in container (B)
 (c) Vapour pressure is equal in both the containers
 (d) Vapour pressure in container (B) is twice the vapour pressure in container (A)
23. If two liquids A and B form minimum boiling azeotrope at some specific composition then
 (a) A — B interactions are stronger than those between A — A or B — B
 (b) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution
 (c) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution
 (d) A — B interactions are weaker than those between A — A or B — B
24. 4 L of 0.02 M aqueous solution of NaCl was diluted by adding 1 L of water. The molality of the resultant solution is
 (a) 0.004 (b) 0.008
 (c) 0.012 (d) 0.016
25. On the basis of information given below mark the correct option.

Information On adding acetone to methanol some of the hydrogen bonds between methanol molecules break.

- (a) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show positive deviation from Raoult's law
 (b) At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show positive deviation from Raoult's law
 (c) At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show negative deviation from Raoult's law
 (d) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show negative deviation from Raoult's law

26. K_H value for Ar (g), CO_2 (g), HCHO (g) and CH_4 (g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively.

Arrange these gases in the order of their increasing solubility.

- (a) $\text{HCHO} < \text{CH}_4 < \text{CO}_2 < \text{Ar}$
 (b) $\text{HCHO} < \text{CO}_2 < \text{CH}_4 < \text{Ar}$
 (c) $\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$
 (d) $\text{Ar} < \text{CH}_4 < \text{CO}_2 < \text{HCHO}$

NEET/AIPMT (2013-2017) Questions

27. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0M HNO_3 ? The concentrated acid is 70% HNO_3 [2013]
 (a) 90.0 g conc. HNO_3
 (b) 70.0 g conc. HNO_3
 (c) 54.0 g conc. HNO_3
 (d) 45.0 g conc. HNO_3
28. Which condition is not satisfied by an ideal solution? [NEET Kar. 2013]
 (a) $\Delta_{\text{mix}} H = 0$
 (b) $\Delta_{\text{mix}} V = 0$
 (c) $\Delta_{\text{mix}} S = 0$
 (d) Obedience to Raoult's Law
29. Of the following 0.10 m aqueous solutions, which one will exhibit the largest freezing point depression? [2014]
 (a) KCl (b) $\text{C}_6\text{H}_{12}\text{O}_6$
 (c) $\text{Al}_2(\text{SO}_4)_3$ (d) K_2SO_4
30. Which one of the following electrolytes has the same value of van't Hoff's factor (i) as that of the $\text{Al}_2(\text{SO}_4)_3$ (if all are 100% ionised)? [2015]
 (a) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (b) $\text{Al}(\text{NO}_3)_3$
 (c) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (d) K_2SO_4
31. The boiling point of 0.2 mol kg^{-1} solution of X in water is greater than equimolal solution of Y in water. Which one of the following statements is true in this case? [2015]
 (a) Molecular mass of X is greater than the molecular mass of Y.
 (b) Molecular mass of X is less than the molecular mass of Y.
 (c) Y is undergoing dissociation in water while X undergoes no change.
 (d) X is undergoing dissociation in water.
32. Which one is not equal to zero for an ideal solution: [2015]
 (a) ΔS_{mix} (b) ΔV_{mix}
 (c) $\Delta P = P_{\text{observed}} - P_{\text{Raoult}}$ (d) ΔH_{mix}
33. What is the mole fraction of the solute in a 1.00 m aqueous solution? [2015 RS]
 (a) 0.177 (b) 1.770
 (c) 0.0354 (d) 0.0177
34. At 100°C the vapour pressure of a solution of 6.5g of a solute in 100 g water is 732 mm. If $K_b = 0.52$, the boiling point of this solution will be [2016]
 (a) 101°C (b) 100°C
 (c) 102°C (d) 103°C
35. If molality of the dilute solutions is doubled, the value of molal depression constant (K_f) will be:- [2017]
 (a) halved (b) tripled
 (c) unchanged (d) doubled
36. Which of the following is dependent on temperature? [2017]
 (a) Molarity (b) Mole fraction
 (c) Weight percentage (d) Molality
37. Which of the following statement about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C. (Given : Vapour Pressure Data at 25°C, benzene = 12.8 kPa, toluene = 3.85 kPa) [2016]
 (a) The vapour will contain a higher percentage of benzene
 (b) The vapour will contain a higher percentage of toluene
 (c) The vapour will contain equal amounts of benzene and toluene
 (d) Not enough information is given to make a predication

Hints & Solutions

EXERCISE - 1

- (b) Lowering in vapour pressure is the highest for that molecules for which Vont-Hoff factor is maximum because. Now, Von't Hoff factor is maximum for BaCl_2 [As number of ions formed here after dissociation in water is zero], this will have the highest lowering of vapour pressure.
- (b) For an ideal solution, $\Delta H_{\text{mixing}} = 0$
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$ (According to Hess's law)
 i.e., for ideal solutions there is no change in magnitude of the attractive forces in the two components present.

$$3. (a) \Delta T = K_b \cdot \frac{m}{M} \times \frac{1000}{W}$$

$$0.25 = K_b \cdot \frac{1}{M} \times \frac{1000}{W} = K_b \times \frac{1}{60} \times \frac{1000}{W}$$

$$\Delta T = K_b \times \frac{0.3}{180} \times \frac{1000}{W}$$

$$\frac{\Delta T}{0.25} = \frac{3}{180} \times 60 = 1 \Rightarrow \Delta T = 0.25^\circ\text{C}$$

New boiling point of glucose solution = 100.25°C .

- (d)
- (b) The molality involves weights of the solute and the solvent. Since weight does not change with the temperature, therefore molality does not depend upon the temperature.
- (b) Density = 1.17 gm/cc (Given)

$$\text{As } d = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{volume} = 1 \text{ cc} \quad \therefore \text{mass} = d = 1.17 \text{ g}$$

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{Volume in litre}} = \frac{1.17 \times 1000}{36.5 \times 1}$$

$$= \frac{1170}{36.5} = 32.05 \text{ M}$$

$$7. (a) \text{Molarity} = \frac{\text{mole}}{\text{litre}} = \frac{5/40}{250/1000}$$

$$= \frac{5}{40} \times \frac{1000}{250} = 0.5 \text{ M}$$

$$8. (b) \text{Molarity} = \frac{\text{mole}}{\text{litre}} = \frac{37/36.5}{100/1.18 \times 1000}$$

[37 gm HCl in 100 gm of solution]

$$= \frac{100}{1.18} \text{ C.C} = \frac{100}{1.18 \times 1000} \text{ l}$$

$$= \frac{37}{36.5} \times \frac{1.18 \times 1000}{100} = 11.96 \approx 12.$$

- (b) Relation between molality and mole fraction is

$$m = \frac{1000 \times x_2}{x_1 M_1} = \frac{1000 \times .2}{.8 \times 78} = 3.2$$

$$\text{Thus, } X(m) = 3.2$$

$$10. (b) M = \frac{\text{Wt} \times 1000}{\text{M.Wt.} \times V}; \quad M = \frac{7.1 \times 1000}{142 \times 100} = 0.5 \text{ M}$$

$$11. (a) \frac{\Delta p}{p^\circ} = \frac{n_2}{n_1 + n_2} \quad \text{or} \quad \frac{n_2}{n_1 + n_2} = \frac{640 - 630}{640} = \frac{0.0156}{1}$$

or 1 mole i.e., 78g benzene contains solute = 0.0156 mol

$$\therefore \text{Molality of solution} = \frac{0.0156 \times 10^3}{78} = 0.2 \text{ m}$$

$$12. (c) \text{Molarity} = \frac{\text{Number of moles}}{\text{Volume of solution (L)}}$$

$$\text{Moles of water} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{1000}{18} = 55.6$$

$$\text{Molarity} = \frac{55.6}{1} = 55$$

$$13. (c) \pi V = nRT$$

$$\pi = \frac{nRT}{V} = \frac{1.75 \times 0.0821 \times (273 + 17)}{342 \times 150 / 1000}$$

[M.W. of sucrose = 342]

$$= \pi = \frac{1.75}{342} \times \frac{1000}{150} \times 0.0821 \times 290 = 0.8 \text{ atm.}$$

$$14. (b) \because 10 \text{ g glucose is dissolved in} = 100 \text{ ml solution.}$$

$$\therefore 180 \text{ g (g mole) is dissolved in}$$

$$= \frac{100}{10} \times 180 = 1800 \text{ ml} = 1.8 \text{ L}$$

$$15. (d) \text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

$$\therefore \text{ppm} = \frac{10}{10^6} \times 10^6 = 10 \text{ ppm}$$

$$16. (a) \frac{p^\circ - p}{p^\circ} = x_{\text{solute}}$$

$$\text{Given, } p^\circ = 0.8 \text{ atm, } p = 0.6 \text{ atm, } x_{\text{solute}} = ?$$

$$\frac{0.8 - 0.6}{0.8} = x_{\text{solute}} \quad \text{or} \quad \frac{0.2}{0.8} = x_{\text{solute}},$$

$$\text{or } x_{\text{solute}} = 0.25$$

$$17. (c) \Delta T = K_b \frac{m \times 1000}{M W}$$

$$\Rightarrow 0.567 = 5.12 \times \frac{0.44 \times 1000}{M \times 22.2}$$

$$\Rightarrow M = \frac{512 \times 0.44 \times 1000}{0.567 \times 22.2} = 178.9$$

18. (b) $\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume in litres}} = \frac{5}{2.5} = 2 \text{ M}$

19. (a) Mole fraction of any component A in solution

$$x = \frac{\text{No. of moles of A}}{\text{Total No. of moles of solution}}$$

As total no. of moles of solution > No. of moles of A
Thus x can never be equal to one or zero.

20. (d) $\Delta T = k_b \frac{m}{M} \times \frac{1000}{W}$

$$\Rightarrow 1 = 2.53 \times \frac{10}{M} \times \frac{1000}{100}$$

$$\Rightarrow M = \frac{2.53 \times 100}{1} = 253 \text{ g}$$

21. (b) One molal solution means one mole of solute is present in 1 kg (1000 g) solvent
i.e., mole of solute = 1

$$\text{Mole of solvent (H}_2\text{O)} = \frac{1000 \text{ g}}{18 \text{ g}} = \frac{1000}{18}$$

$$\text{Mole fraction of solute} = \frac{1}{\left(1 + \frac{1000}{18}\right)} = \frac{18}{1008} = 0.018.$$

22. (d)

23. (d) $NV = N_1V_1 + N_2V_2 + N_3V_3$

$$\text{or, } 1000N = 1 \times 5 + \frac{1}{2} \times 20 + \frac{1}{3} \times 30 \text{ or } N = \frac{1}{40}.$$

24. (d) $\Delta T = k_f \times \frac{m}{M} \times \frac{1000}{W}$

$$= 1.86 \times \frac{0.1 \times 1000}{1000} = 0.186$$

Since NaCl is 100% ionised so Vant Hoff factor = 2

$$\text{So, } \Delta T' = i \times \Delta T = 2 \times 0.186 = -0.372^\circ\text{C}$$

25. (a) Given vapour pressure of pure solvent (P°) = 121.8 mm Hg; Weight of solute (w) = 15 g
Weight of solvent (W) = 250 g; Vapour pressure of solution (P) = 120.2 mm Hg and Molecular weight of solvent (M) = 78
From Raoult's law

$$= \frac{P^\circ - P}{P^\circ} = \frac{w}{m} \times \frac{M}{W}$$

$$\frac{121.8 - 120.2}{121.8} = \frac{15}{m} \times \frac{78}{250}$$

$$\text{or } m = \frac{15 \times 78}{250} \times \frac{121.8}{1.6} = 356.2$$

26. (b) $\pi = CRT$

$$\frac{600}{760} = \frac{20 \times 1000 \times 0.083 \times (273 + 15)}{M \times 500}$$

$$\left[600 \text{ mm} = \frac{600}{760} \text{ atmosphere} \right]$$

$$\Rightarrow M = \frac{38 \times 20 \times 1000 \times 0.083 \times 288}{30 \times 500}$$

$$= 1211 \approx 1200$$

27. (c) These two components A and B follows the condition of Raoult's law if the force of attraction between A and B is equal to the force of attraction between A and A or B and B.

28. (a) Given $V.P_p = 80 \text{ torr}$

$$V.P_Q = 60 \text{ torr}$$

$$P_{\text{total}} = V \cdot P_p \times x_p + V \cdot P_q \times x_q$$

$$= \left[80 \times \frac{3}{5} + 60 \times \frac{2}{5} \right] = 16 \times 3 + 12 \times 2$$

$$P_{\text{total}} = 48 + 24 = 72 \text{ torr}$$

29. (d) A solution containing A and B components shows negative deviation when A-A and B-B interactions are weaker than that of A-B interactions. For such solutions.

$$\Delta H = -ve \text{ and } \Delta V = -ve$$

30. (b) Chloroform and acetone form a non-ideal solution in which A.....B type of interactions are readily seen due to intensive H-bonding instead of A.....A and B.....B type. Therefore, the solution shows negative deviation from Raoult's law i.e.

$$\Delta V_{\text{mix}} = -ve; \Delta H_{\text{mix}} = -ve$$

$\therefore$ Total volume of solution is less than 80 ml.

31. (c) Here, $\Delta V = 500 - 300 = 200 \text{ cc} = 0.2 \text{ L}$

$$p = 0.6 \text{ atm}$$

$$q = 10 \text{ J}$$

$$W = p \Delta v = (0.2 \times 0.6) = 0.12 \text{ Latm}$$

$$\text{Also, } 1 \text{ Latm} = 101.3 \text{ J}$$

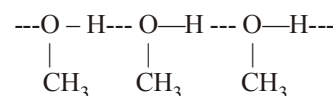
$$\therefore W = 0.12 \times 101.3 = 12.156 \text{ J}$$

But $q = -ve$, when heat is liberated

$$\therefore \Delta E = q + W = -10 + 12.16 = 2.16 \text{ J}$$

32. (b) Positive deviations are shown by such solutions in which solvent-solvent and solute-solute interactions are stronger than the solute-solvent interactions. In such solution, the interactions among molecules becomes weaker. Therefore their escaping tendency increases which results in the increase in their partial vapour pressures.

In pure methanol there exists intermolecular H-bonding.



On adding benzene, its molecules come between ethanol molecules there by breaking H-bonds which weaken intermolecular forces. This results in increase in vapour pressure.

33. (b) Moles of glucose = $\frac{18}{180} = 0.1$

Moles of water = $\frac{178.2}{18} = 9.9$

Total moles = $0.1 + 9.9 = 10$

$P_{H_2O} = \text{Mole fraction} \times \text{Total pressure} = \frac{9.9}{10} \times 760$
 $= 752.4 \text{ Torr}$

34. (d) Antifreeze is a water based liquid coolant used in gasoline and diesel engines. Compounds like methanol, ethanol, glycol, glycerol are added to the water to reduce the freezing point of the mixture below the lowest temperature that the engine is likely to be exposed and to inhibit corrosion in cooling systems which often contain a range of electrochemically incompatible metals. If all the mentioned compounds are available at same price then the compound having lowest molecular weight will be the choice because

$$\Delta T_f = iK_f \frac{w}{M.W.} \times \frac{1000}{w_{\text{solvent}}}$$

So, less quantity of the compound will result in large depression in freezing point of antifreeze solution.

35. (d) $\frac{P^\circ - P}{P^\circ} = \frac{n_2}{n_1 + n_2}$

$$\frac{640 - 600}{640} = \frac{2.5/x}{39/78}$$

$$x = \frac{640 \times 78 \times 2.5}{39 \times 40} = 80$$

36. (c) For ideal solution,

$$\Delta V_{\text{mixing}} = 0 \text{ and } \Delta H_{\text{mixing}} = 0.$$

37. (d) C_2H_5I and C_2H_5OH form non-ideal solution.

38. (d) Gaseous densities of ethanol and dimethyl ether would be same at same temperature and pressure. The heat of vaporisation, V.P. and b.p.ts will differ due to H-bonding in ethanol.

39. (c) The given vapour pressure graph shows that on mixing two components having vapour pressures p_A and p_B in any ratio, the total vapour pressure of the solution, shown by the line CD, does not show any deviation from ideal behaviour. Lines AD and CB are also do not show any deviation from their expected behaviour but these lines show the individual behaviour of components A and B.

40. (d)

41. (a) Molal elevation constant is given by the formula,

$$K_b = \frac{\Delta T_b}{m}, \text{ where } m \text{ is molality and } \Delta T_b \text{ is elevation in}$$

boiling point.

42. (d) Azeotropic mixture is constant boiling mixture, it is not possible to separate the components of azeotropic mixture by boiling.

43. (a) Freezing point of water is, $T = 0^\circ\text{C}$

When 342 g of cane sugar ($C_{12}H_{22}O_{11}$) is dissolved in 1000 g of water, the freezing point of water is depressed by ΔT_f which is given by,

$$\Delta T_f = K_f m = K_f \frac{w_{\text{sol}}}{M.W.} \times \frac{1000}{w_{\text{solvent}}}$$

$$= (1.86^\circ\text{C/mol}) \times \frac{342 \text{ g}}{(342 \text{ g/mol})} \times \frac{1000}{1000}$$

$$= 1.86^\circ\text{C}.$$

So, freezing point of solution

$$= T - \Delta T_f$$

$$= (0 - 1.86)^\circ\text{C}$$

$$= -1.86^\circ\text{C}$$

44. (a) The solutions (liquid mixture) which boils at constant temperature and can distil as such without any change in composition are called azeotropes.

Solution of HNO_3 and H_2O will form maximum boiling point azeotrope. Maximum boiling azeotropes show negative deviation from Raoult's law.

	Composition (%)	Boiling Point
HNO_3	68.0	359 K
H_2O	32.0	373 K

Boiling point of the azeotrope of these two solutions is 393.5 K.

45. (c) According to Raoult's law

$$\frac{p^\circ - p}{p^\circ} = x_B$$

$$\left[\begin{array}{l} x_B = \text{Mole fraction of solute} = \frac{.2}{.2 + .8} = \frac{1}{5} \\ p = 60 \text{ mm of Hg} \end{array} \right]$$

$$\frac{p^\circ - p}{p^\circ} = \frac{1}{5} \text{ or } 4p^\circ = (p) \times 5$$

$$\Rightarrow p^\circ = \frac{60 \times 5}{4} = 75 \text{ mm of Hg}$$

46. (a) When hard boiled egg after shelling is immersed in saturated brine, its size remains same because of the coagulation of inner liquid there is no flow of solvent molecules across the membrane.

47. (b) According to Raoult's law

$$\frac{\Delta p}{p^\circ} = \frac{n}{n + N} \text{ (mole fraction of solute)}$$

$$\frac{10}{p^\circ} = 0.2 \therefore p^\circ = 50 \text{ mm of Hg}$$

For other solution of same solvent

$$\frac{20}{p^\circ} = \frac{n}{n + N} \text{ (Mole fraction of solute)}$$

$$\Rightarrow \frac{20}{50} = \text{Mole fraction of solute}$$

$$\Rightarrow \text{Mole fraction of solute} = 0.4$$

As mole fraction of solute + mole fraction of solvent = 1

Hence, mole fraction of solvent = $1 - 0.4 = 0.6$

48. (a) A solution of acetone in ethanol shows positive deviation from Raoult's law. It is because ethanol molecules are strongly hydrogen bonded. When acetone is added, these molecules break the hydrogen bonds and ethanol becomes more volatile. Therefore its vapour pressure is increased.
49. (a) Liquid mixture having a definite composition and boil like a pure liquid is called an azeotrope.
 $\Rightarrow$ Mixture showing +ive deviation from Raoult's Law forms minimum boiling azeotrope while mixture showing -ive deviation from Raoult's law forms maximum boiling azeotrope.
50. (a) $\Delta T_f = i \times K_f \times m$
 Van't Hoff factor, $i = 2$ for NaCl, $m = 0.01$
 hence $\Delta T_f = 0.02 K_f$ which is maximum in the present case.
 Hence ΔT_f is maximum or freezing point is minimum.
51. (c) We know that

$$\Delta T_f = \frac{100 \times K_f \times w}{m \times W} \therefore m = \frac{100 \times K_f \times w}{\Delta T_f \times W}$$
 Now, K_f = molecular depression constant
 $= 50.2^\circ\text{C per } 100 \text{ gm}$
 $\Delta T_f = 0.502^\circ\text{C}$
 $W = 25 \text{ gm}$

$$m = \frac{100 \times 50.2 \times 0.750}{0.502 \times 25} = 300$$
52. (b) density of ethanol = 0.789 gm/ml.
 wt. of 1000 ml = volume $\times$ density = 789g
 $\therefore$ Molality = $\frac{\text{Mass of } \text{CH}_3\text{COOH}}{\text{Mol. mass of } \text{CH}_3\text{COOH}} \times \frac{1000}{\text{wt. of ethanol}}$

$$= \frac{5}{60} \times \frac{1000}{789} = 0.1056 \text{ mol/g}$$
53. (c) Osmotic pressure is a colligative property.
54. (a) As both the solutions are isotonic hence there is no net movement of the solvent occurs through the semipermeable membrane between two solutions.
55. (a) Total wt. of solution = 800 gm.
 Wt. of solute = $\frac{40}{100} \times 800 = 320 \text{ g}$.
 So, 100 gm solute precipitated
 Remaining total wt. of solute = $320 - 100 \text{ g}$
 $= 220 \text{ g}$
 Remaining total wt. of solution = $800 - 100$
 $= 700 \text{ g}$
 $\therefore$ % composition = $\frac{220}{700} \times 100 = 31.43\%$
56. (a) Concentration of particles in CaCl_2 solution will be maximum as $i = 3$ for CaCl_2 and $i = 2$ for KCl. Glucose and Urea do not dissociate into ions, as they are nonelectrolytes.
57. (a) $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{Al}_2(\text{SO}_4)_3$ both dissociates to give 5 ions or $i = 5$
 $\text{K}_4[\text{Fe}(\text{CN})_6] \rightleftharpoons 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$
 and $\text{Al}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{Al}^{3+} + 3\text{SO}_4^{2-}$
58. (a) Depression in freezing point $\propto$ No. of particles.
 (when concentration of different solutions is equal)
 $\text{Al}_2(\text{SO}_4)_3$ provides five ions on ionisation

$$\text{Al}_2(\text{SO}_4)_3 \longrightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-}$$
 while KCl provides two ions

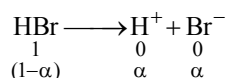
$$\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$$
 $\text{C}_6\text{H}_{12}\text{O}_6$ and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ are not ionised so they have single particle in solution.
 Hence, $\text{Al}_2(\text{SO}_4)_3$ have maximum value of depression in freezing point or lowest freezing point.
59. (a) Molecular masses of polymers are best determined by osmotic pressure method. Firstly because other colligative properties give so low values that they cannot be measured accurately and secondly, osmotic pressure measurements can be made at room temperature and do not require heating which may change the nature of the polymer.
60. (b) Solvent having high cryoscopic constant (camphor) can be used in determination of molecular masses of organic compounds like naphthalene, anthracene etc., by cryoscopic method.
61. (c) $\Delta T_A = K_f m_A$, $\Delta T_B = K_f m_B$
 $\Delta T_A = \Delta T_B$, $m_A = m_B$

$$\frac{\text{Mass of solute A}}{\text{Molecular mass of A}} = \frac{\text{Mass of B}}{\text{Molecular mass of B}}$$

$$\frac{3}{60} = \frac{9}{\text{Molecular mass of B}}$$
 Molecular mass of B = 180.
62. (c) $\Delta T = K_f m = \frac{K_f \times W_2 \times 1000}{M_2 W_1} = 5.12 \times \frac{1}{250} \times \frac{1000}{51.2} = 0.4\text{K}$
63. (b) Total no. of milli equivalents of acids
 $= (100 \times 0.4 + 200 \times 0.2) \text{ meq.}$
 $= 40 + 40 = 80 \text{ meq.}$
 Total volume of mixture = 300
 $\therefore N \times 300 = 80$

$$N = \frac{80}{300} = 0.2670 \text{ N.}$$
64. (c) Colloidal particles exhibit ceaseless chaotic and random motions, such motions of the particles are called Brownian motion.
65. (d) $V_1 = 250\text{ml}$; $N_1 = 0.4\text{N}$
 $V_2 = 1250 \text{ ml}$; $N_2 = ?$
 Applying the law of equivalence :-
 No. of equivalents before dilution = No. of equivalents after dilution
 $\therefore N_1 V_1 = N_2 V_2$
 $(0.25) \times (0.4) = (1.25) \times N_2$
 $N_2 = 0.080 \text{ N.}$

66. (d) $\left(\text{HX} \right)_{1-0.3} \rightleftharpoons \left(\text{H}^+ \right)_{0.3} + \left(\text{X}^- \right)_{0.3}, i = 1.3; \Delta T_f = K_f \times m \times i$
 $\Delta T_f = 1.85 \times 0.2 \times 1.3 = 0.481^\circ\text{C}$
 $\therefore T_f = T_f^\circ - \Delta T_f = 0 - 0.481^\circ\text{C} = -0.481^\circ\text{C}$
67. (c) $\Delta T_b = K_b \times m$
 Elevation in boiling point is a colligative property, which depends upon the no. of particles (concentration of solution). Thus greater the number of particles, greater is the elevation in boiling point and hence greater will be its boiling point.
 $\text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-}$
 Since Na_2SO_4 has maximum number of particles (c) hence has maximum boiling point.
68. (b) Normality = $\frac{\text{No. of equivalents}}{\text{Volume of solution in litre}}$
 $\Rightarrow \text{No. of equivalents} = \text{Normality} \times \text{Volume of solution in litre}$
 $= 0.1 \times 0.1 = 0.01$
 $\Rightarrow \frac{\text{Wt}}{\text{Equivalent wt.}} = 0.01$
 $\Rightarrow \text{wt} = 0.01 \times \frac{\text{Molecular wt.}}{\text{basicity}}$
 $\text{wt.} = 0.01 \times \frac{200}{2} = 1 \text{ gm}$
69. (a) (i) $i = \frac{\text{No. of particles after ionisation}}{\text{No. of particles before ionisation}}$
 (ii) $\Delta T_b = i \times K_b \times m$
 $\text{CuCl}_2 \longrightarrow \text{Cu}^{2+} + 2\text{Cl}^-$
 $\begin{array}{ccc} 1 & 0 & 0 \\ (1-\alpha) & \alpha & 2\alpha \end{array}$
 $i = \frac{1+2\alpha}{1}, i = 1 + 2\alpha$
 Assuming 100% ionization
 So, $i = 1 + 2 = 3$
 $\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16 \quad [m = \frac{13.44}{134.4} = 0.1]$
70. (b) Benzoic acid exists as dimer in benzene.
71. (b) $\Delta T_f = K_f \times m = 1.86 \times 0.5 = 0.93^\circ\text{C}; T_f = -0.93^\circ\text{C}$
72. (c) $K_b = \frac{0.1 \times 180 \times 100}{1.8 \times 1000} = 1 \text{ K/m}$
73. (b) Isotonic solutions are those solutions which have same osmotic concentrations.
 The solution with higher osmotic concentration is called hypertonic and lower is called hypotonic solution.
74. (d) Boiling temperature is a temperature at which vapour pressure is equal to the atmospheric pressure when external pressure is equal to 1 atm.
75. (b) $\pi = \frac{nRT}{V}$ or $T = \frac{\pi V}{nR}$
 10% (w/v) aqueous solution of glucose means 10 g glucose is present in 100 mL of H_2O
 $= \frac{14 \times 100 \times 10^{-3} \times 180}{0.082 \times 10} = 307.3 \text{ K}$
76. (c) Normality
 $= \frac{\text{Mass}}{\text{Equivalent mass}} \times \frac{1000}{\text{Volume of solution}}$
 $= \frac{4}{40} \times \frac{1000}{100} = 1$
77. (c) Solvent molecules flow from low concentration solution to high concentration solution.
78. (d) $\Delta T_f = i K_f m$
 $\text{KBr} \longrightarrow \text{K}^+ + \text{Br}^-$
 $\begin{array}{ccc} 1 & 0 & 0 \\ (1-\alpha) & \alpha & \alpha \end{array}$
 $i = 1 + \alpha$
 Here $\alpha = 0.8$ (80% ionization)
 $i = 1.8$
 $\Delta T_f = (1.8)(1.86)(0.4) = 1.339$
 $T_f = -1.339^\circ\text{C}$
79. (a) The solution which provide same number of ions are isotonic.
 $\text{Ca}(\text{NO}_3)_2 \longrightarrow \text{Ca}^{2+} + 2\text{NO}_3^-$
 Total ions produced = 3
 $\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$
 Total ions produced = 3
 $\therefore 0.1 \text{ M Ca}(\text{NO}_3)_2$ and $0.1 \text{ M Na}_2\text{SO}_4$ are isotonic.
80. (b) KNO_3 is a strong electrolyte which dissociates into two ions. Therefore, its van't Hoff factor is 2. Acetic acid (CH_3COOH) is a weak electrolyte, it does not dissociate completely. So, its van't Hoff factor is less than that of KNO_3
 $\therefore$ Osmotic pressure of $0.1 \text{ M KNO}_3 >$
 Osmotic pressure of $0.1 \text{ M CH}_3\text{COOH}$
 or $P_1 > P_2$
81. (a) For highest boiling point of a solution, the ΔT_b should be highest, Since, ΔT_b is directly proportional to the molality of solution.
 $\Delta T_b \propto m$
 Of the given solutions urea and glucose remain unionized and remain as one particle in solution. In case of Na_2SO_4 (a strong electrolyte) there are three particles for each molecule (2 Na^+ and one SO_4^{2-}) whereas for KNO_3 (strong electrolyte) there are 2 particles (one K^+ and one NO_3^-). Thus for equimolar solutions of these two, the number of particles is more in Na_2SO_4 (aq) and so is molality. Thus it will exhibit highest boiling point.
82. (b) Given mass of solute = 8.1 g
 Mass of solvent = 100 g
 For HBr



$$\alpha = 90\% = 0.9$$

$$i = 1 + \alpha = 1 + 0.9 = 1.9$$

$$\Delta T_f = K_f \times m \times i$$

$$= 1.86 \times \frac{\text{moles of solute}}{\text{mass of solvent in kg}} \times 1.9$$

$$= 1.86 \times \frac{8.1/81}{100/1000} \times 1.9$$

$$= 1.86 \times 1 \times 1.9 = 3.534 \text{ K}$$

$$T_f = T_f^\circ - \Delta T_f$$

$$\text{or } T_f = 0 - 3.534 \text{ K}$$

$$\therefore T_f = -3.534 \text{ K}$$

83. (d) Osmotic pressure is a colligative property. Hence resulting osmotic pressure of the solution is given by

$$\pi_T = \pi_1 + \pi_2 + \pi_3 \dots \dots \dots$$

$$\pi_T = 1.64 + 2.46 = 4.10 \text{ atm.}$$

84. (d) Addition of solute to water decreases the freezing point of water (pure solvent).

$\therefore$ When 1% lead nitrate (solute) is added to water, the freezing point of water will be below 0°C .

85. (b) As $\Delta T_f = K_f \cdot m$

$$\Delta T_b = K_b \cdot m$$

$$\text{Hence, we have } m = \frac{\Delta T_f}{K_f} = \frac{\Delta T_b}{K_b}$$

$$\text{or } \Delta T_f = \Delta T_b \frac{K_f}{K_b}$$

$$\Rightarrow [\Delta T_b = 100.18 - 100 = 0.18^\circ\text{C}]$$

$$= 0.18 \times \frac{1.86}{0.512} = 0.654^\circ\text{C}$$

As the Freezing Point of pure water is 0°C ,

$$\Delta T_f = 0 - T_f$$

$$0.654 = 0 - T_f$$

$$\therefore T_f = -0.654$$

Thus the freezing point of solution will be -0.654°C .

86. (c) Applying the law of equivalence,

$$N_1V_1 + N_2V_2 + N_3V_3 = N_RV_R$$

$$\frac{N}{10} \times 50 + \frac{N}{3} \times 30 + \frac{N}{2} \times 10 = N_R \times 1000$$

$$5N + 10N + 5N = 1000 \times N_R$$

$$\Rightarrow N_R = \frac{N}{50}$$

87. (a) Given : $K_b = 0.52$, molarity = 2m

Here, molality = molarity = 2 molal

Now, using $\Delta T_b = K_b \times m$, we get

$$\Delta T_b = 0.52 \times 2 = 1.04^\circ\text{C}$$

Now, ΔT_b

$$= \text{Boiling pt. of solution} - \text{Boiling pt. of solvent (pure water)}$$

$\Rightarrow$ Boiling pt. of solution (2M sucrose solution)

$$= \Delta T_b + \text{Boiling pt. of pure water}$$

$$= 1.04^\circ\text{C} + 100^\circ\text{C} = 101.04^\circ\text{C}$$

88. (d) $\Delta T_f = 0 - (0.00732^\circ\text{C}) = 0.00732$

$$\Delta T_f = i \times K_f \times m$$

$$i = \frac{\Delta T_f}{K_f \times m} = \frac{0.00732}{1.86 \times 0.002} = 1.97 \approx 2$$

89. (d) When the aqueous solution of one molal KI is diluted with water, concentration decreases, therefore the vapour pressure of the resulting solution increases.

$$90. (a) \Delta T_f = K_f \frac{1000W_2}{M_2W_1} = \frac{1.86 \times 1000 \times 68.5}{342 \times 1000} = 0.372$$

$$T_f = T_f^\circ - \Delta T_f$$

$$T_f = -0.372^\circ\text{C}$$

91. (b) Concentration of $\text{Na}_2\text{CO}_3 = \frac{25.3}{106} \times \frac{1000}{250} = 0.955 \text{ M}$

$$[\text{Na}^+] = 2 \times 0.955 = 1.91 \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.955 \text{ M}$$

92. (b) Given $K_f = -1.86^\circ\text{C m}^{-1}$, mass of solute = 5.00 g, mass of solvent = 45.0 g and $\Delta T_f = -3.82^\circ\text{C}$

$$\Delta T_f = i \times K_f \cdot m$$

$$3.82 = i \times 1.86 \times \frac{5 \times 1000}{142 \times 45}$$

$$\therefore i = 2.62 \text{ (Molecular mass of } \text{Na}_2\text{SO}_4 = 142 \text{ g)}$$

93. (c) If compound dissociates in solvent $i > 1$ and on association $i < 1$.

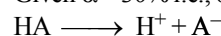
94. (b) 1 molal solution means 1 mole of solute dissolved in 1000 gm solvent.

$$\therefore n_{\text{solute}} = 1 \quad w_{\text{solvent}} = 1000 \text{ gm}$$

$$\therefore n_{\text{solvent}} = \frac{1000}{18} = 55.56$$

$$x_{\text{solute}} = \frac{1}{1 + 55.56} = 0.0177$$

95. (d) Given $\alpha = 30\%$ i.e., 0.3



$$\begin{array}{ccc} 1 - \alpha & \alpha & \alpha \\ 1 - 0.3 & 0.3 & 0.3 \end{array}$$

$$i = 1 - 0.3 + 0.3 + 0.3$$

$$i = 1.3$$

$$\Delta T_f = 1.3 \times 1.86 \times 0.1 = 0.2418$$

$$T_f = 0 - 0.2418 = -0.2418^\circ\text{C}$$

96. (d) $M = \frac{WRT}{\pi V} = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 200 \times 10^{-3}}$

$$= \frac{31.374 \times 10^6}{514} = 61038 \text{ g}$$

97. (d) $p = p_A x_A + p_B x_B$
 $= p_A x_A + p_B (1 - x_A)$
 $\Rightarrow p_A x_A + p_B - p_B x_A$
 $\Rightarrow p_B + x_A (p_A - p_B)$

98. (b) $p_A^\circ = ?$, Given $p_B^\circ = 200$ mm of Hg, $x_A = 0.6$,
 $x_B = 1 - 0.6 = 0.4$, $P = 290$ of Hg

$$P = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$$

$$\Rightarrow 290 = P_A^\circ \times 0.6 + 200 \times 0.4 \therefore p_A^\circ = 350 \text{ mm of Hg.}$$

99. (b) For this solution intermolecular interactions between *n*-heptane and ethanol are weaker than *n*-heptane-*n*-heptane & ethanol-ethanol interactions hence the solution of *n*-heptane and ethanol is non-ideal and shows positive deviation from Raoult's law.

100. (a) From molarity equation :

$$M_1 V_1 + M_2 V_2 = M \times V$$

$$M = \frac{M_1 V_1 + M_2 V_2}{V} \text{ where } V = \text{total volume}$$

$$= \frac{750 \times 0.5 + 250 \times 2}{1000}$$

$$= 0.875 \text{ M}$$

EXERCISE - 2

1. (c) Moles of urea = $\frac{5}{60}$; moles of fructose = $\frac{5}{180}$;

$$\text{moles of sucrose} = \frac{5}{342};$$

$$\text{moles of KCl(effective)} = 2 \times \frac{5}{74.5} = \frac{5}{37.25}$$

2. (b) Using the relation,

$$M = \frac{w.R.T}{\pi V}, \text{ we get } M = \frac{6 \times 0.080 \times 300}{2 \times 10^{-3} \times 0.2} = 3.6 \times 10^5$$

3. (d) The salt that ionises to least extent will have highest freezing point. [i.e., minimum ΔT_f]

4. (b) Greater is the effective molarity ($i \times C$), higher the ΔT_f value and lower the freezing point.

5. (c) $N_1 V_1 + N_2 V_2 = NV$

$$4x + 10(1-x) = 6 \times 1; -6x = -4; x = 0.67$$

Thus 0.67 litre of 4N HCl

$$1-x = 1-0.67 = 0.33 \text{ litre of } 10 \text{ N HCl}$$

6. (a) Molarity = $\frac{\% \times 10 \times d}{\text{GMM}} = \frac{22 \times 10 \times 1.253}{342} = 0.805 \text{ M.}$

$$\text{Normality} = \frac{\% \times 10 \times d}{\text{GEM}} = \frac{22 \times 10 \times 1.253}{342/6} = 4.83 \text{ N}$$

$$\text{Molality} = \frac{22 \times 1000}{342(100-22)} = 0.825 \text{ m}$$

7. (b) Mole fraction of $\text{H}_2\text{O} = \frac{\frac{80}{18}}{\frac{80}{18} + \frac{20}{34}} = \frac{68}{77}$.

8. (c) Molality (m) = $\frac{\text{Molarity}}{\text{Density} - \frac{\text{Molarity} \times \text{Molecular mass}}{1000}}$

$$= \frac{18}{1.8 - \frac{18 \times 98}{1000}} = 5000$$

9. (b) $\pi V = \frac{w}{m} RT$

$$\therefore 6 \times 10^{-4} \times 1 = \frac{4}{m} \times 0.0821 \times 300; m = 1.64 \times 10^5$$

10. (b) $\pi V = CRT$

$$\frac{\pi_1}{\pi_2} = \frac{C_1 T_1}{C_2 T_2}$$

$$\pi_1 = P, \pi_2 = 2 \text{ atm. } C_1 = C, C_2 = \frac{C}{2}$$

$$T_1 = 600 \text{ K, } T_2 = 700 \text{ K}$$

$$\frac{P}{2} = \frac{2 \times C \times 600}{C \times 700}$$

$$P = \frac{24}{7}$$

11. (a) CaCl_2 acts as a non-volatile solute and results in depression in freezing point. Thus, snow fall is reduced and prevents blocking of roads in the polar region.

12. (c) $\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$
- | | | | |
|--------------------------|------------|-----------|-----------|
| Mol. before dissociation | 1 | 0 | 0 |
| Mol. after dissociation | $1-\alpha$ | 2α | 1α |

$$i = 1 - \alpha + 2\alpha + \alpha = 1 + 2\alpha$$

13. (b) AlCl_3 furnishes more ions than CaCl_2 and thus possess higher boiling point i.e., $T_1 > T_2$.

14. (a) Van't Hoff equation is

$$\pi V = inRT$$

For depression in freezing point.

$$\Delta T_f = i \times K_f \times m$$

For elevation in boiling point.

$$\Delta T_b = i \times K_b \times m$$

For lowering of vapour pressure,

$$\frac{P_{\text{solvent}}^\circ - P_{\text{solution}}}{P_{\text{solvent}}^\circ} = i \left(\frac{n}{N+n} \right).$$

15. (b) $\Delta T_f = i \cdot K_f \cdot m$; $0.0054 = i \times 1.8 \times 0.001$

$$i = 3 \text{ so it is } [\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2.$$

16. (c) Given, $W = 500 \text{ cc} = 500 \text{ g}$

$$(\because \text{density of water} = 1 \text{ g/cc})$$

$$\text{As, Density} = \frac{\text{Weight}}{\text{Volume}}$$

$$\text{Weight} = \text{Density} \times \text{Volume} = \frac{1 \text{ g}}{\text{cc}} \times 500 \text{ cc} = 500 \text{ g}$$

$$w = \text{amount of urea} = ?$$

$$K_f = 1.86^\circ\text{C}; \Delta T_f = 0.186^\circ\text{C}$$

$$M = \text{Molecular mass of urea} = 60$$

$$M = \frac{1000 \times K_f \times w}{W \times \Delta T_f}$$

$$60 = \frac{1000 \times 1.86 \times w}{500 \times 0.186}$$

$$60 = 20 \times w$$

$$\therefore w = \frac{60}{20} = 3\text{g}$$

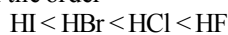
17. (b) Among the given options, CaCl_2 solution will produce maximum (three) ions per molecule, so it will show minimum freezing point.

18. (d) $\Delta T_b = K_b \frac{w}{M} \times \frac{1000}{W}$

$$0.52 = 0.6 \times \frac{3}{M} \times \frac{1000}{200} (W = 200 \times 1)$$

$$M = \frac{1.8 \times 5}{0.52} = 17.3\text{g mol}^{-1}$$

19. (d) The value of ΔT_b depends upon two factors 'i' and 'm'. It is given that 1 mol of each compound is dissolved in 1 L of solution. Hence molarity is same for all the compounds. Now the van't Hoff factor depends on number of particle i.e. on degree of ionisation which further depends on the bond dissociation energy which is in the order



i.e., bond dissociation energy of HI is least. Lower the bond dissociation energy, higher is the degree of ionisation and hence higher the number of particles, thus *i* will be maximum for HI and hence ΔT_b value will be larger for HI.

20. (d) Let the mass of methane and oxygen = *m* gm.

Mole fraction of O_2

$$= \frac{\text{Moles of } \text{O}_2}{\text{Moles of } \text{O}_2 + \text{Moles of } \text{CH}_4}$$

$$= \frac{m/32}{m/32 + m/16} = \frac{m/32}{3m/32} = \frac{1}{3}$$

Partial pressure of O_2 = Total pressure $\times$ mole fraction

$$\text{of } \text{O}_2, P_{\text{O}_2} = P \times \frac{1}{3} = \frac{1}{3}P$$

21. (a) Osmotic pressure (π) of isotonic solutions are equal. For solution of unknown substance C_1 (concentration).

$$C_1 = \frac{5.25/M}{V}$$

Where *M* represents molar mass.

$$\text{For solution of urea, } C_2 \text{ (concentration)} = \frac{1.5/60}{V}$$

$$\text{Given, } \pi_1 = \pi_2 \quad \therefore \pi = \text{CRT}$$

$$\therefore C_1 RT = C_2 RT \text{ or } C_1 = C_2 \text{ or } \frac{5.25/M}{V} = \frac{1.5/60}{V}$$

$$\therefore M = 210\text{g/mol}$$

22. (d) At 1 atmospheric pressure the boiling point of mixture is 80°C .

At boiling point the vapour pressure of mixture, $p_T = 1$ atmosphere = 760 mm Hg.

Using the relation,

$$p_T = p_A^\circ x_A + p_B^\circ x_B, \text{ we get}$$

$$p_T = 520x_A + 1000(1 - x_A)$$

$$\{\because p_A^\circ = 520\text{ mm Hg},$$

$$p_B^\circ = 1000\text{ mm Hg}, x_A + x_B = 1\}$$

$$\text{or } 760 = 520x_A + 1000 - 1000x_A \text{ or } 480x_A = 240$$

$$\text{or } x_A = \frac{240}{480} = \frac{1}{2} \text{ or } 50\text{ mol. percent}$$

i.e., the correct answer is (d)

23. (a) The vapour pressure of a solution of glucose in water can be calculated using the relation

$$\frac{p^\circ - p_s}{p_s} = \frac{\text{Moles of glucose in solution}}{\text{Moles of water in solution}}$$

$$\text{or } \frac{17.5 - p_s}{p_s} = \frac{18/180}{178.2/18} \quad [\because p^\circ = 17.5]$$

$$\text{or } 17.5 - p_s = \frac{0.1 \times p_s}{9.9} \text{ or } p_s = 17.325\text{ mm Hg.}$$

Hence (a) is correct answer.

24. (b) $p_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B$

$$550 = p_A^\circ \times \frac{1}{4} + p_B^\circ \times \frac{3}{4}$$

$$p_A^\circ + 3p_B^\circ = 550 \times 4 \quad \dots(i)$$

In second case

$$p_{\text{total}} = p_A^\circ \times \frac{1}{5} + p_B^\circ \times \frac{4}{5}$$

$$p_A^\circ + 4p_B^\circ = 560 \times 5 \quad \dots(ii)$$

Subtract (i) from (ii)

$$\therefore p_B^\circ = 560 \times 5 - 550 \times 4 = 600$$

$$\therefore p_A^\circ = 400$$

25. (a) $p_{\text{Total}} = p_A^\circ x_A + p_B^\circ x_B$

$$= p^\circ_{\text{Heptane}} x_{\text{Heptane}} + p^\circ_{\text{Octane}} x_{\text{Octane}}$$

$$= 105 \times \frac{25/100}{\frac{25}{100} + \frac{35}{114}} + 45 \times \frac{35/114}{\frac{25}{100} + \frac{35}{114}}$$

$$= 105 \times \frac{0.25}{0.25 + 0.3} + 45 \times \frac{0.3}{0.25 + 0.3}$$

$$= \frac{105 \times 0.25}{0.55} + \frac{45 \times 0.3}{0.55} = \frac{26.25 + 13.5}{0.55}$$

$$= 72\text{ kPa}$$

26. (b) For isotonic solutions

$$\pi_1 = \pi_2$$

$$C_1 = C_2$$

$$\frac{5/342}{0.1} = \frac{1/M}{0.1}$$

$$\frac{5}{342} = \frac{1}{M}$$

$$\Rightarrow M = \frac{342}{5} = 68.4 \text{ gm/mol}$$

27. (b) $\Delta T_f = i \times K_f \times m$
 Given $\Delta T_f = 2.8$, $K_f = 1.86 \text{ K kg mol}^{-1}$ $i = 1$
 (ethylene glycol is a non-electrolyte)
 wt. of solvent = 1 kg
 Let of wt of solute = x
 Mol. wt of ethylene glycol = 62

$$2.8 = 1 \times 1.86 \times \frac{x}{62 \times 1}$$

$$\text{or } x = \frac{2.8 \times 62}{1.86} = 93 \text{ gm}$$

28. (a) Molecular weight of naphthoic acid
 $\text{C}_{11}\text{H}_8\text{O}_2 = 172 \text{ g mol}^{-1}$.
 The theoretical value of depression in freezing point

$$= K_f \times \text{molality} = 1.72 \times \frac{20 \times 1000}{172 \times 50} = 4\text{K}$$

Van't Hoff factor,

$$i = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}}$$

$$= \frac{2}{4} = 0.5.$$

29. (a) $P_{\text{N}_2} = \kappa_{\text{H}} x_{\text{N}_2}$
 $0.8 \times 5 = 1 \times 10^5 \times x_{\text{N}_2}$
 $\therefore x_{\text{N}_2} = 4 \times 10^{-5}$

$$\text{Solubility in 10 moles} = 4 \times 10^{-4}.$$

30. (c) Number of moles of urea = $\frac{120}{60} = 2$
 Total mass of solution = $1000 + 120 = 1120 \text{ g}$

$$\begin{aligned} \text{Total volume of solution (in L)} &= \frac{\text{Mass}}{\text{Density}} \\ &= \frac{1120}{1.15 \times 10^3} = \frac{112}{115} \text{ L} \end{aligned}$$

$$\begin{aligned} \text{Molarity of the solution} &= \frac{\text{Number of moles}}{\text{Volume of solution in litre}} \\ &= \frac{2 \times 115}{112} = 2.05 \text{ mol L}^{-1} \end{aligned}$$

31. (a) $\Delta T_f = i \times K_f \times m$
 Where m = Molality of the solution
 (i.e. number of moles of solute per 1000 g of the solvent)

$$\text{Here } m = \frac{0.1}{329} \times 10$$

$$\text{Thus } \Delta T_f = 4 \times 1.86 \times \frac{0.1 \times 10}{329} = 2.3 \times 10^{-2}$$

$$\text{Thus } T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2} \text{ } ^\circ\text{C}$$

32. (a) From Raoult law

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent} + \text{No. of moles of solute}}$$

When the concentration of solute is much lower than the concentration of solvent,

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

$$\Delta T_b = K_b \times m$$

$$m = \frac{\text{Number of moles of the solute}}{\text{Mass of solvent in grams}} \times 1000$$

$$\Delta T_b = K_b \times \frac{\text{Number of moles of the solute}}{\text{Mass of solvent in grams}} \times 1000$$

Number of moles of solute

$$= \frac{\Delta T_b \times \text{Mass of solvent in grams}}{K_b \times 1000}$$

$$= \frac{2 \times 100}{0.76 \times 1000} = 0.26,$$

$$\text{Number of moles of solvent} = \frac{100}{18} = 5.56$$

$$\text{From equation (i) we get, } \frac{760 - p}{760} = \frac{0.26}{5.56}$$

$$\text{On solving, } p = 724.46 \approx 724$$

33. (b) Sodium sulphate dissociates as
 $\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{--}$
 hence van't hof factor $i = 3$

$$\text{Now } \Delta T_f = i K_f \cdot m$$

$$= 3 \times 1.86 \times 0.01 = 0.0558 \text{ K}$$

34. (d) Colligative properties depends upon the no. of particles.
 Since methanol is non electrolyte hence cannot be considered.

35. (a) $k_{\text{H}} = 100 \text{ kbar} = 10^5 \text{ bar}$, $p = 1 \text{ bar}$
 $p = k_{\text{H}} \times x_{\text{A}}$

$$x_{\text{A}} = \frac{p}{k_{\text{H}}} = \frac{1}{100 \times 10^3} = 10^{-5}$$

$$\text{Moles of water} = \frac{1000}{18} = 55.5$$

$$\text{Weight of water} = 1000 \text{ g } (\because 1000 \text{ mL} = 1000 \text{ g})$$

$$\text{Mole fraction} = 10^{-5} = \frac{x}{55.5 + x}$$

As $55.5 \gg x$, thus neglecting x from denominator

$$10^{-5} = \frac{x}{55.5} \Rightarrow x = 55.5 \times 10^{-5} \text{ moles}$$

or 0.555 millimoles.

36. (d) $\Delta T_b = k_b \cdot m$

$$\Delta T_b = k_b \times \frac{\text{weight of solute} \times 1000}{\text{molecular weight of solute} \times \text{weight of solvent}}$$

$$0.75 = 2.5 \times \frac{1.5}{M} \times \frac{1000}{50}$$

$$M = \frac{2.5 \times 1.5 \times 1000}{0.75 \times 50} = 100$$

37. (b) $\Delta T_f = K_f \times m$

K_f is a characteristic of a particular solvent *i.e.*, it will be different for different solvents.

38. (a) According to Raoult's law,

$$P_T = x_A P_A^\circ + x_B P_B^\circ$$

Given, $P_T = 500 \text{ mm Hg}$

$$n_A = 1 \text{ and } n_B = 2 \therefore x_A = 1/3 \text{ and } x_B = 2/3$$

$$\Rightarrow 500 = \frac{1}{3} P_A^\circ + \frac{2}{3} P_B^\circ$$

$$\Rightarrow 1500 = P_A^\circ + 2P_B^\circ \quad \dots (i)$$

Also given Qn that one more mole of B is added to the solution, the pressure of the ideal solution increases by 25 mm Hg.

$$\therefore P_{T_2} = 500 + 25 = 525 \text{ mm Hg}$$

Also, $n_B = 3 \therefore x_A = 1/4 \text{ and } x_B = 3/4$

$$525 = \frac{1}{4} P_A^\circ + \frac{3}{4} P_B^\circ \quad \dots (ii)$$

$$2100 = P_A^\circ + 3P_B^\circ$$

Subtract (i) and (ii),

$$P_B^\circ = 600 \text{ mm Hg}$$

$$P_A^\circ + 2P_B^\circ = 1500 \Rightarrow P_A^\circ = 300 \text{ mm Hg.}$$

39. (d) According to Henry's law,

$$m = k \times p$$

given $K_H = 1.4 \times 10^{-3}$

$$P_{O_2} = 0.5 \text{ or}$$

$$P_{O_2} = K_H \times x_{O_2}$$

$$\therefore x_{O_2} = \frac{0.5}{1.4 \times 10^{-3}}$$

$$\text{No. of moles; } n = \frac{m}{M}$$

$$0.7 \times 10^{-4} = \frac{m}{32}$$

$$m = 22.4 \times 10^{-4} \text{ g} = 2.24 \text{ mg}$$

40. (d) Mass of non-volatile solute = 1 g

Molar mass of solute = 250 g mol⁻¹

Mass of benzene = 51.2 g, $K_f = 5.12 \text{ K kg mol}^{-1}$

$$\Delta T_f = \frac{K_f \times 1000 \times w_2}{M_2 \times w_1}$$

where, w_2 = mass of the solute

M_2 = molar mass of solute

w_1 = mass of the solvent

On substituting given values, $\Delta T_f = \frac{5.12 \times 1000 \times 1}{51.2 \times 250}$

$$\therefore \Delta T_f = 0.4 \text{ K}$$

41. (c) Acetone and chloroform shows negative deviation from Raoult's law when these are mixed, the hydrogen bonding takes place between the two molecular species due to which escaping tendency of either liquid molecules becomes less and boiling point of solution increases.

42. (c)

43. (d) According to Henry's law the mass of a gas dissolved per unit volume of solvent is proportional to the pressure of the gas at constant temperature $m = K p$ *i.e.* as the solubility increases, value of Henry's law constant decreases. Since CO₂ is most soluble in water among the given set of gases. Therefore CO₂ has the lowest value of Henry's law constant.

44. (a) Given $w = 10 \text{ g}$ Mol. mass = 40
Weight of solvent = 1250 × 0.8 g = 1000 g = 1 kg

$$\therefore \text{molality} = \frac{10}{40 \times 1} = 0.25$$

45. (d) Glucose is non electrolyte hence depression in freezing point will be minimum, hence freezing point will be highest.

46. (b)

47. (b) Both assertion and reason are correct but reason is not the correct explanation of assertion.

The relationship between lowering of vapour pressure and osmotic pressure can be derived as follows:

Van't Hoff equation for dilute solutions is

$$\pi = \frac{n}{V} RT \quad \dots (i)$$

In case of a dilute solution, the volume of solution can be taken as equal to that of solvent. If N is the number of moles of solvent of molecular weight M and density ρ , the volume V is given by

$$V = \frac{NM}{\rho} \quad \dots (ii)$$

$$\text{or } \frac{n}{N} = \frac{\pi M}{\rho RT} \quad \dots (iii)$$

From Raoult's law,

$$\frac{P^\circ - P}{P^\circ} = \frac{n}{N} \quad \dots (iv)$$

$$\therefore \frac{P^\circ - P}{P^\circ} = \frac{\pi M}{\rho RT} \quad [\text{From (iii) and (iv)}]$$

$$\text{or } (P^\circ - P) = \frac{\pi M}{\rho RT} \times P^\circ$$

The factor $\frac{MP^\circ}{\rho RT}$ is constant at constant temperature.

$$\therefore (P^\circ - P) \propto \pi$$

or lowering of V.P. $\propto$ osmotic pressure

Thus assertion is correct.

Osmotic pressure is a colligative property is correct.

48. (c) Both the solute and solvent will form the vapours but vapour phase will become richer in the more volatile component.
49. (b)
50. (c) Camphor has high molal depression constant.

EXERCISE - 3

Exemplar Questions

- (a) According to Henry's law partial pressure of a gas in the solution is proportional to the mole fraction of gas in the solution.
 $p = K_H x$; K_H = (Henry's constant)
- (d) Dissolution of sugar in water will be most rapid when powdered sugar is dissolved in hot water because in powdered form it can easily insert in the vacancies of water particle.
 Also, dissolution of sugar in water is an endothermic process. So it is favourable at high temperature.
- (c)
- (b) When solute gets precipitated in the solution, then the solution is known as supersaturated solution.
- (c) Maximum amount of solid that can be dissolved in a specified amount of a given solvent does not depend upon pressure. The reason is solid and liquid are highly incompressible and practically remain unaffected by change in pressure.
- (b) At high altitude, the partial pressure of oxygen is less than at the ground level. This decreased atmospheric pressure causes release of oxygen from blood. Hence people living at high altitude have low concentration of oxygen in the blood and tissues.
- (a) Mixture of methanol and acetone show a positive deviation from Raoult's law. Molecules in pure methanol are hydrogen bonded. On adding acetone, its molecules enters in between the host molecules and break some of the hydrogen bonds between them.
 Therefore, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules.
 Other three remaining options will show negative deviation.
- (b) Colligative properties depend upon number of solute particles in solution irrespective of their nature.
- (b) Colligative properties depends upon the number of particles. As we know greater the value of van't Hoff factor higher will be elevation in boiling point and hence higher will be the boiling point of solution. Among the given solution 1.0M Na_2SO_4 have highest no. of particles i.e highest value of ' i '.
 Hence, 1.0 M Na_2SO_4 has highest value of boiling point.
- (a) $\Delta T_b = K_b m$ elevation in boiling point

$$K_b = \frac{\Delta T_b}{m}$$
- (c) $\Delta T_f = i K_f m$ i.e., depression in freezing point is directly related to van't Hoff factor (i). Glucose is a non-electrolyte hence will remain undissociated. Hence for glucose value of i is 1 whereas for MgCl_2 value of i is 3. Hence, depression in freezing point of MgCl_2 is about 3 times of glucose.
- (d) When an unripe mango is placed in a concentrated salt solution to prepare pickle then mango loose water due to osmosis and get shrivel.
- (a) Osmotic pressure (π) = CRT.
 For concentrated solution C has higher value than dilute solution.
 Hence, as concentration of solution increases osmotic pressure also increase.
- (a) The value of molal depression constant, K_f depends upon nature of solvent. Therefore two different solutions of sucrose of same molality prepared in different solvents will have different depression in freezing point.
- (b) Number of total ions present in the solution is known as van't Hoff factors (i).
 for KCl , $i = 2$
 for NaCl , $i = 2$
 for K_2SO_4 , $i = 3$
- (b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of higher concentration of solute to lower concentration.
- (a) The value of Henry's constant (K_H) increases with increase in temperature.
- (b) According to Henry's law
 $p \propto x$
 $\Rightarrow p = K_H x$
 As value of K_H rises solubility of gases decreases.
- (b) If a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semi-permeable membrane. This process is called reverse osmosis.
 Thus, in this case, if a pressure greater than osmotic pressure is applied on piston (B). Water will move from side (B) to side (A).
- (c) As van't hof factor depends only on no. of dissociated ions. Hence, i will be independent on concentration of solutions.
- (b) A mixture of bromoethane and chloroethane is an example of ideal solution. For an ideal solution, the A — A or B — B type intermolecular interaction is nearly equal to A — B type interaction.
 Chloroform and acetone mixture is an example of non-ideal solution having negative deviation while ethanol-acetone mixture shows positive deviation.
- (a) On adding salt to water to make the salt solution the vapour pressure of solution gets lowered. This is due

$$\begin{aligned} \text{Unit of } K_b &= \frac{\text{unit of } \Delta T_b}{\text{unit of } m} = \frac{K}{\text{molality}} \\ &= \frac{K}{\text{mol kg}^{-1}} = K \text{ mol}^{-1} \text{ kg} \end{aligned}$$

to the decrease in surface covered by solvent molecule which leads to decrease in number of solvent molecule escaping from the surface corresponding to pure solvent.

Hence, vapour pressure also get reduces.

23. (a) If two liquids A and B form minimum boiling azeotrope at some specific composition then A — B interactions are weaker than those of A — A and B — B. Because in case of positive deviation, we get minimum boiling azeotropes whereas in case of negative deviation we get maximum boiling azeotropes.

24. (d) As we know, $M_1 V_1 = M_2 V_2$
On putting values, we get
 $0.02 \times 4 \text{ L} = M_2 \times 5 \text{ L}$

$$M_2 = \frac{0.08}{5} = 0.016 \text{ M}$$

25. (a) At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show positive deviation. This is due to weaker A — B interaction than A — A and B — B interaction.

26. (c) Value of K_H depends upon nature of gases dissolved in water. Higher the value of K_H at a given temperature the lower is the solubility of the gas in the liquid. Hence, correct order is :
 $\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$.

NEET/AIPMT (2013-2017) Questions

27. (d) Molarity (M) = $\frac{\text{wt} \times 1000}{\text{mol. wt.} \times \text{vol (ml)}}$
 $2 = \frac{\text{wt.}}{63} \times \frac{1000}{250}$
 $\text{wt.} = \frac{63}{2} \text{ gm}$
 $\text{wt. of 70\% acid} = \frac{100}{70} \times 31.5 = 45 \text{ gm}$
28. (c) An ideal solution is that solution in which each component obeys Raoult's law under all conditions of temperatures and concentrations. For an ideal solution, $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$.
29. (c) Colligative properties $\propto$ no. of particles. Since $\text{Al}_2(\text{SO}_4)_3$ contains maximum number of particles, hence will have the largest value of freezing point depression.
30. (c) $\text{K}_4[\text{Fe}(\text{CN})_6] \rightleftharpoons 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^-$
and $\text{Al}_2(\text{SO}_4)_3 \rightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-}$
 $\therefore$ van't Hoff factor is 5 for both $\text{Al}_2(\text{SO}_4)_3$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$
31. (d) $\Delta T_b = iK_b m$
Given, $(\Delta T_b)_x > (\Delta T_b)_y$
 $\therefore i_x K_b m > i_y K_b m$ (K_b is same for same solvent)
 $i_x > i_y$
So, x is undergoing dissociation in water.
32. (a) For an ideal solution $\Delta S_{\text{mix}} > 0$
33. (d) Molality = $\frac{W}{M} \times \frac{1}{V(\text{kg})}$

$$= \frac{n}{V(\text{kg})} \quad (\text{where } n_{\text{solute}} = W/M)$$

$$1.00 \text{ m} = \frac{n}{V(\text{kg})} \quad \text{i.e., 1 mole in 1 kg of water}$$

Moles of 1 kg H_2O

$$= \frac{1000 \text{ g}}{18 \text{ g/mol}} = 55.55 \text{ mole}$$

Moles of solute = 1

Mole fraction

$$= \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{water}}} = \frac{1}{(1 + 55.55)}$$

$$= 0.01768 = 0.0177$$

$$34. (a) \left(\frac{P^\circ - P_s}{P^\circ} \right) = \frac{n}{N} = \frac{W_1}{M_1} \times \frac{M_2}{W_2}$$

Where, W_1 = wt of solute

W_2 = wt of solvent

M_1 = Mass of solute

M_2 = Mass of solvent

at 100°C , $P^\circ = 760 \text{ mm}$

$$\frac{760 - 732}{760} = \frac{6.5 \times 18}{M_1 \times 100}$$

$$M_1 = 31.75 \text{ g mol}^{-1}$$

$$\Delta T_b = m \times K_b = \frac{W_1 \times 1000}{M_1 \times W_2} \times K_b$$

$$\Delta T_b = \frac{0.52 \times 6.5 \times 1000}{31.75 \times 100} = 1.06^\circ\text{C}$$

$\therefore$ boiling point of solution

$$= 100^\circ\text{C} + 1.06^\circ\text{C} = 101^\circ\text{C}$$

35. (c) K_f (molal depression constant) only depends on the nature of the solvent and is independent of the concentration of the solution.
36. (a) Molarity depends on the volume of a solution which can be changed with change in temperature.
37. (a) Let us consider that A is benzene and B is toluene
1 : 1 molar mixture of A and B

$$\therefore x_A = \frac{1}{2} \text{ and } x_B = \frac{1}{2}$$

$$\text{Total pressure of solution (P)} = P_A^0 x_A + P_B^0 x_B$$

$$P = 12.8 \times \frac{1}{2} + 3.85 \times \frac{1}{2} = 8.325 \text{ kPa}$$

$$Y_A = \frac{P_A^0 x_A}{P} = \frac{12.8 \times \frac{1}{2}}{8.325} = 0.768$$

$$\therefore y_B = 1 - y_A = 1 - 0.768 = 0.232$$

so, the vapour will contain higher percentage of benzene.

Chapter 17 Electrochemistry

Electrochemistry is that branch of chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions i.e., how chemical energy produced in a redox reaction can be converted into electrical energy or how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous.

Under electrochemistry, we study two types of cells: electrochemical and electrolytic cell.

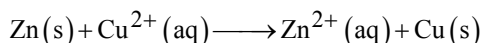
Difference Between Electrochemical and Electrolytic Cell:

Electrochemical cell	Electrolytic cell
1. It converts chemical energy into electrical energy	1. It converts electrical energy into chemical energy.
2. It is based upon redox reaction which is spontaneous.	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied.
3. The electrode on which oxidation takes place is called Anode (negative pole) and electrode on which reduction takes place is called cathode (positive pole).	3. The electrode which is connected to negative terminal of the battery is called cathode; the cations migrate to it, gain electrons and hence reduction takes place. The other electrode is called anode.
4. A salt bridge is used to set up the cell.	4. No salt bridge is used in this case.
5. Two electrolytes are used.	5. Only one electrolyte is taken.

GALVANIC CELL

It is also called voltaic cell. It converts chemical energy liberated during redox reaction to electrical energy.

For example reaction between Zn and CuSO_4 .



The chemical reaction responsible for production of electricity takes place in two separate compartments called half cells which consists of an electrolyte solution and an electrode.

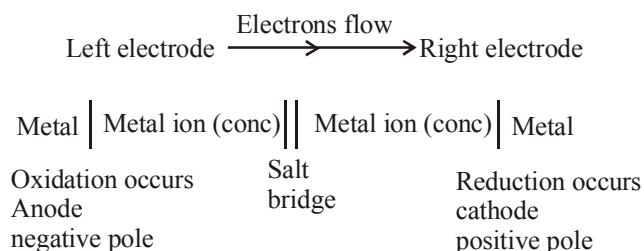
Anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
(Ist half cell reaction)

Cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
(IInd half cell reaction)

Two half cells are connected by salt bridge.

Note:

- Electrode on which oxidation occurs is called anode (negative pole) while the electrode on which reduction occurs is called cathode (positive pole)
- Electrons flow from anode to cathode in the external circuit.
- Inner circuit is completed by flow of ions through the salt bridge.
- Representation of electrochemical cell is like:



Characteristics of Salt Bridge

- It allows the flow of current by completing the circuit.
- It maintains electrical neutrality of electrolytes in two half cells.

ELECTROMOTIVE FORCE (EMF)

The difference in the electrode potentials of two electrodes of the cell is termed as electromotive force (EMF).

Cell potential or EMF of the cell is given by:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} = E_{\text{R}} - E_{\text{L}} \\ &= E_{\text{cathode}} - E_{\text{anode}} = E_{\text{red}} - E_{\text{ox}} \end{aligned}$$

Conventionally, all electrode potentials are expressed at top as reduction potentials, and

Reduction potential = – Oxidation potential

For a redox reaction to be spontaneous, EMF of the cell must be positive.

Reduction occurs at the electrode having higher reduction potential and oxidation occurs at the electrode having lower reduction potential.

Electrode potential is a fixed quantity and is not multiplied by 'n' i.e. number of e^- s involved in a reaction.

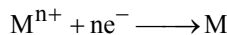
Standard electrode potential for fluorine is the highest indicating that fluorine gas (F_2) has the maximum tendency to get reduced to F^- ions and thus, F_2 gas is the strongest oxidising agent. Lithium has lowest electrode potential indicating that Li^+ ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

Note : Galvanic cell has an external voltage $< 1.1\text{ V}$ when $E_{\text{ext}} = 1.1\text{ V}$, the reaction stops and no current flows. And, if $E_{\text{ext}} > 1.1\text{ V}$, the reaction occurs in opposite direction and the cell functions as an **electrolytic cell** where the electrons flow from Cu to Zn and current flows from Zn to Cu.

NERNST EQUATION

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

- (i) For electrode potential, the reaction is,



Then Nernst equation, is applied as

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

for pure solids liquids or gases at 1 atm pressure $[M] = 1$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

putting $R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$

$F = 96500\text{ C}$

$T = 298\text{ K}$

$$E_{\text{Red}} = E^{\circ}_{\text{Red}} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

- (ii) For EMF of the cell, the cell reaction is:



Then by Nernst equation at 298 K,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Where n is the number of electrons involved in the cell reaction.

- (iii) For a cell reaction in equilibrium,

$$E_{\text{cell}} = 0$$

$$K_C = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n} \log K_C \text{ at } 298\text{ K}$$

where n = no. of electrons involved in the cell reaction

K_C = equilibrium constant for the cell reaction.

Gibb's Free Energy and Cell Potential

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

$$\text{as } E^{\circ}_{\text{cell}} = \frac{RT}{nF} \ln K_C$$

$$\Delta G^{\circ} = -2.303 RT \log K_C$$

where ΔG° = standard free energy change of the reaction

F = Faraday's constant = 96500 C

$R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$

ELECTROLYSIS

It is a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten state.

On passing electric current, positively charged ions move towards cathode and negatively charged ions move towards anode; where they lose their charge and become neutral species. **Oxidation occurs at anode while reduction takes place at cathode.**

Faraday's Laws

The **quantitative aspects** of electrolysis were studied by Faraday. He put forward two laws as follows:

- (i) **Faraday's First law of Electrolysis:**

According to this law, the amount of chemical reaction and hence the mass of any substance deposited at any electrode during electrolysis by a current is directly proportional to the quantity of electricity passed through the electrolyte i.e.,

$$m \propto Q$$

$$m = ZQ$$

$$\text{as, } Q = It$$

$$\therefore m = ZIt$$

where $m \rightarrow$ amount of subs. deposited

$Q \rightarrow$ quantity of electricity in 'C'

$Z \rightarrow$ Constant called Electrochemical equivalent

$I \rightarrow$ Current in ampere

$t \rightarrow$ time in seconds

Electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.

$$\text{Electro-chemical equivalent (Z)} = \frac{\text{equivalent wt. of element}}{96500}$$

- (ii) **Faraday's second law of electrolysis**

When same amount of electricity is passed through solutions of different electrolytes connected in series, the weight of the substances produced at the electrodes are directly proportional to their equivalent weights.

Ex: for AgNO_3 and CuSO_4 solutions connected in series, if same quantity of electricity is passed, then

$$\frac{\text{wt. of Ag deposited}}{\text{Wt. of Cu deposited}} = \frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of Cu}}$$

Note:

- (i) If n electrons are involved in the electrode reaction, the passage of n faradays (i.e., $nF = n \times 96500\text{ C}$) of electricity will liberate one mole of the substance.

- (ii) Equivalent weight of a substance can be calculated as:

$$\text{Eq. wt.} = \frac{m}{Q} \times 96500 \left[\begin{array}{l} m \rightarrow \text{amount of substance deposited} \\ Q \rightarrow \text{Quantity of electricity} \end{array} \right]$$

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

Conductance (G)

The amount of electric current that can be passed through the solution is called conductance. Conductance is inverse of resistance.

$$\text{Conductance} = \frac{1}{\text{Resistance}} \quad \text{or} \quad G = \frac{1}{R}$$

Unit of conductance is inverse of ohm. It is represented as mho or ohm^{-1} or siemens (s).

- (i) Resistance of a conductor is given as follows:

$$R = \rho \frac{l}{A}$$

R = resistance; ρ = resistivity; l = length,
 A = area of cross-section.

(ii) The reciprocal of resistivity is called conductivity

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \frac{l}{A} \quad \kappa \rightarrow \text{specific conductivity or conductivity.}$$

$$\text{or } \kappa = G \times \frac{l}{A} = \text{observed conductance} \times \text{cell constant}$$

$$= G \times G^* \quad (\text{where cell constant} = l/A)$$

$$\therefore \text{Cell constant } (G^*) = \frac{\kappa}{G} = \frac{\text{Conductivity}}{\text{Conductance}}$$

Equivalent Conductivity

If one equivalent of an electrolyte is dissolved in a solution, then the conductivity of two parallel electrodes situated 1 cm apart is called equivalent conductivity. It is denoted by Λ_{eq} .

$$\Lambda_{eq} = \kappa \times V \quad (\text{where } V = \text{volume})$$

In terms of concentration,

$$\Lambda_{eq} = \frac{\kappa \times 1000}{C_{eq}} = \frac{\kappa \times 1000}{\text{Normality}}$$

Where C_{eq} = Concentration

Unit of Λ_{eq} = $\text{cm}^2 \text{ ohm}^{-1} \text{ gm eq}^{-1}$

Molar Conductivity

If one mole of an electrolyte is dissolved in a solution, then the conductivity of that solution between two parallel electrodes situated 1 cm apart, is called molar conductivity. It is represented by λ_m .

$\lambda_m = \kappa \times V_m$
 where V_m = Volume of the solution in which 1 mole solute is

dissolved. $\left(V_m = \frac{1}{C} \right)$

κ = specific conductivity

$$\lambda_m = \frac{1000 \text{ cm}^3}{M} \times \kappa$$

or Unit = $\text{cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1} = \text{S cm}^2 \text{ mol}^{-1}$

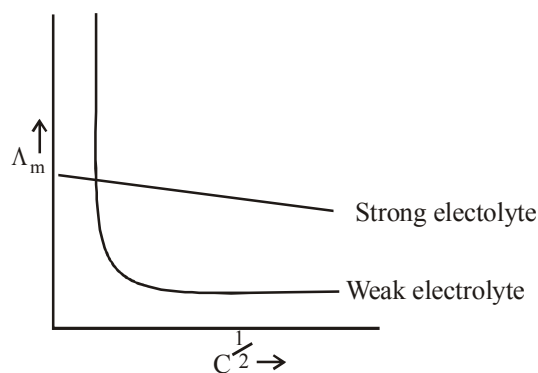
Unit of Different Quantities

Physical Quantity	Commonly used units	SI units
1. Resistance(R)	ohm(Ω)	ohm(Ω)
2. Resistivity(ρ)	ohm cm($\Omega \text{ cm}$)	ohm m($\Omega \text{ m}$)
3. Conductance(G)	Ω^{-1}	siemen(S)
4. Conductivity(κ)	$\Omega^{-1} \text{ cm}^{-1}$	S m^{-1}
5. Equivalent Conductivity(Λ_{eq})	$\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$	$\text{S m}^2 \text{ eq}^{-1}$
6. Molar Conductivity(Λ_m)	$\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$\text{S cm}^2 \text{ mol}^{-1}$
7. Cell constant(G^*)	cm^{-1}	m^{-1}

Effect of Dilution on Conductance, Specific Conductivity and Λ_m

- Conductance increases with increase in dilution due to increase in number of ions in solution.
- Conductivity** decreases with the decrease in concentration. This is because conductivity is the conductance of one unit volume of solution. As the number of ions per unit volume decrease on dilution, hence conductivity decreases with decrease in concentration.
- Molar conductivity** and equivalent conductivity increases with decrease in concentration. This is because $\Lambda_m = \kappa V$ and $\Lambda_{eq} = \kappa V$. Though ' κ ' decreases with decrease in concentration but it is compensated by increase in volume and hence Λ_m and Λ_{eq} increase with dilution.

The variation of Λ_m for strong and weak electrolytes with concentration is as follows:



The increase in Λ_m for strong electrolyte with dilution is not very sharp. This is because strong electrolyte is already completely dissociated into ions. On dilution, ions get separated and their movement becomes easier and hence, Λ_m increases but not sharply.

On the other hand, weak electrolyte has lower degree of dissociation at higher concentrations. On dilution, the degree of dissociation increases and number of ions in the solution increases. Thus, Λ_m increases sharply.

KOHLRAUSCH'S LAW

According to this law, limiting molar conductivity of an electrolyte is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte.

Mathematically, Λ_m° for $A_x B_y = x\lambda^{\circ y+}_{(A)} + y\lambda^{\circ x-}_{(B)}$
 where,

Λ_m° = Limiting molar conductivity of the electrolyte

$\lambda^{\circ y+}_{(A)}$ and $\lambda^{\circ x-}_{(B)}$ = Limiting molar conductivities of cation and anion respectively.

Applications of Kohlrausch's Law

(i) Calculation of Λ_m° for weak electrolytes.

$$\lambda^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ\text{CH}_3\text{COO}^- + \lambda^\circ\text{H}^+ \quad \dots\dots(1)$$

for strong electrolytes :

$$\lambda^\circ(\text{CH}_3\text{COOK}) = \lambda^\circ\text{CH}_3\text{COO}^- + \lambda^\circ\text{K}^+ \quad \dots\dots(2)$$

$$\lambda^\circ(\text{HCl}) = \lambda^\circ\text{H}^+ + \lambda^\circ\text{Cl}^- \quad \dots\dots(3)$$

$$\lambda^\circ(\text{KCl}) = \lambda^\circ\text{K}^+ + \lambda^\circ\text{Cl}^- \quad \dots\dots(4)$$

$$\therefore \text{eq}^n(2) + \text{eq}^n(3) - \text{eq}^n(4) = \text{eq}^n(1)$$

$$\text{i.e., } \lambda^\circ_{(\text{CH}_3\text{COOK})} + \lambda^\circ_{(\text{HCl})} - \lambda^\circ_{(\text{KCl})} = \lambda^\circ_{(\text{CH}_3\text{COOH})}$$

(ii) Calculation of degree of dissociation (α):

It Λ_m^c is the molar conductivity of solution at any concentration C and Λ_m° is the molar conductivity at infinite dilution the degree of dissociation will be:

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

(iii) Calculation of dissociation constant of a weak electrolyte

$$\text{i.e., } K_c = \frac{C\alpha^2}{1-\alpha}$$

where C is concentration and α is degree of dissociation of weak electrolyte.

(iv) Calculation of solubility of a sparingly soluble salt: Salts which dissolve to a very small extent in water are called sparingly soluble salts. Their solutions are considered as infinite dilute solutions as they dissolve in very little amount. Their solubility is given as:

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

PREDICTING THE PRODUCTS OF ELECTROLYSIS

In electrolysis, the conversion of ions into neutral species at their respective electrodes is called primary change. The product formed as a result of primary change may be collected as such or it may undergo secondary change to form final products.

When electrolysis is carried out in molten state, the products are actually the substances obtained from the ions of the electrolyte. However, in aqueous solution, the situation is different. At each electrode, two different ions can be discharged which ion gets discharged depends:

- On their relative discharge potentials
 - Sometimes on the material of the electrode used.
- Usually, the ions with **lower discharge potential** are discharged in preference to those which have high discharge potentials.

SOME COMMERCIAL CELLS (Batteries)

They are mainly of two types:

Primary Batteries or Cells

Primary cells are those in which redox reaction occurs only once and the cell becomes dead after some time and cannot be used again. Examples:

Dry cell or Leclanche cell : Particulars are:

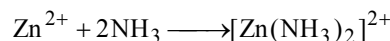
Anode - Zinc Container

Cathode - graphite rod surrounded by MnO_2 powder

Electrolyte - paste of NH_4Cl + ZnCl_2

Cathode Reaction : $\text{MnO}_2 + \text{NH}_4^+ + e^- \longrightarrow \text{MnO}(\text{OH}) + \text{NH}_3$

Anode Reaction : $\text{Zn} - 2e^- \longrightarrow \text{Zn}^{++}$



Cell potential 1.25V to 1.5V

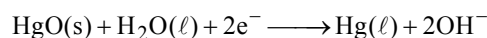
Mercury Cell

Anode - Zn-Hg amalgam

Cathode - paste of (HgO + C)

Electrolyte - moist paste of KOH -ZnO

Cathode Reaction :



Anode Reaction : $\text{Zn} + 2\text{OH}^- \longrightarrow \text{ZnO} + \text{H}_2\text{O}(\ell) + 2e^-$

Net Reaction : $\text{Zn}(\text{Hg}) + \text{HgO}(\text{s}) \longrightarrow \text{ZnO}(\text{s}) + \text{Hg}(\ell)$

cell potential = 1.30 volt

Secondary Batteries or Cells

These can be recharged by passing current in opposite direction so that they can be used again.

Examples: (i) Lead storage battery and Nickel cadmium storage cell.

Lead storage battery :

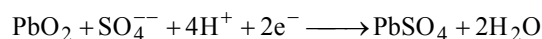
Anode - Spongy lead

Cathode - grid of lead packed with PbO_2

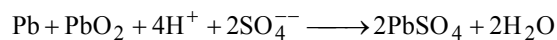
Electrolyte - 38% H_2SO_4 by mass

Anode Reaction : $\text{Pb} + \text{SO}_4^{--} \longrightarrow \text{PbSO}_4 + 2e^-$

Cathode Reaction :



Net Reaction :



When recharged the cell reactions are reversed.

Nickel-cadmium storage cell

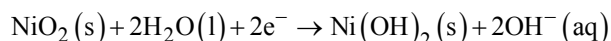
Anode - Cadmium

Cathode - metal grid containing NiO_2

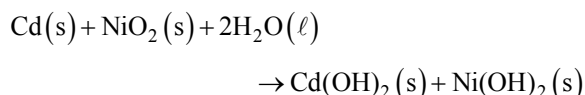
Electrolyte - KOH solution

Anode Reaction $\text{Cd}(\text{s}) + 2\text{OH}^- \rightarrow \text{Cd}(\text{OH})_2(\text{s}) + 2e^-$

Cathode Reaction :



Net Reaction :



Cell potential = 1.4V.

Fuel Cells

Galvanic cells which are designed to convert energy of combustion of fuels like H_2 , CH_4 , CH_3OH , etc. directly into electrical energy are called fuel cells. Ex: $\text{H}_2 - \text{O}_2$ fuel cell.

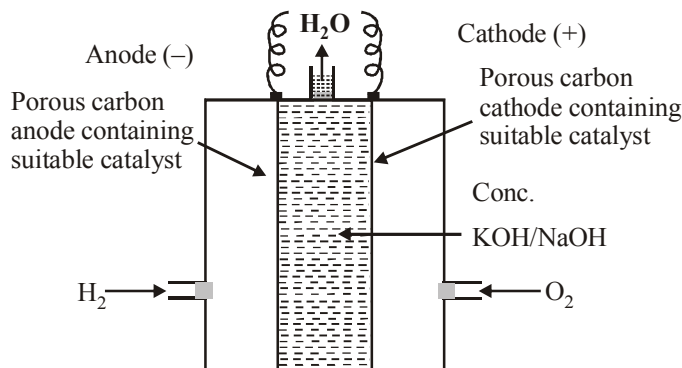


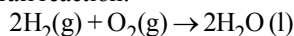
Fig : $\text{H}_2 - \text{O}_2$ fuel cell

The electrode reactions are:

cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

anode: $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$

Overall reaction:



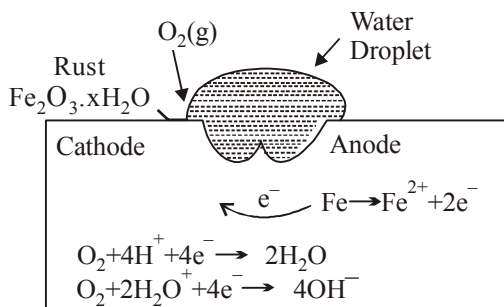
Advantages of fuel cells

- The cell runs continuously as long as the reactants are supplied.
- Their efficiency is about 70% compared to thermal plants whose efficiency is 40%.
- They are pollution free.

CORROSION

It is the slow eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, carbonates, sulphates etc.

Examples: rusting of iron, tarnishing of silver, green coating on silver and bronze, etc.



The reactions involved in the rusting of iron are:

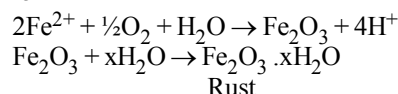
Cathode: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$

$$E^\circ_{\text{H}^+/\text{O}_2/\text{H}_2\text{O}} = 1.23\text{V}$$

Anode: $2\text{Fe}(\text{s}) \rightarrow 2\text{Fe}^{2+} + 4\text{e}^-$ $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$

Overall reaction: $2\text{Fe}(\text{s}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in form of hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$).



Factors Which Promote Corrosion

- More active metals are readily corroded.
- Presence of impurities enhance corrosion. Pure metals do not corrode.
- Air and moisture accelerate corrosion. In vacuum, there is no corrosion.
- Corrosion occurs rapidly at bands, scratches, nicks and cuts in the metal.
- Electrolytes also increase the rate of corrosion.

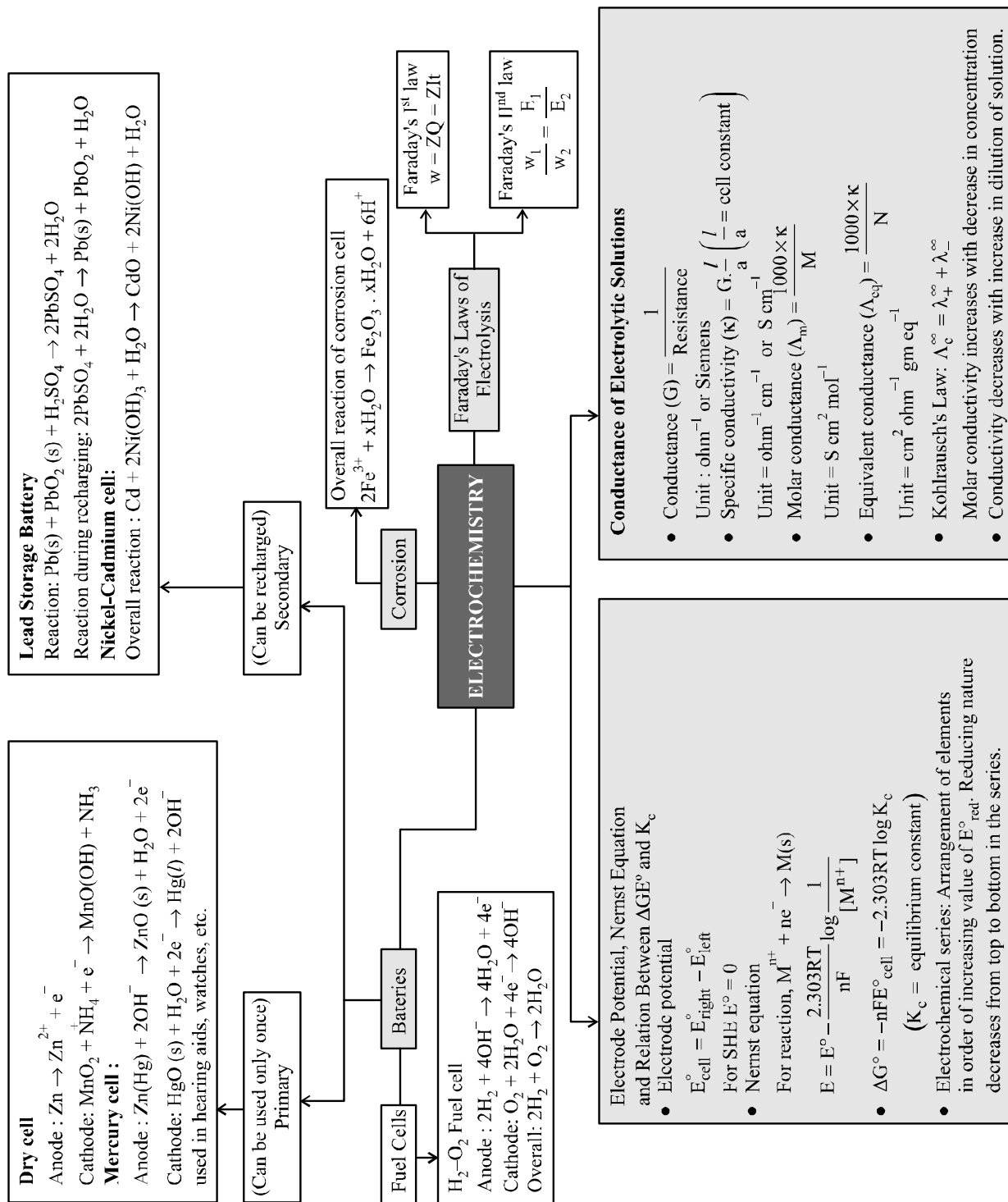
Prevention of Corrosion

- Painting, oiling, greasing (i.e., barrier protection) prevent corrosion
- Covering with a layer of more reactive metal (called sacrificial protection). For ex: iron is coated with more active zinc. The process is called Galvanisation.
- Coating of iron surface with phosphate or other chemicals which forms a protective, tough, adherent in soluble film.

Note:

- Iron in contact with a solution whose pH is above 9-10 does not corrode. This is because H^+ ions are involved in the reduction of O_2 . As concentration of H^+ decreases, i.e., pH is increased, the reduction of O_2 becomes less favourable.
- If water is saline, it helps in the flow of current in the miniature cell and hence enhances the process of corrosion.
- Rust is formed at a site other than the site where pitting has occurred.
- Iron corrodes more rapidly than it does in the absence of copper and tin. This is because when iron is coated with copper or tin; if the coating is broken, iron is exposed and it being more reactive than both copper and tin, gets corroded.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- The amount of chlorine evolved by passing 2A of current in aq. solution of NaCl for 30 minutes is :
 (a) 0.84 gm (b) 1.32 gm
 (c) 3.34 gm (d) 5.47 gm
 - The conjugate acid of NH_3 is :
 (a) NH_4^+ (b) NH_2OH
 (c) NH_3 (d) N_2H_4
 - If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4 cm^{-1} , then its molar conductance in $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ is
 (a) 10^2 (b) 10^4
 (c) 10 (d) 10^3
 - Specific conductance of a 0.1 N KCl solution at 23°C is $0.012 \text{ ohm}^{-1} \text{ cm}^{-1}$. Resistance of cell containing the solution at same temperature was found to be 55 ohm. The cell constant is
 (a) 0.0616 cm^{-1} (b) 0.66 cm^{-1}
 (c) 6.60 cm^{-1} (d) 660 cm^{-1}
 - The highest electrical conductivity of the following aqueous solutions is of
 (a) 0.1 M difluoroacetic acid (b) 0.1 M fluoroacetic acid
 (c) 0.1 M chloroacetic acid (d) 0.1 M acetic acid
 - When an electric current of 0.5 ampere is passed through acidulated water for two hours, then volume of hydrogen (H_2) at NTP produced will be (1 Coulomb of electricity deposits 0.00001 gm of hydrogen)
 (a) 0.1 litre (b) 0.6 litre
 (c) 0.4 litre (d) 0.8 litre
- | Electrolyte: | KCl | KNO ₃ | HCl | NaOAc | NaCl |
|---|-------|------------------|-------|-------|-------|
| $\Lambda^\infty (\text{S cm}^2 \text{ mol}^{-1})$: | 149.9 | 145 | 426.2 | 91 | 126.5 |
- Calculate $\Lambda^\infty_{\text{HOAc}}$ using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C
 (a) 217.5 (b) 390.7
 (c) 552.7 (d) 517.2
- The unit of equivalent conductivity is
 (a) ohm cm
 (b) $\text{ohm}^{-1} \text{ cm}^2 (\text{g equivalent})^{-1}$
 (c) $\text{ohm cm}^2 (\text{g equivalent})$
 (d) S cm^{-2}
 - The resistance of 0.01 N solution of an electrolyte was found to be 220 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm^{-1} . The value of equivalent conductance of solution is –
 (a) $400 \text{ mho cm}^2 \text{ g eq}^{-1}$ (b) $295 \text{ mho cm}^2 \text{ g eq}^{-1}$
 (c) $419 \text{ mho cm}^2 \text{ g eq}^{-1}$ (d) $425 \text{ mho cm}^2 \text{ g eq}^{-1}$
 - How much chlorine will be liberated on passing one ampere current for 30 min. through NaCl solution?
 (a) 0.66 mole (b) 0.33 mole
 (c) 0.66 g (d) 0.33 g
 - A 0.5 M NaOH solution offers a resistance of 31.6 ohm in a conductivity cell at room temperature. What shall be the approximate molar conductance of this NaOH solution if cell constant of the cell is 0.367 cm^{-1} .
 (a) $234 \text{ S cm}^2 \text{ mole}^{-1}$ (b) $23.2 \text{ S cm}^2 \text{ mole}^{-1}$
 (c) $4645 \text{ S cm}^2 \text{ mole}^{-1}$ (d) $5464 \text{ S cm}^2 \text{ mole}^{-1}$
 - For the electrochemical cell,
 $\text{M} | [\text{M}^+ || \text{X}^- | \text{X}]$, $E^\circ(\text{M}^+/\text{M}) = 0.44 \text{ V}$ and $E^\circ(\text{X}/\text{X}^-) = 0.33 \text{ V}$. From this data one can deduce that:
 (a) $\text{M} + \text{X} \longrightarrow \text{M}^+ + \text{X}^-$ is spontaneous reaction
 (b) $\text{M}^+ + \text{X}^- \longrightarrow \text{M} + \text{X}$ is spontaneous reaction
 (c) $E_{\text{cell}} = 0.77 \text{ V}$
 (d) $E_{\text{cell}} = -0.77 \text{ V}$
 - If 0.5 amp current is passed through acidified silver nitrate solution for 100 minutes. The mass of silver deposited on cathode, is (eq. wt. of silver nitrate = 108)
 (a) 2.3523 g (b) 3.3575 g
 (c) 5.3578 g (d) 6.3575 g
 - Using same quantity of current, which among Na, Mg, and Al is deposited to the highest extent during electrolysis.
 (a) Mg (b) Al
 (c) Na (d) All in same amount
 - Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is– $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$
 To prepare 5.12 kg of aluminium metal by this method we require electricity of
 (a) $5.49 \times 10^1 \text{ C}$ (b) $5.49 \times 10^4 \text{ C}$
 (c) $1.83 \times 10^7 \text{ C}$ (d) $5.49 \times 10^7 \text{ C}$
 - When electric current is passed through acidified water, 112 ml of hydrogen gas at STP collected at the cathode in 965 seconds. The current passed in amperes is
 (a) 1.0 (b) 0.5
 (c) 0.1 (d) 2.0
 - An electrolytic cell contains a solution of Ag_2SO_4 and has platinum electrodes. A current is passed until 1.6 gm of O_2 has been liberated at anode. The amount of silver deposited at cathode would be
 (a) 107.88 gm (b) 1.6 gm
 (c) 0.8 gm (d) 21.60 gm
 - Which of the following will form a cell with the highest voltage?
 (a) 0.1 M Ag^+ , 2 M Co^{2+} (b) 2 M Ag^+ , 0.1 M Co^{2+}
 (c) 1 M Ag^+ , 1 M Co^{2+} (d) 2 M Ag^+ , 2 M Co^{2+}
 - When 9650 coulombs of electricity is passed through a solution of copper sulphate, the amount of copper deposited is (given at. wt. of Cu = 63.6)
 (a) 0.318 g (b) 3.18 g
 (c) 31.8 g (d) 63.6 g

20. Find the charge in coulombs required to convert 0.2 mole VO_3^{-2} into VO_4^{-3} –
 (a) 1.93×10^4 (b) 9.65×10^4
 (c) 1.93×10^5 (d) 9.65×10^5
21. Iron pipes, lying in acidic soil, are often attached to the blocks of magnesium for their protection from rusting, because magnesium :
 (a) is lighter than iron
 (b) is readily converted into positive ion
 (c) forms a corrosion-resistant alloy with iron
 (d) prevents air from reaching the surface of iron
22. A silver cup is plated with silver by passing 965 coulombs of electricity. The amount of Ag deposited is :
 (a) 107.89 g (b) 9.89 g
 (c) 1.0002 g (d) 1.08 g
23. Total charge on 1 mole of a monovalent metal ion is equal to
 (a) 9.65×10^4 coulombs (b) 1.6×10^{-19} coulombs
 (c) 6.2×10^{18} coulombs (d) None of these
24. On passing current through two cells, connected in series containing solution of AgNO_3 and CuSO_4 , 0.18 g of Ag is deposited. The amount of the Cu deposited is:
 (a) 0.529 g (b) 10.623 g
 (c) 0.0529 g (d) 1.2708 g
25. How many atoms of calcium will be deposited from a solution of CaCl_2 by a current of 25 mA flowing for 60 seconds?
 (a) 4.68×10^{18} (b) 4.68×10^{15}
 (c) 4.68×10^{12} (d) 4.68×10^9
26. To deposit one equivalent weight of silver at cathode, the charge required will be
 (a) $9.65 \times 10^4 \text{ C}$ (b) $9.65 \times 10^3 \text{ C}$
 (c) $9.65 \times 10^5 \text{ C}$ (d) $9.65 \times 10^7 \text{ C}$
27. In the electrolysis of water, one faraday of electrical energy would liberate
 (a) one mole of oxygen
 (b) one gram atom of oxygen
 (c) 8 g oxygen
 (d) 22.4 lit. of oxygen
28. When an acid cell is charged, then :
 (a) voltage of cell increases
 (b) electrolyte of cell dilutes
 (c) resistance of cell increases
 (d) none of the above
29. The volume of oxygen gas liberated at NTP by passing a current of 9650 coulombs through acidified water is :
 (a) 1.12 litre (b) 2.24 litre
 (c) 11.2 litre (d) 22.4 litre
30. Three faradays electricity was passed through an aqueous solution of iron (II) bromide. The weight of iron metal (at. wt = 65) deposited at the cathode (in gm) is
 (a) 56 (b) 84
 (c) 112 (d) 168
31. On passing C ampere of electricity through a electrolyte solution for t second. m gram metal deposits on cathode. The equivalent weight E of the metal is
 (a) $E = \frac{C \times t}{m \times 96500}$ (b) $E = \frac{C \times m}{t \times 96500}$
 (c) $E = \frac{96500 \times m}{C \times t}$ (d) $E = \frac{C \times t \times 96500}{m}$
32. What is the time (in sec) required for depositing all the silver present in 125 mL of 1 M AgNO_3 solution by passing a current of 241.25 A? (1 F = 96500 C)
 (a) 10 (b) 50
 (c) 1000 (d) 100
33. The number of electrons passing per second through a cross-section of copper wire carrying 10^{-6} amperes of current per second is found to be
 (a) 1.6×10^{-19} (b) 6×10^{-35}
 (c) 6×10^{-16} (d) 6×10^{12}
34. What is the E°_{cell} for the reaction
 $\text{Cu}^{2+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightleftharpoons \text{Cu}(\text{s}) + \text{Sn}^{4+}(\text{aq})$
 at 25°C if the equilibrium constant for the reaction is 1×10^6 ?
 (a) 0.5328 V (b) 0.3552 V
 (c) 0.1773 V (d) 0.7104 V
35. Which of the following reaction is possible at anode?
 (a) $2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$
 (b) $\text{F}_2 \rightarrow 2\text{F}^-$
 (c) $(1/2) \text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}$
 (d) None of these.
36. In electrolysis of dilute H_2SO_4 , what is liberated at anode?
 (a) H_2 (b) SO_4^{2-}
 (c) SO_2 (d) O_2
37. The reference electrode is made by using
 (a) ZnCl_2 (b) CuSO_4
 (c) HgCl_2 (d) Hg_2Cl_2
38. The standard hydrogen electrode potential is zero, because
 (a) hydrogen oxidized easily
 (b) electrode potential is considered as zero
 (c) hydrogen atom has only one electron
 (d) hydrogen is a very light element
39. The element that is easiest to be reduced:
 (a) Ag (b) Fe
 (c) Cu (d) Sn
40. Which one is not called a anode reaction from the following
 (a) $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$ (b) $\text{Cu} \rightarrow \text{Cu}^{++} + 2\text{e}^-$
 (c) $\text{Hg}^+ \rightarrow \text{Hg}^{++} + \text{e}^-$ (d) $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$
41. The chemical reaction,
 $2\text{AgCl}_{(\text{s})} + \text{H}_{2(\text{g})} \longrightarrow 2\text{HCl}_{(\text{aq})} + 2\text{Ag}_{(\text{s})}$
 taking place in a galvanic cell is represented by the notation
 (a) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1\text{M}\text{KCl}_{(\text{aq})} | \text{AgCl}_{(\text{s})} | \text{Ag}_{(\text{s})}$
 (b) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1\text{M}\text{HCl}_{(\text{aq})} | 1\text{M}\text{Ag}^+_{(\text{aq})} | \text{Ag}_{(\text{s})}$
 (c) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1\text{M}\text{HCl}_{(\text{aq})} | \text{AgCl}_{(\text{s})} | \text{Ag}_{(\text{s})}$
 (d) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1\text{M}\text{HCl}_{(\text{aq})} | \text{Ag}_{(\text{s})} | \text{AgCl}_{(\text{s})}$

42. The cell reaction $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$ is best represented by
- $\text{Cu}(s) | \text{Cu}^{2+}(aq) || \text{Ag}^+(aq) | \text{Ag}(s)$
 - $\text{Pt} | \text{Cu}^{2+} || \text{Ag}^+(aq) | \text{Ag}(s)$
 - $\text{Cu}^{2+} | \text{Cu} || \text{Pt} | \text{Ag}$
 - None of the above representations
43. The resistance of 1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant 1.15 cm^{-1} . The equivalent conductance (in $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$) of 1 N acetic acid will be
- 4.6
 - 9.2
 - 18.4
 - 0.023
44. Specific conductance of 0.1 M HNO_3 is 6.3×10^{-2} . The molar conductance of the solution is
- $100 \text{ ohm}^{-1} \text{ cm}^2$
 - $515 \text{ ohm}^{-1} \text{ cm}^2$
 - $630 \text{ ohm}^{-1} \text{ cm}^2$
 - $6300 \text{ ohm}^{-1} \text{ cm}^2$
45. Which of the following statements about galvanic cell is incorrect
- anode is positive
 - oxidation occurs at the electrode with lower reduction potential
 - cathode is positive
 - reduction occurs at cathode
46. Which of the following reactions occurs at the cathode?
- $\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + 2e^-$
 - $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$
 - $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$
 - $2\text{OH}^- \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2e^-$
47. At 298K the standard free energy of formation of $\text{H}_2\text{O}(\ell)$ is -237.20 kJ/mole while that of its ionisation into H^+ ion and hydroxyl ions is 80 kJ/mole , then the emf of the following cell at 298 K will be [Take Faraday constant $F = 96500 \text{ C}$]
- $$\text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(1\text{M}) || \text{OH}^-(1\text{M}) | \text{O}_2(\text{g}, 1 \text{ bar})$$
- 0.40V
 - 0.81V
 - 1.23 V
 - 0.40 V
48. If the following half cells have E° values as
- $$\text{A}^{3+} + e^- \longrightarrow \text{A}^{2+}, E^\circ = y_2 \text{ V}$$
- $$\text{A}^{2+} + 2e^- \longrightarrow \text{A}, E^\circ = -y_1 \text{ V}$$
- The E° of the half cell $\text{A}^{3+} + 3e^- \longrightarrow \text{A}$ will be
- $\frac{2y_1 - y_2}{3}$
 - $\frac{y_2 - 2y_1}{3}$
 - $2y_1 - 3y_2$
 - $y_2 - 2y_1$
49. To deposit 0.634 g of copper by electrolysis of aqueous cupric sulphate solution, the amount of electricity required (in coulombs) is
- 1930
 - 3960
 - 4825
 - 9650
50. Without losing its concentration ZnCl_2 solution cannot be kept in contact with
- Au
 - Al
 - Pb
 - Ag
51. $\text{Cu}^+(aq)$ is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction :
- $$2\text{Cu}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{Cu}(s)$$
- choose correct E° for given reaction if $E^\circ \text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$ and $E^\circ \text{Cu}^+/\text{Cu} = 0.15 \text{ V}$
- 0.38 V
 - +0.49 V
 - +0.38 V
 - 0.19 V
52. In the silver plating of copper, $\text{K}[\text{Ag}(\text{CN})_2]$ is used instead of AgNO_3 . The reason is
- a thin layer of Ag is formed on Cu
 - more voltage is required
 - Ag^+ ions are completely removed from solution
 - less availability of Ag^+ ions, as Cu cannot displace Ag from $[\text{Ag}(\text{CN})_2]^-$ ion
53. On passing electric current of one ampere for 16 min and 5 sec through one litre solution of CuCl_2 , all copper of solution was deposited at cathode. The strength of CuCl_2 solution was (molar mass of Cu = 63.5, Faraday constant = 96500 C/mol):
- 0.2 N
 - 0.01 N
 - 0.1 N
 - 0.02 N
54. The standard e.m.f. of a galvanic cell involving cell reaction with $n = 2$ is found to be 0.295 V at 25°C . The equilibrium constant of the reaction would be (Given $F = 96500 \text{ C mol}^{-1}$; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)
- 2.0×10^{11}
 - 4.0×10^{12}
 - 1.0×10^2
 - 1.0×10^{10}
55. What will be the emf for the given cell
- $$\text{Pt} | \text{H}_2(P_1) | \text{H}^+(aq) || \text{H}_2(P_2) | \text{Pt}$$
- $\frac{RT}{F} \log_e \frac{P_1}{P_2}$
 - $\frac{RT}{2F} \log_e \frac{P_1}{P_2}$
 - $\frac{RT}{F} \log_e \frac{P_2}{P_1}$
 - None of these.
56. In a cell that utilises the reaction
- $$\text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(\text{g})$$
- addition of H_2SO_4 to cathode compartment, will
- increase the E and shift equilibrium to the right
 - lower the E and shift equilibrium to the right
 - lower the E and shift equilibrium to the left
 - increase the E and shift equilibrium to the left
57. The same amount of electricity was passed through two cells containing molten Al_2O_3 and molten NaCl. If 1.8 g of Al were liberated in one cell, the amount of Na liberated in other cell is:
- 2.8 g
 - 3.2 g
 - 4.6 g
 - 6.8 g
58. According to Nernst equation, which is not correct if $Q = K_c$:
- $E_{\text{cell}} = 0$
 - $\frac{RT}{nF} \ln Q = E_{\text{cell}}^\circ$
 - $K_c = e^{\frac{nFE_{\text{cell}}^\circ}{RT}}$
 - $E_{\text{cell}} = E_{\text{cell}}^\circ$

59. The volume of oxygen gas liberated at NTP by passing a current of 9650 coulombs through acidified water is :
 (a) 1.12 litre (b) 2.24 litre
 (c) 11.2 litre (d) 22.4 litre
60. The emf of the cell
 $\text{Ni} | \text{Ni}^{2+} (1.0 \text{ M}) || \text{Au}^{3+} (1.0 \text{ M}) | \text{Au}$ is
 [Given $E^\circ \text{Ni}^{2+} / \text{Ni} = -0.25 \text{ V}$ and $E^\circ \text{Au}^{3+} / \text{Au} = +1.5 \text{ V}$]
 (a) 2.00 V (b) 1.25 V
 (c) -1.25 V (d) 1.75 V
61. What is the e.m.f for the given cell ?
 $\text{Cr} | \text{Cr}^{3+} (1.0 \text{ M}) || \text{Co}^{2+} (1.0 \text{ M}) | \text{Co}$
 $(E^\circ \text{ for } \text{Cr}^{3+} / \text{Cr} = -0.74 \text{ volt and } E^\circ \text{ for } \text{Co}^{2+} / \text{Co} = -0.28 \text{ volt})$
 (a) -0.46 volt (b) -1.02 volt
 (c) +0.46 volt (d) 1.66 volt
62. If a salt bridge is removed between the two half cells, the voltage
 (a) Drops to zero (b) Does not change
 (c) Increase gradually (d) Increases rapidly
63. The standard emf of a cell, involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is ($F = 96500 \text{ C mol}^{-1}$)
 (a) 1.0×10^1 (b) 1.0×10^5
 (c) 1.0×10^{10} (d) 1.0×10^{30}
64. Given the electrode potentials
 $\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}, E^\circ = 0.771 \text{ volts}$
 $\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-, E^\circ = 0.536 \text{ volts}$
 E°_{cell} for the cell reaction
 $2\text{Fe}^{3+} + 2\text{I}^- \longrightarrow 2\text{Fe}^{2+} + \text{I}_2$, is
 (a) 1.006 V (b) 0.503 V
 (c) 0.235 V (d) -0.235 V
65. For the galvanic cell
 $\text{Zn} | \text{Zn}^{2+} (0.1 \text{ M}) || \text{Cu}^{2+} (1.0 \text{ M}) | \text{Cu}$ the cell potential increase if
 (a) $[\text{Zn}^{2+}]$ is increased
 (b) $[\text{Cu}^{2+}]$ is increased
 (c) $[\text{Cu}^{2+}]$ is decreased
 (d) surface area of anode is increased
66. Adding powered lead and iron to a solution that is 1.0 M in both Pb^{2+} and Fe^{2+} ions, would result in a reaction, in which:
 (a) More iron and Pb^{2+} ions are formed
 (b) More lead and Fe^{2+} ions are formed
 (c) Concentration of both Pb^{2+} and Fe^{2+} ion increases
 (d) There is no net change
67. The standard cell potential of $\text{Zn} | \text{Zn}^{2+} (aq) || \text{Cu}^{2+} (aq) | \text{Cu}$ cell is 1.10 V. The maximum work obtained by this cell will be
 (a) 106.15 kJ (b) -212.30 kJ
 (c) -318.45 kJ (d) -424.60 kJ
68. A hydrogen electrode is immersed in a solution with pH = 0 (HCl). By how much will the potential (reduction) change if an equivalent amount of NaOH is added to the solution. (Take $p_{\text{H}_2} = 1 \text{ atm}$), $T = 298 \text{ K}$.
 (a) increase by 0.41 V (b) increase by 59 mV
 (c) decrease by 0.41 V (d) decrease by 59 mV
69. Following cell has EMF 0.7995V.
 $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{HNO}_3 (1 \text{ M}) || \text{AgNO}_3 (1 \text{ M}) | \text{Ag}$
 If we add enough KCl to the Ag cell so that the final Cl^- is 1M. Now the measured emf of the cell is 0.222V. The K_{sp} of AgCl would be –
 (a) $1 \times 10^{-9.8}$ (b) $1 \times 10^{-19.6}$
 (c) 2×10^{-10} (d) 2.64×10^{-14}
70. $E^\circ = \frac{RT}{nF} \ln K_{\text{eq}}$
 The above equation is called :
 (a) Gibb's equation
 (b) Gibb's-Helmholtz equation
 (c) Nernst equation
 (d) Van der Waal's equation
71. Standard cell voltage for the cell $\text{Pb} | \text{Pb}^{2+} || \text{Sn}^{2+} | \text{Sn}$ is -0.01 V. If the cell is to exhibit $E_{\text{cell}} = 0$, the value of $[\text{Sn}^{2+}] / [\text{Pb}^{2+}]$ should be antilog of –
 (a) +0.3 (b) 0.5
 (c) 1.5 (d) -0.5
72. An electrochemical cell is set up as: $\text{Pt}; \text{H}_2 (1 \text{ atm}) | \text{HCl} (0.1 \text{ M}) || \text{CH}_3\text{COOH} (0.1 \text{ M}) | \text{H}_2 (1 \text{ atm}); \text{Pt}$. The e.m.f of this cell will not be zero, because
 (a) the temperature is constant
 (b) e.m.f depends on molarities of acids used
 (c) acids used in two compartments are different
 (d) pH of 0.1 M HCl and 0.1 M CH_3COOH is not same
73. The quantity of electricity needed to liberate 0.5 gram equivalent of an element is
 (a) 48250 faraday (b) 48250 coulomb
 (c) 19300 faraday (d) 19300 coulomb
74. For the cell reaction,
 $\text{Cu}^{2+} (\text{C}_1, aq) + \text{Zn}(s) \rightarrow \text{Zn}^{2+} (\text{C}_2, aq) + \text{Cu}(s)$ of an electrochemical cell, the change in free energy, ΔG , at a given temperature is a function of
 (a) $\ln (\text{C}_1)$ (b) $\ln (\text{C}_2/\text{C}_1)$
 (c) $\ln (\text{C}_2)$ (d) $\ln (\text{C}_1 + \text{C}_2)$
75. The most durable metal plating on iron to protect against corrosion is
 (a) nickel plating (b) copper plating
 (c) tin plating (d) zinc plating
76. A certain current liberated 0.504 gm of hydrogen in 2 hrs. How many grams of copper can be liberated by the same current flowing for the same time in a copper sulphate solution ?
 (a) 12.7 gms (b) 15.9 gms
 (c) 31.8 gms (d) 63.5 gms
77. Several blocks of magnesium are fixed to the bottom of a ship to
 (a) make the ship lighter
 (b) prevent action of water and salt
 (c) prevent puncturing by under-sea rocks
 (d) keep away the sharks
78. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to
 (a) produce high purity water
 (b) create potential difference between two electrodes
 (c) generate heat
 (d) remove adsorbed oxygen from electrode surfaces

79. During the charging of lead storage battery, the reaction at anode is represented by :
- $\text{Pb}^{2+} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4$
 - $\text{PbSO}_4 + 2\text{H}_2\text{O} \longrightarrow \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$
 - $\text{Pb} \longrightarrow \text{Pb}^{2+} + 2\text{e}^-$
 - $\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$
80. Two electrolytic cells, one containing acidified ferrous chloride and another acidified ferric chloride, are connected in series. The ratio of iron deposited at cathodes in the two cells will be :
- 3 : 1
 - 2 : 1
 - 1 : 1
 - 3 : 2
81. Which colourless gas evolves, when NH_4Cl reacts with zinc in a dry cell battery
- NH_4
 - N_2
 - H_2
 - Cl_2
82. When a lead storage battery is discharged
- SO_2 is evolved
 - Lead sulphate is consumed
 - Lead is formed
 - Sulphuric acid is consumed
83. $\text{Zn}^{2+} \rightarrow \text{Zn}_{(s)}; E^0 = -0.76 \text{ V}$
 $\text{Cu}^{2+} \rightarrow \text{Cu}_{(s)}; E^0 = -0.34 \text{ V}$
 Which of the following is spontaneous?
- $\text{Zn}^{2+} + \text{Cu} \rightarrow \text{Zn} + \text{Cu}^{2+}$
 - $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$
 - $\text{Zn}^{2+} + \text{Cu}^{2+} \rightarrow \text{Zn} + \text{Cu}$
 - None of these
84. The efficiency of a fuel cell is given by
- $\frac{\Delta G}{\Delta S}$
 - $\frac{\Delta G}{\Delta H}$
 - $\frac{\Delta S}{\Delta G}$
 - $\frac{\Delta H}{\Delta G}$
85. The equilibrium constant of the reaction:
 $\text{Cu}(s) + 2\text{Ag}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{Ag}(s); E^0 = 0.46 \text{ V}$ at 298 K is
- 2.0×10^{10}
 - 4.0×10^{10}
 - 4.0×10^{15}
 - 2.4×10^{10}
86. On the basis of the following E^0 values, the strongest oxidizing agent is :
- $$[\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + \text{e}^-; E^0 = -0.35 \text{ V}$$
- $$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-; E^0 = -0.77 \text{ V}$$
- $[\text{Fe}(\text{CN})_6]^{4-}$
 - Fe^{2+}
 - Fe^{3+}
 - $[\text{Fe}(\text{CN})_6]^{3-}$
87. Kohlrausch's law states that at :
- finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.
 - infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte.
 - infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.
 - infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.
88. Standard free energies of formation (in kJ/mol) at 298 K are -237.2 , -394.4 and -8.2 for $\text{H}_2\text{O}(l)$, $\text{CO}_2(g)$ and pentane (g), respectively. The value E^0_{cell} for the pentane-oxygen fuel cell is :
- 1.968 V
 - 2.0968 V
 - 1.0968 V
 - 0.0968 V
89. Given:
- $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}, E^0 = 0.337 \text{ V}$
 - $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+, E^0 = 0.153 \text{ V}$
- Electrode potential, E^0 for the reaction, $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$, will be :
- 0.90 V
 - 0.30 V
 - 0.38 V
 - 0.52 V
90. Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 amperes of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency. At. mass of Al = 27 g mol^{-1})
- $8.1 \times 10^4 \text{ g}$
 - $2.4 \times 10^5 \text{ g}$
 - $1.3 \times 10^4 \text{ g}$
 - $9.0 \times 10^3 \text{ g}$
91. The equivalent conductance of $\frac{M}{32}$ solution of a weak monobasic acid is 8.0 mho cm^2 and at infinite dilution is 400 mho cm^2 . The dissociation constant of this acid is:
- 1.25×10^{-6}
 - 6.25×10^{-4}
 - 1.25×10^{-4}
 - 1.25×10^{-5}
92. For the reduction of silver ions with copper metal, the standard cell potential was found to be $+0.46 \text{ V}$ at 25°C . The value of standard Gibbs energy, ΔG^0 will be ($F = 96500 \text{ C mol}^{-1}$)
- -89.0 kJ
 - -89.0 J
 - -44.5 kJ
 - -98.0 kJ
93. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to:
- increase in ionic mobility of ions
 - 100% ionisation of electrolyte at normal dilution
 - increase in both i.e. number of ions and ionic mobility of ions
 - increase in number of ions
94. Which of the following expressions correctly represents the equivalent conductance at infinite dilution of $\text{Al}_2(\text{SO}_4)_3$, Given that $\Lambda_{\text{Al}^{3+}}^0$ and $\Lambda_{\text{SO}_4^{2-}}^0$ are the equivalent conductances at infinite dilution of the respective ions?
- $\frac{1}{3}\Lambda_{\text{Al}^{3+}}^0 + \frac{1}{2}\Lambda_{\text{SO}_4^{2-}}^0$
 - $2\Lambda_{\text{Al}^{3+}}^0 + 3\Lambda_{\text{SO}_4^{2-}}^0$
 - $\Lambda_{\text{Al}^{3+}}^0 + \Lambda_{\text{SO}_4^{2-}}^0$
 - $(\Lambda_{\text{Al}^{3+}}^0 + \Lambda_{\text{SO}_4^{2-}}^0) \times 6$

95. Consider the following relations for emf of an electrochemical cell:

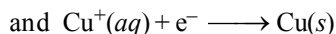
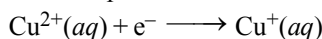
- (i) $\text{emf of cell} = (\text{Oxidation potential of anode}) - (\text{Reduction potential of cathode})$
 (ii) $\text{emf of cell} = (\text{Oxidation potential of anode}) + (\text{Reduction potential of cathode})$
 (iii) $\text{emf of cell} = (\text{Reduction potential of anode}) + (\text{Reduction potential of cathode})$
 (iv) $\text{emf of cell} = (\text{Oxidation potential of anode}) - (\text{Oxidation potential of cathode})$

Which of the above relations are correct?

- (a) (ii) and (iv) (b) (iii) and (i)
 (c) (i) and (ii) (d) (iii) and (iv)
96. Standard electrode potential of three metals X, Y and Z are -1.2 V , $+0.5\text{ V}$ and -3.0 V , respectively. The reducing power of these metals will be :

- (a) $Y > Z > X$ (b) $X > Y > Z$
 (c) $Z > X > Y$ (d) $X > Y > Z$

97. The electrode potentials for



are $+0.15\text{ V}$ and $+0.50$, respectively. The value of $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$ will be :

- (a) 0.500 V (b) 0.325 V
 (c) 0.650 V (d) 0.150 V

98. Standard electrode potential for $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is $+0.15\text{ V}$ and that for the Cr^{3+}/Cr couple is -0.74 V . These two couples in their standard state are connected to make a cell. The cell potential will be :

- (a) $+1.19\text{ V}$ (b) $+0.89\text{ V}$
 (c) $+0.18\text{ V}$ (d) $+1.83\text{ V}$

99. If the E°_{cell} for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG° and K_{eq} ?

- (a) $\Delta G^{\circ} > 0$; $K_{\text{eq}} > 1$ (b) $\Delta G^{\circ} < 0$; $K_{\text{eq}} > 1$
 (c) $\Delta G^{\circ} < 0$; $K_{\text{eq}} < 1$ (d) $\Delta G^{\circ} > 0$; $K_{\text{eq}} < 1$

100. Limiting molar conductivity of NH_4OH

(i.e., $\Lambda^{\circ}_{\text{m}}(\text{NH}_4\text{OH})$) is equal to :

- (a) $\Lambda^{\circ}_{\text{m}}(\text{NH}_4\text{Cl}) + \Lambda^{\circ}_{\text{m}}(\text{NaCl}) - \Lambda^{\circ}_{\text{m}}(\text{NaOH})$
 (b) $\Lambda^{\circ}_{\text{m}}(\text{NaOH}) + \Lambda^{\circ}_{\text{m}}(\text{NaCl}) - \Lambda^{\circ}_{\text{m}}(\text{NH}_4\text{Cl})$
 (c) $\Lambda^{\circ}_{\text{m}}(\text{NH}_4\text{OH}) + \Lambda^{\circ}_{\text{m}}(\text{NH}_4\text{Cl}) - \Lambda^{\circ}_{\text{m}}(\text{HCl})$
 (d) $\Lambda^{\circ}_{\text{m}}(\text{NH}_4\text{Cl}) + \Lambda^{\circ}_{\text{m}}(\text{NaOH}) - \Lambda^{\circ}_{\text{m}}(\text{NaCl})$

EXERCISE - 2

Applied Questions

- Molar conductances of BaCl_2 , H_2SO_4 and HCl at infinite dilutions are x_1 , x_2 and x_3 respectively. Equivalent conductance of BaSO_4 at infinite dilution will be :
 (a) $(x_1 + x_2 - x_3)/2$ (b) $x_1 + x_2 - 2x_3$
 (c) $(x_1 - x_2 - x_3)/2$ (d) $(x_1 + x_2 - 2x_3)/2$
- Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is $100\ \Omega$. The conductivity of this solution is 1.29 S m^{-1} . Resistance of the same cell when filled with 0.02 M of the same solution is $520\ \Omega$. The molar conductivity of 0.02 M solution of electrolyte will be
 (a) $1.24 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}$ (b) $12.4 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}$
 (c) $124 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}$ (d) $1240 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}$
- What is the amount of chlorine evolved when 2 amperes of current is passed for 30 minutes in an aqueous solution of NaCl ?
 (a) 66 g (b) 1.32 g
 (c) 33 g (d) 99 g
- A galvanic cell is set up from electrodes A and B
 Electrode A: $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$, $E^{\circ}_{\text{red}} = +1.33\text{ V}$
 Electrode B: $\text{Fe}^{3+}/\text{Fe}^{2+}$, $E^{\circ}_{\text{red}} = 0.77\text{ V}$
 Which of the following statements is false ?
 (a) Standard e.m.f. of the cell is 0.56 V
 (b) Current will flow from electrode A to B in the external circuit
 (c) A will act as cathode and have positive polarity
 (d) None of these
- The electric charge for electrode decomposition of one gram equivalent of a substance is
 (a) one ampere per second
 (b) $96500\text{ coulombs per second}$
 (c) one ampere for one hour
 (d) charge on one mole of electrons
- On passing a current of 1.0 ampere for 16 min and 5 sec through one litre solution of CuCl_2 , all copper of the solution was deposited at cathode. The strength of CuCl_2 solution was (Molar mass of $\text{Cu} = 63.5$; Faraday constant = $96,500\text{ C mol}^{-1}$)
 (a) 0.01 N (b) 0.01 M
 (c) 0.02 M (d) 0.2 N
- In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam. This is because
 (a) Hg is more inert than Pt
 (b) more voltage is required to reduce H^{+} at Hg than at Pt
 (c) Na is dissolved in Hg while it does not dissolve in Pt
 (d) conc. of H^{+} ions is larger when Pt electrode is taken

8. Given : $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^- \quad E^\circ = -1.09 \text{ V}$;
 $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^- \quad E^\circ = 0.54 \text{ V}$
 $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe} \quad E^\circ = -0.44 \text{ V}$
 Which of the following reactions will not be spontaneous?
 (a) $\text{Fe} + \text{Br}_2 \rightarrow \text{FeBr}_2$ (b) $\text{Fe} + \text{I}_2 \rightarrow \text{FeI}_2$
 (c) $\text{I}_2 + 2\text{Br}^- \rightarrow 2\text{I}^- + \text{Br}_2$ (d) $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$
9. $\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+} \quad E^\circ = 0.13 \text{ V}$
 $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^- \quad E^\circ = 1.08 \text{ V}$
 Calculate K_{eq} for the cell formed by two electrodes
 (a) 10^{41} (b) 10^{32}
 (c) 10^{-32} (d) 10^{-42}
10. The e.m.f. of a Daniell cell at 298 K is E_1 .

$$\text{Zn} \left| \text{ZnSO}_4 (0.01 \text{ M}) \right| \left| \text{CuSO}_4 (1.0 \text{ M}) \right| \text{Cu}$$

 When the concentration of ZnSO_4 is 1.0 M and that of CuSO_4 is 0.01 M, the e.m.f. changed to E_2 . What is the relationship between E_1 and E_2 ?
 (a) $E_2 = 0 \neq E_1$ (b) $E_1 > E_2$
 (c) $E_1 < E_2$ (d) $E_1 = E_2$
11. Sodium is made by the electrolysis of a molten mixture of about 40% NaCl and 60% CaCl_2 because
 (a) CaCl_2 helps in conduction of electricity
 (b) this mixture has a lower melting point than NaCl
 (c) Ca^{++} can displace Na from NaCl
 (d) Ca^{++} can reduce NaCl to Na
12. In anodising :
 (a) The metal ion present in electrolyte gets reduced and a film of metal gets coated on the surface of metal cathode
 (b) The anode metal gets oxidised to form a metal oxide coat
 (c) both the above are correct
 (d) none of the above is correct
13. At 25°C , the molar conductance at infinite dilution for the strong electrolytes NaOH, NaCl and BaCl_2 are 248×10^{-4} , 126×10^{-4} and $280 \times 10^{-4} \text{ Sm}^2\text{mol}^{-1}$ respectively. $\Lambda_m^0 \text{Ba(OH)}_2$ in $\text{Sm}^2\text{mol}^{-1}$ is
 (a) 52.4×10^{-4} (b) 524×10^{-4}
 (c) 402×10^{-4} (d) 262×10^{-4}
14. The specific conductance of a 0.1 N KCl solution at 23°C is $0.012 \text{ ohm}^{-1}\text{cm}^{-1}$. The resistance of cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be
 (a) 0.142 cm^{-1} (b) 0.66 cm^{-1}
 (c) 0.918 cm^{-1} (d) 1.12 cm^{-1}
15. A solution containing one mole per litre of each $\text{Cu(NO}_3)_2$, AgNO_3 , $\text{Hg}_2(\text{NO}_3)_2$ and $\text{Mg(NO}_3)_2$, is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are $\text{Ag}^+ / \text{Ag} = +0.80$, $\text{Hg}_2^{2+} / 2\text{Hg} = +0.79$, $\text{Cu}^{2+} / \text{Cu} = +0.34$, $\text{Mg}^{2+} / \text{Mg}$

$= -2.37$ with increasing voltage, the sequence of deposition of metals on the cathode will be

- (a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
 (c) Ag, Hg, Cu (d) Cu, Hg, Ag
16. The e.m.f. of the cell $\text{Zn} | \text{Zn}^{2+} (0.01\text{M}) || \text{Fe}^{2+} (0.001\text{M}) | \text{Fe}$ at 298 K is 0.2905 then the value of equilibrium for the cell reaction is
 (a) $\frac{0.32}{e^{0.0295}}$ (b) $\frac{0.32}{10^{0.0295}}$
 (c) $\frac{0.26}{10^{0.0295}}$ (d) $\frac{0.32}{10^{0.0591}}$
17. Aluminium displaces hydrogen from acids but copper does not. A galvanic cell prepared by combining Cu / Cu^{2+} and Al / Al^{3+} has an e.m.f. of 2.0 V at 298 K. If the potential of copper electrode is +0.34 V, that of aluminium is
 (a) +1.66 V (b) -1.66 V
 (c) +2.34 V (d) -2.3 V
18. 1.0 L each of a buffer containing 1 mole NH_3 and 1 mol of NH_4^+ were placed in the cathodic and anodic half-cells and 965 C of electricity was passed. If anodic and cathodic half cells reactions involve oxidation and reduction of water only as

$$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 - 4\text{e}^-$$

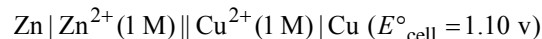
$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$

 Then pH of
 (a) cathodic solution will increase
 (b) anodic solution will decrease
 (c) both the solutions will remain practically constant
 (d) both the solutions will increase
19. A gas X at 1 atm is bubbled through a solution containing a mixture of 1M Y^- and 1M Z^- at 25°C . If the reduction potential of $\text{Z} > \text{Y} > \text{X}$, then
 (a) Y will oxidize X and not Z
 (b) Y will oxidize Z and not X
 (c) Y will oxidize both X and Z
 (d) Y will reduce both X and Z
20. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$
 To prepare 5.12 kg of aluminium metal by this method would require
 (a) $5.49 \times 10^7 \text{ C}$ of electricity
 (b) $1.83 \times 10^7 \text{ C}$ of electricity
 (c) $5.49 \times 10^4 \text{ C}$ of electricity
 (d) $5.49 \times 10^1 \text{ C}$ of electricity
21. At pH = 2, E° (quinhydron) = 1.30 V, E (quinhydron) will be

$$\text{C}_6\text{H}_4(\text{OH})_2 \rightleftharpoons \text{C}_6\text{H}_4(\text{O})_2 + 2\text{H}^+ + 2\text{e}^-$$

 (a) 1.20 V (b) 1.42 V
 (c) 1.36 V (d) 1.30 V

22. The cell,

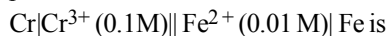


was allowed to be completely discharged at 298 K. The

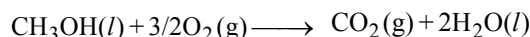
relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$ is

- (a) 9.65×10^4 (b) $\text{antilog}(24.08)$
 (c) 37.3 (d) $10^{37.3}$
23. Given $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.72 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.42 \text{ V}$. The

potential for the cell

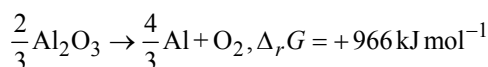


- (a) 0.26 V (b) 0.336 V
 (c) -0.339 (d) 0.26 V
24. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is



At 298 K standard Gibb's energies of formation for $\text{CH}_3\text{OH}(l)$, $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ are -166.2 , -237.2 and $-394.4 \text{ kJ mol}^{-1}$ respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be:

- (a) 87% (b) 90%
 (c) 97% (d) 80%
25. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :



The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least

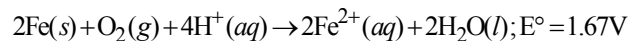
- (a) 4.5 V (b) 3.0 V
 (c) 2.5 V (d) 5.0 V
26. The correct order of $E^\circ_{\text{M}^{2+}/\text{M}}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is

- (a) $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$ (b) $\text{Cr} < \text{Fe} > \text{Mn} > \text{Co}$
 (c) $\text{Fe} > \text{Mn} > \text{Cr} > \text{Co}$ (d) $\text{Cr} > \text{Mn} > \text{Fe} > \text{Co}$

27. The reduction potential of hydrogen half-cell will be negative if:

- (a) $p(\text{H}_2) = 1 \text{ atm}$ and $[\text{H}^+] = 2.0 \text{ M}$
 (b) $p(\text{H}_2) = 1 \text{ atm}$ and $[\text{H}^+] = 1.0 \text{ M}$
 (c) $p(\text{H}_2) = 2 \text{ atm}$ and $[\text{H}^+] = 1.0 \text{ M}$
 (d) $p(\text{H}_2) = 2 \text{ atm}$ and $[\text{H}^+] = 2.0 \text{ M}$

28. Consider the following cell reaction:



At $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$, $p(\text{O}_2) = 0.1 \text{ atm}$ and $\text{pH} = 3$, the cell potential at 25°C is

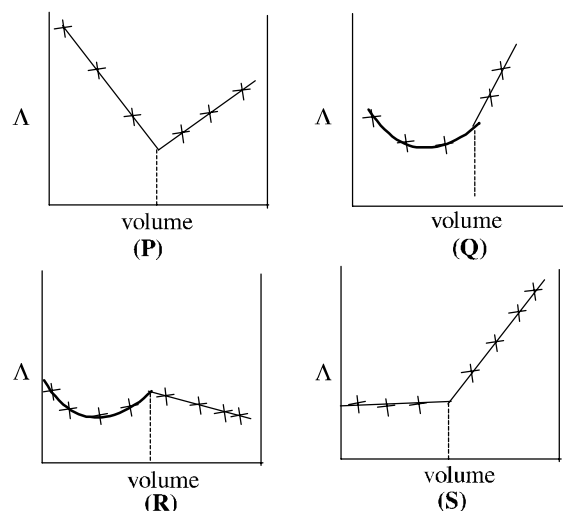
- (a) 1.47 V (b) 1.77 V
 (c) 1.87 V (d) 1.57 V
29. Resistance of 0.2 M solution of an electrolyte is 50Ω . The specific conductance of the solution is 1.3 S m^{-1} . If resistance of the 0.4 M solution of the same electrolyte is 260Ω , its molar conductivity is :
- (a) $6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (b) $625 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 (c) $62.5 \text{ S m}^2 \text{ mol}^{-1}$ (d) $6250 \text{ S m}^2 \text{ mol}^{-1}$

30. The standard reduction potentials for Zn^{2+}/Zn , Ni^{2+}/Ni and Fe^{2+}/Fe are -0.76 , -0.23 and -0.44 V respectively.

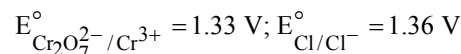
The reaction $\text{X} + \text{Y}^{2+} \longrightarrow \text{X}^{2+} + \text{Y}$ will be spontaneous when :

- (a) $\text{X} = \text{Ni}$, $\text{Y} = \text{Fe}$ (b) $\text{X} = \text{Ni}$, $\text{Y} = \text{Zn}$
 (c) $\text{X} = \text{Fe}$, $\text{Y} = \text{Zn}$ (d) $\text{X} = \text{Zn}$, $\text{Y} = \text{Ni}$
31. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol^{-1})
- (a) $9.65 \times 10^4 \text{ sec}$ (b) $19.3 \times 10^4 \text{ sec}$
 (c) $28.95 \times 10^4 \text{ sec}$ (d) $38.6 \times 10^4 \text{ sec}$
32. $\text{AgNO}_3(aq.)$ was added to an aqueous KCl solution gradually and the conductivity of the solution was measured.

The plot of conductance (Λ) versus the volume of AgNO_3 is



- (a) (P) (b) (Q)
 (c) (R) (d) (S)
33. Given : $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$; $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$



Based on the data given above, strongest oxidising agent will be :

- (a) Cl_2 (b) Cr^{3+}
 (c) Mn^{2+} (d) MnO_4^-
34. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{\text{M}^{3+}/\text{M}^{2+}}$ value ?
- (a) $\text{Cr}(Z=24)$ (b) $\text{Mn}(Z=25)$
 (c) $\text{Fe}(Z=26)$ (d) $\text{Co}(Z=27)$
35. A solution contains Fe^{2+} , Fe^{3+} and I^- ions. This solution was treated with iodine at 35°C . E° for $\text{Fe}^{3+}/\text{Fe}^{2+}$ is $+0.77 \text{ V}$ and E° for $\text{I}_2/2\text{I}^-$ is 0.536 V . The favourable redox reaction is :

- (a) I_2 will be reduced to I^-
 (b) There will be no redox reaction
 (c) I^- will be oxidised to I_2
 (d) Fe^{2+} will be oxidised to Fe^{3+}

36. Standard reduction potentials of the half reactions are given below :
- $$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq}); E^\circ = +2.85 \text{ V}$$
- $$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq}); E^\circ = +1.36 \text{ V}$$
- $$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq}); E^\circ = +1.06 \text{ V}$$
- $$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq}); E^\circ = +0.53 \text{ V}$$
- The strongest oxidising and reducing agents respectively are :
- (a) F_2 and I^- (b) Br_2 and Cl^-
 (c) Cl_2 and Br^- (d) Cl_2 and I_2
37. Molar conductivities (Λ°_{m}) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and $91.0 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Λ°_{m} for CH_3COOH will be :
- (a) $425.5 \text{ S cm}^2 \text{ mol}^{-1}$ (b) $180.5 \text{ S cm}^2 \text{ mol}^{-1}$
 (c) $290.8 \text{ S cm}^2 \text{ mol}^{-1}$ (d) $390.5 \text{ S cm}^2 \text{ mol}^{-1}$
38. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below :
- $$\Lambda^\circ_{\text{CH}_3\text{COONa}} = 91.0 \text{ S cm}^2 / \text{equiv.}$$
- $$\Lambda^\circ_{\text{HCl}} = 426.2 \text{ S cm}^2 / \text{equiv.}$$
- What additional information/ quantity one needs to calculate Λ° of an aqueous solution of acetic acid?
- (a) Λ° of chloroacetic acid (ClCH_2COOH)
 (b) Λ° of NaCl
 (c) Λ° of CH_3COOK
 (d) the limiting equivalent conductance of H^+ ($\lambda^\circ_{\text{H}^+}$).
39. Given: $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.439 \text{ V}$
 The value of standard electrode potential for the change,
 $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$ will be:
- (a) 0.385 V (b) 0.770 V
 (c) -0.270 V (d) -0.072 V
40. Consider the following four electrodes:
 $\text{P} = \text{Cu}^{2+} (0.0001 \text{ M}) / \text{Cu}_{(\text{s})}$
 $\text{Q} = \text{Cu}^{2+} (0.1 \text{ M}) / \text{Cu}_{(\text{s})}$
 $\text{R} = \text{Cu}^{2+} (0.01 \text{ M}) / \text{Cu}_{(\text{s})}$
 $\text{S} = \text{Cu}^{2+} (0.001 \text{ M}) / \text{Cu}_{(\text{s})}$
 If the standard reduction potential of Cu^{2+}/Cu is $+0.34 \text{ V}$, the reduction potentials in volts of the above electrodes follow the order.
- (a) $\text{P} > \text{S} > \text{R} > \text{Q}$ (b) $\text{S} > \text{R} > \text{Q} > \text{P}$
 (c) $\text{R} > \text{S} > \text{Q} > \text{P}$ (d) $\text{Q} > \text{R} > \text{S} > \text{P}$
41. Which pair of electrolytes could not be distinguished by the products of electrolysis using inert electrodes?
- (a) 1 M CuSO_4 solution, 1 M CuCl_2 solution
 (b) 1 M KCl solution, 1 M KI solution
 (c) 1 M AgNO_3 solution, 1 M $\text{Cu(NO}_3)_2$ solution
 (d) 1 M KCl solution, 1 M NaCl solution
42. A current is passed through two cells connected in series. The first cell contains $\text{X(NO}_3)_3(\text{aq})$ and the second cell contains $\text{Y(NO}_3)_2(\text{aq})$. The relative atomic masses of X and Y are in the ratio 1 : 2. What is the ratio of liberated mass of X to that of Y?
- (a) 3 : 2 (b) 1 : 2
 (c) 1 : 3 (d) 3 : 1
43. The electrode potential $E_{(\text{Zn}^{2+}/\text{Zn})}$ of a zinc electrode at 25°C with an aqueous solution of 0.1 M ZnSO_4 is
- $$[E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V. Assume } \frac{2.303RT}{F} = 0.06 \text{ at } 298 \text{ K}].$$
- (a) +0.73 (b) -0.79
 (c) -0.82 (d) -0.70
44. The electrical properties and their respective SI units are given below. Identify the wrongly matched pair.
- | Electrical property | SI unit |
|----------------------------|-----------------------------------|
| (a) Specific conductance | S m^{-1} |
| (b) Conductance | S |
| (c) Equivalent conductance | $\text{S m}^2 \text{ equiv}^{-1}$ |
| (d) Cell constant | m |
45. The ion of least limiting molar conductivity among the following is
- (a) SO_4^{2-} (b) H^+
 (c) Ca^{2+} (d) CH_3COO^-
46. The reduction potential (in volt) of a hydrogen electrode set up with a $2 \times 10^{-2} \text{ M}$ aqueous solution of a weak mono basic acid ($K_a = 5 \times 10^{-5}$) at one atmosphere and 25°C is
- (a) +0.09 (b) +0.18
 (c) -0.09 (d) -0.18
47. A current strength of 3.86 amp was passed through molten calcium oxide for 41 minutes and 40 seconds. The mass of calcium in grams deposited at the cathode is (Atomic mass of Ca is 40 g/mol, $1 \text{ F} = 96500 \text{ C}$)
- (a) 4 (b) 2
 (c) 6 (d) 8
- DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
48. **Statement-1** : The resistivity for a substance is its resistance when it is one meter long and its area of cross section is one square meter.
Statement-2 : The SI units of resistivity is ohm metre (Ωm).
49. **Statement-1** : On increasing dilution, the specific conductance keep on increasing.
Statement-2 : On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases.
50. **Statement-1** : Galvanised iron does not rust.
Statement-2 : Zinc has a more negative electrode potential than iron.

EXERCISE - 3

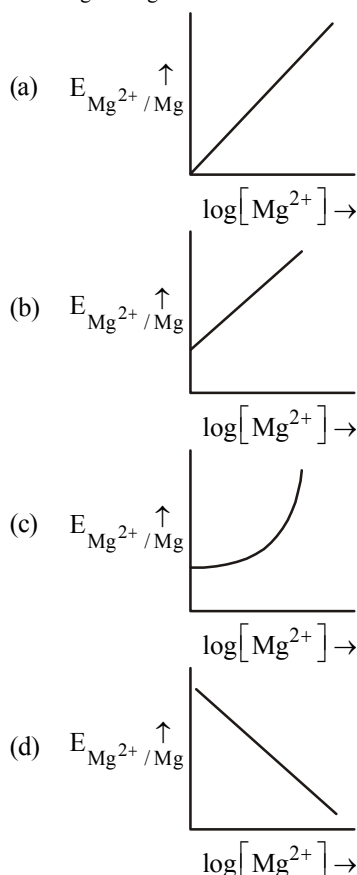
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Which cell measure standard electrode potential of copper electrode?
 - $\text{Pt(s)}|\text{H}_2(\text{g}, 0.1 \text{ bar})||\text{H}^+(\text{aq}, 1 \text{ M})||\text{Cu}^{2+}(\text{aq}, 1 \text{ M})|\text{Cu}$
 - $\text{Pt(s)}|\text{H}_2(\text{g}, 1 \text{ bar})||\text{H}^+(\text{aq}, 1 \text{ M})||\text{Cu}^{2+}(\text{aq}, 2 \text{ M})|\text{Cu}$
 - $\text{Pt(s)}|\text{H}_2(\text{g}, 1 \text{ bar})||\text{H}^+(\text{aq}, 1 \text{ M})||\text{Cu}^{2+}(\text{aq}, 1 \text{ M})|\text{Cu}$
 - $\text{Pt(s)}|\text{H}_2(\text{g}, 0.1 \text{ bar})||\text{H}^+(\text{aq}, 0.1 \text{ M})||\text{Cu}^{2+}(\text{aq}, 1 \text{ M})|\text{Cu}$
- Electrode potential for Mg electrode varies according to the equation

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^{\ominus} - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}$$

of $E_{\text{Mg}^{2+}/\text{Mg}}$ vs $\log [\text{Mg}^{2+}]$ is



- Which of the following statement is correct?
 - E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties.
 - E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties.
 - E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.

- E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.
- The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called.....
 - cell potential
 - cell emf
 - potential difference
 - cell voltage
- Which of the following statement is not correct about an inert electrode in a cell?
 - It does not participate in the cell reaction
 - It provides surface either for oxidation or for reduction reaction
 - It provides surface for conduction of electrons
 - It provides surface for redox reaction
- An electrochemical cell can behave like an electrolytic cell when
 - $E_{\text{cell}} = 0$
 - $E_{\text{cell}} > E_{\text{ext}}$
 - $E_{\text{ext}} > E_{\text{cell}}$
 - $E_{\text{cell}} = E_{\text{ext}}$
- Which of the statements about solutions of electrolytes is not correct?
 - Conductivity of solution depends upon size of ions
 - Conductivity depends upon viscosity of solution
 - Conductivity does not depend upon solvation of ions present in solution
 - Conductivity of solution increases with temperature
- Using the data given below find out the strongest reducing agent.

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^{\ominus} = 1.33 \text{ V}; E_{\text{Cl}_2/\text{Cl}^-}^{\ominus} = 1.36 \text{ V}$$

$$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\ominus} = 1.51 \text{ V}; E_{\text{Cr}^{3+}/\text{Cr}}^{\ominus} = -0.74 \text{ V}$$
 - Cl^-
 - Cr
 - Cr^{3+}
 - Mn^{2+}
- Use the data given in Q. 8 and find out which of the following is the strongest oxidising agent?
 - Cl^-
 - Mn^{2+}
 - MnO_4^-
 - Cr^{3+}
- Using the data given in Q. 8 find out in which option the order of reducing power is correct.
 - $\text{Cr}^{3+} < \text{Cl}^- > \text{Mn}^{2+} < \text{Cr}$
 - $\text{Mn}^{2+} < \text{Cl}^- > \text{Cr}^{3+} < \text{Cr}$
 - $\text{Cr}^{3+} < \text{Cl}^- < \text{Cr}_2\text{O}_7^{2-} < \text{Mn}^{2+}$
 - $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Cl}^- < \text{Cr}$
- Use the data given in Q.8 and find out the most stable ion in its reduced form.
 - Cl^-
 - Cr^{3+}
 - Cr
 - Mn^{2+}
- Use the data of Q. 8 and find out the most stable oxidised species.
 - Cr^{3+}
 - MnO_4^-
 - $\text{Cr}_2\text{O}_7^{2-}$
 - Mn^{2+}

13. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is
 (a) 1 F (b) 6 F
 (c) 3 F (d) 2 F
14. The cell constant of a conductivity cell
 (a) changes with change of electrolyte
 (b) changes with change of concentration of electrolyte
 (c) changes with temperature of electrolyte
 (d) remains constant for a cell
15. While charging the lead storage battery
 (a) PbSO_4 anode is reduced to Pb
 (b) PbSO_4 cathode is reduced to Pb
 (c) PbSO_4 cathode is oxidised to Pb
 (d) PbSO_4 anode is oxidised to PbO_2
16. $\Lambda_m^\circ(\text{NH}_4\text{OH})$ is equal to
 (a) $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \Lambda_m^\circ(\text{HCl})$
 (b) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$
 (c) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NaOH})$
 (d) $\Lambda_m^\circ(\text{NaOH}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$
17. In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?
 (a) $\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$; $E^\circ_{\text{cell}} = -2.71\text{ V}$
 (b) $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$; $E^\circ_{\text{cell}} = 1.23\text{ V}$
 (c) $\text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \frac{1}{2}\text{H}_2(\text{g})$; $E^\circ_{\text{cell}} = 0.00\text{ V}$
 (d) $\text{Cl}^-(\text{aq}) \longrightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^-$; $E^\circ_{\text{cell}} = 1.36\text{ V}$
- The cell potential will be : [2013]
 (a) 0.42 V (b) 0.84 V
 (c) 1.34 V (d) 1.10 V
21. How many grams of cobalt metal will be deposited when a solution of cobalt (II) chloride is electrolyzed with a current of 10 amperes for 109 minutes (1 Faraday = 96,500 C; Atomic mass of Co = 59 u) [NEET Kar. 2013]
 (a) 0.66 (b) 4.0
 (c) 20.0 (d) 40.0
22. Consider the half-cell reduction reaction :
 $\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$, $E^\circ = -1.18\text{ V}$
 $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} + \text{e}^-$, $E^\circ = -1.51\text{ V}$
 The E° for the reaction $3\text{Mn}^{2+} \rightarrow \text{Mn}^0 + 2\text{Mn}^{3+}$, and possibility of the forward reaction are, respectively [NEET Kar. 2013]
 (a) -2.69 V and no (b) -4.18 V and yes
 (c) $+0.33\text{ V}$ and yes (d) $+2.69\text{ V}$ and no
23. When 0.1 mol MnO_4^{2-} is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is: [2014]
 (a) 96500 C (b) $2 \times 96500\text{ C}$
 (c) 9650 C (d) 96.50 C
24. The weight of silver (at wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be : [2014]
 (a) 5.4 g (b) 10.8 g
 (c) 54.9 g (d) 108.0 g
25. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as : [2015]
 (a) Electrolytic cell (b) Dynamo
 (c) Ni-Cd cell (d) Fuel Cell
26. Aqueous solution of which of the following compounds is the best conductor of electric current ? [2015 RS]
 (a) Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$
 (b) Hydrochloric acid, HCl
 (c) Ammonia, NH_3
 (d) Fructose, $\text{C}_6\text{H}_{12}\text{O}_6$
27. The pressure of H_2 required to make the potential of H_2 -electrode zero in pure water at 298 K is : [2016]
 (a) 10^{-14} atm (b) 10^{-12} atm
 (c) 10^{-10} atm (d) 10^{-4} atm
28. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field ? [2017]
 (a) K (b) Rb
 (c) Li (d) Na
29. In the electrochemical cell :- [2017]
 $\text{Zn} | \text{ZnSO}_4(0.01\text{ M}) || \text{CuSO}_4(1.0\text{ M}) | \text{Cu}$, the emf of this Daniel cell is E_1 . When the concentration of ZnSO_4 is changed to 1.0M and that of CuSO_4 changed to 0.01M, the emf changes to E_2 . From the followings, which one is the relationship between E_1 and E_2 ?
 (Given, $\frac{RT}{F} = 0.059$)
 (a) $E_1 < E_2$ (b) $E_1 > E_2$
 (c) $E_2 = 0 \neq E_1$ (d) $E_1 = E_2$

NEET/AIPMT (2013-2017) Questions

18. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be ? [2013]
 (a) 0.59 V (b) 0.118 V
 (c) 1.18 V (d) 0.059 V
19. At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is $9.54\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ and at infinite dilution its molar conductance is $238\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is : [2013]
 (a) 20.800% (b) 4.008%
 (c) 40.800% (d) 2.080%
20. A button cell used in watches functions as following
 $\text{Zn}(\text{s}) + \text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{Ag}(\text{s}) + \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
 If half cell potentials are :
 $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$; $E^\circ = -0.76\text{ V}$
 $\text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + 2\text{OH}^-(\text{aq})$; $E^\circ = 0.34\text{ V}$

Hints & Solutions

EXERCISE - 1

- (b) Charge passed
 $= 30 \times 60 \times 2 = 3600 \text{ coulombs}$
 Chlorine liberated
 $= \frac{35.5 \times 3600}{96500} = 1.32 \text{ gm}$
- (a) NH_4^+ is conjugate acid of NH_3 as it is capable of giving H^+ ion.

$$\begin{array}{ccc} \text{NH}_3 + \text{H}^+ & \longrightarrow & \text{NH}_4^+ \\ \text{Base} & & \text{Conjugate acid} \end{array}$$
- (d) Molarity = 0.01 M ; Resistance = 40 ohm;
 Cell constant $\frac{l}{A} = 0.4 \text{ cm}^{-1}$.
 Specific conductivity (κ)
 $= \frac{\text{cell constant}}{\text{resistance}} = \frac{0.4}{40} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$
 Molar conductance ($\wedge_m$) = $\frac{1000\kappa}{\text{Molarity}}$
 $= \frac{1000 \times 0.01}{0.01} = 10^3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
- (b) Specific conductance of the solution (κ) = $0.012 \text{ ohm}^{-1} \text{ cm}^{-1}$ and resistance (R) = 55 ohm.
 Cell constant = Specific conductance $\times$ Observed resistance
 $= 0.012 \times 55 = 0.66 \text{ cm}^{-1}$.
- (a) Difluoroacetic acid being strongest acid will furnish maximum number of ions showing highest electrical conductivity.
- (c) Volume of $1 \times 10^{-5} \text{ gm}$ of hydrogen
 $= \frac{22400 \times 10^{-5}}{2} \text{ c.c.}$
 When 0.5 amp flows for 2 hours, charge passed
 $= 0.5 \times 60 \times 60 \times 2 = 3600 \text{ coulomb}$
 Now 1 coulomb of electricity releases
 $= \frac{22400 \times 10^{-5}}{2} \text{ c.c. of gas}$
 3600 coulomb of electricity releases,
 $= \frac{22400 \times 10^{-5}}{2} \times \frac{3600}{10^3} \text{ litres} = 0.4 \text{ litres}$
- (b) $\wedge_{\text{HCl}}^\infty = 426.2$ (i)
 $\wedge_{\text{AcONa}}^\infty = 91.0$ (ii)
 $\wedge_{\text{NaCl}}^\infty = 126.5$ (iii)
 $\wedge_{\text{AcOH}}^\infty = (i) + (ii) - (iii) = [426.2 + 91.0 - 126.5] = 390.7$
- (b) $\text{ohm}^{-1} \text{ cm}^2 (\text{geq})^{-1}$
- (a) $\wedge_{\text{eq}} = \kappa \times \frac{1000}{N} = \frac{1}{R} \times \frac{l}{a} \times \frac{1000}{N}$
 $= \frac{1}{R} \times \text{cell constant} \times \frac{1000}{N}$
 $= \frac{1}{220} \times 0.88 \times \frac{1000}{0.01} = 400 \text{ mho cm}^2 \text{ g eq}^{-1}$
- (c) Charge = $1 \times 30 \times 60 = 1800 \text{ coulomb}$
 96500 liberates 35.5 gm of Cl
 1800 coulomb liberates
 $\frac{35.5 \times 1800}{96500} = 0.66 \text{ gm of Cl}$
- (b) Here, R = 31.6 ohm
 $\therefore \text{Conductance} = \frac{1}{R} = \frac{1}{31.6} \text{ ohm}^{-1} = 0.0316 \text{ ohm}^{-1}$
 Specific conductance = conductance $\times$ cell constant.
 $= 0.0316 \text{ ohm}^{-1} \times 0.367 \text{ cm}^{-1} = 0.0116 \text{ ohm}^{-1} \text{ cm}^{-1}$
 Now, molar concentration = 0.5M (given)
 $= 0.5 \times 10^{-3} \text{ mole cm}^{-3}$
 $\therefore \text{Molar conductance} = \frac{\kappa}{C} = \frac{0.0116}{0.5 \times 10^{-3}} = 23.2 \text{ S cm}^2 \text{ mol}^{-1}$
- (b) For the given cell
 $\text{M}|\text{M}^+||\text{X}^-|\text{X}$, the reaction can be given by
 R.H.S. : Reduction -
 $\text{X} + \text{e}^- \rightarrow \text{X}^- ; E^0 = 0.33 \text{ V}$
 L.H.S. : Oxidation
 $\text{M} \rightarrow \text{M}^+ + \text{e}^- ; E^0 = 0.49 \text{ V}$
 Adding both half cell reactions, we get
 $\text{M} + \text{X} \rightarrow \text{M}^+ + \text{X}^-$
 $E_{\text{cell}}^0 = E_{\text{RHS}}^0 - E_{\text{LHS}}^0 = 0.33 - 0.44 = -0.11 \text{ V}$
 Since $E_{\text{Cell}} = -ve$, the reaction can not be spontaneous in forward direction but can proceed spontaneously if the direction is reversed.
- (b) Given current (i) = 0.5 amp;
 Time (t) = 100 minutes $\times 60 = 6000 \text{ sec}$
 Equivalent weight of silver nitrate (E) = 108.
 According to Faraday's first law of electrolysis
 $W = \frac{Eit}{96500} = \frac{108 \times 0.5 \times 6000}{96500} = 3.3575 \text{ g.}$
- (c) According to Faraday's law of electrolysis, the amount of metal deposited on an electrode is directly proportional to the amount of electricity passed and equivalent weight of metal. Now equivalent weight of

- sodium is 23, magnesium is $\frac{24.3}{2}$ i.e. 12.15 and of aluminium is $\frac{27}{3}$ i.e. 9. So, sodium which has highest equivalent weight among Na, Mg and Al, is deposited to highest extent during electrolysis.
15. (d) 1 mole of $e^- = 1F = 96500\text{ C}$
 27g of Al is deposited by $3 \times 96500\text{ C}$
 5120 g of Al will be deposited by

$$= \frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7\text{ C}$$
16. (a) $2H^+ + 2e^- \longrightarrow H_2$
 $E_H(\text{Eq. wt}) = \frac{2}{2} = 1\text{ g}$

$$= \frac{22400}{2} = 11200\text{ ml (STP)}$$

 Total charge passed = $\frac{96500 \times 112}{11200} = 965$
 $Q = It = 965$
 $I = \frac{965}{965} = 1\text{ amp.}$
17. (d) $\frac{W_A}{E_A} = \frac{W_B}{E_B}$; $\frac{1.6}{8} = \frac{\text{Wt. of Ag}}{108}$
 $\therefore \text{Wt. of Ag} = 21.6\text{ g}$
18. (b) Here Ag^+ acts as oxidising agent and Co^{2+} acts as reducing agent. So, cell can be represented as $Co^{2+} | Co^{3+}(\text{aq.}) || Ag^+(\text{aq.}) | Ag$
 Using Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \left| \frac{[Co^{3+}(\text{aq.})][Ag]}{[Ag^+(\text{aq.})][Co^{2+}]}\right|$$

 So, lesser the logarithmic term higher will be the value of E_{cell} . Among the given combinations logarithmic term is lesser for 0.1 M Co^{3+} and 2M Ag^+ and hence it will form a cell of highest voltage.
19. (b) $Cu^{+2} + 2e^- \rightarrow Cu(s)$
 $2 \times 96500\text{ C} \quad 63.6\text{g}$
 $9650\text{ C will deposit} = \frac{63.6}{2 \times 96500} \times 9650 = 3.18\text{ g}$
20. (a) Charge = $0.2 \times 1\text{ Faraday}$
 $= 0.2 \times 96500\text{ coulombs}$
 $= 19300 = 1.93 \times 10^4\text{ coulombs}$
21. (b) Magnesium which is more electropositive than iron prevents the rusting of iron by converting themselves into positive ion and thus reverses the process of conversion of iron to Fe^{3+} ion.
22. (d) $Ag^+ + e^- \longrightarrow Ag$
 $96500\text{ coulombs deposit} = 108\text{ g of Ag}$
 $\therefore 965\text{ coulombs deposit} = \frac{108}{96500} \times 965 = 1.08\text{ g Ag}$
23. (a) Total charge on one mole of monovalent metal ion = Charge on N_0 electrons
 $1F = 96500\text{ coulombs} = 9.65 \times 10^4\text{ coulombs.}$
24. (c) Using Faraday's second law of electrolysis,

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equ. wt. of Cu}}{\text{Equ. wt. of Ag}}$$

$$\Rightarrow \frac{w_{Cu}}{0.18} = \frac{63.5}{2} \times \frac{1}{108}$$

$$\Rightarrow w_{Cu} = \frac{63.5 \times 18}{2 \times 108 \times 100} = 0.0529\text{ g.}$$
25. (a) Charge passed = $25 \times 10^{-3} \times 60$
 $= 15 \times 10^{-1} = 1.5\text{ coulomb}$
 $Ca^{2+} + 2e^- \longrightarrow Ca$
 Now for calcium ion,
 $2 \times 96500\text{ coulomb is required for}$
 $6.02 \times 10^{23}\text{ atoms}$
 $0.3\text{ coulomb will be required for } \frac{6.02 \times 10^{23} \times 1.5}{2 \times 96500}$
 $= 4.68 \times 10^{18}$
26. (a) For deposition of silver, reaction is
 $Ag^+ + e^- \longrightarrow Ag$
 1 mol of Ag will be deposited by
 $= 1F = 96500\text{ C} = 9.65 \times 10^4\text{ C}$
 Since 1 equivalent weight of Ag is also equal to the weight of its 1 mol, hence 1 equivalent weight of Ag will be deposited by $= 9.65 \times 10^4\text{ C}$
27. (c) According to the definition 1 F or 96500 C is the charge carried by 1 mol of electrons when water is electrolysed
 $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$
 So, 4 Faraday of electricity liberate = 32 g of O_2 .
 Thus 1 Faraday of electricity liberate
 $= \frac{32}{4}\text{ g of } O_2 = 8\text{ g of } O_2$
28. (a) Charging increases the voltage. When the discharged cell is recharged, it acts as electrolytic cell.
29. (b) A current of 96500 coulombs liberate 1 mole of O_2 .
 $\Rightarrow 96500\text{ C liberates} = 22.4\text{ L of } O_2\text{ at NTP}$
 $\Rightarrow 9650\text{ C liberates} = \frac{22.4}{96500} \times 9650$
 $= 2.24\text{ L of } O_2\text{ at NTP}$
30. (b) $Fe^{2+} + 2e^- \rightarrow Fe$; $E_{Fe} = \frac{56}{2} = 28$
 1 Faraday liberates = 28 g of Fe
 3 Faraday liberates = $3 \times 28 = 84\text{ gm}$
31. (c)
32. (b) Amount of silver present in 125 ml of 1 M. $AgNO_3$
 $= \frac{108}{1000} \times 125\text{ g}$

Q needed for deposition of 108 g (1 g equivalent of Ag) 42. (a)

$$= 1 F = 96500 C$$

∴ Q needed for deposition of

$$\frac{108}{1000} \times 125 \text{ g Ag} = \frac{1}{108} \times \frac{108}{1000} \times 125 F = 0.125 F$$

$$= 0.125 \times 96500 C$$

Since, $Q = i \times t$

$$\therefore t = \frac{0.125 \times 96500}{241.25} = 50 \text{ s}$$

[Given: $i = 241.25$ amperes]

33. (d) Charge (Coulombs) pass per second = 10^{-6}
number of electrons passed per second

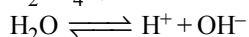
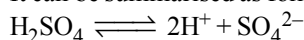
$$= \frac{10^{-6}}{1.602 \times 10^{-19}} = 6.24 \times 10^{12}$$

34. (c) $E_{cell}^{\circ} = \frac{2.303RT}{nF} \log K_{eq} = \frac{.0591}{n} \log K_{eq}$
- $$= \frac{.0591}{2} \log 10^6 = .0591 \times 3 = 0.1773 \text{ V}$$

35. (a) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$

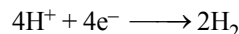
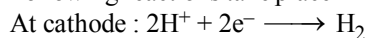
O.S. of Cr changes from +3 to +6 by loss of electrons.
At anode oxidation takes place.

36. (d) In electrolysis of dilute H_2SO_4 , O_2 is liberated at anode.
It can be summarised as follows :-

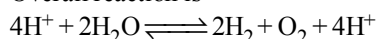


During electrolysis, the hydrogen ions migrate towards the cathode and are collected here in the form of hydrogen gas.

Following reactions take place



Overall reaction is



Thus, we see that hydrogen is produced at cathode and oxygen at anode during electrolysis.

37. (d) Calomel electrode is used as reference electrode.

38. (b) Electrode potential is considered as zero

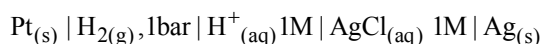
39. (a) Ag is easiest to be reduced among the given choices because its reduction potential is highest among the given choices.

40. (d) $Zn^{2+} + 2e^- \longrightarrow Zn$ It shows reduction reaction.

41. (b) $2AgCl_{(s)} + H_{2(g)} \rightarrow 2HCl_{(aq)} + 2Ag_{(s)}$

The activities of solids and liquids are taken as unity and at low concentrations, the activity of a solute is approximated to its molarity.

The cell reaction will be



43. (a) $k = \frac{\text{Cell constant}}{R} = \frac{1.15}{250}$

$$\Lambda_{eq} = \frac{1.15}{250} \times \frac{1000}{1} = 4.6$$

44. (c) Molar conductance of solution is related to specific conductance as follows :

$$\Lambda_m = K \times \frac{1000}{C} \quad \dots (1)$$

where C is molar concⁿ.

Putting $K = 6.3 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $C = 0.1M$ in equ (1), we get

$$\Lambda_m = (6.3 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}) \times \frac{1000}{(0.1 \text{ mol/cm}^3)}$$

$$= 6.3 \times 10^{-2} \times 10^4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

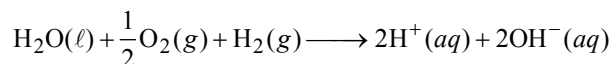
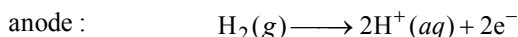
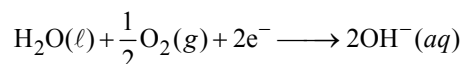
$$= 630 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

45. (a) Anode has negative polarity.

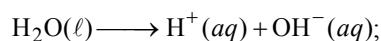
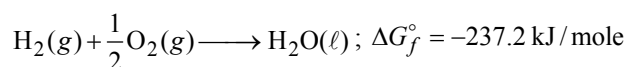
46. (b) Reduction occurs at cathode. Among the given choices, the reaction shown in option (b) is the reduction of Ag^+ to Ag. So, it occurs at cathode.

47. (a) Cell reaction

cathode :



Also we have



$$\Delta G^{\circ} = 80 \text{ kJ/mole}$$

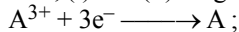
Hence for cell reaction

$$\Delta G^{\circ} = -237.2 + (2 \times 80) = -77.20 \text{ kJ/mole}$$

$$\therefore E^{\circ} = -\frac{\Delta G^{\circ}}{nF} = \frac{77200}{2 \times 96500} = 0.40V$$

48. (b) (i) $A^{3+} + e^- \longrightarrow A^{2+}$, $\Delta G_1 = -1 F y_2$
(ii) $A^{2+} + 2e^- \longrightarrow A$, $\Delta G_2 = -2F(-y_1) = 2Fy_1$

Add, (i) and (ii) we get



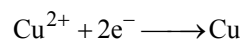
$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

$$-3FE^{\circ} = -Fy_2 + 2Fy_1$$

$$-3FE^{\circ} = -F(y_2 - 2y_1)$$

$$E^{\circ} = \frac{y_2 - 2y_1}{3}$$

49. (a) In the electrolysis of cupric sulphate, the reaction that occurs at cathode is



Thus 2F or $2 \times 96500 C$ of electricity is required to deposit

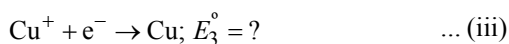
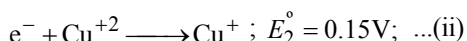
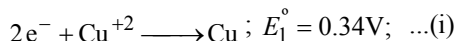
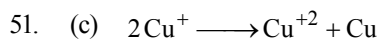
= 1 mol of Cu = 63.5 g of Cu

It means that to deposit 63.5 g of Cu, the amount of electricity required = 2×96500 C

So, to deposit 0.634 g of Cu, the amount of electricity

$$\text{required} = \frac{2 \times 96500}{63.5} \times 0.634 \approx 1930 \text{ C}$$

50. (b) Without losing its concentration ZnCl_2 solution cannot kept in contact with Al because Al is more reactive than Zn due to its highly negative electrode reduction potential.



$$\text{Now, } \Delta G_1^\circ = -nFE_1^\circ = -2 \times 0.34F$$

$$\Delta G_2^\circ = -1 \times 0.15F, \Delta G_3^\circ = -1 \times E_3^\circ F$$

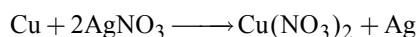
$$\text{Again, } \Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ$$

$$\Rightarrow -0.68F = -0.15F - E_3^\circ F$$

$$\Rightarrow E_3^\circ = 0.68 - 0.15 = 0.53\text{V}$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ(\text{Cu}^+/\text{Cu}) - E_{\text{anode}}^\circ(\text{Cu}^{+2}/\text{Cu}^+) \\ = 0.53 - 0.15 = 0.38\text{V}$$

52. (d) In the silver plating of copper, $\text{K}[\text{Ag}(\text{CN})_2]$ is used instead of AgNO_3 . Copper being more electropositive readily precipitate silver from their salt solution



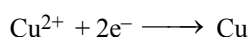
whereas in $\text{K}[\text{Ag}(\text{CN})_2]$ solution a complex anion $[\text{Ag}(\text{CN})_2]^-$ is formed and hence Ag^+ are less available in the solution and therefore copper cannot displace Ag from its complex ion.

53. (b) $I = 1\text{A}, t = 16 \text{ min. } 5 \text{ sec} = 965 \text{ sec}$

Quantity of electricity passed,

$$Q = It = 1 \times 965 \text{ C} = 965 \text{ C}$$

The reaction involved at the cathode is



Thus, $2F (= 2 \times 96500 \text{ C})$ deposits

= 1 mol of Cu = 63.5 g Cu

$$\Rightarrow 965 \text{ C deposits} = \frac{63.5 \times 965}{2 \times 96500} \text{ g Cu} = 0.3125 \text{ g Cu}$$

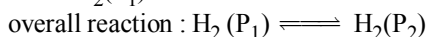
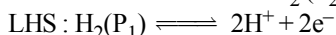
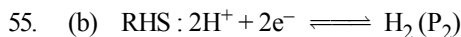
Now, Normality of the solution

$$= \frac{0.3125}{(63.5/2)} \times \frac{1000}{1000} = 0.01 \text{ N}$$

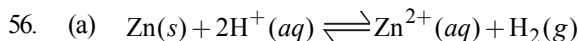
54. (d) $E^\circ = \frac{0.0591}{n} \log K$

Here, $n = 2, E^\circ = 0.295$

$$\therefore \log K = \frac{2 \times 0.295}{0.0591} = 9.98 \approx 10 \text{ or } K = 10^{10}$$



$$E = E^\circ - \frac{RT}{nF} \ln \frac{\text{P}_2}{\text{P}_1} = 0 - \frac{RT}{nF} \ln \frac{\text{P}_2}{\text{P}_1} = \frac{RT}{nF} \ln \frac{\text{P}_1}{\text{P}_2}$$



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}][\text{H}_2]}{[\text{H}^+]^2}$$

Addition of H_2SO_4 will increase $[\text{H}^+]$ and E_{cell} will also increase and the equilibrium will shift towards RHS

57. (c) According to Faraday's law of electrolysis

$$W = ZQ$$

where W is weight of substance liberated at an electrode, Z is electrochemical equivalent and Q is quantity of electricity passed.

When Q coulombs of electricity passed through molten Al_2O_3 , the amount of Al liberated is

$$W_{\text{Al}} = Z_{\text{Al}} Q$$

$$\Rightarrow W_{\text{Al}} = \frac{\text{equ. wt of Al}}{96500} Q$$

$$\Rightarrow 1.8 = \frac{27}{3 \times 96500} Q \dots\dots\dots(\text{i})$$

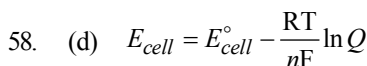
Similarly when Q coulombs of electricity is passed through molten NaCl, the amount of Na liberated is

$$W_{\text{Na}} = \frac{23}{96500} Q \dots\dots\dots(\text{ii})$$

Divide (ii) by (i), we get

$$\frac{W_{\text{Na}}}{1.8} = \frac{23}{96500} \times \frac{96500 \times 3}{27}$$

$$\Rightarrow W_{\text{Na}} = 1.8 \times 3 \times \frac{23}{27} = 4.6 \text{ g.}$$



At equilibrium,

$$E_{\text{cell}} = 0 \text{ and } Q = K_c$$

$$\therefore E_{\text{cell}} \neq E_{\text{cell}}^\circ$$

59. (b) A current of 96500 coulombs liberate 1 mole of O_2 .

$\Rightarrow 96500 \text{ C liberates} = 22.4 \text{ L of } \text{O}_2 \text{ at NTP}$

$\Rightarrow 9650 \text{ C liberates} = 2.24 \text{ L of } \text{O}_2 \text{ at NTP}$

60. (d) Here Ni is anode and Au is cathode

$$\text{Given } E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25\text{V} \text{ and } E_{\text{Au}^{3+}/\text{Au}}^\circ = +1.5\text{V}$$

$$E_{\text{cell}}^\circ = E_{\text{C}}^\circ - E_{\text{A}}^\circ = 1.5 - (-0.25) = 1.5 + 0.25 = 1.75\text{V}$$

61. (c) $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$, $E^\circ_{\text{Co}^{2+}/\text{Co}} = -0.28 \text{ V}$

The given cell reaction is



$\therefore$ Cr is anode and Co is cathode

$$E^\circ_{\text{cell}} = E^\circ_{\text{C}} - E^\circ_{\text{A}} = -0.28 - (-0.74) \\ = -0.28 + 0.74 = +0.46 \text{ V}$$

62. (a) On removing the salt bridge between the two half cells the circuit is broken. Hence, emf becomes zero.

63. (c) The E°_{cell} is given by

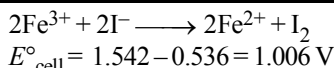
$$E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K_{\text{eq}}$$

$$\therefore 0.591 = \frac{0.0591}{1} \log K_{\text{eq}}$$

$$\text{or } \log K_{\text{eq}} = \frac{0.591}{0.0591} = 10$$

$$\text{or } K_{\text{eq}} = 1 \times 10^{10}$$

64. (a) Given : $[\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}] \times 2$
 $E^\circ = 0.771 \times 2 \text{ V} = 1.542 \text{ V}$
 $2\text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^- \quad E^\circ = -0.536 \text{ V}$



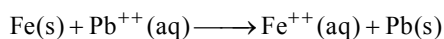
65. (b) For the given cell

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059 \text{ V}}{2} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

The cell potential will decrease with increase in $[\text{Zn}^{2+}(\text{aq})]$ and will increase with increase in $[\text{Cu}^{2+}(\text{aq})]$.

66. (b) Fe is above Pb in the electrochemical series i.e. E°_{oxid}

of Fe (+0.44 V) is higher than E°_{oxid} of Pb (+0.129 V). Hence, on addition of powdered Fe and Pb to a solution of Fe^{++} ion and Pb^{++} ion, the following reaction will take place :



So, more Pb and Fe^{++} ions will be formed.

67. (b) Maximum work done = W_{max}

$$= -nFE^\circ_{\text{cell}} = -2 \times 96500 \times 1.10 = -212.30 \text{ KJ}$$

68. (c) pH changes from 0 to 7.

$\therefore [\text{H}^+]$ changes from 1 to 10^{-7} M .

$$\text{Accordingly } E_{\text{red.}} = \frac{-0.059}{n} \log \frac{1}{[\text{H}^+]} \\ = 0.059 \log 10^{-7}$$

i.e., $0.059 \times (-7) = -0.41 \text{ volt}$.

69. (a) $2\text{Ag}^+ + \text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{Ag}$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2} \times [\text{Ag}^+]^2}$$

$$0.222 = 0.7995 - \frac{0.0591}{2} \log \frac{1}{[\text{Ag}^+]^2}$$

$$[\text{Ag}^+] = 10^{-9.8}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (10^{-9.8}) \times (1) = 10^{-9.8}$$

70. (b) Nernst equation is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{C}]^c [\text{d}]^d}{[\text{A}]^a [\text{B}]^b}$$

When E_{cell} drops to zero the concentration of ions will be equilibrium concentrations. We have for general cell reaction



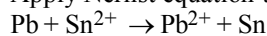
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$$E^\circ_{\text{cell}} = \frac{2.303 RT}{nF} \log K_c$$

[Since at equilibrium $E_{\text{cell}} = 0$]

$$E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K_c \text{ at } 298 \text{ K.}$$

71. (a) Apply Nernst equation to the reaction



$$\text{or } E^\circ + \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = E_{\text{cell}}$$

$$\text{or } \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = \frac{0.01 \times 2}{0.059} = 0.3 \quad (\because E_{\text{cell}} = 0)$$

$$\text{or } \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = \text{antilog}(0.3)$$

72. (d) For a concentration cell having different concentrations of ions.

$$E = \frac{0.0591}{n} \log \frac{c_1}{c_2}$$

If all the concentrations are identical then obviously the cell voltage is zero. But as the pH of 0.1 M HCl (strong acid) and pH of 0.1 M CH_3COOH (weak acid) not same, therefore the cell voltage is not zero.

73. (b) Electricity required = No. of g equiv. $\times 96500 \text{ coulombs}$
 $= 0.5 \times 96500 = 48250 \text{ C}$

74. (b) $\Delta G = -nE^\circ F$

$$\text{For concentration cell, } E = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

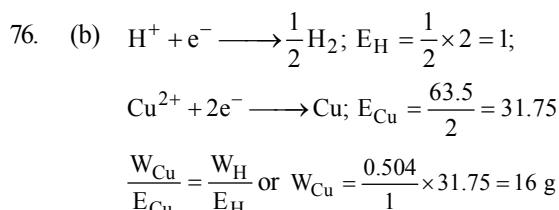
In it R, T, n and F are constant

$$\text{So } E \text{ is based upon } \ln \frac{C_2}{C_1}$$

$$\text{Now } \Delta G = -nEF = -nF \times \frac{RT}{nF} \ln C_2 / C_1 \\ = -RT \ln C_2 / C_1$$

At constant temperature ΔG is a function of $\ln C_2 / C_1$.

75. (d) This is because zinc has higher oxidation potential than Ni, Cu and Sn. The process of coating of iron surface with zinc is known as galvanization. Galvanized iron sheets maintain their lustre due to the formation of protective layer of basic zinc carbonate.

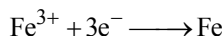


77. (b) Magnesium provides cathodic protection and prevent rusting or corrosion.

78. (b) In $H_2 - O_2$ fuel cell, the combustion of H_2 occurs to create potential difference between the two electrodes

79. (b) During charging, the lead storage battery behaves like an electrolytic cell. So, at anode the reaction is
 $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

80. (d) At cathodes: $Fe^{2+} + 2e^- \longrightarrow Fe$;



$$(E_{Fe})_1 = \frac{\text{At. wt.}}{2}; (E_{Fe})_2 = \frac{\text{At. wt.}}{3}$$

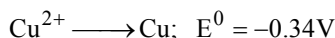
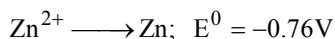
$$\text{Hence, } \frac{(E_{Fe})_1}{(E_{Fe})_2} = \frac{3}{2}$$

81. (c) $2NH_4Cl + Zn \rightarrow 2NH_3 + ZnCl_2 + H_2 \uparrow$.

82. (d) $Pb + PbO_2 + 2H_2SO_4 \xrightleftharpoons[\text{Recharge}]{\text{Discharge}} 2PbSO_4 + 2H_2O$.

Sulphuric acid is consumed on discharging.

83. (b) For spontaneous reaction E_{cell}^0 must be positive.



Here Cu acts as cathode and zinc acts as anode.

$$E_{cell}^0 = E_C^0 - E_A^0 = (-0.34) - (-0.76) = 0.42V.$$

84. (b) Efficiency of a fuel cell (η) = $\frac{\Delta G}{\Delta H}$

85. (c) As $E_{cell}^0 = \frac{0.0591}{n} \log K_c$

$$\therefore 0.46 = \frac{0.0591}{2} \log K_c$$

$$\therefore \log K_c = \frac{2 \times 0.46}{0.0591} = 15.57$$

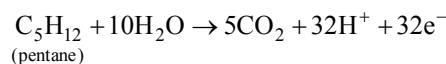
or $K_c = \text{Antilog } 15.57 = 3.7 \times 10^{15} \approx 4 \times 10^{15}$

86. (c) From the given data we find Fe^{3+} is strongest oxidising agent. More the positive value of E^0 , more is the tendency to get oxidized. Thus correct option is (c).

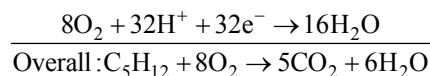
87. (d) Kohlrausch's Law states that at infinite dilution, each

ion migrates independent of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature. From this definition we can see that option (d) is the correct answer.

88. (c) Writing the equation for pentane-oxygen fuel cell at respective electrodes and overall reaction, we get
 At Anode:



At Cathode:



Calculation of ΔG^0 for the above reaction

$$\Delta G^0 = [5 \times (-394.4) + 6 \times (-237.2)] - [-8.2]$$

$$= -1972.0 - 1423.2 + 8.2 = -3387.0 \text{ kJ}$$

$$= -3387000 \text{ Joules.}$$

From the equation we find $n = 32$

Using the relation, $\Delta G^0 = -nFE_{cell}^0$ and substituting various values, we get

$$-3387000 = -32 \times 96500 \times E_{cell}^0 \quad (F = 96500C)$$

$$\text{or } E_{cell}^0 = \frac{3387000}{32 \times 96500}$$

$$= \frac{3387000}{3088000} \text{ or } \frac{3387}{3088} V = 1.0968 V$$

Thus option (c) is correct answer.

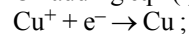
89. (d) $Cu^{2+} + 2e^- \rightarrow Cu$;

$$\Delta G^0 = -nE^0F = -2 \times F \times 0.337 = -0.674 F \quad \dots(i)$$

$$Cu^+ \rightarrow Cu^{2+} + e^-;$$

$$\Delta G^0 = -nE^0F = -1 \times F \times -0.153 = 0.153 F \quad \dots(ii)$$

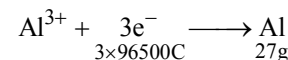
On adding eqn (i) & (ii)



$$\Delta G^0 = -0.521 F = -nE^0F;$$

$$\text{Here } n = 1 \quad \therefore E^0 = +0.52 V$$

90. (a) $\therefore Q = i \times t$
 $\therefore Q = 4.0 \times 10^4 \times 6 \times 60 \times 60 C = 8.64 \times 10^8 C$



[$3 \times 96500 C$ liberates = 27 g of Al]

$\therefore 96500 C$ liberates 9 g of Al

$$8.64 \times 10^8 C \text{ liberates} = \frac{9}{96500} \times 8.64 \times 10^8 \text{ g Al}$$

$$= 8.1 \times 10^4 \text{ g of Al}$$

91. (d) Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{8.0}{400} = 2 \times 10^{-2}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \approx c\alpha^2 = \frac{1}{32} \times (2 \times 10^{-2})^2 = 1.25 \times 10^{-5}$$

92. (a) $Cu + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

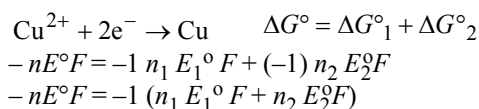
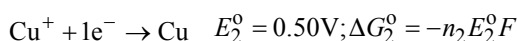
Here, $n = 2$, $E_{\text{cell}}^{\circ} = +0.46 \text{ V}$

$$\Delta G^{\circ} = -nE^{\circ}F = \frac{-2 \times 0.46 \times 96500}{1000} \text{ kJ} \approx -89 \text{ kJ}$$

93. (a) Dilution of strong electrolytes increases ionisation, hence ionic mobility of ions which in turn increases equivalent conductance of the solution.
94. (c) Conductivity of an electrolyte depends on the mobility of ions and concentration of ions. The motion of an ionic species in an electric field is retarded by the oppositely charged ions due to their interionic attraction. On dilution, concentration of electrolyte decreases and the retarding influence of oppositely charged ions decreases. Therefore mobility of ions increases.
95. (a) Option (ii) and (iv) are correct
96. (c) As the value of standard reduction potential decreases the reducing power increases i.e.,

$$\begin{matrix} Z & > & X & > & Y \\ (-3.0) & & (-1.2) & & (+0.5) \end{matrix}$$

97. (b) $\text{Cu}^{2+} + 1e^{-} \rightarrow \text{Cu}^{+} \quad E_1^{\circ} = 0.15 \text{ V}; \Delta G_1^{\circ} = -n_1 E_1^{\circ} F$



$$E^{\circ} = \frac{n_1 E_1^{\circ} + n_2 E_2^{\circ}}{n} = \frac{0.15 \times 1 + 0.50 \times 1}{2}$$

$$E^{\circ} = 0.325 \text{ V}$$

98. (b) Given $E_{\text{Sn}^{+4}/\text{Sn}^{+2}} = +0.15 \text{ V}$

$$E_{\text{Cr}^{+3}/\text{Cr}} = -0.74 \text{ V}$$

$$E_{\text{cell}}^{\circ} = E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ} = 0.74 + 0.15 = 0.89 \text{ V}$$

99. (d) Standard Gibbs free energy is given as $\Delta G^{\circ} = -nE^{\circ}F$
If $E_{\text{cell}}^{\circ} < 0$ i.e., $-ve$
 $\Delta G^{\circ} > 0$

$$\text{Further } \Delta G^{\circ} = -RT \ln K_{eq}$$

$$\therefore \Delta G^{\circ} > 0 \text{ and } K_{eq} < 0$$

100. (d) $\Lambda_{\text{m}}^{\circ}(\text{NH}_4\text{Cl}) = \Lambda_{\text{m}}^{\circ}(\text{NH}_4^{+}) + \Lambda_{\text{m}}^{\circ}(\text{Cl}^{-})$

$$\Lambda_{\text{m}}^{\circ}(\text{NaOH}) = \Lambda_{\text{m}}^{\circ}(\text{Na}^{+}) + \Lambda_{\text{m}}^{\circ}(\text{OH}^{-})$$

$$\Lambda_{\text{m}}^{\circ}(\text{NaCl}) = \Lambda_{\text{m}}^{\circ}(\text{Na}^{+}) + \Lambda_{\text{m}}^{\circ}(\text{Cl}^{-})$$

$$\therefore \Lambda_{\text{m}}^{\circ}(\text{NH}_4^{+}) + \Lambda_{\text{m}}^{\circ}(\text{OH}^{-})$$

$$= \Lambda_{\text{m}}^{\circ}(\text{NH}_4^{+}) + \Lambda_{\text{m}}^{\circ}(\text{Cl}^{-}) + \Lambda_{\text{m}}^{\circ}(\text{Na}^{+})$$

$$+ \Lambda_{\text{m}}^{\circ}(\text{OH}^{-}) - \left[\Lambda_{\text{m}}^{\circ}(\text{Na}^{+}) + \Lambda_{\text{m}}^{\circ}(\text{Cl}^{-}) \right]$$

$$\Lambda_{\text{m}}^{\circ}(\text{NH}_4\text{OH}) = \Lambda_{\text{m}}^{\circ}(\text{NH}_4\text{Cl}) + \Lambda_{\text{m}}^{\circ}(\text{NaOH}) - \Lambda_{\text{m}}^{\circ}(\text{NaCl})$$

EXERCISE - 2

1. (d) $\lambda_{\text{m}}^{\infty}(\text{BaSO}_4) = \lambda_{\text{Ba}^{2+}}^{\infty} + \lambda_{\text{SO}_4^{2-}}^{\infty}$
 $= \lambda_{\text{m}}^{\infty}(\text{BaCl}_2) + \lambda_{\text{m}}^{\infty}(\text{H}_2\text{SO}_4) - 2\lambda_{\text{HCl}}^{\infty}$

$$= x_1 + x_2 - 2x_3; \quad \lambda_{\text{e}}^{\circ} = \frac{1}{2} \lambda_{\text{m}}^{\circ}(\text{BaSO}_4)$$

2. (a) Conductivity (κ) = $\frac{\ell}{R.a.}$

$$\kappa = \frac{l}{R.a.}; \quad \text{cell constant.} \left(\frac{l}{a} \right) = 1.29 \times 100 = 129$$

$$\text{Again conductivity of } 0.02 \text{ M solution } \kappa = \frac{1}{520} \times 129$$

$$\Lambda_{\text{m}} = \frac{\kappa \times 1000}{\text{M}} = \frac{129}{520} \times \frac{1000}{0.02} = 1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

3. (b) At Anode, $\text{Cl}^{-} \rightarrow \frac{1}{2} \text{Cl}_2 + e^{-}$

$$\text{Equivalent wt. of chlorine } (E_{\text{Cl}_2}) = \frac{35.5 \times 2}{2} = 35.5$$

$$W_{\text{Cl}_2} = \frac{E_{\text{Cl}_2} \times I \times t}{96500} = \frac{35.5 \times 2 \times 30 \times 60}{96500} = 1.32 \text{ gm.}$$

4. (d)
5. (d) Charge on one mole of electrons = 96500 C

6. (a) By Faraday's 1st Law of electrolysis, $\frac{W}{E} = \frac{Q}{96500}$

(where $Q = it$ = charge of ion)

We know that no. of gram equivalent

$$= \frac{W}{E} = \frac{it}{96500} = \frac{1 \times 965}{96500} = \frac{1}{100}$$

(where $i = 1 \text{ A}$, $t = 16 \times 60 + 5 = 965 \text{ sec.}$)

Since, we know that

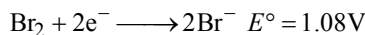
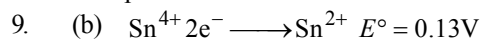
$$\text{Normality} = \frac{\text{No. of gram equivalent}}{\text{Volume (in litre)}} = \frac{\frac{1}{100}}{1} = 0.01 \text{ N}$$

7. (b) In electrolysis of NaCl when Pt electrode is taken then H_2 liberated at cathode while with Hg cathode it forms sodium amalgam because more voltage is required to reduce H^{+} at Hg than Pt.
8. (c) As per reaction in (c), reduction occurs at iodine electrode and oxidation at bromine electrode.

$$\text{Hence, } E_{\text{cell}}^{\circ} = E_{\text{I}_2/\text{I}^-}^{\circ} - E_{\text{Br}_2/\text{Br}^-}^{\circ}$$

$$= 0.54 - 1.09 = -0.55 \text{ V}$$

The negative cell potential suggests the non-spontaneity of the reaction. In other cases E_{cell} will be positive.



E° value shows Br_2 has higher reduction potential.

Hence

$$E_{\text{cell}} = E_{\text{Br}_2/\text{Br}^-} - E_{\text{Sn}^{4+}/\text{Sn}^{2+}}$$

$$= 1.08 - 0.13 = 0.95 \text{ V}$$

$$\text{Now } -\Delta G = nF E_{\text{cell}}$$

$$n = 2, F = 96500.$$

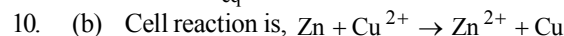
$$-\Delta G = 2 \times 96500 \times 0.95 \text{ kJ/mol.}$$

$$\text{Also, } \Delta G = -2.303 RT \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = -\frac{\Delta G}{2.303 \times R \times T} = \frac{-(-2 \times 96500 \times 0.95)}{2.303 \times 8.314 \times 298}$$

$$= 32.13$$

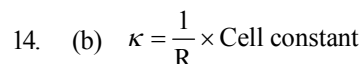
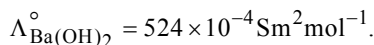
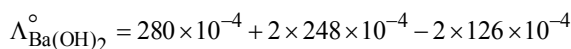
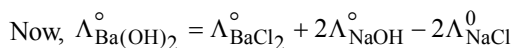
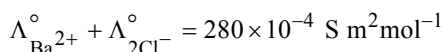
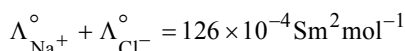
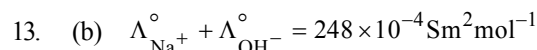
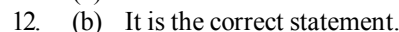
$$K_{\text{eq}} = \text{antilog } 32.682 \approx 10^{32}$$



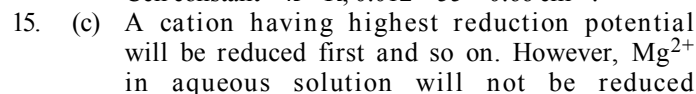
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Greater the factor $\left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right]$, less is the EMF

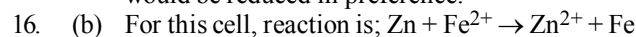
$$\text{Hence } E_1 > E_2$$



$$\text{Cell constant} = \kappa \times R; 0.012 \times 55 = 0.66 \text{ cm}^{-1}.$$



$\left(E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} < E_{\text{H}_2\text{O}/\frac{1}{2}\text{H}_2 + \text{OH}^-} \right)$. Instead water would be reduced in preference.

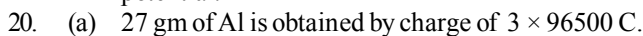
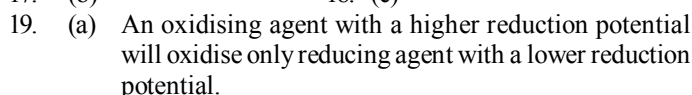


$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{c_1}{c_2}; E^{\circ} = E + \frac{0.0591}{n} \log \frac{c_1}{c_2}$$

$$= 0.2905 + \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-3}} = 0.32 \text{ V.}$$

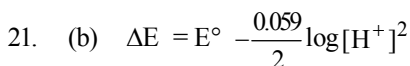
$$E^{\circ} = \frac{0.0591}{2} \log K_c; \log K_c = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$

$$\therefore K_c = 10^{\frac{0.32}{0.0295}}.$$

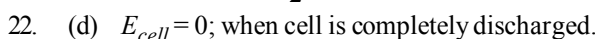


$$\therefore 1 \text{ gm of Al is obtained by charge of } 3 \times \frac{96500}{27} \text{ C.}$$

$$\therefore 5.12 \times 10^3 \text{ gm of Al is obtained by charge of } 3 \times \frac{96500}{27} \times 5.12 \times 1000 = 5.49 \times 10^7 \text{ C.}$$



$$= 1.30 - \frac{0.059}{2} \log (10^{-2})^2 = 1.418 \text{ V}$$

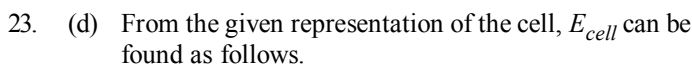


$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

$$\text{or } 0 = 1.1 - \frac{0.059}{2} \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

$$\log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right) = \frac{2 \times 1.1}{0.059} = 37.3$$

$$\therefore \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 10^{37.3}$$



$$E_{\text{cell}} = \left(E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} - E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} \right) - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

[Nernst-Equ.]

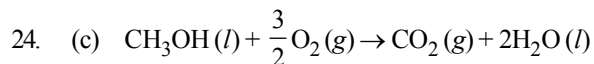
$$= -0.42 - (-0.72) - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= -0.42 + 0.72 - \frac{0.059}{6} \log \frac{0.1 \times 0.1}{0.01 \times 0.01 \times 0.01}$$

$$= 0.3 - \frac{0.059}{6} \log \frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6} \times 4$$

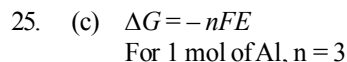
$$= 0.30 - 0.0393 = 0.26 \text{ V}$$

Hence option (d) is correct answer.



$$\begin{aligned}\Delta G_r &= [\Delta G_f(\text{CO}_2, g) + 2\Delta G_f(\text{H}_2\text{O}, l)] - \\ &\quad \left[\Delta G_f(\text{CH}_3\text{OH}, l) + \frac{3}{2}\Delta G_f(\text{O}_2, g) \right] \\ &= -394.4 + 2(-237.2) - (-166.2) - 0 \\ &= -394.4 - 474.4 + 166.2 = -702.6 \text{ kJ}\end{aligned}$$

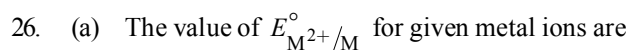
$$\% \text{ efficiency} = \frac{702.6}{726} \times 100 = 97\%$$



For $\frac{4}{3}$ mol of Al, $n = \frac{4}{3} \times 3 = 4$

$$\text{or } E = \frac{\Delta G}{-nF} = \frac{966 \times 10^3}{-4 \times 96500} = -2.5 \text{ V}$$

$\therefore$ The potential difference needed for the reduction = 2.5 V.



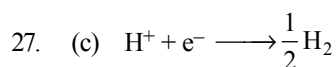
$$E_{\text{Mn}^{2+}/\text{Mn}}^\circ = -1.18 \text{ V},$$

$$E_{\text{Cr}^{2+}/\text{Cr}}^\circ = -0.9 \text{ V},$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V and}$$

$$E_{\text{Co}^{2+}/\text{Co}}^\circ = -0.28 \text{ V}.$$

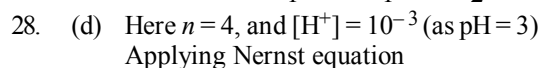
The correct order of $E_{\text{M}^{2+}/\text{M}}^\circ$ values without considering negative sign would be
 $\text{Mn}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+}.$



$$E = E^\circ - \frac{0.059}{1} \log \frac{[\text{P}(\text{H}_2)]^{1/2}}{[\text{H}^+]}$$

Now if $p_{\text{H}_2} = 2 \text{ atm}$ and $[\text{H}^+] = 1 \text{ M}$

$$\text{then } E = 0 - \frac{0.059}{1} \log \frac{2^{1/2}}{1} = \frac{-0.059}{2} \log 2$$



$$\begin{aligned}E &= E^\circ - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]^2}{[\text{H}^+]^4 (p_{\text{O}_2})} \\ &= 1.67 - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1}\end{aligned}$$

$$= 1.67 - \frac{0.059}{4} \log 10^7 = 1.67 - 0.103 = 1.567$$

29. (a) $\kappa = \frac{1}{R} \times \frac{\ell}{A}$

$$1.3 = \frac{1}{50} \times \frac{\ell}{A}$$

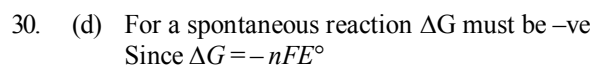
$$\frac{\ell}{A} = 65 \text{ m}^{-1}$$

$$\Lambda = \frac{\kappa \times 1000}{\text{molarity}}$$

[molarity is in moles/litre but 1000 is used to convert liter into cm^3]

$$= \frac{\left(\frac{1}{260} \times 65 \text{ m}^{-1} \right) \times 1000 \text{ cm}^3}{0.4 \text{ moles}}$$

$$= \frac{650 \text{ m}^{-1}}{260 \times 4 \text{ mol}} \times \frac{1}{1000} \text{ m}^3 = 6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$



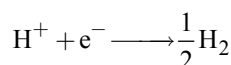
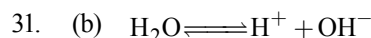
Hence for ΔG to be -ve ΔE° has to be positive. Which is possible when $X = \text{Zn}$, $Y = \text{Ni}$



$$E_{\text{Zn}/\text{Zn}^{2+}}^\circ + E_{\text{Ni}^{2+}/\text{Ni}}^\circ = 0.76 + (-0.23)$$

$$= +0.53$$

(positive)

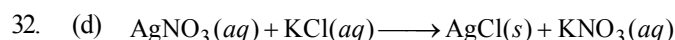


$\therefore$ 0.5 mole of H_2 is liberated by 1 F = 96500 C
0.01 mole of H_2 will be liberated by

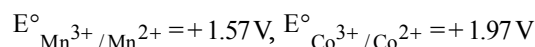
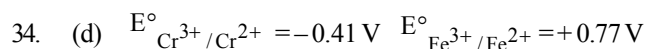
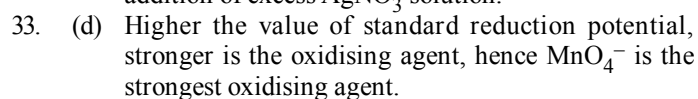
$$= \frac{96500}{0.5} \times 0.01 = 1930 \text{ C}$$

$$Q = I \times t$$

$$t = \frac{Q}{I} = \frac{1930 \text{ C}}{10 \times 10^{-3} \text{ A}} = 19.3 \times 10^4 \text{ sec}$$



Conductivity of the solution is almost compensated due to formation of $\text{KNO}_3(aq)$. However, after end point, conductivity increases more rapidly due to addition of excess AgNO_3 solution.



35. (c) Given $\text{Fe}^{3+}/\text{Fe}^{2+} = +0.77 \text{ V}$
 and $I_2/2\text{I}^- = 0.536 \text{ V}$
 $2(\text{e}^- + \text{Fe}^{3+} \longrightarrow \text{Fe}^{2+}) \quad E^\circ = 0.77 \text{ V}$
 $2\text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^- \quad E^\circ = -0.536 \text{ V}$

 $2\text{Fe}^{3+} + 2\text{I}^- \longrightarrow 2\text{Fe}^{2+} + \text{I}_2$
 $E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$
 $= 0.77 - 0.536$
 $= 0.164 \text{ V}$
 $\therefore$ Since value of E° is +ve reaction will take place.
36. (a) Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.
37. (d) $\Lambda^\circ_{\text{CH}_3\text{COOH}} = \Lambda^\circ_{\text{CH}_3\text{COONa}} + \Lambda^\circ_{\text{HCl}} - \Lambda^\circ_{\text{NaCl}}$
 $= 91 + 425.9 - 126.4 = 390.5 \text{ S cm}^2\text{mol}^{-1}$
38. (b) According to Kohlrausch's law, molar conductivity of weak electrolyte acetic acid (CH_3COOH) can be calculated as follows:
 $\Lambda^\circ_{\text{CH}_3\text{COOH}} = (\Lambda^\circ_{\text{CH}_3\text{COONa}} + \Lambda^\circ_{\text{HCl}}) - \Lambda^\circ_{\text{NaCl}}$
 $\therefore$ Value of $\Lambda^\circ_{\text{NaCl}}$ should also be known for calculating value of $\Lambda^\circ_{\text{CH}_3\text{COOH}}$.
39. (b) Given
 $\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe},$
 $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036 \text{ V} \quad \dots \text{(i)}$
 $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe},$
 $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.439 \text{ V} \quad \dots \text{(ii)}$
 we have to calculate
 $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}, \Delta G = ?$
 To obtain this equation subtract equ (ii) from (i) we get
 $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad \dots \text{(iii)}$
 As we know that $\Delta G = -nFE$
 Thus for reaction (iii)
 $\Delta G = \Delta G_1 - \Delta G_2$
 $-nFE^\circ = -nFE_1 - (-nFE_2)$
 $-nFE^\circ = nFE_2 - nFE_1$
 $-1FE^\circ = 2 \times (-0.439) - 3 \times (-0.036)$
 $-1FE^\circ = -0.770 \text{ F}$
 $\therefore E^\circ = +0.770 \text{ V}$
40. (d) $E_{\text{red}} = E^\circ_{\text{red}} + \frac{0.591}{n} \log[M^{n+}]$
 Lower the concentration of M^{n+} , lower is the reduction potential.
 Hence order of reduction potential is :
 $Q > R > S > P$
41. (d) Electrolysis of both KCl and NaCl liberates H_2 at the cathode and Cl_2 at the anode. But the resulting solutions will be different.
42. (c) The oxidation states of X and Y are X^{3+} and Y^{2+} . Given atomic masses are in the ratio of 1 : 2
 $\therefore$ Eq. mass = $\frac{\text{Atomic mass}}{\text{Oxidation state}}$

$\therefore$ Equivalent masses are in the ratio

$$\frac{1}{3} : \frac{2}{2} \text{ or } \frac{1}{3} : 1 \text{ or } 1 : 3$$

43. (b) For $\text{Zn}^{2+} \rightarrow \text{Zn}$

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{2.303RT}{nF} \log \left[\frac{[\text{Zn}]}{[\text{Zn}^{2+}]} \right]$$

$$= -0.76 - \frac{0.06}{2} \log \frac{1}{[0.1]} = -0.76 - 0.03$$

$$E_{\text{Zn}^{2+}/\text{Zn}} = -0.79 \text{ V}$$

44. (d) Cell constant = l/a
 Unit = $\text{m}/\text{m}^2 = \text{m}^{-1}$.

45. (d) Larger the size, lower the speed.

46. (d) $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$

$$E_{\text{cell}} = 0.06 \log [\text{H}^+] = 0.06 \times \log \sqrt{K_a C}$$

$$= 0.06 \times \log 10^{-3} = -0.18 \text{ V}$$

47. (b) Given $I = 3.86 \text{ amp}$
 $t = 41 \text{ min } 40 \text{ seconds} = 2500 \text{ seconds}$
 Mass deposited = ZIt
 Where

$$Z = \frac{\text{Equivalent weight}}{96500}$$

$$\text{Equivalent weight of Ca} = \frac{40}{2} (\text{Ca}^{2+} \rightarrow \text{Ca}) = 20$$

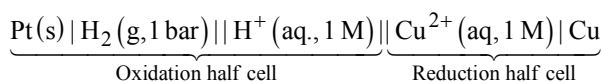
$$Z = \frac{20}{96500} \times 3.86 \times 2500 = 2$$

48. (b) We know, $R \propto \frac{\ell}{A}$ or $R = \rho \left(\frac{\ell}{A} \right)$, where proportionality constant ρ is called resistivity. If $\ell = 1 \text{ m}$ and $A = 1 \text{ m}^2$, then $R = \rho$ i.e., Resistance = Resistivity.
49. (d) The specific conductivity decreases while equivalent and molar conductivities increase with dilution.
50. (a) Zinc metal which has a more negative electrode potential than iron will provide electrons in preference of the iron, and therefore corrodes first. Only when all the zinc has been oxidised, the iron start to rust.

EXERCISE - 3

Exemplar Questions

1. (c) Standard electrode potential of copper electrode can be calculated by constructing a concentration cell composed of two half cell reactions in which concentration of species on left hand and right hand side are unity.



2. Electrode potential for Mg electrode varies according to the equation :

$$E_{\text{Mg}^{2+}/\text{Mg}} = E^\circ_{\text{Mg}^{2+}/\text{Mg}} - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}$$

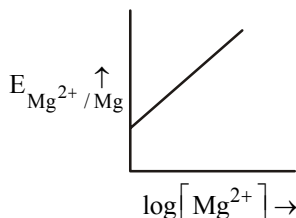
$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} + \frac{0.059}{2} \log [\text{Mg}^{2+}]$$

$$E_{\text{Mg}^{2+}/\text{Mg}} = \frac{0.059}{2} \log [\text{Mg}^{2+}] + E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$$

This equation represents equation of straight line.

Hence intercept (c) = $E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$ and slope = $\frac{0.059}{2}$

Thus, equation can be diagrammatically represented as:



3. (c) E_{cell} is an intensive property as it is independent of the mass of species but $\Delta_r G$ of cell reaction is an extensive property because this depends upon mass of species.
4. (b) Cell emf is the difference between the electrode potential of two electrodes when no current is drawn through the cell.
5. (d) Inert electrode does not participate in redox reaction and acts only as source or sink for electrons. It provides surface either for oxidation or for reduction reaction.
6. (c) If an external opposite potential is applied on the galvanic cell and increased slowly. It is observed that the reaction continues to take place till the opposing voltage reaches the value 1.1 V. At this stage no current flow through the cell. Any further increase in the external potential restarts the reaction but in the opposite direction.
Hence, now the cell will behave like an electrolytic cell.
7. (c) Greater the solvation of ions of an electrolyte lesser will be the electrical conductivity of the solution.
8. (b) Among the given options chromium has highest negative value of E° hence, it is the most strongest reducing agent.
9. (c) Higher the positive value of standard reduction potential of metal ion higher will be its oxidising capacity.
Since, $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ}$ has highest positive value hence it is the strongest oxidising agent.
10. (b) On moving down in electrochemical series reducing power decreases as the value of electrode potential decreases.
11. (d) $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ}$ has highest positive value. So Mn^{2+} is most stable ion in its reduced form.
12. (d) $E_{\text{Cr}^{3+}/\text{Cr}}^{\circ}$ has the lowest value of SRP. Hence, Cr^{3+} is the most stable oxidised species.

13. (c) $\text{Al}^{3+}(\text{aq}) \xrightarrow{+3e^-} \text{Al}(\text{s})$
Hence, total 3F is required.

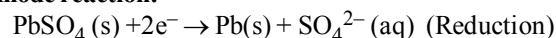
14. (d) Cell constant (G) = $\frac{l}{A}$

where l = length of object and A = area of cross section
Since, l and A remain constant for any particular object hence value of cell constant always remains constant.

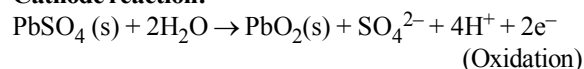
15. (a) When the lead storage battery is recharged the reaction occurring on cell is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 respectively

The electrode reactions are as follows

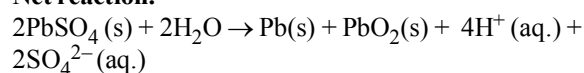
Anode reaction:



Cathode reaction:



Net reaction:



16. (b) $\Lambda_{\text{m}}^{\circ}(\text{NH}_4\text{Cl}) = \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} \quad \dots(\text{i})$

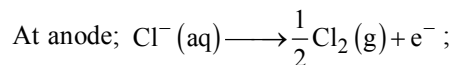
$$\Lambda_{\text{m}}^{\circ}(\text{NaOH}) = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ} \quad \dots(\text{ii})$$

$$\Lambda_{\text{m}}^{\circ}(\text{NaCl}) = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} \quad \dots(\text{iii})$$

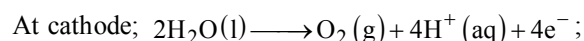
On adding (i) & (ii) and subtract (iii), we get :

$$\Lambda_{\text{m}}^{\circ}(\text{NH}_4\text{Cl}) + \Lambda_{\text{m}}^{\circ}(\text{NaOH}) - \Lambda_{\text{m}}^{\circ}(\text{NaCl}) = \Lambda_{\text{m}}^{\circ}(\text{NH}_4\text{OH})$$

17. (d) In the electrolysis of aqueous NaCl, following reactions are possible at anode.



$$E_{\text{cell}}^{\circ} = 1.36\text{V}$$



$$E_{\text{cell}}^{\circ} = -1.23\text{V}$$

The reaction at anode with lower value of E° is preferred and therefore water should get oxidised in preference to $\text{Cl}^-(\text{aq})$. However on account of overpotential of oxygen reaction (d) is preferred.

NEET/AIPMT (2013-2017) Questions

18. (a) $\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$

$$1 \text{ atm} \quad 10^{-10}$$

$$E_{\text{H}_2/\text{H}^+} = 0 - \frac{0.059}{2} \log \frac{(10^{-10})^2}{1}$$

$$E_{\text{H}_2/\text{H}^+} = +0.59\text{V}$$

19. (b) $\alpha = \frac{\Lambda_{\text{m}}}{\Lambda_{\text{m}}^{\infty}} = \frac{9.54}{238} = 0.04008 = 4.008\%$

20. (d) $E^\circ_{\text{Cell}} = E^\circ_{\text{OP}} + E^\circ_{\text{RP}}$
 $= 0.76 + 0.314 = 1.10 \text{ V}$
21. (c) Applying,
 $w = Zit = \frac{Eit}{96500}$
 Equivalent weight of cobalt (II) = $59/2$
 $I = 10 \text{ A}$
 Time (t) = $109 \text{ min} = 109 \times 60 \text{ sec}$
 Substituting these values we get,
 $w = \frac{59 \times 10 \times 109 \times 60}{2 \times 96500} = 20.0$
22. (a) $\Delta E^\circ = E^\circ_{\text{red}} + E^\circ_{\text{oxd}}$
 $= -1.81 - 1.51 = -2.69$
 Since ΔE° is negative
 $\therefore \Delta G = -nFE^\circ$, ΔG will have positive value so, forward reaction is not possible.
23. (c) $\overset{(+6)}{\text{MnO}_4^{2-}} \longrightarrow \overset{(+7)}{\text{MnO}_4^-} + e^-$
 0.1 mole
 Quantity of electricity required = $0.1F$
 $= 0.1 \times 96500 = 9650 \text{ C}$
24. (d) $w_{\text{O}_2} = n_{\text{O}_2} \times 32$
 $w_{\text{O}_2} = \frac{5600}{22400} \times 32 = 8 \text{ g} = 1 \text{ equivalent of O}_2$
 $= 1 \text{ equivalent of Ag} = 108$
25. (d) A device that converts energy of combustion of fuels, directly into electrical energy is known as fuel cell.
26. (b) HCl completely dissociates to give H^+ and Cl^- ions, hence act as very good electrolyte. While others are non-electrolytes.
27. (a) $2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g})$
 $\therefore E = E^0 - \frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$
 $0 = 0 - 0.0295 \log \frac{P_{\text{H}_2}}{(10^{-7})^2}$
 $\frac{P_{\text{H}_2}}{(10^{-7})^2} = 1$
 $P_{\text{H}_2} = 10^{-14} \text{ atm}$
28. (c) Li^+ being smallest, has maximum charge density.
 $\therefore \text{Li}^+$ is most heavily hydrated among all alkali metal ions. Effective size of Li^+ in aqueous solution is therefore, largest. So, moves slowest under electric field.
29. (b) For cell,
 $\text{Zn}|\text{ZnSO}_4(0.01 \text{ M})||\text{CuSO}_4(1.0 \text{ M})|\text{Cu}$
 $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$
 $\therefore E_1 = E^\circ_{\text{cell}} - \frac{2.303RT}{2 \times F} \times \log \frac{(0.01)}{1}$
 When concentrations are changed for ZnSO_4 and CuSO_4 , we can write
 $E_2 = E^\circ_{\text{cell}} - \frac{2.303RT}{2F} \times \log \frac{1}{0.01}$
 $\therefore E_1 > E_2$

Chapter

18

Chemical Kinetics

RATE OF A CHEMICAL REACTION

It is defined as the change in the concentration of reactant or product in unit time. It is always a positive quantity. It can be expressed in terms of:

- rate of decrease in concentration of any one of the reactant
- rate of increase in concentration of any one of the product.

For ex; For a reaction, $A \rightarrow B$

$$\text{Rate of disappearance of A} = \frac{\text{Decrease in conc. of A}}{\text{Time taken}}$$

$$= \frac{-\Delta[B]}{\Delta t}$$

$$\text{Rate of appearance of B} = \frac{\text{Increase in conc. of B}}{\text{Time taken}} = \frac{+\Delta[B]}{\Delta t}$$

$$\text{where } \Delta[A] = A_2 - A_1 = A_{\text{final}} - A_{\text{initial}}$$

$$\Delta[B] = B_2 - B_1 = B_{\text{final}} - B_{\text{initial}}$$

$$\Delta t = t_2 - t_1 = \text{change in time}$$

This is **average rate of reaction, r_{av}** , which is rate of reaction over a certain measurable period of time during the course of reaction.

To express the rate at a particular moment of time, we determine the **instantaneous rate, r_{inst}** . It is given by:

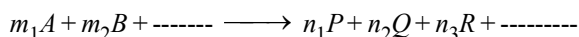
$$r_{\text{av}} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} \quad (\because \text{time interval is the smallest})$$

$$\text{As } t \rightarrow 0,$$

$$r_{\text{inst}} = \frac{-d[A]}{dt} = \frac{d[B]}{dt}$$

Rate of Reaction in the Form of Stoichiometry of a Chemical Reaction

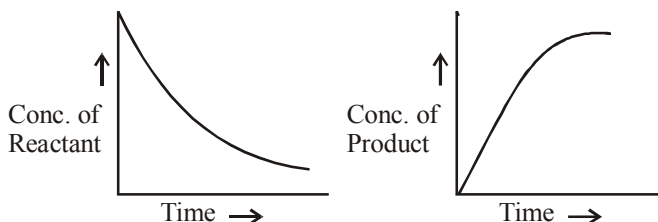
Let us consider a reaction :



Rate of reaction

$$= -\frac{1}{m_1} \frac{d[A]}{dt} = -\frac{1}{m_2} \frac{d[B]}{dt} = \frac{1}{n_1} \frac{d[P]}{dt} = \frac{1}{n_2} \frac{d[Q]}{dt}$$

Units of rate of reaction are conc/time i.e., $\text{mol L}^{-1}\text{s}^{-1}$. Graphically, it is shown as:



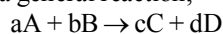
FACTORS AFFECTING RATE OF A REACTION

- Nature of reactants** : Reactions involving lesser bond rearrangement proceed much faster than those which involve larger bond rearrangement.
- Concentration of reactants** : More will be the concentration of reactant greater will be the rate of reaction.
- Temperature** : When temperature increases, the rate of reaction increases because large number of molecules cross the energy barrier. For all reactions, rate of reaction increases with increase in temperature whether reaction is exothermic or endothermic.
- Presence of catalyst** : Catalyst increased rate without itself getting consumed in reaction
- Surface area of reactants** : The more the surface area, the more is the rate of reaction.
- Presence of light** : Some reactions do not occur in dark but occur in presence of light. Such reactions are known as photochemical reactions.

RATE LAW, RATE CONSTANT, ORDER OF REACTION

Rate Law

For a general reaction,



the rate expression is given by:

$$\text{Rate} \propto [A]^a[B]^b \quad (\text{Law of mass action})$$

$$\text{Rate} \propto [A]^x[B]^y \quad \text{Rate Law or Rate expression}$$

where x and y may or may not be equal to a and b

$$\text{Again, Rate} = k[A]^x[B]^y$$

$$\frac{-d[R]}{dt} = k[A]^x[B]^y$$

This is called **Differential rate equation**. This equation which relates the rate of reaction to concentration of reactants is called rate law or rate expression. Rate law or for any reaction is determined experimentally.

Rate Constant

k is constant of proportionality called **Rate constant/ Velocity constant/ specific reaction rate**.

$$[A] = [B] = 1$$

$$\text{Rate} = k$$

In general rate constant may be defined as the rate of the reaction when the concentration of each of the reactants is unity.

Characteristics of rate constant :

- The value of k is different for different reactions.
- At fixed temperature the value of k is constant.
- It is independent of concentration but depends on temperature.
- The larger the value of k the faster is the reaction and vice versa.

'k' for different reaction order are given below:

Order of reaction	Units of rate constant
Zero (n = 0)	$(\text{mol L}^{-1})^{1-0} \text{s}^{-1} = \text{mol L}^{-1} \text{s}^{-1}$
First order (n = 1)	$(\text{mol L}^{-1})^{1-1} \text{s}^{-1} = \text{s}^{-1}$
Second order (n = 2)	$(\text{mol L}^{-1})^{1-2} \text{s}^{-1} = \text{mol L}^{-1} \text{s}^{-1}$

Order of reaction

It is defined as the sum of the exponents to which the concentration terms in the rate law expression are raised to express the observed rate of reaction.

For the reaction



then, $\text{Rate} = k[A]^\alpha [B]^\beta$,

then the sum of exponents of concentration terms

$$= \alpha + \beta = \text{Order of reaction}$$

where α = Order with respect to reactant A

β = Order with respect to reactant B

- The order of a reaction may be zero, (-)ve, (+)ve or fractional.
- The order of a reaction is determined by the slowest step of mechanism.
- Reactions of higher order (more than 3) are rare.

Note : Order of a reaction is experimentally determined quantity. It can be obtained from rate law equation not from balanced chemical equation.

Molecularity of a Reaction

The reactions taking place in one step are called elementary reactions. The reactions which do not occur in one step are called complex reactions.

The total number of moles of atoms or ions or molecules or reacting species in a balanced chemical equation is called molecularity of the reaction.

For an elementary reaction, molecularity is the sum of the molecules of different reactants as represented by balanced chemical equation whereas complex reaction, molecularity has no meaning.

It can only be defined for an elementary reaction.

The main points of different between order and molecularity of a

reaction are:

Difference Between Order and Molecularity of Reaction

	Order of reaction		Molecularity of reaction
1.	It can be fractional as well as zero.	1.	It is always a whole number. It cannot be zero or fractional.
2.	It can be determined experimentally only.	2.	It can be calculated by simply adding the molecules of the slowest step.
3.	It is applicable to elementary as well as complex reactions.	3.	It is applicable only to elementary reactions. For a complex reaction, molecularity of the slowest step is same as the overall order of reaction.
4.	It cannot be obtained from balanced or stoichiometric equation.	4.	It can be obtained.
5.	It is changed when one reactant is taken in large excess	5.	It undergoes no change.

INTEGRATED RATE EQUATIONS

The integrated rate equations are different for reactions of different orders. Some of these are:

Zero Order Reaction



$$\text{Rate} = \frac{-d[X]}{dt} = k[X]^0$$

$$\frac{-d[X]}{dt} = k \Rightarrow d[X] = -kdt$$

On integrating both sides

$$[X] = -kt + C \quad \dots\dots\dots (i)$$

$$\text{At } t = 0 \quad [X] = [X]_0$$

$$[X]_0 = C$$

Substituting in equation (i) we get,

$$[X] = -kt + [X]_0$$

$$k = \frac{[X]_0 - [X]}{t} \quad \dots\dots\dots (ii)$$

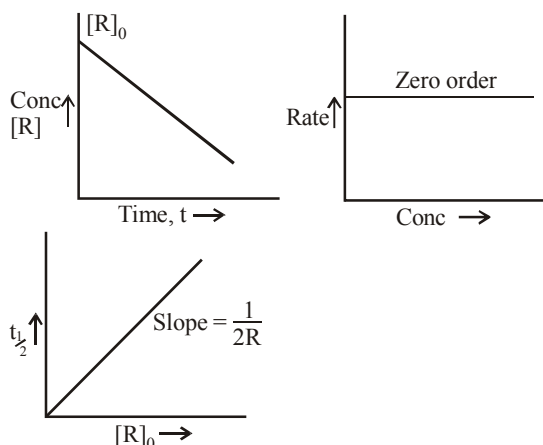
Half-life for zero order reaction :

$$\text{At } t = t_{1/2} \quad [X] = \frac{1}{2}[X]_0$$

By putting these values in equation (ii)

$$k = \frac{[X]_0 - \frac{1}{2}[X]_0}{t_{1/2}} \quad t_{1/2} = \frac{[X]_0}{2k}$$

Graphical representation for zero order reaction

**First Order Reaction**

$$\text{Rate} = \frac{-d[X]}{dt} = k[X], \quad \frac{d[X]}{[X]} = -kdt$$

On integrating both sides

$$\ln [X] = -kt + C \quad \dots\dots\dots (i)$$

when $t = 0$, $[X] = [X]_0$

$$\ln [X]_0 = C$$

Substituting in equation (i) we get

$$\ln [X] = -kt + \ln [X]_0$$

$$\ln [X] - \ln [X]_0 = -kt$$

$$kt = \ln [X]_0 - \ln [X]$$

$$kt = \ln \frac{[X]_0}{[X]} \Rightarrow k = \frac{1}{t} \ln \frac{[X]_0}{[X]}$$

$$k = \frac{2.303}{t} \log \frac{[X]_0}{[X]} \quad \dots\dots\dots (ii)$$

Half-life for first order reaction :

$$\text{When } t = t_{1/2}, [X] = \frac{[X]_0}{2}$$

By putting values in equation (ii)

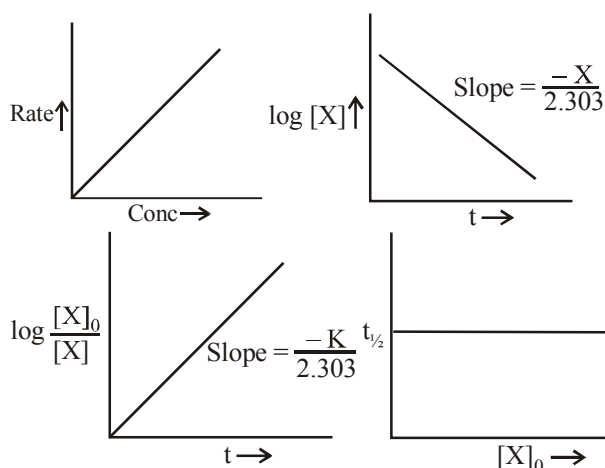
$$k = \frac{2.303}{t_{1/2}} \log \frac{[X]_0}{[X]_0/2}$$

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{0.693}{k}$$

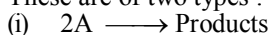
Graphical representation for first order reaction

On summarising we get,

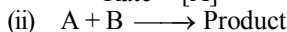
Order	Reaction	Differential Rate Law	Integrated Rate Law	Half - life	Units of R
0	$X \rightarrow Y$	$\frac{d[X]}{dt} = -k$	$kt = [X]_0 - [X]$	$[X]_0 / 2k$	Conc. time ⁻¹ or mol L ⁻¹ s ⁻¹
1	$X \rightarrow Y$	$\frac{d[X]}{dt} = -k[X]$	$[X] = [X]_0 e^{-kt}$ or $kt = \ln \frac{[X]_0}{[X]}$	$\ln 2 / k$	time ⁻¹ or s ⁻¹
2	$2X \rightarrow \text{Product}$		$k = \frac{[X]}{t[X]_0([X]_0 - [X])}$	$\frac{1}{k[X]_0}$	conc ⁻¹ time ⁻¹ or mol s ⁻¹

**Second Order Reaction**

These are of two types :



$$\text{Rate} \propto [A]^2$$



$$\text{Rate} \propto [A][B]$$

For reaction, $2X \longrightarrow \text{Product}$

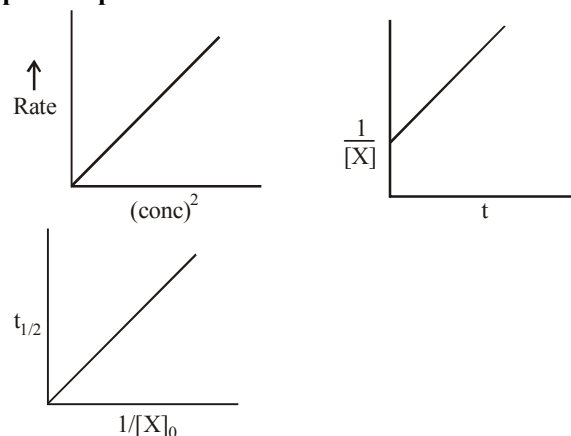
$$k = \frac{1}{t} \frac{X}{[X]_0([X]_0 - [X])} \quad \dots\dots (i)$$

Half life period for second order reaction :

$$\text{When } t = t_{1/2}, [X] = \frac{[X]_0}{2}$$

By putting values in equation (i)

$$t_{1/2} = \frac{1}{k[X]_0}$$

Graphical representation for second order reaction

Half-life Period for the n^{th} Order Reaction

When the order of reaction is n , $t_{1/2}$ is given by

$$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{a^{n-1}} \right]$$

$$\therefore t_{1/2} \propto \frac{1}{a^{n-1}}$$

Unit of $k = (\text{conc})^{1-n} \cdot \text{time}^{-1}$

For a first order gas phase reaction, $A(g) \rightarrow B(g) + C(g)$

$$k = \frac{2.303}{t} \log \frac{p_i}{p_A} = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$$

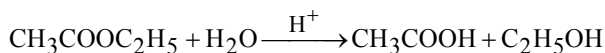
where p_i is initial pressure of A, $p_t \rightarrow$ total pressure at time t
 $(p_t = p_A + p_B + p_C)$

PSEUDO FIRST ORDER REACTIONS

Reactions are not truly of first order but under certain conditions become reactions of first order are called pseudo-first order reactions.

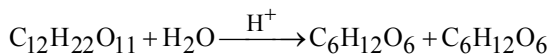
For ex:

- (i) acid-catalysed hydrolysis of ethyl acetate



Rate of reaction $\propto [\text{CH}_3\text{COOC}_2\text{H}_5]$

- (ii) acid-catalysed inversion of cane sugar



Rate of reaction $\propto [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$

This is because that water is present in such large excess that its concentration remains almost constant during the reaction.

ACTIVATION ENERGY

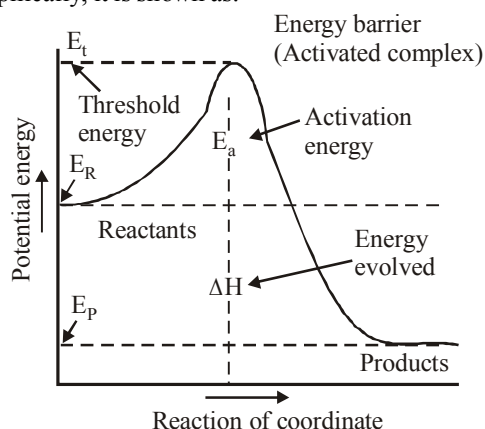
The minimum energy which the colliding molecules must have in order that the collision between them may be effective is called **threshold energy**.

The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to threshold value is called **activation energy**. Thus,

Activation energy = Threshold energy – Avg KE of reactant

For fast reaction activation energy is low while for slow reaction activation energy is high.

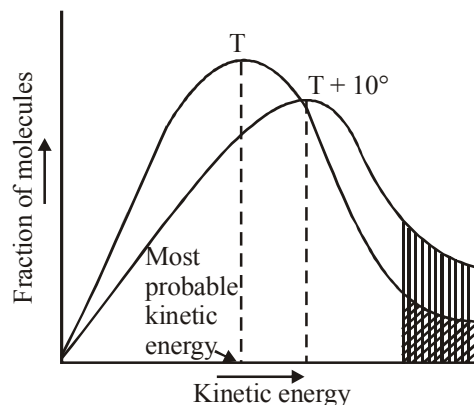
Graphically, it is shown as:



Temperature Dependence of Reaction

For a chemical reaction, with 10°C rise in temperature, the rate constant is nearly doubled. This is because on increasing the temperature, the fraction of molecules colliding with energies greater than E_a increases. At $(T + 10)^\circ\text{C}$, the fraction of molecules having energy equal to or greater than E_a gets doubled leading to doubling the rate of a reaction.

Diagrammatically, it is shown as:



Mathematically, temperature dependence of rate of reaction is given by **Arrhenius equation** given as:

$$k = Ae^{-E_a/RT} \quad \dots(i)$$

Where $A \rightarrow$ Arrhenius factor or frequency factor or pre-exponential factor

$R \rightarrow$ gas constant

$E_a \rightarrow$ activation energy

If rate constant of a reaction at a particular temperature is known, its value at another temperature can be calculated, provided E_a is known. It is as follows:

Taking logarithm on both sides of equation (i)

$$\ln k = \ln A - \frac{E_a}{RT}$$

If the value of rate constant at temperatures T_1 and T_2 are k_1 and k_2

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

On subtracting the two equations we get

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

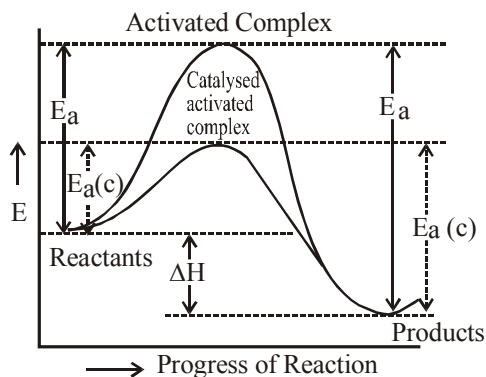
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

EFFECT OF CATALYST ON RATE OF REACTION

A catalyst alters the rate of a reaction without itself undergoing any permanent chemical change.

The catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

The graphical representation is as follows:



Where,

E_a = Activation energy without catalyst

$E_a(c)$ = Activation energy with catalyst.

COLLISION THEORY OF CHEMICAL REACTIONS

Chemical reaction occurs as a result of effective collision between reaction molecules. For this two things are important.

- (i) proper orientation of reaction molecules
- (ii) possession of energy more than threshold energy.

Collision Frequency

Total number of collisions which occur among the reacting molecules per second per unit volume is called collision frequency. Its value is given by

$$z = \sqrt{2} \pi \bar{v} \sigma^2 n^2$$

$\bar{v}$ = average velocity, σ = molecular diameter in cm.,

n = number of molecules per cc.

Rate of Reaction from Collision Theory

It is given by

$$\text{Rate of reaction} = f \times z$$

z = collision frequency,

f = fraction of effective collisions

$$= \frac{\Delta n}{N} = e^{-E_a/RT}$$

$$\therefore \text{Rate}(k) = Z e^{-E_a/RT}$$

For effective collision another factor P , called **steric factor** has to be taken into consideration.

Then rate of reaction can be expressed as

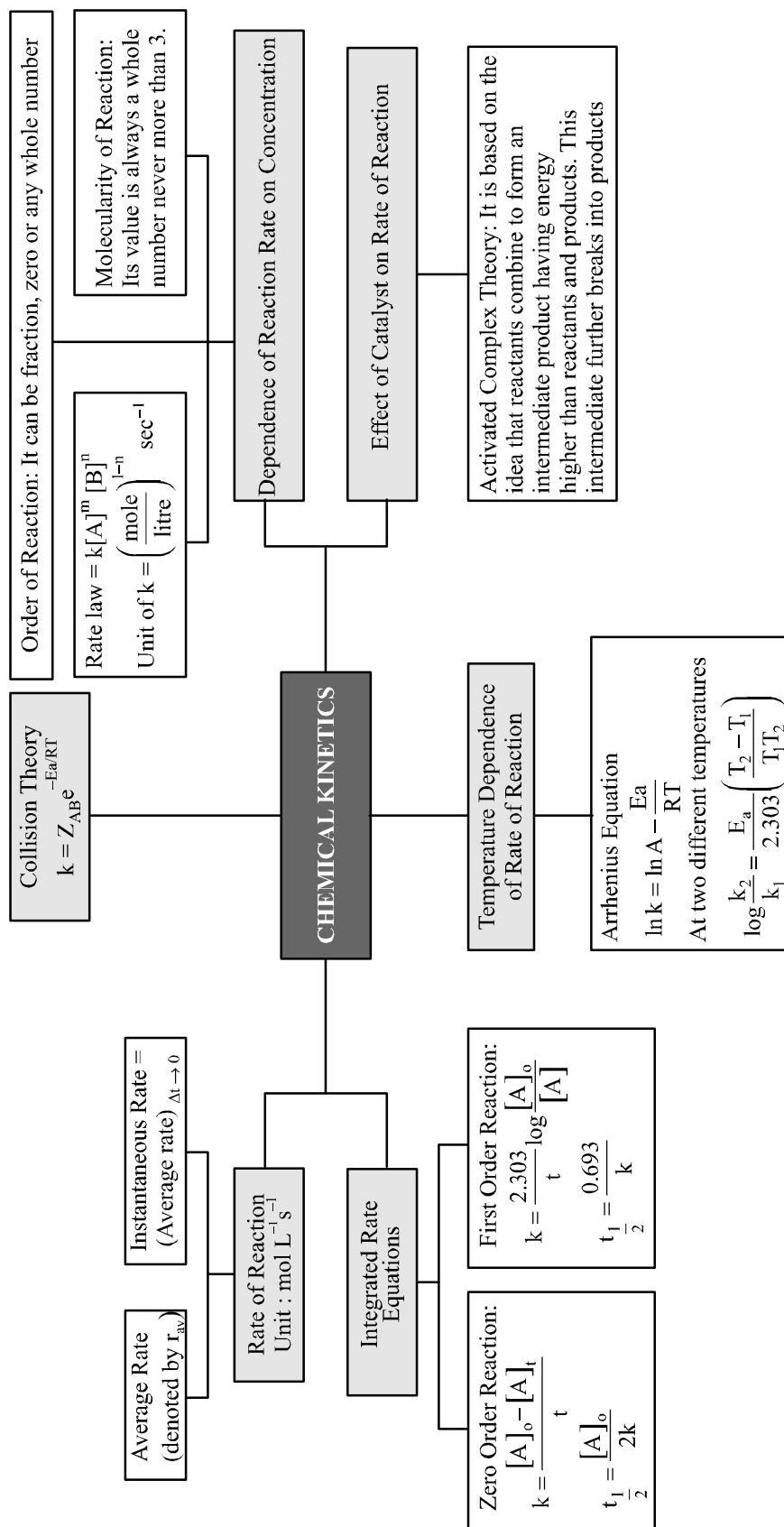
$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

Where $P \rightarrow$ Probability or steric factor

$Z_{AB} \rightarrow$ collision frequency of reactants A and B

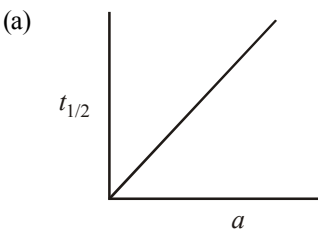
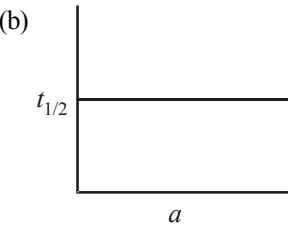
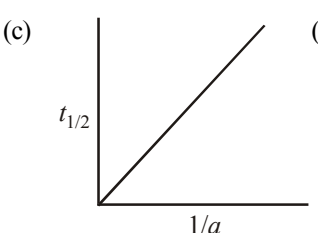
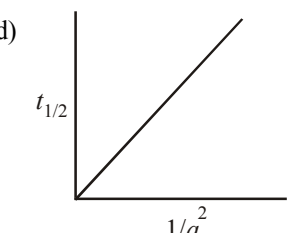
$e^{-E_a/RT} \rightarrow$ fraction of molecules with energies equal to or greater than E_a .

CONCEPT MAP

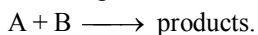


EXERCISE - 1

Conceptual Questions

- The rate constant of first order reaction is 3×10^{-6} per second. The initial concentration is 0.10 M. The initial rate is:
 - 3×10^{-7} moles/litre/sec
 - 3×10^{-8} moles/litre/sec
 - 3×10^{-5} moles/litre/sec
 - 3×10^{-8} moles/litre/sec
- Which of the following statement is true for the reaction, $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$. The rate law is $\frac{dx}{dt} = k[\text{H}_2][\text{Br}_2]^{1/2}$:
 - order of reaction is 1.5
 - molecularity of the reaction is 2
 - by increasing the concentration of Br_2 four times the rate of reaction is doubled
 - all the above are correct.
- The rate constant k , for the reaction $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ is $1.3 \times 10^{-2}\text{s}^{-1}$. Which equation given below describes the change of $[\text{N}_2\text{O}_5]$ with time? $[\text{N}_2\text{O}_5]_0$ and $[\text{N}_2\text{O}_5]_t$ correspond to concentration of N_2O_5 initially and at time t .
 - $[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 + kt$
 - $[\text{N}_2\text{O}_5]_0 = [\text{N}_2\text{O}_5]_t e^{kt}$
 - $\log [\text{N}_2\text{O}_5]_t = \log [\text{N}_2\text{O}_5]_0 + kt$
 - $\ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = kt$
- For the reaction $2\text{A} + \text{B} \rightarrow 3\text{C} + \text{D}$ Which of the following does not express the reaction rate?
 - $-\frac{d[\text{B}]}{dt}$
 - $\frac{d[\text{D}]}{dt}$
 - $-\frac{1}{2} \frac{d[\text{A}]}{dt}$
 - $-\frac{1}{3} \frac{d[\text{C}]}{dt}$
- Consider the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
The equality relationship between $\frac{d[\text{NH}_3]}{dt}$ and $-\frac{d[\text{H}_2]}{dt}$ is
 - $+\frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$
 - $+\frac{d[\text{NH}_3]}{dt} = -\frac{3}{2} \frac{d[\text{H}_2]}{dt}$
 - $\frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{H}_2]}{dt}$
 - $\frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$
- For the reaction system: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO , the rate of reaction will
 - diminish to one-eighth of its initial value
 - increase to eight times of its initial value
 - increase to four times of its initial value
 - diminish to one-fourth of its initial value
- For reaction $a\text{A} \rightarrow x\text{P}$, when $[\text{A}] = 2.2 \text{ mM}$, the rate was found to be 2.4 mM s^{-1} . On reducing concentration of A to half, the rate changes to 0.6 mM s^{-1} . The order of reaction with respect to A is:
 - 1.5
 - 2.0
 - 2.5
 - 3.0
- The rate of reaction is doubled for every 10°C rise in temperature. The increase in reaction rate as a result of temperature rise from 10°C to 100°C is:
 - 614
 - 400
 - 512
 - 112
- In the reaction $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will:
 - increase 2 times
 - increase 4 times
 - decrease 2 times
 - remain the same
- Which of the following graphs represent relation between initial concentration of reactants and half-life for third order reaction?
 - 
 - 
 - 
 - 
- The differential rate law for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is
 - $-\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = -\frac{d[\text{HI}]}{dt}$
 - $\frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$
 - $\frac{1}{2} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{I}_2]}{dt} = -\frac{d[\text{HI}]}{dt}$
 - $-2 \frac{d[\text{H}_2]}{dt} = -2 \frac{d[\text{I}_2]}{dt} = \frac{d[\text{HI}]}{dt}$
- Select the rate law that corresponds to data shown for the

following reaction



Exp.	[A]	[B]	Initial rate
1	0.012	0.035	0.1
2	0.024	0.070	0.8
3	0.024	0.035	0.1
4	0.012	0.070	0.8

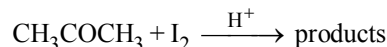
- (a) $\text{rate} = k[B]^3$ (b) $\text{rate} = k[B]^4$
 (c) $\text{rate} = k[A][B]^3$ (d) $\text{rate} = k[A]^2[B]^2$
13. For the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, rate and rate constant are $1.02 \times 10^{-4} \text{ mol lit}^{-1} \text{ sec}^{-1}$ and $3.4 \times 10^{-5} \text{ sec}^{-1}$ respectively then concentration of N_2O_5 at that time will be
 (a) 1.732M (b) 3M
 (c) $3.4 \times 10^5 \text{ M}$ (d) $1.02 \times 10^{-4} \text{ M}$
14. For a first order reaction, to obtain a positive slope, we need to plot {where [A] is the concentration of reactant A}
 (a) $-\log_{10}[A]$ vs t (b) $-\log_e[A]$ vs t
 (c) $\log_{10}[A]$ vs $\log t$ (d) $[A]$ vs t
15. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ sec}$. The rate constant of reaction in sec^{-1} is:
 (a) 2×10^4 (b) 3.45×10^{-5}
 (c) 1.386×10^{-4} (d) 2×10^{-4}
16. The rate constant for the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ is $3.10 \times 10^{-5} \text{ sec}^{-1}$. If the rate is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$ then the concentration of N_2O_5 (in mol litre^{-1}) is:
 (a) 0.04 (b) 0.8 (c) 0.07 (d) 1.4
17. T_{50} of first -order reaction is 10 min. Starting with 10 mol L^{-1} , rate after 20 min is
 (a) $0.0693 \text{ mol L}^{-1} \text{ min}^{-1}$
 (b) $0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1}$
 (c) $0.0693 \times 5 \text{ mol L}^{-2} \text{ min}^{-1}$
 (d) $0.0693 \times 10 \text{ mol L}^{-1} \text{ min}^{-1}$
18. Velocity constant K of a reaction is affected by
 (a) Change in the concentration of the reactant
 (b) Change of temperature
 (c) Change in the concentration of the product
 (d) None of the above
19. The first order rate constant for a certain reaction increases from $1.667 \times 10^{-6} \text{ s}^{-1}$ at 727°C to $1.667 \times 10^{-4} \text{ s}^{-1}$ at 1571°C . The rate constant at 1150°C , assuming constancy of activation energy over the given temperature range is [Given : $\log 19.9 = 1.299$]
 (a) $3.911 \times 10^{-5} \text{ s}^{-1}$ (b) $1.139 \times 10^{-5} \text{ s}^{-1}$
 (c) $3.318 \times 10^{-5} \text{ s}^{-1}$ (d) $1.193 \times 10^{-5} \text{ s}^{-1}$
20. For the following reaction scheme (homogeneous), the rate constant has units : $A + B \xrightarrow{K} C$
 (a) $\text{sec}^{-1} \text{ mole}$ (b) sec^{-1}
 (c) $\text{sec}^{-1} \text{ litre mole}^{-1}$ (d) sec
21. A substance 'A' decomposes by a first order reaction starting initially with $[A] = 2.00 \text{ M}$ and after 200 min, $[A]$ becomes 0.15 M . For this reaction $t_{1/2}$ is
 (a) 53.72 min (b) 50.49 min (c) 48.45 min (d) 46.45 min
22. After how many seconds will the concentration of the reactants in a first order reaction be halved, if the decay constant is $1.155 \times 10^{-3} \text{ sec}^{-1}$.
 (a) 200 (b) 400 (c) 600 (d) 800
23. The plot of concentration of the reactant vs time for a reaction is a straight line with a negative slope. The reaction follows a rate equation
 (a) zero order (b) first order
 (c) second order (d) third order
24. Half life of a first order reaction is 4s and the initial concentration of the reactant is 0.12 M . The concentration of the reactant left after 16 s is
 (a) 0.0075 M (b) 0.06 M (c) 0.03 M (d) 0.015 M
25. $3A \rightarrow B + C$, it would be a zero order reaction when
 (a) the rate of reaction is proportional to square of concentration of A
 (b) the rate of reaction remains same at any concentration of A
 (c) the rate remains unchanged at any concentration of B and C
 (d) the rate of reaction doubles if concentration of B is increased to double
26. A first order reaction is 50% completed in 30 minutes at 27°C . Its rate constant is :
 (a) $2.31 \times 10^{-2} \text{ minute}^{-1}$ (b) $3.21 \times 10^{-5} \text{ minute}^{-1}$
 (c) $4.75 \times 10^{-2} \text{ minute}^{-1}$ (d) $1.33 \times 10^{-3} \text{ minute}^{-1}$
27. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B?
 (a) 2 hours (b) 1 hour (c) 0.5 hour (d) 0.25 hour
28. Out of the following reaction which will proceed in forward direction if volume of container is increased?
 (a) $H_2 + Cl_2 \rightarrow 2HCl$
 (b) $CaCO_3 \rightarrow CaO + CO_2$
 (c) $N_2 + 3H_2 \rightarrow 2NH_3$
 (d) $N_2 + 2O_2 \rightarrow N_2O_4$
29. The rate of a first order reaction is $1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ at 0.5 M concentration of the reactant. The half life of the reaction is
 (a) 0.383 min (b) 23.1 min (c) 8.73 min (d) 7.53 min
30. For a first order reaction $A \rightarrow B$ the reaction rate at reactant concentration of 0.01 M is found to be $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$. The half life period of the reaction is
 (a) 30 s (b) 220 s (c) 300 s (d) 347 s
31. For a chemical reaction which can never be a fraction :
 (a) rate constant (b) order
 (c) molecularity (d) half life
32. If half-life of a substance is 5 yrs, then the total amount of substance left after 15 years, when initial amount is 64 grams

is

- (a) 16 grams (b) 2 grams (c) 32 grams (d) 8 grams.
33. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is
(a) 7.5 minutes (b) 15 minutes
(c) 30 minutes (d) 60 minutes
34. The concentration of a reactant X decreases from 0.1 M to 0.005 M in 40 min. If the reaction follows first order kinetics, the rate of the reaction when the concentration of X is 0.01 M will be
(a) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (b) $3.47 \times 10^{-4} \text{ M min}^{-1}$
(c) $3.47 \times 10^{-5} \text{ M min}^{-1}$ (d) $7.5 \times 10^{-4} \text{ M min}^{-1}$
35. The order of a reaction with rate equal to $k[A]^{3/2}[B]^{-1/2}$ is :
(a) 1 (b) $-\frac{1}{2}$ (c) $-\frac{3}{2}$ (d) 2
36. The rate constant for a first order reaction whose half-life, is 480 seconds is :
(a) $2.88 \times 10^{-3} \text{ sec}^{-1}$ (b) $2.72 \times 10^{-3} \text{ sec}^{-1}$
(c) $1.44 \times 10^{-3} \text{ sec}^{-1}$ (d) 1.44 sec^{-1}
37. In a reaction, when the concentration of reactant is increased two times, the increase in rate of reaction was four times. Order of reaction is :
(a) zero (b) 1 (c) 2 (d) 3
38. The rate constant of a first order reaction is $6.9 \times 10^{-3} \text{ s}^{-1}$. How much time will it take to reduce the initial concentration to its $1/8^{\text{th}}$ value?
(a) 100 s (b) 200 s (c) 300 s (d) 400 s
39. In a 1st order reaction, reactant concentration C varies with time t as :
(a) $\frac{1}{C}$ increases linearly with t
(b) $\log C$ decreases linearly with t
(c) C decreases with $\frac{1}{t}$
(d) $\log C$ decreases with $\frac{1}{t}$
40. A substance 'A' decomposes by a first order reaction starting initially with $[A] = 2.00 \text{ mol/litre}$ and after 200 sec, $[A] = 0.15 \text{ mol/litre}$. For this reaction, what is the value of k ?
(a) $1.29 \times 10^{-2} \text{ sec}^{-1}$ (b) $2.03 \times 10^{-3} \text{ sec}^{-1}$
(c) $1.80 \times 10^{-3} \text{ sec}^{-1}$ (d) $1.55 \times 10^{-2} \text{ sec}^{-1}$
41. A reaction proceeds by first order, 75% of this reaction was completed in 32 min. The time required for 50% completion is
(a) 8min (b) 16min (c) 20min (d) 24min
42. For the third order reaction, $3A \longrightarrow \text{products}$, with 0.1 M as the initial concentration of A, $t_{1/2}$ is 8 hr 20 minute. The rate constant of the reaction is
(a) $5 \times 10^{-3} \text{ lit}^2 \text{ mole}^{-1} \text{ sec}^{-1}$
(b) $50 \text{ lit}^2 \text{ mole}^{-2} \text{ sec}^{-1}$
(c) $5.0 \times 10^{-3} \text{ lit}^2 \text{ mole}^{-2} \text{ sec}^{-1}$
(d) $5 \times 10^{-2} \text{ lit}^2 \text{ mole}^{-2} \text{ sec}^{-1}$
43. What is order with respect to A, B, C, respectively

[A]	[B]	[C]	rate (M/sec.)
0.2	0.1	0.02	8.08×10^{-3}
0.1	0.2	0.02	2.01×10^{-3}
0.1	1.8	0.18	6.03×10^{-3}
0.2	0.1	0.08	6.464×10^{-2}

- (a) $-1, 1, 3/2$ (b) $-1, 1, 1/2$
(c) $1, 3/2, -1$ (d) $1, -1, 3/2$
44. For a chemical reaction $t_{1/2}$ is 2.5 hours at room temperature. How much of the reactant will be left after 7.5 hours if initial weight of reactant was 160 gm?
(a) 10 gm (b) 40 gm (c) 80 gm (d) 20 gm
45. For the reaction,

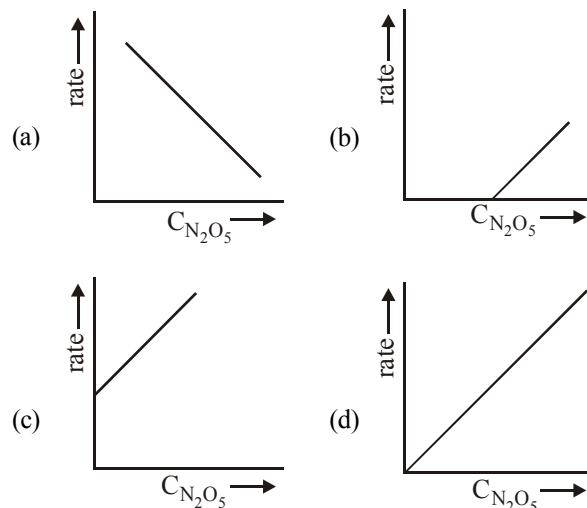


The rate is governed by expression

$$\frac{dx}{dt} = k[\text{acetone}][\text{H}^+]$$

The order w.r.t. I_2 is:

- (a) 1 (b) 0 (c) 3 (d) 2
46. In the following first order competing reactions
 $\text{X} + \text{reagent} \rightarrow \text{product}$
 $\text{Y} + \text{reagent} \rightarrow \text{product}$
The ratio of $\frac{k_1}{k_2}$ if only 50% of Y will have been reacted when 94% of X has been reacted is
(a) 3.06 (b) 1.06
(c) 4.06 (d) 0.06
47. The rate constant of a reaction is $3.00 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$. The order of this reaction will be:
(a) 0 (b) 1 (c) 2 (d) 3
48. Point out the wrong statement:
For a first order reaction
(a) time for half-change ($t_{1/2}$) is independent of initial concentration
(b) change in the concentration unit does not change the rate constant (k)
(c) time for half-change $\times$ rate constant = 0.693
(d) the unit of k is $\text{mole}^{-1} \text{ min}^{-1}$
49. Which one of the following plots is true for the first order decomposition of N_2O_5 ?

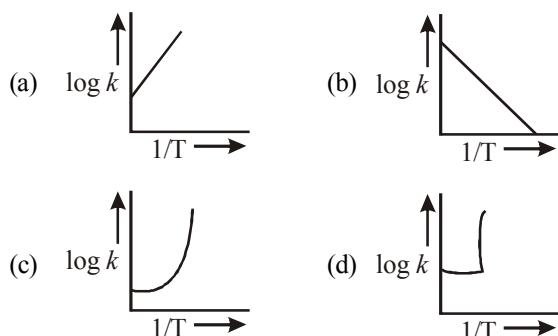


50. The first order rate constant for the decomposition of N_2O_5

- is $6.2 \times 10^{-4} \text{ sec}^{-1}$. The half life period for this decomposition in seconds is
 (a) 1117.7 (b) 111.7 (c) 223.4 (d) 160.9
51. For a certain reaction, rate = $k \times [\text{H}^+]^n$. If pH of reaction changes from two to one, the rate becomes 100 times of its value at pH = 2, the order of reaction is –
 (a) 1 (b) 2 (c) 0 (d) 3
52. The half-life of a reaction is inversely proportional to the square of the initial concentration of the reactant. Then the order of the reaction is
 (a) 0 (b) 1 (c) 2 (d) 3
53. Ethylene is produced by $\text{C}_4\text{H}_8 \xrightarrow{\Delta} 2\text{C}_2\text{H}_4$. The rate constant is $2.3 \times 10^{-4} \text{ sec}^{-1}$. Approximately in what time will the molar ratio of ethylene to cyclobutane in mixture attain the value equal to one?
 (log 2 = 0.3, log 3 = 0.47)
 (a) 1700 sec (b) 1600 sec
 (c) 2000 sec (d) 1200 sec
54. $t_{\frac{1}{4}}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is k , the $t_{\frac{1}{4}}$ can be written as
 (a) $0.75/k$ (b) $0.69/k$ (c) $0.29/k$ (d) $0.10/k$
55. What is the half life of a radioactive substance if 87.5% of any given amount of the substance disintegrates in 40 minutes?
 (a) 20 minutes (b) 10 minutes
 (c) 13 minutes 32 sec (d) 160 minutes
56. The rate law for the reaction $2\text{X} + \text{Y} \rightarrow \text{Z}$ is Rate = $k[\text{X}][\text{Y}]$. The correct statement with regard to this relation is
 (a) the unit of k is s^{-1}
 (b) the rate of the reaction is independent of $[\text{X}]$ and $[\text{Y}]$
 (c) for this reaction $t_{1/2}$ is independent of initial concentrations of reactant
 (d) the rate of formation of Z is half of the rate of disappearance of X
57. For an exothermic reaction, the energy of activation of the reactants is
 (a) equal to the energy of activation of products
 (b) less than the energy of activation of products
 (c) greater than the energy of activation of products
 (d) sometimes greater and sometimes less than that of the products
58. A chemical reaction is catalyzed by a catalyst X . Hence X
 (a) reduces enthalpy of the reaction
 (b) decreases rate constant of the reaction
 (c) increases activation energy of the reaction
 (d) does not affect equilibrium constant of the reaction
59. Consider the following statements:
 I. Increase in concentration of reactant increases the rate of a zero order reaction.
 II. Rate constant k is equal to collision frequency A if $E_a = 0$.
 III. Rate constant k is equal to collision frequency A if $E_a = \infty$.
- IV. In k vs T is a straight line.
 V. In k vs $1/T$ is a straight line.
 Correct statements are
 (a) I and IV (b) II and V
 (c) III and IV (d) II and III
60. Activation energy of a chemical reaction can be determined by
 (a) evaluating rate constant at standard temperature
 (b) evaluating velocities of reaction at two different temperatures
 (c) evaluating rate constants at two different temperatures
 (d) changing concentration of reactants
61. The rate law for the reaction
 $\text{xA} + \text{yB} \longrightarrow \text{mP} + \text{nQ}$ is Rate = $k[\text{A}]^c[\text{B}]^d$. What is the total order of the reaction?
 (a) $(x+y)$ (b) $(m+n)$
 (c) $(c+d)$ (d) x/y
62. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = Ae^{-E_a^*/RT}$. Activation energy (E_a^*) of the reaction can be calculated by plotting
 (a) $\log k$ vs $\frac{1}{\log T}$ (b) k vs T
 (c) k vs $\frac{1}{\log T}$ (d) $\log k$ vs $\frac{1}{T}$
63. For a first order reaction, the time taken to reduce the initial concentration by a factor of $\frac{1}{4}$ is 20 minutes. The time required to reduce initial concentration by a factor of $\frac{1}{16}$ is
 (a) 20 min (b) 10 min
 (c) 80 min (d) 40 min
64. The activation energy for a simple chemical reaction $\text{A} \rightarrow \text{B}$ is E_a in forward direction. The activation energy for reverse reaction
 (a) is always double of E_a
 (b) is negative of E_a
 (c) is always less than E_a
 (d) can be less than or more than E_a
65. Rate of a reaction can be expressed by Arrhenius equation as : $k = Ae^{-E_a/RT}$
 In this equation, E_a represents
 (a) the total energy of the reacting molecules at a temperature, T
 (b) the fraction of molecules with energy greater than the activation energy of the reaction
 (c) the energy below which all the colliding molecules will react
 (d) the energy below which colliding molecules will not react
66. The minimum energy a molecule should possess in order to enter into a fruitful collision is known as
 (a) reaction energy (b) collision energy
 (c) activation energy (d) threshold energy
67. Which one of the following reactions is a true first order

reaction?

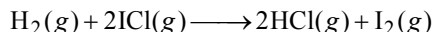
- (a) Alkaline hydrolysis of ethyl acetate
 (b) Acid catalyst hydrolysis of ethyl acetate
 (c) Decomposition of N_2O
 (d) Decomposition of gaseous ammonia on a hot platinum surface
68. The reason for almost doubling the rate of reaction on increasing the temperature of the reaction system by $10^\circ C$ is
 (a) The value of threshold energy increases
 (b) Collision frequency increases
 (c) The fraction of the molecule having energy equal to threshold energy or more increases
 (d) Activation energy decreases
69. For a reaction, activation energy (E_a) = 0 and rate constant (k) = $3.2 \times 10^6 s^{-1}$ at 300 K. What is the value of the rate constant at 310 K
 (a) $3.2 \times 10^{-12} s^{-1}$ (b) $3.2 \times 10^6 s^{-1}$
 (c) $6.4 \times 10^{12} s^{-1}$ (d) $6.4 \times 10^6 s^{-1}$
70. In the Arrhenius plot of $\ln k$ vs $\frac{1}{T}$, a linear plot is obtained with a slope of $-2 \times 10^4 K$. The energy of activation of the reaction (in $kJ mol^{-1}$) is (R value is $8.3 J K^{-1} mol^{-1}$)
 (a) 83 (b) 166 (c) 249 (d) 332
71. A graph plotted between $\log k$ vs $1/T$ for calculating activation energy is shown by



72. Consider an endothermic reaction $X \rightarrow Y$ with the activation energies, respectively, in general
 (a) $E_b < E_f$
 (b) $E_b > E_f$
 (c) $E_b = E_f$
 (d) There is no definite relation between E_b and E_f
73. When a biochemical reaction is carried out in laboratory in the absence of enzyme then rate of reaction obtained is 10^{-6} times, then activation energy of reaction in the presence of enzyme is
 (a) $\frac{6}{RT}$
 (b) different from E_a obtained in laboratory
 (c) P is required
 (d) can't say anything
74. In a first order reaction, the concentration of the reactant is reduced to $\frac{1}{8}$ of the initial concentration in 75 minutes at

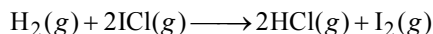
298 K. What is the half-life period of the reaction in minutes?

- (a) 50 (b) 15 (c) 45 (d) 25
75. The reaction of hydrogen and iodine monochloride is given as:

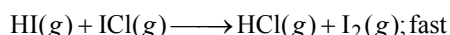
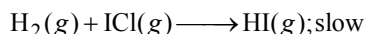


The reaction is of first order with respect to $H_2(g)$ and $ICl(g)$, following mechanisms were proposed.

Mechanism A:



Mechanism B:

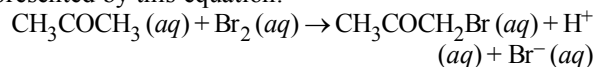


Which of the above mechanism(s) can be consistent with the given information about the reaction?

- (a) A and B both (b) neither A nor B
 (c) A only (d) B only
76. In a first-order reaction $A \rightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is

- (a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$

77. The bromination of acetone that occurs in acid solution is represented by this equation.



These kinetic data were obtained for given reaction concentrations.

Initial Concentrations, M			Initial rate, disappearance of Br_2 , Ms^{-1}
$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$	
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

Based on given data, the rate equations is:

- (a) $\text{Rate} = k[CH_3COCH_3][H^+]$
 (b) $\text{Rate} = k[CH_3COCH_3][Br_2]$
 (c) $\text{Rate} = k[CH_3COCH_3][Br_2][H^+]^2$
 (d) $\text{Rate} = k[CH_3COCH_3][Br_2][H^+]$
78. For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$,

$$\frac{d[NH_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}, \text{ the value of } -\frac{d[H_2]}{dt}$$

would be :

- (a) $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (b) $6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (c) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (d) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
79. In the reaction



The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following:

- (a) $\frac{d[\text{Br}_2]}{dt} = -\frac{5}{3} \frac{d[\text{Br}^-]}{dt}$ (b) $\frac{d[\text{Br}_2]}{dt} = \frac{5}{3} \frac{d[\text{Br}^-]}{dt}$
 (c) $\frac{d[\text{Br}_2]}{dt} = \frac{3}{5} \frac{d[\text{Br}^-]}{dt}$ (d) $\frac{d[\text{Br}_2]}{dt} = -\frac{3}{5} \frac{d[\text{Br}^-]}{dt}$

80. Half life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction is :

- (a) $0.5 \times 10^{-2} \text{ s}^{-1}$ (b) $0.5 \times 10^{-3} \text{ s}^{-1}$
 (c) $5.0 \times 10^{-2} \text{ s}^{-1}$ (d) $5.0 \times 10^{-3} \text{ s}^{-1}$

81. For the reaction $\text{A} + \text{B} \longrightarrow \text{products}$, it is observed that:

- (1) On doubling the initial concentration of A only, the rate of reaction is also doubled and
 (2) On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by:

- (a) $\text{rate} = k[\text{A}][\text{B}]^2$ (b) $\text{rate} = k[\text{A}]^2[\text{B}]^2$
 (c) $\text{rate} = k[\text{A}][\text{B}]$ (d) $\text{rate} = k[\text{A}]^2[\text{B}]$

82. For the reaction $[\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})]$

the value of rate of disappearance of N_2O_5 is given as $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as :

- (a) $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
 (b) $1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
 (c) $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
 (d) $1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ and $6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

83. For an endothermic reaction, energy of activation is E_a and enthalpy of reaction of ΔH (both of these in kJ/mol). Minimum value of E_a will be.

- (a) less than ΔH (b) equal to ΔH
 (c) more than ΔH (d) equal to zero

84. During the kinetic study of the reaction, $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, following results were obtained:

Run	$[\text{A}](\text{mol L}^{-1})$	$[\text{B}](\text{mol L}^{-1})$	Initial rate of formation of D ($\text{mol L}^{-1} \text{ min}^{-1}$)
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Based on the above data which one of the following is correct?

- (a) $\text{rate} = k[\text{A}]^2[\text{B}]$ (b) $\text{rate} = k[\text{A}][\text{B}]$
 (c) $\text{rate} = k[\text{A}]^2[\text{B}]^2$ (d) $\text{rate} = k[\text{A}][\text{B}]^2$

85. The rate of the reaction $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$ is given

by the rate equation $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$

The value of the rate constant can be increased by:

- (a) increasing the concentration of NO.
 (b) increasing the temperature.
 (c) increasing the concentration of the Cl_2
 (d) doing all of these

86. Which one of the following statements for the order of a reaction is incorrect ?

- (a) Order can be determined only experimentally.
 (b) Order is not influenced by stoichiometric coefficient of the reactants.
 (c) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction.
 (d) Order of reaction is always whole number.

87. The unit of rate constant for a zero order reaction is

- (a) $\text{mol L}^{-1} \text{ s}^{-1}$ (b) $\text{L mol}^{-1} \text{ s}^{-1}$
 (c) $\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ (d) s^{-1}

88. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C , the rate of the reaction will become :

- (a) 256 times (b) 512 times (c) 64 times (d) 128 times

89. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by :

(a) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ (b) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

(c) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} + \frac{1}{T_1} \right)$ (d) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

90. The energies of activation for forward and reverse reactions for $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1} . The enthalpy change of the reaction ($\text{A}_2 + \text{B}_2 \rightarrow 2\text{AB}$) in the presence of a catalyst will be (in kJ mol^{-1})

- (a) 20 (b) 300 (c) 120 (d) 280

91. Consider the reaction, $2\text{A} + \text{B} \rightarrow \text{products}$. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is

- (a) s^{-1} (b) $\text{L mol}^{-1} \text{ s}^{-1}$
 (c) no unit (d) $\text{mol L}^{-1} \text{ s}^{-1}$

92. For a reaction $\frac{1}{2}\text{A} \rightarrow 2\text{B}$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression

(a) $-\frac{d[\text{A}]}{dt} = \frac{1}{2} \frac{d[\text{B}]}{dt}$ (b) $-\frac{d[\text{A}]}{dt} = \frac{1}{4} \frac{d[\text{B}]}{dt}$

(c) $-\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt}$ (d) $-\frac{d[\text{A}]}{dt} = 4 \frac{d[\text{B}]}{dt}$

93. The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be ($\log 2 = 0.301$)

- (a) 23.03 minutes (b) 46.06 minutes
 (c) 460.6 minutes (d) 230.03 minutes

94. For a first order reaction $(A) \rightarrow \text{products}$ the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is :
- (a) $1.73 \times 10^{-5} \text{ M/min}$ (b) $3.47 \times 10^{-4} \text{ M/min}$
 (c) $3.47 \times 10^{-5} \text{ M/min}$ (d) $1.73 \times 10^{-4} \text{ M/min}$
95. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be : ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.301$)
- (a) 53.6 kJ mol^{-1} (b) 48.6 kJ mol^{-1}
 (c) 58.5 kJ mol^{-1} (d) 60.5 kJ mol^{-1}
96. The rate of reaction depends upon the [1995]
 (a) volume (b) force
 (c) pressure (d) conc. of reactants
97. Half life of a first order reaction is 4 s and the initial concentration of the reactants is 0.12 M. The concentration of the reactant left after 16 s is [1999]
 (a) 0.0075 M (b) 0.06 M
 (c) 0.03 M (d) 0.015 M
98. The plot of concentration of the reactant vs. time for a reaction is a straight line with a negative slope. The reaction follows a [1996]
 (a) zero order rate equation
 (b) first order rate equation
 (c) second order rate equation
 (d) third order rate equation
99. Select the rate law that corresponds to data shown for the following reaction [1994]
 $A + B \longrightarrow \text{products.}$
- | Exp. | [A] | [B] | Initial rate |
|------|-------|-------|--------------|
| 1 | 0.012 | 0.035 | 0.1 |
| 2 | 0.024 | 0.070 | 0.8 |
| 3 | 0.024 | 0.035 | 0.1 |
| 4 | 0.012 | 0.070 | 0.8 |
- (a) $\text{rate} = k [B]^3$
- (b) $\text{rate} = k [B]^4$
 (c) $\text{rate} = k [A] [B]^3$
 (d) $\text{rate} = k [A]^2 [B]^2$
100. Activation energy of a chemical reaction can be determined by [1998]
 (a) evaluating rate constant at standard temperature
 (b) evaluating velocities of reaction at two different temperatures
 (c) evaluating rate constants at two different temperatures
 (d) changing concentration of reactants

EXERCISE - 2

Applied Questions

1. The rate equation for a reaction,
 $N_2O \longrightarrow N_2 + 1/2O_2$
 is $\text{Rate} = k[N_2O]^0 = k$. If the initial concentration of the reactant is $a \text{ mol Lit}^{-1}$, the half-life period of the reaction is
- (a) $t_{1/2} = \frac{a}{2k}$ (b) $t_{1/2} = \frac{ka}{2}$
 (c) $t_{1/2} = \frac{a}{k}$ (d) $t_{1/2} = \frac{k}{a}$
2. The rate law for a reaction between the substances A and B is given by $\text{Rate} = k [A]^n [B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as
- (a) $(m+n)$ (b) $(n-m)$ (c) $2^{(n-m)}$ (d) $\frac{1}{2^{(m+n)}}$
3. The rate equation for the reaction $2A + B \rightarrow C$ is found to be : $\text{rate} = k[A][B]$. The correct statement in relation to this reaction is that the
- (a) rate of formation of C is twice the rate of disappearance of A
 (b) $t_{1/2}$ is a constant
 (c) unit of k must be s^{-1}
 (d) value of k is independent of the initial concentrations of A and B
4. For a first order reaction the rate constant is 6.909 min^{-1} .

The time taken for 75% conversion in minutes is

- (a) $\frac{3}{2} \log 2$ (b) $\frac{2}{3} \log 3$
 (c) $\frac{2}{3} \log 2$ (d) $\frac{3}{2} \log \left(\frac{3}{4}\right)$
5. Rate of a reaction can be expressed by following rate expression
 $\text{Rate} = k[A]^2[B]$, if concentration of A is increased by 3 times, and concentration of B is increased by 2 times, how many times rate of reaction increases?
 (a) 9 times (b) 27 times
 (c) 18 times (d) 8 times
6. The decomposition of N_2O_5 occurs as
 $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ and follows 1st order kinetics, hence:
 (a) the reaction is unimolecular
 (b) the reaction is bimolecular
 (c) $t_{1/2} \propto a^0$
 (d) None of these
7. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. The half-life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is
 (a) 120 (b) 60 (c) 240 (d) 180
8. Diazonium salt decomposes as
 $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$
 At 0°C , the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is
 (a) a first order reaction
 (b) a second order reaction
 (c) independent of the initial concentration of the salt
 (d) a zero order reaction
9. If ' P ' is the intensity of absorbed light and ' C ' is the concentration of AB for the photochemical process,
 $AB + h\nu \longrightarrow AB^*$, the rate of formation of AB^* is directly proportional to
 (a) C (b) I (c) I^2 (d) CI
10. The rate constant of a reaction becomes equal to the pre-exponential factor when
 (a) the absolute temperature is zero
 (b) the activation energy is infinity
 (c) the absolute temperature is infinity
 (d) the temperature in Celsius is zero.
11. The rate of reaction is doubled for every 10°C rise in temperature. The increase in reaction rate as a result of temperature rise from 10°C to 100°C is
 (a) 112 (b) 512 (c) 400 (d) 614
12. For the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

if $\frac{\Delta[\text{NH}_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$, the value of $\frac{-\Delta[\text{H}_2]}{\Delta t}$ would be

- (a) $1 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$ (b) $3 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$
 (c) $4 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$ (d) $6 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$

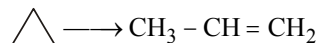
13. Lead is the final product formed by a series of changes in which the rate determining stage is the radioactive decay of uranium-238 with a half-life of 4.5×10^9 years. What would be the age of a rock sample originally lead free in which the molar proportion of uranium to lead is now 1 : 3?
 (a) 1.5×10^9 years (b) 2.25×10^9 years
 (c) 4.5×10^8 years (d) 9.0×10^9 years
14. For the reaction $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$, the experimental data suggest, $\text{rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$. The molecularity and order of the reaction are respectively
 (a) $2, \frac{3}{2}$ (b) $\frac{3}{2}, \frac{3}{2}$ (c) 1, 1 (d) $1, \frac{1}{2}$
15. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will
 (a) remain unchanged (b) triple
 (c) increase by a factor of 4 (d) double
16. Which among the following plots are linear ($a - x$) is the concentration of reactant remaining after time, t
 (1) $(a - x)$ vs t , for a first order reaction
 (2) $(a - x)$ vs t , for a zero order reaction
 (3) $(a - x)$ vs t , for a second order reaction
 (4) $1/(a - x)$ vs t , for a second order reaction
 (a) 1 and 2 (b) 1 and 3
 (c) 2 and 3 (d) 2 and 4
17. A reaction was observed for 15 days and the percentage of the reactant remaining after the days indicated was recorded in the following table :

Time(days)	0	2	4	6	8	10	12	14	15
% reactant remaining	100	50	39	25	21	18	15	12.5	10

Which one of the following best describes the order and the half-life of the reaction?

Reaction Order	Half-life (days)
(a) First	2
(b) First	6
(c) Second	2
(d) Zero	6
18. A first order reaction is half completed in 45 minutes. How long does it need 99.9% of the reaction to be completed
 (a) 5 hours (b) 7.5 hours
 (c) 10 hours (d) 20 hours
19. In the first order reaction, the concentration of the reactant is reduced to 25% in one hour. The half life period of the reaction is
 (a) 2 hr (b) 4 hr (c) 1/2 hr (d) 1/4 hr
20. The half-life of 2 samples are 0.1 and 0.4 seconds. Their respective concentration are 200 and 50 respectively. What is the order of the reaction
 (a) 0 (b) 2 (c) 1 (d) 4
21. The rate constant of a first order reaction is doubled when the temperature is increased from 20°C to 25°C . How many times the rate constant will increase if the temperature is raised from 20°C to 40°C ?
 (a) 4 (b) 8 (c) 16 (d) 32

22. Cyclopropane rearranges to form propene



This follows first order kinetics. The rate constant is $2.714 \times 10^{-3} \text{ sec}^{-1}$. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec

- (a) 0.035 M (b) 0.22 M
(c) 0.145 M (d) 0.0018 M
23. The rate constant is doubled when temperature increases from 27°C to 37°C . Activation energy in kJ is
(a) 34 (b) 54 (c) 100 (d) 50
24. The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is
(a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$
(c) Infinity (d) $3.6 \times 10^{30} \text{ s}^{-1}$
25. The activation energy for a reaction is 9.0 kcal/mol. The increase in the rate constant when its temperature is increased from 298K to 308K is
(a) 63% (b) 50% (c) 100% (d) 10%
26. For the following reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$, the rate law is: $\text{Rate} = k [\text{NO}_2]^2$. If 0.1 mole of gaseous carbon monoxide is added at constant temperature to the reaction mixture which of the following statements is true?
(a) Both k and the reaction rate remain the same
(b) Both k and the reaction rate increase
(c) Both k and the reaction rate decrease
(d) Only k increases, the reaction rate remain the same
27. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately
(a) 45 minutes (b) 60 minutes
(c) 40 minutes (d) 50 minutes
28. The rate constants k_1 and k_2 for two different reactions are $10^{16} \cdot e^{-2000/T}$ and $10^{15} \cdot e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is:
(a) 1000 K (b) $\frac{2000}{2.303}$ K (c) 2000 K (d) $\frac{1000}{2.303}$ K
29. The rate of the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + 2\text{O}_2$ can be written in three ways:
$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = k [\text{N}_2\text{O}_5], \quad \frac{d[\text{NO}_2]}{dt} = k' [\text{N}_2\text{O}_5]$$
$$\frac{d[\text{O}_2]}{dt} = k'' [\text{N}_2\text{O}_5]$$

The relationship between k and k' and between k and k'' are:
(a) $k' = 2k$; $k'' = k$ (b) $k' = 2k$; $k'' = k/2$
(c) $k' = 2k$; $k'' = 2k$ (d) $k' = k$; $k'' = k$
30. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial velocity is ten times the permissible value, after how many days will it be safe to enter the room?
(a) 100 days (b) 1000 days
(c) 300 days (d) 10 days.
31. The time for half life period of a certain reaction $\text{A} \longrightarrow \text{Products}$ is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1} , how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction?

- (a) 4 h (b) 0.5 h (c) 0.25 h (d) 1 h

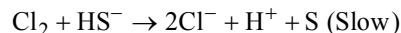
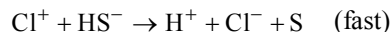
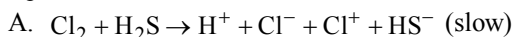
32. Consider the reaction:



The rate equation for this reaction is

$$\text{rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$$

Which of these mechanisms is/are consistent with this rate equation?



- (a) B only (b) Both A and B
(c) Neither A nor B (d) A only

33. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C , the rate of the reaction increases by about:

- (a) 10 times (b) 24 times (c) 32 times (d) 64 times

34. Consider a reaction $a\text{G} + b\text{H} \rightarrow \text{Products}$. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

- (a) 0 (b) 1 (c) 2 (d) 3

35. Under the same reaction conditions, initial concentration of $1.386 \text{ mol dm}^{-3}$ of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reaction is –

- (a) $0.5 \text{ mol}^{-1} \text{ dm}^3$ (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) $2.0 \text{ mol}^{-1} \text{ dm}^3$

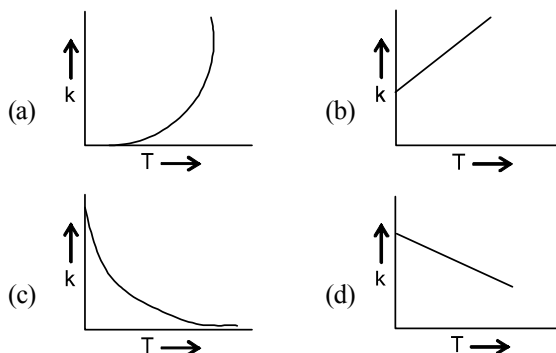
36. For a first order reaction $\text{A} \rightarrow \text{P}$, the temperature (T) dependent rate constant (k) was found to follow the equation

$$\log k = - (2000) \frac{1}{T} + 6.0.$$

The pre-exponential factor A and the activation energy E_a , respectively, are

- (a) $1.0 \times 10^6 \text{ s}^{-1}$ and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) $1.0 \times 10^6 \text{ s}^{-1}$ and 16.6 kJ mol^{-1}
(d) $1.0 \times 10^6 \text{ s}^{-1}$ and 38.3 kJ mol^{-1}

37. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is



38. For a reaction $\text{A} + \text{B} \longrightarrow \text{C} + 2\text{D}$, experimental results were collected for three trials and the data obtained are given

below:

Trial	[A], M	[B], M	Initial Rate, M s ⁻¹
1	0.40	0.20	5.5×10^{-4}
2	0.80	0.20	5.5×10^{-4}
3	0.40	0.40	2.2×10^{-3}

The correct rate law of the reaction is

- (a) $\text{rate} = k[A]^0[B]^2$ (b) $\text{rate} = k[A][B]^2$
 (c) $\text{rate} = k[A][B]$ (d) $\text{rate} = k[A][B]^0$

39. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. The half-life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is

- (a) 120 (b) 60
 (c) 240 (d) 180

40. The initial rates of reaction

$3A + 2B + C \longrightarrow \text{Products}$, at different initial concentrations are given below:

Initial rate, M s ⁻¹	[A] ₀ , M	[B] ₀ , M	[C] ₀ , M
5.0×10^{-3}	0.010	0.005	0.010
5.0×10^{-3}	0.010	0.005	0.015
1.0×10^{-2}	0.010	0.010	0.010
1.25×10^{-3}	0.005	0.005	0.010

The order with respect to the reactants, A, B and C are respectively

- (a) 3, 2, 0 (b) 3, 2, 1
 (c) 2, 2, 0 (d) 2, 2, 1

41. Which one of the following reactions is a true first order reaction?

- (a) Alkaline hydrolysis of ethyl acetate
 (b) Acid catalyst hydrolysis of ethyl acetate
 (c) Decomposition of N₂O
 (d) Decomposition of gaseous ammonia on a hot platinum surface

42. In a first order reaction, the concentration of the reactant is reduced to $\frac{1}{8}$ of the initial concentration in 75 minutes at 298 K. What is the half-life period of the reaction in minutes?

- (a) 50 (b) 15
 (c) 45 (d) 25

43. In the Arrhenius plot of $\ln k$ vs $\frac{1}{T}$, a linear plot is obtained with a slope of -2×10^4 K. The energy of activation of the reaction (in kJ mole⁻¹) is (R value is $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$)

- (a) 83 (b) 166
 (c) 249 (d) 332

44. For a first order reaction, the time taken to reduce the initial

concentration by a factor of $\frac{1}{4}$ is 20 minutes. The time

required to reduce initial concentration by a factor of $\frac{1}{16}$ is

- (a) 20 min (b) 10 min
 (c) 80 min (d) 40 min

45. The rate law for the reaction

$x\text{A} + y\text{B} \longrightarrow m\text{P} + n\text{Q}$ is $\text{Rate} = k[A]^c[B]^d$. What is the total order of the reaction?

- (a) $(x+y)$ (b) $(m+n)$
 (c) $(c+d)$ (d) x/y

46. Consider the following statements:

- I. Increase in concentration of reactant increases the rate of a zero order reaction.
 II. Rate constant k is equal to collision frequency A if $E_a = 0$.
 III. Rate constant k is equal to collision frequency A if $E_a = \infty$.
 IV. $\ln k$ vs T is a straight line.
 V. $\ln k$ vs $1/T$ is a straight line.

Correct statements are

- (a) I and IV (b) II and V
 (c) III and IV (d) II and III

DIRECTIONS for Qs. 47 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True

47. **Statement-1** : If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.

Statement-2 : Lower the activation energy, faster is the reaction.

48. **Statement-1** : If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.

Statement-2 : For a zero order reaction, the rate of reaction is independent of initial concentration.

49. **Statement-1** : If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.

Statement-2 : Lower the activation energy, faster is the reaction.

50. **Statement-1** : According to steady state hypothesis, in a multistep reaction, the change in concentration with time for reactive intermediates is zero.

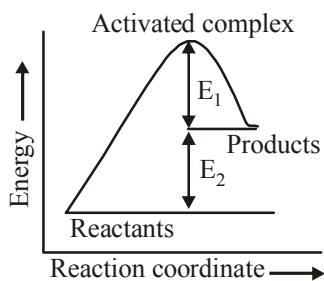
Statement-2 : The intermediates are so reactive that after a brief initial period their concentrations rise from zero to a small value and remains constant for most of the duration of the reaction.

EXERCISE - 3

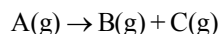
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- The role of a catalyst is to change
 (a) Gibbs energy of reaction
 (b) enthalpy of reaction
 (c) activation energy of reaction
 (d) equilibrium constant
- In the presence of a catalyst, the heat evolved or absorbed during the reaction
 (a) increases
 (b) decreases
 (c) remains unchanged
 (d) may increase or decrease
- Activation energy of a chemical reaction can be determined by
 (a) determining the rate constant at standard temperature
 (b) determining the rate constant at two temperatures
 (c) determining probability of collision
 (d) using catalyst
- Consider figure and mark the correct option.



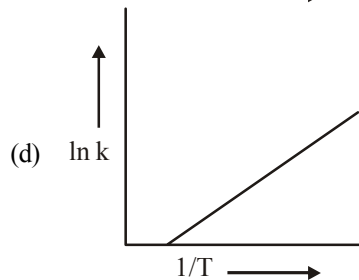
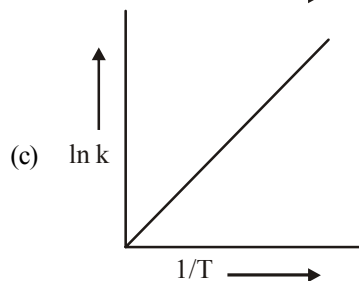
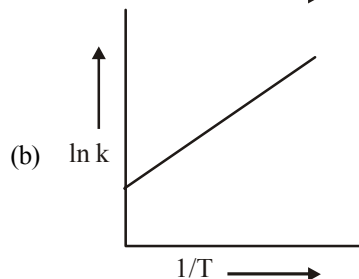
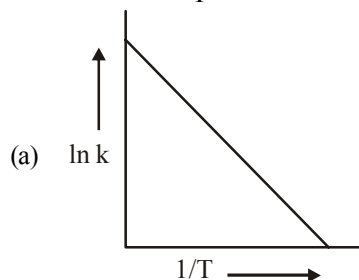
- Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant
 - Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant
 - Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product
 - Activation energy of backward reaction is E_1 and product is more stable than reactant
- Consider a first order gas phase decomposition reaction given below



The initial pressure of the system before decomposition of A was p_i . After lapse of time 't' total pressure of the system increased by x units and became ' p_t '. The rate constant k for the reaction is given as

- $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$
- $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
- $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$
- $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

- According to Arrhenius equation rate constant k is equal to $A e^{-E_a/RT}$. Which of the following options represents the graph of $\ln k$ vs $\frac{1}{T}$?

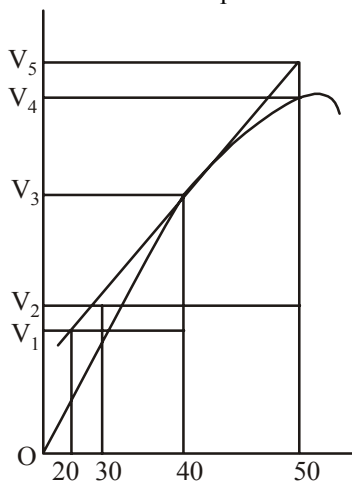


- Consider the Arrhenius equation given below and mark the correct option.

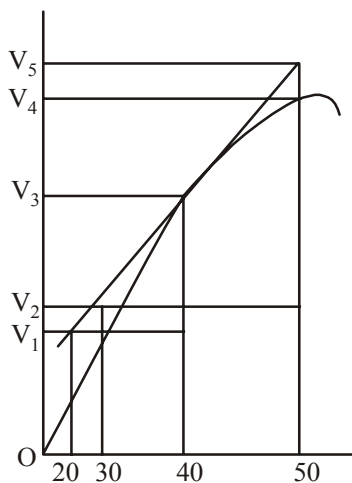
$$k = Ae^{-\frac{E_a}{RT}}$$

- Rate constant increases exponentially with increasing activation energy and decreasing temperature
- Rate constant decreases exponentially with increasing activation energy and decreasing temperature
- Rate constant increases exponentially with decreasing activation energy and decreasing temperature
- Rate constant increases exponentially with decreasing activation energy and increasing temperature

8. A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in figure. On the basis of this mark the correct option.

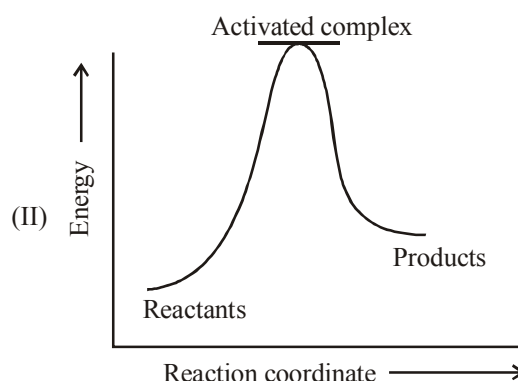
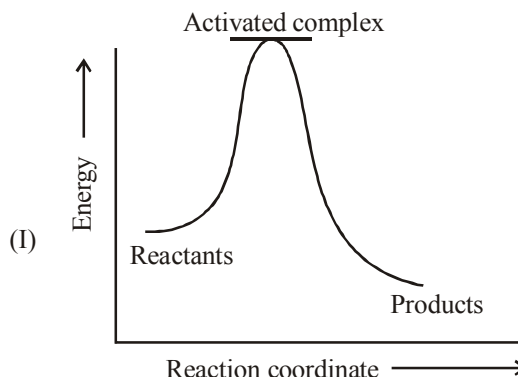


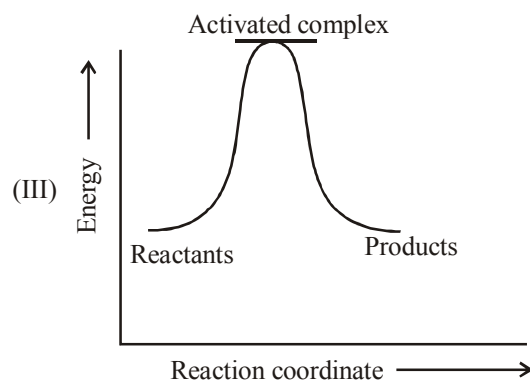
- (a) Average rate upto 40s is $\frac{V_3 - V_2}{40}$
 (b) Average rate upto 40s is $\frac{V_3 - V_2}{40 - 30}$
 (c) Average rate upto 40s is $\frac{V_3}{40}$
 (d) Average rate upto 40s is $\frac{V_3 - V_1}{40 - 20}$
9. Which of the following statements is not correct about order of a reaction?
- The order of a reaction can be a fractional number
 - Order of a reaction is experimentally determined quantity
 - The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction
 - The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression
10. Consider the graph given in figure. Which of the following options does not show instantaneous rate of reaction at 40th second?



- (a) $\frac{V_5 - V_2}{50 - 30}$ (b) $\frac{V_4 - V_2}{50 - 30}$
 (c) $\frac{V_3 - V_2}{40 - 30}$ (d) $\frac{V_3 - V_1}{40 - 20}$

11. Which of the following statements is correct?
- The rate of a reaction decreases with passage of time as the concentration of reactants decreases.
 - The rate of a reaction is same at any time during the reaction.
 - The rate of a reaction is independent of temperature change.
 - The rate of a reaction decreases with increase in concentration of reactant(s).
12. Which of the following expressions is correct for the rate of reaction given below?
- $$5\text{Br}^- (\text{aq}) + \text{BrO}_3^- (\text{aq}) + 6\text{H}^+ (\text{aq}) \rightarrow 3\text{Br}_2 (\text{aq}) + 3\text{H}_2\text{O} (\text{l})$$
- (a) $\frac{\Delta[\text{Br}^-]}{\Delta t} = 5 \frac{\Delta[\text{H}^+]}{\Delta t}$ (b) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{6}{5} \frac{\Delta[\text{H}^+]}{\Delta t}$
 (c) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$ (d) $\frac{\Delta[\text{Br}^-]}{\Delta t} = 6 \frac{\Delta[\text{H}^+]}{\Delta t}$
13. Which of the following graphs represents exothermic reaction?



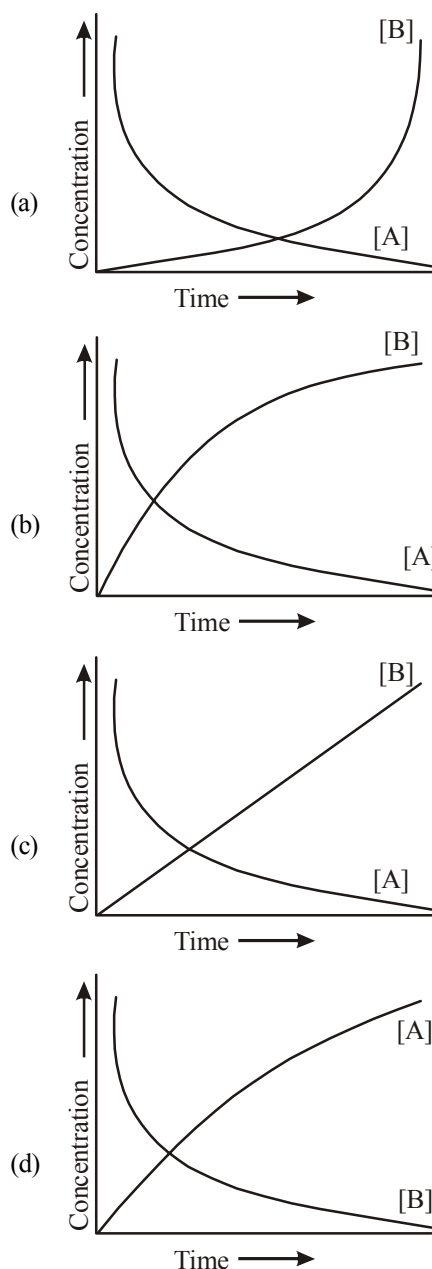


- (a) Only (I) (b) Only (II)
(c) Only (III) (d) Both (I) and (II)
14. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be $\text{Rate} = k[A][B]$
Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be
- (a) the same (b) doubled
(c) quadrupled (d) halved
15. Which of the following statements is incorrect about the collision theory of chemical reaction?
- (a) It considers reacting molecules or atoms to be hard spheres and ignores their structural features
(b) Number of effective collisions determines the rate of reaction
(c) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation
(d) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective
16. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?
- (a) 1.26×10^{15} s (b) 2.52×10^{14} s
(c) 2.52×10^{28} s (d) Infinite
17. Compounds 'A' and 'B' react according to the following chemical equation.
 $A(g) + 2B(g) \longrightarrow 2C(g)$
Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Experiment	Initial concentration of [A]/mol L ⁻¹	Initial concentration of [B]/mol L ⁻¹	Initial concentration of [C]/mol L ⁻¹ s ⁻¹
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

- (a) $\text{Rate} = k[A]^2[B]$ (b) $\text{Rate} = k[A][B]^2$
(c) $\text{Rate} = k[A][B]$ (d) $\text{Rate} = k[A]^2[B]^0$
18. Which of the following statement is not correct for the catalyst?
- (a) It catalyses the forward and backward reactions to the same extent

- (b) It alters ΔG of the reaction
(c) It is a substance that does not changes the equilibrium constant of a reaction
(d) It provides an alternate mechanism by reducing activation energy between reactants and products.
19. The value of rate constant of a pseudo first order reaction.....
- (a) depends on the concentration of reactants present in small amount
(b) depends on the concentration of reactants present in excess
(c) is independent of the concentration of reactants
(d) depends only on temperature
20. Consider the reaction $A \rightarrow B$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?



NEET/AIPMT (2013-2017) Questions

21. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) [2013]
 (a) 269 kJ mol⁻¹ (b) 34.7 kJ mol⁻¹
 (c) 15.1 kJ mol⁻¹ (d) 342 kJ mol⁻¹
22. A reaction having equal energies of activation for forward and reverse reaction has : [2013]
 (a) $\Delta G = 0$ (b) $\Delta H = 0$
 (c) $\Delta H = \Delta G = \Delta S = 0$ (d) $\Delta S = 0$
23. A reaction is 50% completed in 2 hours and 75% completed in 4 hours. The order of reaction is [NEET Kar. 2013]
 (a) 0 (b) 1
 (c) 2 (d) 3
24. For a reaction between A and B the order with respect to A is 2 and the order with respect to B is 3. The concentrations of both A and B are doubled, the rate will increase by a factor of: [NEET Kar. 2013]
 (a) 10 (b) 12
 (c) 16 (d) 32
25. The activation energy of a reaction can be determined from the slope of which of the following graphs ? [2015]
 (a) $\frac{\ln K}{T}$ vs. T (b) $\ln K$ vs. $\frac{1}{T}$
 (c) $\frac{T}{\ln K}$ vs. $\frac{1}{T}$ (d) $\ln K$ vs. T
26. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is : [2015]
 (a) First
 (b) Second
 (c) More than zero but less than first
 (d) Zero
27. The rate constant of the reaction $A \rightarrow B$ is 0.6×10^{-3} mole per second. If the concentration of A is 5 M then concentration of B after 20 minutes is : [2015 RS]
 (a) 1.08 M (b) 3.60 M
 (c) 0.36 M (d) 0.72 M
28. The rate of a first-order reaction is $0.04 \text{ mol l}^{-1} \text{ s}^{-1}$ at 10 seconds and $0.03 \text{ mol l}^{-1} \text{ s}^{-1}$ at 20 seconds after initiation of the reaction. The half-life period of the reaction is [2016]
 (a) 24.1 s (b) 34.1 s
 (c) 44.1 s (d) 54.1 s
29. The addition of a catalyst during a chemical reaction alters which of the following quantities? [2016]
 (a) Entropy (b) Internal energy
 (c) Enthalpy (d) Activation energy
30. Mechanism of a hypothetical reaction [2017]
 $X_2 + Y_2 \rightarrow 2XY$ is given below :
 (i) $X_2 \rightarrow X + X$ (fast)
 (ii) $X + Y_2 \rightleftharpoons XY + Y$ (slow)
 (iii) $X + Y \rightarrow XY$ (fast)
 The overall order of the reaction will be :
 (a) 2 (b) 0
 (c) 1.5 (d) 1
31. A first order reaction has a specific reaction rate of 10^{-2} sec^{-1} . How much time will it take for 20g of the reactant to reduce to 5 g ? [2017]
 (a) 138.6 sec (b) 346.5 sec
 (c) 693.0 sec (d) 238.6 sec

Hints & Solutions

EXERCISE - 1

- (a) $\frac{dc}{dt} = k[c] = 3 \times 10^{-6} \times 0.1$
 $\frac{dc}{dt} = 3 \times 10^{-7} \text{ mol litre}^{-1} \text{ sec}^{-1}$
- (d) All the statements are correct.
 Order of reaction $= 1 + \frac{1}{2} = 1.5$
 Molecularity $= 1 + 1 = 2$
 $\frac{dx}{dt} \propto [\text{Br}_2]^{1/2}$
 So, reaction rate will be doubled if concentration of Br_2 is increased by 4 times.
- (d) As the unit of rate constant is sec^{-1} , so the reaction is first order reaction. Hence
 $k = \frac{1}{t} = \log \frac{a}{(a-x)} \text{ or } kt = \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$
- (d) In the given options $-\frac{d[\text{C}]}{3dt}$ will not represent the reaction rate. It should not have -ve sign as it is a product.
 $\frac{1}{3} \frac{d[\text{C}]}{dt}$ shows the rate of formation of product C.
- (a) If we write rate of reaction in terms of concentration of NH_3 and H_2 , then
 Rate of reaction $= \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$
 So, $\frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$
- (b) $r = k[\text{O}_2][\text{NO}]^2$. When the volume is reduced to 1/2, the conc. will double
 $\therefore$ New rate $= k[2\text{O}_2][2\text{NO}]^2 = 8k[\text{O}_2][\text{NO}]^2$
 The new rate increases to eight times of its initial.
- (b) When the concentration of reactant is reduced to half its initial value, the rate is reduced by $\frac{2.4}{0.6} = 4$ times
 It means, rate $\propto [\text{reactant}]^2$
 So, order of reaction $= 2$
- (c) Increase in temperature $= 100^\circ\text{C} - 10^\circ\text{C} = 90^\circ\text{C}$
 $\therefore n = 9$
 Increase in reaction rate $= 2^n = 2^9 = 512$ times
- (a) $2\text{A} + \text{B} \longrightarrow \text{A}_2\text{B}$
 $r_1 = k[\text{A}]^2[\text{B}] \quad \dots(i)$
 When, $[\text{A}] = [2\text{A}]$, $[\text{B}] = \left[\frac{\text{B}}{2}\right]$
 $r_2 = k[2\text{A}]^2 \left[\frac{\text{B}}{2}\right] = k4[\text{A}]^2 \left[\frac{\text{B}}{2}\right]$

$$= k2[\text{A}]^2[\text{B}] = 2r_1 \quad (\because r_1 = k[\text{A}]^2[\text{B}])$$

$\therefore$ Rate of reaction is increased two times.

- (d) Graph (d) represents graph between $t_{1/2}$ and initial concentration for 3rd order reaction :
 (a) Zero order reaction
 (b) 1st order reaction
 (c) 2nd order reaction.
- (d) rate of appearance of HI $= \frac{1}{2} \frac{d[\text{HI}]}{dt}$
 rate of formation of $\text{H}_2 = \frac{-d[\text{H}_2]}{dt}$
 rate of formation of $\text{I}_2 = \frac{-d[\text{I}_2]}{dt}$
 hence $\frac{-d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$
 or $-\frac{2d[\text{H}_2]}{dt} = -\frac{2d[\text{I}_2]}{dt} = \frac{d[\text{HI}]}{dt}$
- (a) From data 1 and 3, it is clear that keeping (B) const, [A] is doubled, rate remains unaffected. Hence rate is independent of [A]. From 1 and 4, keeping [A] constant, [B] is doubled, rate become 8 times. Hence rate $\propto [\text{B}]^3$.
- (b) $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$
 from the unit of rate constant it is clear that the reaction follow first order kinetics. Hence
 by rate law equation, $r = k[\text{N}_2\text{O}_5]$
 where $r = 1.02 \times 10^{-4}$, $k = 3.4 \times 10^{-5}$
 $1.02 \times 10^{-4} = 3.4 \times 10^{-5} [\text{N}_2\text{O}_5]$
 $[\text{N}_2\text{O}_5] = 3\text{M}$
- (b) For a first order reaction the positive slope is obtained when we plot $-\log_e [\text{A}]$ vs t .
- (c)
 $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$
 $\therefore k = \frac{2.303}{2 \times 10^4} \log \frac{800}{50} = 1.386 \times 10^{-4} \text{ s}^{-1}$
- (b) Given $dx/dt = 2.400 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$
 $k = 3.10 \times 10^{-5} \text{ sec}^{-1}$
 For first order reaction
 $2\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \text{O}_2$
 $\frac{dx}{dt} = k[\text{N}_2\text{O}_5]$
 or $2.4 \times 10^{-5} = 3.0 \times 10^{-5} [\text{N}_2\text{O}_5]$
 or $[\text{N}_2\text{O}_5] = \frac{2.4 \times 10^{-5}}{3.0 \times 10^{-5}} = 0.8 \text{ mol. litre}^{-1}$
- (b) Initial concentration $= 10 \text{ mol L}^{-1}$
 $\therefore$ Conc. after 20 min (two half lives) $= 2.5 \text{ mol L}^{-1}$

$$\text{Now, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \text{ min}}$$

$$\text{or } 0.0693 \text{ min}^{-1}$$

$$\therefore \text{rate} = k \times [\text{reactant}]$$

$$= 0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1}$$

18. (b) Velocity constant 'K' is characteristic constant of a reaction and depends only on temperature and catalyst.

19. (c) $\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$\text{or } 2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$2.303 \log \left[\frac{1.667 \times 10^{-4}}{1.667 \times 10^{-6}} \right] = -\frac{E_a}{R} \left[\frac{1}{1844} - \frac{1}{1000} \right]$$

$$2.303 \times 2 = \frac{E_a}{R} \times \frac{844}{1844 \times 1000} \quad \dots\dots(1)$$

$$\therefore \frac{E_a}{R} = \frac{4.606 \times 1844 \times 1000}{844}$$

$$2.303 \log \left[\frac{k_3}{1.667 \times 10^{-6}} \right] = \frac{E_a}{R} \times \frac{1423 - 1000}{1423 \times 1000}$$

$$= \frac{E_a}{R} \times \frac{423}{1423 \times 1000} \quad \dots\dots(2)$$

Dividing equation (2) by equation (1)

$$\frac{\log \left[\frac{k_3}{1.667 \times 10^{-6}} \right]}{2}$$

$$= \frac{423}{1423 \times 1000} \times \frac{1844 \times 1000}{844}$$

$$\therefore \log \left[\frac{k_3}{1.667 \times 10^{-6}} \right] = 2 \times \frac{423 \times 1844}{1423 \times 844} = 1.299$$

On taking Antilog, $k_3 = 19.9$

$$\therefore k_3 = 19.9 \times 1.667 \times 10^{-6} = 3.318 \times 10^{-5} \text{ s}^{-1}$$

20. (c)

21. (a) Given initial concentration (a) = 2.00 M; Time taken (t) = 200 min and final concentration ($a - x$) = 0.15 M.

For a first order reaction rate constant,

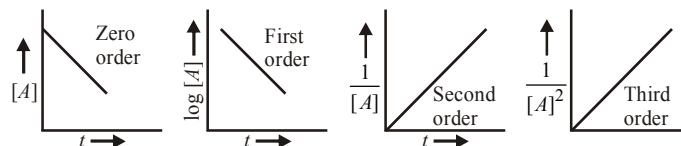
$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{200} \log \frac{2.00}{0.15}$$

$$= \frac{2.303}{200} \times (0.301 + 0.824) = 1.29 \times 10^{-2} \text{ min}^{-1}$$

$$\text{Further } (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{1.29 \times 10^{-2}} = 53.72 \text{ min.}$$

22. (c) $T_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.155 \times 10^{-3}} = \frac{693}{1.155} = 600 \text{ sec}$

23. (a) Plots of conc. [A] Vs time, t



24. (a) $t_{1/2} = 4 \text{ s}$ $T = 16 \text{ s}$

$$n = \frac{T}{t_{1/2}} = \frac{16}{4} = 4 \quad (\therefore T = n \times t_{1/2})$$

$$[A] = [A]_0 \left(\frac{1}{2} \right)^n = 0.12 \times \left(\frac{1}{2} \right)^4 = \frac{0.12}{16} = 0.0075 \text{ M}$$

Where $[A]_0$ = initial concentration and $[A]$ = concentration left after time t

25. (b) For reaction $3A \longrightarrow B + C$

If it is zero order reaction $r = k = [A]^0$, i.e., the rate remains same at any concentration of 'A'. i.e., independent of concentration of A.

26. (a) $k = \frac{0.693}{T_{1/2}} = \frac{0.693}{30} = 2.31 \times 10^{-2} \text{ min}^{-1}$

27. (b) $A \rightarrow B$ For a first order reaction
Given $a = 0.8 \text{ mol}$, $(a - x) = 0.8 - 0.6 = 0.2$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \text{ or } k = 2.303 \log 4$$

again $a = 0.9$, $a - x = 0.9 - 0.675 = 0.225$

$$k = \frac{2.303}{t} \log \frac{0.9}{0.225}$$

$$2.303 \log 4 = \frac{2.303}{t} \log 4$$

Hence $t = 1 \text{ hour}$

28. (b) $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$

This reaction will proceed in forward direction if volume of container is increased.

29. (b) For a first order reaction, $A \rightarrow \text{products}$

$$r = k[A] \text{ or } k = \frac{r}{[A]}$$

$$\Rightarrow k = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}$$

$$\text{Further, } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^{-2}} = 23.1$$

30. (d) Given $[A] = 0.01 \text{ M}$
Rate = $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

For a first order reaction

$$\text{Rate} = k[A]$$

$$k = \frac{2.0 \times 10^{-5}}{[0.01]} = 2 \times 10^{-3}$$

$$t_{1/2} = \frac{0.693}{2 \times 10^{-3}} = 347 \text{ sec}$$

31. (c) Molecularity can never be fraction. It is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction. It is a theoretical concept.

32. (d) $t_{1/2} = 5$ years, $T = 15$ years hence total number of half life periods $= \frac{15}{5} = 3$.

$$\therefore \text{Amount left} = \frac{64}{(2)^3} = 8\text{g}$$

33. (c) As the concentration of reactant decreases from 0.8 to 0.4 in 15 minutes hence the $t_{1/2}$ is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half lives as

$$[A] = \left(\frac{1}{2}\right)^n [A]_0$$

$$\frac{0.1}{0.025} = \left(\frac{1}{2}\right)^n$$

$$n = 2$$

i.e., 30 minutes

34. (d) For a first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\therefore k = \frac{2.303}{40 \text{ min}} \log \frac{0.1}{0.005}$$

$$= \frac{2.303}{40 \text{ min}} \times \log 20 = \frac{2.303}{40} \times 1.3010$$

Now rate $= k \times [\text{reactant}]$

When $[x] = 0.01 \text{ M}$

$$\therefore \text{rate} = \frac{2.303}{40} \times 1.3010 \times 0.01 \text{ M min}^{-1} \\ = 7.5 \times 10^{-4} \text{ M min}^{-1}$$

35. (a) Given $r = k[A]^{3/2}[B]^{-1/2}$

$$\text{Order} = 3/2 - 1/2 = \frac{3-1}{2} = \frac{2}{2} = 1$$

36. (c) For first order reaction, $k = \frac{0.693}{t_{1/2}}$

where k = rate constant

$t_{1/2}$ = half life period = 480 sec.

$$\therefore k = \frac{0.693}{480} = 1.44 \times 10^{-3} \text{ sec}^{-1}$$

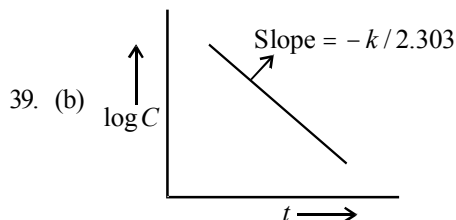
37. (c) Since rate of reaction becomes four times on doubling concentration of reactant, it is second order reaction.

38. (c) $[A] = [A]_0 \left(\frac{1}{2}\right)^n$ where $[A]_0$ = initial concentration

$$\frac{1}{8} = 1 \left(\frac{1}{2}\right)^n ; n = 3$$

$$t_{1/2} = \frac{0.693}{6.9 \times 10^{-3}} = 100 \text{ sec}$$

$$\therefore T = n \times t_{1/2} = 3 \times 100 = 300 \text{ sec.}$$



40. (a) For a first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

Substituting the given values

$$k = \frac{2.303}{200 \text{ sec}} \log \frac{2.0}{0.15} = \frac{2.303}{200} (\log 2.0 - \log 0.15) \text{ sec}^{-1} \\ = \frac{2.303}{200} \times 1.1249 \text{ sec}^{-1} = 1.29 \times 10^{-2} \text{ sec}^{-1}$$

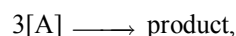
41. (b) Given: 75% reaction gets completed in 32 min

$$\text{Thus, } k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{32} \log \frac{100}{(100-75)} \\ = \frac{2.303}{32} \log 4 = 0.0433 \text{ min}^{-1}$$

Now we can use this value of k to get the value of time required for 50% completion of reaction

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)} = \frac{2.303}{0.0433} \log \frac{100}{50} \\ = \frac{2.303}{0.0433} \log 2 = 16 \text{ min}$$

42. (a) The half life period of a 3rd order reaction,



is given by the equation

$$t_{1/2} = \frac{3}{2k[A]_0^2}$$

where $[A]_0$ is initial concentration.

Here $t_{1/2} = 8 \text{ hr } 20 \text{ min} = 500 \text{ min.} = 30000 \text{ sec}$ and $[A]_0 = 0.1 \text{ M}$

$$\therefore k = \frac{3}{2t_{1/2}[A]_0^2} = \frac{3}{2 \times (30000 \text{ sec})(0.10 \text{ mol L}^{-1})^2} \\ = \frac{3}{60000 \times 0.01} = 5 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

43. (d) If rate $= k[A]^x[B]^y[C]^z$

From first two given data

$$8.08 \times 10^{-3} = k[0.2]^x[0.1]^y[0.02]^z \quad \dots (1)$$

$$2.01 \times 10^{-3} = k[0.1]^x[0.2]^y[0.02]^z \quad \dots (2)$$

Divide (1) by (2) we get, $4 = 2^x (1/2)^y$

Similarly, from second and third data

$$(9)^y (9)^z = 3$$

$$2y + 2z = 1$$

From first and fourth data $4^z = 8 = 2^3$

$2z = 3$. So $z = 3/2$, $y = -1$, $x = 1$

44. (d) Using the relation

$$[A] = [A]_0 (1/2)^n \quad [n = \text{number of half-lives}]$$

$$T = n \times t_{1/2}$$

Here, $n = \frac{7.5}{2.5} = 3$

$$\therefore [A] = 160 \times \left(\frac{1}{2}\right)^3 = 160 \times \frac{1}{8}$$

or 20 gm i.e., (d)

45. (b) The order w.r.t. I_2 is zero because the rate is not dependent on the concentration of I_2 .

46. (c) For the reaction,

$X + \text{reagent} \xrightarrow{k_1} \text{product}$,
the value of k_1 when 94% of X has been reacted is given by

$$k_1 = \frac{2.303}{t} \log \frac{100}{100 - 94}$$

$$\Rightarrow k_1 = \frac{2.303}{t} \log \left(\frac{100}{6}\right) \dots\dots(1)$$

Similarly, for the reaction

$Y + \text{reagent} \xrightarrow{k_2} \text{product}$,
the value of k_2 when 50% of Y have been reacted is given by,

$$k_2 = \frac{2.303}{t} \log \frac{100}{100 - 50}$$

$$\Rightarrow k_2 = \frac{2.303}{t} \log(2) \dots\dots\dots(2)$$

Dividing equ. (1) by equ. (2), we get

$$\frac{k_1}{k_2} = \frac{\log \left(\frac{100}{6}\right)}{\log 2} = 4.059$$

47. (c) As we know that, units of rate constant.

$$= (\text{unit of conc.})^{1-n} (\text{unit of time})^{-1}$$

$$= (\text{mol L}^{-1})^{1-n} (\text{sec})^{-1}$$

On comparing these units with the given units of rate constant, we get

$$(\text{mol L}^{-1})^{1-n} (\text{sec})^{-1} = \text{L mol}^{-1} \text{sec}^{-1}$$

$$\Rightarrow \text{L}^{n-1} \text{mol}^{1-n} \text{sec}^{-1} = \text{L mol}^{-1} \text{sec}^{-1}$$

On comparing the powers, we get

$$n - 1 = 1 \Rightarrow n = 2$$

So, reaction is of second order.

48. (d) Unit of k for 1st order reaction is $(\text{Time})^{-1}$

49. (d) For first order decomposition of N_2O_5 , rate law is given by

$$\text{rate, } r = k[N_2O_5]$$

On plotting rate on y-axis and $\text{conc}^n [N_2O_5]$ on x-axis and then comparing it with $y = mx + c$, we get a line starting from origin with slope 'k'. Its positive slope suggests that

line is going up. Hence graph shown in option (d) is the correct choice.

50. (a) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2 \times 10^{-4}} = 1117.7 \text{ sec.}$

51. (b) $\text{pH} = 2$; $r_1 = k \times (10^{-2})^n$ { $\because [H^+] = 10^{-\text{pH}}$ }
 $\text{pH} = 1$; $r_2 = k \times (10^{-1})^n$

$$\text{Given } r_2 = 100 r_1 \Rightarrow \left(\frac{10^{-1}}{10^{-2}}\right)^n = 100$$

$$\Rightarrow 10^n = 100$$

$$\therefore n = 2$$

52. (d) $t_{1/2} \propto \frac{1}{a^2}$

$$\text{We know that } t_{1/2} \propto \frac{1}{a^{n-1}}$$

$$\text{i.e. } n = 3$$

Thus reaction is of 3rd order.



Moles at $t = 0$	a	0
Moles at $t = t$	$(a - x)$	$2x$

$$\text{when } \frac{2x}{a-x} = 1 \text{ then } x = \frac{a}{3}$$

$$\therefore t = \frac{2.303}{k} \log \frac{a}{(a-x)}$$

$$= \frac{2.303}{2.3 \times 10^{-4}} \log \frac{a}{a - \frac{a}{3}} = 1700 \text{ sec}$$

54. (c) $t_{1/4} = \frac{2.303}{k} \log \frac{1}{3/4} = \frac{2.303}{k} \log \frac{4}{3}$
 $= \frac{2.303}{k} (\log 4 - \log 3) = \frac{2.303}{k} (2 \log 2 - \log 3)$

$$= \frac{2.303}{k} (2 \times 0.301 - 0.4771) = \frac{0.29}{k}$$

55. (c) Given initial mass = a

$$\text{Mass left after time } t = x = 0.875 a$$

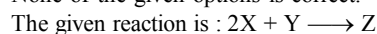
$$t = 40 \text{ minutes.}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{a}{a-0.875 a}$$

$$= \frac{2.303}{40} \log 8 = 0.052 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.052} = 13 \text{ minutes } 32 \text{ sec.}$$

56. (d) None of the given options is correct.



$$-\frac{d[X]}{2dt} = \frac{d[Z]}{dt}$$

∴ Rate of formation of Z is half of the rate of disappearance of X.

$$\frac{-d[X]}{2dt} = \frac{-d[Y]}{dt}$$

Rate of X is not equal to rate of disappearance of Y.

57. (b) Activation energy of reactant is less than the energy of activation of products.

58. (d) A catalyst affects equally both forward and backward reactions, therefore it does not affect equilibrium constant of reaction.

59. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$
∴ when $E_a = 0$, $k = A$

Also $\ln k$ vs $1/T$ is a straight line with slope $= -E_a/R$.

∴ Statements (ii) and (v) are correct.

60. (c) We know that the activation energy of chemical reaction

is given by formula $= \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$, where k_1 is

the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 and E_a is the activation energy. Therefore activation energy of chemical reaction is determined by evaluating rate constant at two different temperatures.

61. (c) Order is the sum of the powers to which the concentration terms are raised in the rate equation.

62. (d) $k = Ae^{-E_a/RT}$

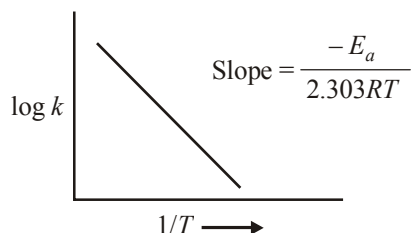
$$\text{or } \log k = \log A - \frac{E_a}{2.303 RT}$$

Comparing the above equation with

$$y = mx + c$$

$$y = \log k, \quad x = \frac{1}{T}$$

Thus a plot of $\log k$ vs $1/T$ should be a straight line, with slope equal to $-E_a/2.303 RT$ and intercept equal to $\log A$



$$\therefore \text{Slope} = \frac{-E_a}{2.303R}$$

$$\text{or } E_a = -2.303R \times \text{Slope}$$

$$63. (d) \therefore \frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

For first condition

$$\frac{1}{4} = \left(\frac{1}{2}\right)^n \therefore n = 2$$

$$t_{1/2} = \frac{20}{2} = 10$$

For second condition

$$\left(\frac{1}{16}\right) = \left(\frac{1}{2}\right)^n$$

$$n = 4 \therefore T = 4 \times 10 = 40 \text{ min}$$

64. (d) The activation energy of reverse reaction will depend upon whether the forward reaction is exothermic or endothermic.

$$\text{As } \Delta H = E_{a(\text{forward reaction})} - E_{a(\text{backward reaction})}$$

For exothermic reaction

$$\Delta H = -ve$$

$$\therefore -\Delta H = E_{a(f)} - E_{a(b)}$$

$$\text{or } E_{a(f)} = E_{a(b)} - \Delta H$$

$$\therefore E_{a(f)} < E_{a(b)}$$

for endothermic reaction

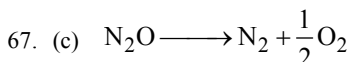
$$\Delta H = +ve$$

$$\therefore \Delta H = E_{a(f)} - E_{a(b)} \text{ or } E_{a(f)} = \Delta H + E_{a(b)}$$

$$\therefore E_{a(f)} > E_{a(b)}$$

65. (d) In Arrhenius equation $k = Ae^{-E_a/RT}$, E_a is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.

66. (d) The definition of threshold energy.



$$\frac{dx}{dt} \propto [\text{N}_2\text{O}]^1$$

i.e. order of reaction = 1

68. (b) When the temperature is increased, energy in form of heat is supplied which increases the kinetic energy of the reacting molecules. this will increase the number of collisions and ultimately the rate of reaction will be enhanced.

69. (b) When $E_a = 0$ rate constant is independent of temperature.

$$70. (b) k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT$$

For $\ln k$ vs $1/T$

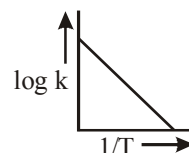
$$\ln A = \text{intercept}$$

$$-E_a/R = \text{slope} = -2 \times 10^4 \text{ K}$$

$$\therefore E_a = 8.3 \times 2 \times 10^4 \text{ J mol}^{-1}$$

$$= 16.6 \times 10^4 \text{ J mol}^{-1} \text{ or } 166 \text{ kJ mol}^{-1}$$

71. (b) A graph plotted between $\log k$ vs $\frac{1}{T}$ for calculating activation energy is shown as



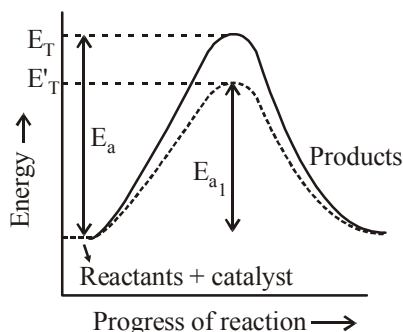
from Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

72. (a) For endothermic reaction $\Delta H = +ve$

$$\text{Then from equation } \Delta H = E_{FR} - E_{BR}; E_{BR} < E_{FR}$$

73. (b) The presence of enzyme (catalyst) increases the speed of reaction by lowering the energy barrier, i.e., a new path is followed with lower activation energy.



Here E_T is the threshold energy.

E_a and E_{a_1} is energy of activation of reaction in absence and presence of catalyst respectively.

74. (d) For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{75} \log \frac{1}{1/8} = \frac{2.303 \times 0.903}{75} \text{ min}^{-1}$$

First order reaction

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 75}{2.303 \times 0.903} = 25 \text{ min}$$

75. (d) As the slowest step is the rate determining step thus the mechanism B will be more consistent with the given information also because it involve one molecule of H_2 and one molecule of ICl it can expressed as

$$r = k [\text{H}_2][\text{ICl}]$$

Which shows that the reaction is first order w.r.t. both H_2 & ICl .

76. (c) For a first order reaction

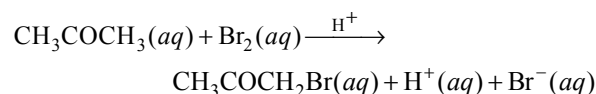
$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

when $t = t_{1/2}$

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a-a/2}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log 2 = \frac{\ln 2}{k}$$

77. (a) Rewriting the given data for the reaction



S. No.	Initial concentration of CH_3COCH_3 in M	Initial concentration of Br_2 in M	Initial concentration of H^+ in M	Rate of disappearance of Br_2 in Ms^{-1} i.e. $-\frac{d}{dt}[\text{Br}_2]$ or $\frac{dx}{dt}$
1	0.30	0.05	0.05	5.7×10^{-5}
2	0.30	0.10	0.05	5.7×10^{-5}
3	0.30	0.10	0.10	1.2×10^{-4}
4	0.40	0.05	0.20	3.1×10^{-4}

Actually this reaction is autocatalyzed and involves complex calculation for concentration terms.

We can look at the above results in a simple way to find the dependence of reaction rate (i.e., rate of disappearance of Br_2).

From data (1) and (2) in which concentration of CH_3COCH_3 and H^+ remain unchanged and only the concentration of Br_2 is doubled, there is no change in rate of reaction. It means the rate of reaction is independent of concentration of Br_2 .

Again from (2) and (3) in which $(\text{CH}_3\text{COCH}_3)$ and (Br_2) remain constant but H^+ increases from 0.05 M to 0.10 i.e. doubled, the rate of reaction changes from 5.7×10^{-5} to 1.2×10^{-4} (or 12×10^{-5}), thus it also becomes almost doubled. It shows that rate of reaction is directly proportional to $[\text{H}^+]$. From (3) and (4), the rate should have doubled due to increase in conc of $[\text{H}^+]$ from 0.10 M to 0.20 M but the rate has changed from 1.2×10^{-4} to 3.1×10^{-4} . This is due to change in concentration of CH_3COCH_3 from 0.30 M to 0.40 M. Thus the rate is directly proportional to $[\text{CH}_3\text{COCH}_3]$. We now get
 $\text{rate} = k [\text{CH}_3\text{COCH}_3]^1 [\text{Br}_2]^0 [\text{H}^+]^1$
 $= k [\text{CH}_3\text{COCH}_3][\text{H}^+]$.

78. (d) Rate of disappearance of H_2 = rate of formation of NH_3 .

$$\begin{aligned} -\frac{1}{3} \frac{d[\text{H}_2]}{dt} &= \frac{1}{2} \frac{d[\text{NH}_3]}{dt} \\ \Rightarrow -\frac{d[\text{H}_2]}{dt} &= \frac{3}{2} \frac{d[\text{NH}_3]}{dt} = \frac{3}{2} \times 2 \times 10^{-4} \\ &= 3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

79. (d) Rate of disappearance of Br^-

= rate of appearance of Br_2

$$\begin{aligned} \Rightarrow -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} &= \frac{1}{3} \frac{d[\text{Br}_2]}{dt} \\ \Rightarrow \frac{1}{3} \frac{d[\text{Br}_2]}{dt} &= -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} \\ \Rightarrow \frac{d[\text{Br}_2]}{dt} &= -\frac{3}{5} \frac{d[\text{Br}^-]}{dt} \end{aligned}$$

80. (b) For a first order reaction

$$t_{1/2} = \frac{0.693}{k}; k = \frac{0.693}{1386} = 0.5 \times 10^{-3} \text{ s}^{-1}$$

81. (a) When concentration A is doubled, rate is doubled. Hence order with respect to A is one.

When concentrations of both A and B are doubled, rate increases by 8 times hence order with respect to B is 2.

$$\therefore \text{rate} = k [\text{A}]^1 [\text{B}]^2$$

$$\text{Total order} = 1 + 2 = 3$$

82. (b) $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$

$$-\frac{d}{dt}[\text{N}_2\text{O}_5] = +\frac{1}{2} \frac{d}{dt}[\text{NO}_2] = 2 \frac{d}{dt}[\text{O}_2]$$

$$\frac{d}{dt}[\text{NO}_2] = 1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1} \text{ and}$$

$$\frac{d}{dt}[\text{O}_2] = 3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

83. (b)

84. (d) In case of (II) and (III), keeping concentration of [A] constant, when the concentration of [B] is doubled, the rate quadruples. Hence it is second order with respect to B. In case of I & IV Keeping the concentration of [B] constant, when the concentration of [A] is increased four times, rate also increases four times. Hence, the order with respect to A is one. hence

$$\text{Rate} = k [\text{A}][\text{B}]^2$$

85. (b)
- $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$

$$\text{Rate} = k [\text{NO}]^2 [\text{Cl}]$$

The value of rate constant can be increased by increasing the temperature.

$\therefore$ Correct choice : (b)

86. (d) order of reaction may be zero, whole number or fractional.

87. (a)
- Rate**
- =
- $k[\text{A}]^0$

$$\text{Unit of } k = \text{mol L}^{-1} \text{ sec}^{-1}$$

88. (b)
- $\frac{r_{100^\circ\text{C}}}{r_{10^\circ\text{C}}} = 2^{\left(\frac{T_2 - T_1}{10}\right)} = 2^{\left(\frac{100 - 10}{10}\right)} = 2^9 = 512$
- (where 2 is

temperature coefficient of reaction)

89. (b, d)

According to Arrhenius equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

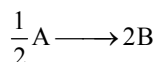
$$= - \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_1}{K_2} = - \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

90. (a) Presence of catalyst does not affect enthalpy change of reaction
- $\Delta H_R = E_f - E_b = 180 - 200 = -20 \text{ kJ/mol}$

91. (b) Since doubling the concentration of B does not change half life, the reaction is of 1st order w.r.t. B. Order of reaction with respect to A = 1 because rate of reaction doubles when concentration of A is doubled keeping concentration of B constant. $\therefore$ Order of reaction = $1 + 1 = 2$ and units of second order reaction are $\text{L mol}^{-1} \text{ sec}^{-1}$.

92. (b) The rates of reactions for the reaction



can be written either as

$$-2 \frac{d}{dt}[\text{A}] \text{ with respect to 'A'}$$

or $\frac{1}{2} \frac{d}{dt}[\text{B}] \text{ with respect to 'B'}$

From the above, we have

$$-2 \frac{d}{dt}[\text{A}] = \frac{1}{2} \frac{d}{dt}[\text{B}]$$

$$\text{or } -\frac{d}{dt}[\text{A}] = \frac{1}{4} \frac{d}{dt}[\text{B}]$$

i.e., correct answer is (b)

93. (b) For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6.93}$$

$$k = \frac{2.303}{t} \log \frac{100}{100 - 99}$$

$$\frac{0.693}{6.93} = \frac{2.303}{t} \log \frac{100}{1}$$

$$\frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$

$$t = 46.06 \text{ min}$$

94. (b) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{0.1}{0.025}$$

$$= \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.6020}{40}$$

$$= 3.47 \times 10^{-2} \text{ min}^{-1}$$

$$\text{Rate} = k[\text{A}] = 3.47 \times 10^{-2} \times 0.01$$

$$= 3.47 \times 10^{-4} \text{ M/min}$$

95. (a) Activation energy can be calculated from the equation

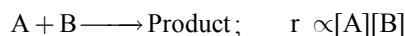
$$\frac{\log k_2}{\log k_1} = \frac{-E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{Given } \frac{k_2}{k_1} = 2; T_2 = 310 \text{ K}; T_1 = 300 \text{ K}$$

$$= \log 2 = \frac{-E_a}{2.303 \times 8.314} \left(\frac{1}{310} - \frac{1}{300} \right)$$

$$E_a = 53598.6 \text{ J/mol} = 53.6 \text{ kJ/mol.}$$

96. (d) The rate of a reaction is the speed at which the reactants are converted into products. It depends upon the concentration of reactants. e.g for the reaction



97. (a)
- $t_{1/2} = 4 \text{ s}$
- $T = 16$

$$n = \frac{T}{t_{1/2}} = \frac{16}{4} = 4 \quad (\because T = n \times t_{1/2})$$

$$\text{A} = \text{A}_0 \left(\frac{1}{2} \right)^n = 0.12 \times \left(\frac{1}{2} \right)^4 = \frac{0.12}{16} = 0.0075 \text{ M}$$

where A_0 = initial concentration &

A = concentration left after time t.

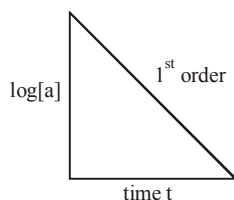
98. (b) For a first reaction
- $\frac{dx}{dt} = k(a-x)$
- on intergration

$$\int \frac{dx}{(a-x)} = \int k dt$$

$$\text{i.e. } -\ln(a-x) = kt + c \text{ or } kt = \ln a - \ln(a-x)$$

$$\text{or } kt = 2.303 [\log a - \log(a-x)]$$

Thus if we plot a graph between $\log a$ & t we get



99. (a) From data 1 and 3, it is clear that keeping (B) const, When [A] is doubled, rate remains unaffected. Hence rate is independent of [A]. from 1 and 4, keeping [A] constant, when [B] is doubled, rate become 8 times. Hence

$$\text{rate} \propto [B]^3.$$

100. (c) We know that the activation energy of chemical reaction

$$\text{is given by formula} = \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right], \text{ where}$$

k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 and E_a is the activation energy. Therefore activation energy of chemical reaction is determined by evaluating rate constant at two different temperatures.

EXERCISE - 2

- (a) For a zero order reaction

$$t_{1/2} = \frac{a}{2k}$$
- (c) $\text{Rate}_1 = k[A]^n[B]^m$; $\text{Rate}_2 = k[2A]^n[\frac{1}{2}B]^m$

$$\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[2A]^n[\frac{1}{2}B]^m}{k[A]^n[B]^m} = [2]^n[\frac{1}{2}]^m = 2^n \cdot 2^{-m} = 2^{n-m}$$
- (d) The velocity constant depends on temperature only. It is independent of concentration of reactants.
- (c) Given, $k = 6.909 \text{ min}^{-1}$
For a first order reaction

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$6.909 = \frac{2.303}{t} \log \left(\frac{100}{100-75} \right) = \frac{2.303}{t} \log \left(\frac{100}{25} \right)$$

$$\Rightarrow t = \frac{2.303}{6.909} \log 4 \Rightarrow t = \frac{1}{3} \log(2^2) = \frac{2}{3} \log 2.$$
- (c) Reaction Rate $R_1 = k[A]^2[B]$
Now increase conc. of A by three times and conc. of B by two times. Then new rate
 $R_2 = k[3A]^2[2B]$

$$\frac{R_1}{R_2} = \frac{k[A]^2[B]}{k[3A]^2[2B]} = \frac{1}{3^2} \times \frac{1}{2} = \frac{1}{18}$$

$$R_2 = 18 \times R_1$$
- (c) Half life time ($t_{1/2}$) for n^{th} order reaction is given by,

$$t_{1/2} \propto [a]^{1-n}$$
 where n is the order of reaction and a is concentration of reactant.
 As decomposition of N_2O_5 follows 1st order kinetic.
 So, $\Rightarrow t_{1/2} \propto [a]^{1-1} \Rightarrow t_{1/2} \propto a^0$
- (d) For a zero order reaction,

$$t_{1/2} \propto a_0 \text{ (initial concentration or initial pressure)}$$

$$(t_{1/2})_1 \propto P_1$$

$$(t_{1/2})_2 \propto P_2$$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1}, \frac{(t_{1/2})_2}{45} = \frac{16}{4}$$

$$(t_{1/2})_2 = \frac{16}{4} \times 45 = 180 \text{ min}$$
- (a) As doubling the initial conc. doubles the rate of reaction, order = 1
- (b) The rate of photochemical process varies with the intensity of absorption.
 Since greater the intensity of absorbed light more photons will fall at a point, and further each photon causes one molecule to undergo reaction.

$$H_2O \xrightarrow{\text{Photolysis}} OH^- + H^+$$
- (c) According to Arrhenius equation, the rate constant of reaction is given by,

$$k = Ae^{-E_a/RT}$$
 where A is pre-exponential factor, E_a is activation energy and T is absolute temperature.
 when $T \rightarrow \infty$, $\frac{E_a}{RT} \rightarrow 0$
 then $k = Ae^0$
 or $k = A$
- (b) As the rate of reaction get doubled for every 10°C rise in temperature. Hence the increase in reaction rate as a result of temperature rise from 10°C to 100°C is equal to $= 2^9 = 512$
- (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\frac{-\Delta[N_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[NH_3]}{\Delta t}$$

$$\therefore \frac{-\Delta[H_2]}{\Delta t} = \frac{3}{2} \times \frac{\Delta[NH_3]}{\Delta t} = \frac{3}{2} \times 2 \times 10^{-4}$$

$$= 3 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$$
- (d) Here, $t_{1/2} = 4.5 \times 10^9 \text{ years}$
 Molar ratio of U^{238} : $Pb^{206} = 1 : 3$
 Age of the rock can be determined according to the formula

$$t = \frac{2.303 \times t_{1/2}}{0.693} \log \left[1 + \frac{Pb^{206}}{U^{238}} \right] = \frac{2.303 \times 4.5 \times 10^9}{0.693} \log [1+3]$$

$$= \frac{2.303 \times 4.5 \times 10^9}{0.693} \times 0.6020$$

$$\therefore t = 9 \times 10^9 \text{ years.}$$

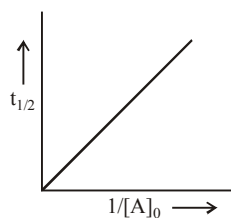
14. (a) The order of reaction is $\frac{3}{2}$ and molecularity is 2.

15. (c) Since $-\frac{dx}{dt} \propto [\text{CO}]^2$ so on doubling the concentration of CO the rate of reaction will increase by 4 times.

16. (d)

17. (c) $100 \xrightarrow{2 \text{ days}} 50 \quad 50 \xrightarrow{4 \text{ days}} 25$
 $25 \xrightarrow{8 \text{ days}} 12.5$

From the data given above we conclude $t_{1/2} \propto \frac{1}{[A]_0}$. If we plot a graph between half life and $1/[A]_0$ it will look like



Above graph is a characteristic of second order reaction. $t_{1/2}$ of reaction = 2 days.

18. (b) $k = \frac{0.693}{45} \text{ min}^{-1} = \frac{2.303}{t_{99.9\%}} \log \frac{a}{a - 0.999a}$ or

$$t_{99.9\%} = \frac{2.303 \times 45}{0.693} \log 10^3 = 448 \text{ min} \approx 7.5 \text{ hrs}$$

19. (c) $k = \frac{2.303}{1 \text{ hr}} \log \frac{100}{25} = \frac{2.303}{t} \log \frac{100}{50}$

$$\therefore \log 4 = \frac{1}{t} \log 2 \quad \therefore 2 \log 2 = \frac{1}{t} \log 2; t = \frac{1}{2} \text{ hr.}$$

20. (b) $t_{1/2} \propto a^{1-n} \Rightarrow \frac{0.1}{0.4} = \frac{(200)^{1-n}}{(50)^{1-n}} \Rightarrow \frac{1}{4} = \left[\frac{4}{1}\right]^{1-n} = \left[\frac{1}{4}\right]^{n-1}$

$$\Rightarrow \frac{1}{4} = \frac{1}{4^{n-1}} \therefore n-1=1; n=2$$

21. (c) Increase in rate = $2^{(T_2-T_1)/5} = 2^{(40-20)/5} = 2^4 = 16$ times

22. (b) $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$
 $(a-x)$ is the concentration left after 100 sec.

$$2.7 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.29}{(a-x)}$$

$$\Rightarrow \frac{0.27}{2.303} = \log \frac{0.29}{(a-x)} \Rightarrow 0.117 = \log \frac{0.29}{(a-x)}$$

$$\Rightarrow (a-x) = 0.22 \text{ M.}$$

23. (b) $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\text{If } \frac{k_2}{k_1} = 2$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{310} \right]$$

$$E_a = 0.3010 \times 2.303 \times 8.314 \left(\frac{300 \times 310}{10} \right)$$

$$= 53598.59 = 54 \text{ kJ.}$$

24. (b) $T_2 = T$ (say), $T_1 = 25^\circ\text{C} = 298\text{K}$,
 $E_a = 104.4 \text{ kJ mol}^{-1} = 104.4 \times 10^3 \text{ J mol}^{-1}$
 $k_1 = 3 \times 10^{-4}$, $k_2 = ?$,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left[\frac{1}{298} - \frac{1}{T} \right]$$

$$\text{As } T \rightarrow \infty, \frac{1}{T} \rightarrow 0$$

$$\therefore \log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log \frac{k_2}{3 \times 10^{-4}} = 18.297, \frac{k_2}{3 \times 10^{-4}} = 1.98 \times 10^{18}$$

$$k_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14} \text{ s}^{-1}$$

25. (a) $2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$\log \frac{k_2}{k_1} = \frac{9.0 \times 10^3}{2.303 \times 2} \left[\frac{308 - 298}{308 \times 298} \right]$$

$$\frac{k_2}{k_1} = 1.63; k_2 = 1.63k_1;$$

$$\text{Increase in } k_1 = \frac{k_2 - k_1}{k_1} \times 100$$

$$= \frac{1.63k_1 - k_1}{k_1} \times 100 = 63.0\%$$

26. (a) k remains constant at constant temperature and CO does not effect the rate of reaction.

27. (a) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

when $t = 60$ and $x = 60\%$

$$k = \frac{2.303}{60} \log \frac{100}{100-60} = \frac{2.303}{60} \log \frac{100}{40}$$

Now,

$$t_{1/2} = \frac{2.303}{0.0153} \log \frac{100}{100-50} = \frac{2.303}{0.0153} \times \log 2$$

$$= \frac{2.303}{0.0153} \times 0.3010 = 45.31 \text{ min.}$$

28. (d) Given, $k_1 = 10^{16} \cdot e^{-\frac{2000}{T}}$

$$\text{and } k_2 = 10^{15} \cdot e^{-\frac{1000}{T}}$$

when k_1 and k_2 are equal at any temperature T , we have

$$10^{16} \cdot e^{-\frac{2000}{T}} = 10^{15} \cdot e^{-\frac{1000}{T}}$$

$$\text{or } 10 \times 10^{15} \cdot e^{-\frac{2000}{T}} = 10^{15} \cdot e^{-\frac{1000}{T}}$$

$$\text{or } 10.e^{-\frac{2000}{T}} = e^{-\frac{1000}{T}}$$

$$\text{or } \ln 10 - \frac{2000}{T} = -\frac{1000}{T}$$

$$\text{or } \ln 10 = \frac{2000}{T} - \frac{1000}{T}$$

$$\text{or } 2.303 \log 10 = \frac{1000}{T}$$

$$\text{or } 2.303 \times 1 \times T = 1000 \quad [\because \log 10 = 1]$$

$$\text{or } T = \frac{1000}{2.303} \text{ K}$$

29. (b) Rate of disappearance of reactant = Rate of appearance of products

$$-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$\frac{1}{2} k[\text{N}_2\text{O}_5] = \frac{1}{4} k'[\text{N}_2\text{O}_5] = k''[\text{N}_2\text{O}_5]$$

$$\frac{k}{2} = \frac{k'}{4} = k'' \quad k' = 2k, \quad k'' = \frac{k}{2}$$

30. (a) Since initial velocity is ten times the permissible value
 $\therefore A_0 = 10A$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t_{1/2} = \frac{2.303}{\lambda} \log \frac{A_0}{A} = \frac{2.303}{0.693/30} \log \frac{10A}{A}$$

$$= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \text{ days.}$$

31. (c) For the reaction
 $A \rightarrow \text{Product}$
 given $t_{1/2} = 1 \text{ hour}$
 for a zero order reaction

$$t_{1/2} = \frac{[A_0]}{2k}$$

$$\text{or } k = \frac{[A_0]}{2t_{1/2}} = \frac{2}{2 \times 1} = 1 \text{ mol lit}^{-1} \text{ hr}^{-1}$$

Further for a zero order reaction

$$k = \frac{dx}{dt} = \frac{\text{change in concentration}}{\text{time}}$$

$$1 = \frac{0.50 - 0.25}{\text{time}}$$

$$\therefore \text{time} = 0.25 \text{ hr.}$$

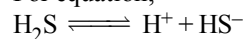
32. (d) Since the slow step is the rate determining step hence if we consider option (A) we find

$$\text{Rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$$

Now if we consider option (B) we find

$$\text{Rate} = k[\text{Cl}_2][\text{HS}^-] \quad \dots(i)$$

For equation,



$$K = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad \text{or} \quad [\text{HS}^-] = \frac{K[\text{H}_2\text{S}]}{[\text{H}^+]}$$

Substituting this value in equation (i) we find

$$\text{Rate} = k[\text{Cl}_2]K \frac{[\text{H}_2\text{S}]}{[\text{H}^+]} = k' \frac{[\text{Cl}_2][\text{H}_2\text{S}]}{[\text{H}^+]}$$

Thus slow step should involve 1 molecule of Cl_2 and 1 molecule of H_2S .

hence only, mechanism (A) is consistent with the given rate equation.

33. (c) Since for every 10°C rise in temperature rate doubles for 50°C rise in temperature increase in reaction rate = $2^5 = 32$ times

34. (d) Overall order = sum of orders w.r.t each reactant.
 Let the order be x and y for G and H respectively

Exp.No.	[G]mole litre ⁻¹	[H]mole litre ⁻¹	rate(mole litre ⁻¹ time ⁻¹)
1	a	b	r
2	$2a$	$2b$	$8r$
3	$2a$	b	$2r$

$\therefore$ For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant i.e.,

$$\text{rate} \propto [\text{G}] \quad \therefore x = 1$$

From (2) and (3), $y = 2$

$\therefore$ Overall order is 3.

35. (a) The values of rate constants k_0 , k_1 for zero order and first order reaction, respectively, are given by the following equation:

$$k_0 = \frac{A_0}{2 \times t_{1/2}} \quad [\text{where } A_0 = \text{initial concentration, and } t_{1/2} = \text{half-life period}]$$

$$\text{and } k_1 = \frac{0.693}{t_{1/2}}$$

Substituting various given values, we get

$$k_0 = \frac{1.386 \text{ mol litre}^{-1}}{2 \times 20 \text{ sec}} \quad \dots(i)$$

$$\text{and } k_1 = \frac{0.693}{40 \text{ sec}} \quad \dots(ii)$$

Dividing (ii) by (i), we get

$$\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{2 \times 20}{1.386 \text{ mol dm}^{-3}}$$

$$= \frac{0.693}{1.386} = 0.5$$

$$= 0.5 \text{ mol}^{-1} \text{ dm}^3$$

Thus the correct answer is (a).

$$36. (d) \log k = \log A - \frac{E_a}{2.303RT} \quad \dots(1)$$

$$\text{Also given } \log k = 6.0 - (2000) \frac{1}{T} \quad \dots(2)$$

On comparing equations, (1) and (2)

$$\log A = 6.0 \Rightarrow A = 10^6 \text{ s}^{-1}$$

$$\text{and } \frac{E_a}{2.303 R} = 2000 ;$$

$$\Rightarrow E_a = 2000 \times 2.303 \times 8.314 = 38.29 \text{ kJ mol}^{-1}$$

37. (a) As per Arrhenius equation ($k = Ae^{-E_a/RT}$), the rate constant increases exponentially with temperature.

38. (a) From the first set of data (i) and (ii) it is observed that on keeping concentration of [B] constant and on doubling the concentration of [A] rate does not change hence order of reaction with respect to A is zero.

From the second set of data (i) and (iii) it is observed that rate becomes 4 times on doubling the concentration of [B] keeping [A] constant hence order with respect to [B] will be 2

$$\text{rate} = k[A]^0[B]^2$$

39. (d) For a zero order reaction,

$$t_{1/2} \propto a_0 \text{ (initial concentration or initial pressure)}$$

$$(t_{1/2})_1 \propto P_1$$

$$(t_{1/2})_2 \propto P_2$$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1}, \quad \frac{(t_{1/2})_2}{45} = \frac{16}{4}$$

$$(t_{1/2})_2 = \frac{16}{4} \times 45 = 180 \text{ min}$$

40. (d) From 1st and 2nd sets of data - no change in rate is observed with the change in concentration of 'C'. So the order with respect to 'C' is zero.

From 1st and 4th sets of data

Dividing eq. (4) by eq. (1)

$$\frac{1.25 \times 10^{-3}}{5.0 \times 10^{-3}} = \left[\frac{0.005}{0.010} \right]^x$$

$$\text{or } 0.25 = (0.5)^x \text{ or } (0.5)^2 = (0.5)^x$$

$$\therefore x = 2$$

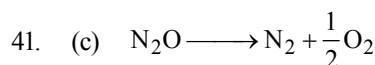
The order with respect to 'A' is 2 from the 1st and 3rd sets of data Dividing eq. (1) by eq. (3)

$$\frac{5.0 \times 10^{-3}}{1.0 \times 10^{-2}} = \left[\frac{0.005}{0.010} \right]^y$$

$$\text{or } (0.5)^1 = (0.5)^y \Rightarrow y = 1$$

The order with respect to 'B' is 1

So the order with respect to the reactants A, B and C is 2, 1 and 0.



$$\frac{dx}{dt} \propto [\text{N}_2\text{O}]^1$$

i.e. order of reaction = 1

42. (d) For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{75} \log \frac{1}{1/8} = \frac{2.303 \times 0.903}{75} \text{ min}^{-1}$$

First order reaction

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 75}{2.303 \times 0.903} = 25 \text{ min}$$

$$43. (b) k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT$$

For $\ln k$ vs $1/T$

$\ln A$ = intercept

$$-E_a/R = \text{slope} = -2 \times 10^4 \text{ K}$$

$$\therefore E_a = 8.3 \times 2 \times 10^4 \text{ J mol}^{-1}$$

$$= 16.6 \times 10^4 \text{ J mol}^{-1} \text{ or } 166 \text{ kJ mol}^{-1}$$

$$44. (d) \therefore \frac{N}{N_0} = \left(\frac{1}{2} \right)^n$$

For first condition

$$\frac{1}{4} = \left(\frac{1}{2} \right)^n \therefore n = 2$$

$$t_{1/2} = \frac{20}{2} = 10$$

For second condition

$$\left(\frac{1}{16} \right) = \left(\frac{1}{2} \right)^n$$

$$n = 4 \therefore T = 4 \times 10 = 40 \text{ min}$$

45. (c) Order is the sum of the powers to which the concentration terms are raised in the rate equation.

46. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$

$$\therefore \text{when } E_a = 0, k = A$$

Also $\ln k$ vs $1/T$ is a straight line with slope $= -E_a/R$.

$\therefore$ Statements (ii) and (v) are correct.

47. (b) According to Arrhenius equation, $k = Ae^{-E/RT}$

When $E_a = 0, k = A$

48. (b) For a zero order reaction, $t_{1/2}[A_0]/2k$

49. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$.

EXERCISE - 3

Exemplar Questions

- (c) The role of a catalyst is to change the activation energy of reaction.
- (c) The heat absorbed or evolved during the reaction remains unchanged in presence of catalyst as there is no change in stability of reactant and product.
- (b) Arrhenius equation relates activation energy of a chemical reaction with rate constant of a reaction at two different temperatures.

$$\ln \left(\frac{k_1}{k_2} \right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

- (a) The minimum energy required to convert reactant molecules into product molecules.

i.e. Activation energy = $E_1 + E_2$

Energy of product is greater than the reactants so less stable.

5. (b) $A(g) \longrightarrow B(g) + C(g)$
Initially p_i 0 0
At time t $p_i - x$ x x
Total pressure at equilibrium, $p_t = p_i - x + x + x = p_i + x$
For first order reaction $x = p_t - p_i$

$$k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$$

$$= \frac{2.303}{t} \log \frac{p_i}{p_i - (p_t - p_i)}$$

$$= \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$$

6. (a) According to Arrhenius equation, $k = A e^{-E_a/RT}$

Taking log on both side $\ln k = \ln \left(A e^{-\frac{E_a}{RT}} \right)$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A$$

From the graph, it is clear that slope = $-\frac{E_a}{R}$ and intercept = $\ln A$.

7. (d) As per Arrhenius equation $k = A e^{-E_a/RT}$

So, $k \propto e^{-E_a}$

$$k \propto e^{-\frac{1}{T}}$$

$$\propto e^T$$

These relations show that rate constant increases with decreasing activation energy and increasing temperature.

8. (c) $Zn + \text{dil. HCl} \longrightarrow ZnCl_2 + H_2 \uparrow$

Rate of reaction

$$= \frac{\text{Change in concentration of } H_2}{\text{Change in time}} = \frac{V_3 - 0}{40 - 0} = \frac{V_3}{40}$$

9. (c) Order of reaction may or may not be equal to sum of stoichiometric coefficients of reactants in the balanced chemical equation.

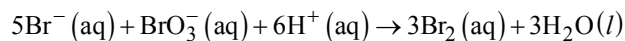
10. (b) Instantaneous rate of reaction

$$= \frac{\text{Change in volume}}{\text{Time interval close to 40s}}$$

$$r_{\text{inst}}(20s) = \frac{V_4 - V_2}{50 - 30} \text{ incorrect, correct is } \frac{V_5 - V_2}{50 - 30}$$

11. (a) Concentration of reactant decreases with passage of time, so rate of reaction decreases because rate changes with change in concentration of reactant or product with time.

12. (c)



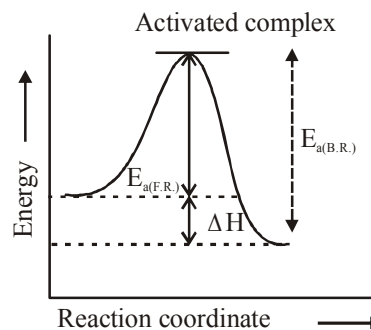
Rate law expression as

$$-\frac{1}{5} \frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-1}{6} \frac{\Delta[H^+]}{\Delta t} = \frac{+1}{3} \frac{\Delta[Br_2]}{\Delta t}$$

$$\Rightarrow -\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-5}{6} \frac{\Delta[H^+]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[H^+]}{\Delta t}$$

13. (a) $E_{a(F.R.)} + \Delta H = E_{a(B.R.)}$
 $\Delta H = -ve$



14. (b) Rate of reaction w.r.t B is of first order
 $R_1 = k[A][B]$
when concentration of reactant 'B' is doubled then rate (R_2) will be :
 $R_2 = k[A][2B]$
 $R_2 = 2k[A][B]$
 $R_2 = 2R_1$
15. (c) In collision theory of reaction rates the key factors which determine whether a particular collision will result in a reaction is the energy of collision and the orientation of the collision.
16. (d) The time in which the concentration of a reactant is reduced to half of its original value is called half-life period of the reaction.
But it is impossible to perform 100% of the reaction. Because substance never reacts completely as in every half-life, 50% of the substance reacts. So, time taken for 100% completion of a reaction is infinite.
17. (b) $r = k[A]^x[B]^y$

$$\frac{\text{Rate of exp. 1}}{\text{Rate of exp. 2}} = \frac{[0.30]^x [0.30]^y}{[0.30]^x [0.60]^y}$$

$$\frac{0.10}{0.40} = \frac{[0.30]^y}{[0.60]^y}$$

$$\frac{1}{4} = \left[\frac{1}{2} \right]^y$$

$$\left[\frac{1}{2} \right]^2 = \left[\frac{1}{2} \right]^y$$

$$y = 2$$

$$\frac{\text{Rate of exp. 1}}{\text{Rate of exp. 3}} = \frac{[0.30]^x [0.30]^y}{[0.60]^x [0.30]^y}$$

$$\frac{0.10}{0.20} = \left[\frac{0.30}{0.60} \right]^x \left[\frac{0.30}{0.30} \right]^y$$

$$\frac{1}{2} = \left[\frac{1}{2} \right]^x [1]^y$$

$$\frac{1}{2} = \left[\frac{1}{2} \right]^x$$

i.e., $x = 1$

$$\therefore \text{Rate} = k[A]^x[B]^y$$

$$\text{Rate} = k[A]^1[B]^2$$

18. (b) Catalyst does not change Gibbs free energy because Gibbs free energy is related to concentration of reactant & product which is not changed by catalyst.
19. (b) Pseudo first order reaction is a chemical reaction in which rate of reaction depends upon concentration of only one reactant while concentration of another reactant has no effect on rate of reaction.
20. (b) $A \rightarrow B$
As time increases concentration of reactant decreases and concentration of product increases exponentially.

NEET/AIPMT (2013-2017) Questions

21. (b) $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
 $\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{293} - \frac{1}{308} \right]$
 $0.3 = \frac{E_a}{2.303 \times 8.314} \times \frac{293 \times 308}{15}$
 $E_a = \frac{0.3 \times 2.303 \times 8.314 \times 293 \times 308}{15}$
 $= 34673 \text{ J mol}^{-1} = 34.7 \text{ kJ mol}^{-1}$
22. (b) $DH = E_{af} - E_{ab} = 0$
23. (b) For a first order reaction,
 $t_{75\%} = 2 \times t_{50\%}$
24. (d) $\text{Rate}_1 = k[A]^2[B]^3$
 when concentrations of both A and B are doubled then
 $\text{Rate}_2 = k[2A]^2[2B]^3 = 32k[A]^2[B]^3$
 $\therefore$ rate will increase by a factor of 32.
25. (b) Arrhenius equation
 $K = A \cdot e^{-E_a/RT} \Rightarrow \ln K = \ln A - \frac{E_a}{RT}$
 $\text{slope} = \frac{-E_a}{R}$
 so, activation energy of reaction can be determined from
 the slope of $\ln K$ vs $\frac{1}{T}$
26. (a) $t_{1/2} = \frac{0.693}{k}$

For first order $t_{1/2}$ is independent of initial concentration of reactant.

27. (d) Rate constant $k = 0.6 \times 10^{-3}$ mole per second. (unit mole per second shows zero order reaction)

For a zero order reaction

$$[A] = [A]_0 - kt$$

$$\text{and } [A]_0 - [A] = [B] = kt$$

$$= 0.6 \times 10^{-3} \times 20 \times 60 = 0.72 \text{ M}$$

28. (a) For a first order reaction

$$K = \frac{2.303}{(t_2 - t_1)} \log \frac{(a - x_1)}{(a - x_2)}$$

$$K = \frac{2.303}{(20 - 10)} \log \left(\frac{0.04}{0.03} \right)$$

$$K = \frac{2.303 \times 0.1249}{10}$$

$$\frac{0.6932}{t_{1/2}} = \frac{2.303 \times 0.1249}{10}$$

$$t_{1/2} = \frac{0.6932 \times 10}{2.303 \times 0.1249} = 24.1 \text{ sec}$$

29. (d) A catalyst provides an alternative route for the reaction with a lower activation energy.

30. (c) The overall reaction rate depends on the rate of the slowest step.

i.e., Overall rate = Rate of slowest step (ii)

$$= k[X][Y_2] \quad \dots (1)$$

k = rate constant

Assuming step (i) to be reversible, its equilibrium constant,

$$k_{eq} = \frac{[X]^2}{[X_2]} \Rightarrow [X]^2 = k_{eq} [X_2];$$

$$[X] = k_{eq}^{\frac{1}{2}} [X_2]^{\frac{1}{2}} \quad \dots (2)$$

From eq (1) and (2)

$$\text{Rate} = k k_{eq}^{\frac{1}{2}} [X_2]^{\frac{1}{2}} [Y_2]$$

$$\text{Overall order} = \frac{1}{2} + 1 = \frac{3}{2} = 1.5$$

31. (a) Half life for a first order reaction,

$$t_{1/2} = \frac{0.693}{K}$$

$$\text{So, } t_{1/2} = \frac{0.693}{10^{-2}} \text{ sec.}$$

Also, for the reduction of 20 g of reactant to 5 g, two half lives will be required.

$\therefore$ For 20 g of the reactant to reduce to 5g, time taken,

$$t = 2 \times \frac{0.693}{10^{-2}} \text{ sec} = 138.6 \text{ sec.}$$

Chapter

19

Surface Chemistry

Surface chemistry deals with the phenomena that occur at the surfaces or interfaces.

ADSORPTION

The accumulation of molecular species at the surface rather than in the bulk of a solid or a liquid is termed **Adsorption**. The substance which accumulates at the surface is called **adsorbate** and the material on the surface of which adsorption takes place is called **adsorbent**. Examples of adsorbents are activated charcoal, Pt, Ni, Pd. etc.

The process of removing an adsorbed substance from a surface on which it is adsorbed is called **Desorption**.

Absorption

Adsorption is different from absorption. In adsorption, the substance is concentrated only at the surface while in absorption, the substance is uniformly distributed throughout the bulk of the solid. For ex: water vapour. Water vapours are absorbed by anhydrous CaCl_2 but adsorbed by silica gel.

Both absorption and adsorption can take place simultaneously. This process in which absorption and adsorption take place simultaneously is called sorption.

Types of Adsorption

Depending upon the nature of forces between molecules of adsorbate and adsorbent, adsorption is of two types :

- (i) Physical adsorption (ii) Chemical adsorption

Mechanism of Adsorption

Particles at the surface of adsorbent are in different state than inside the bulk. On the surface particles are not surrounded by atoms or molecules of their kind on all sides and hence they possess unbalanced or residual attractive forces. These unbalanced inward forces or free valencies at the surface of adsorbent are responsible for attracting the adsorbate particles on its surface.

Characteristics of Adsorption:

- Adsorption is a surface phenomenon
- It is spontaneous process.
- Adsorption is exothermic because during adsorption, residual forces of the surface decrease i.e., surface energy decreases which appears as heat i.e., ΔH is negative.
- For adsorption, ΔS is negative because the molecules of adsorbate are held on the surface of the adsorbent.
- As $\Delta G = \Delta H - T\Delta S$, $\therefore$ for adsorption to be spontaneous, ΔG must be negative. As ΔS is negative, ΔG can be negative only if $\Delta H = -ve$ and $\Delta H > T\Delta S$.

$$\begin{aligned}\therefore \text{ for adsorption, } \Delta H &= -ve \\ \Delta S &= -ve \\ \Delta G &= -ve \text{ if } \Delta H > T\Delta S\end{aligned}$$

Physical adsorption (Physiosorption)		Chemical Adsorption (Chemisorption)	
1	The forces operating in these cases are weak van der Waals forces	1	The forces operating are similar to those of a chemical bond.
2	The heats of adsorption are low, viz about 20-40 kJ mol ⁻¹	2	The heats of adsorption are high, viz, about 40-400 kJ mol ⁻¹
3	No compound formation takes place.	3	Surface compounds are formed.
4	The process is reversible	4	It is an irreversible process.
5	It does not require any activation energy	5	It requires activation energy.
6	It usually occurs at low temperature and decreases with increase of temperature.	6	It first increases with increase of temperature.
7	It is not specific in nature i.e., all gases are adsorbed on all solids to some extent.	7	It is specific in nature and occurs only when there is some possibility of compound formation between adsorbate and adsorbent.
8	It forms multimolecular layer	8	It forms unimolecular layer.

Factors Affecting Adsorption

- Nature of adsorbate:** Readily liquefiable gases such as HCl, SO₂, CO₂, CH₄, NH₃ etc. are more easily adsorbed by the adsorbent than the permanent gases H₂, N₂ etc.
- Nature of adsorbent:** Activated charcoal is a better adsorbent than transitional metals.
- Surface area of adsorbent:** The greater the surface area of adsorbent, the greater will be the extent of adsorption.
- Pressure:** Extent of physical adsorption increases as the pressure of the gas increases, till a saturation point is reached.
- Temperature:** Adsorption is accompanied by evolution of heat i.e., ΔH is negative, so the rate of adsorption should decrease with rise in temperature. It is found to be so in case of physical adsorption. The effect of temperature is represented by an adsorption isobar.
- Activation of adsorbent:** An adsorbent can be activated either by heating or by bringing it in finely divided state, or by making its surface rough by rubbing. For example charcoal is activated by heating it in vacuum at 1000°C.

ADSORPTION ISOTHERM

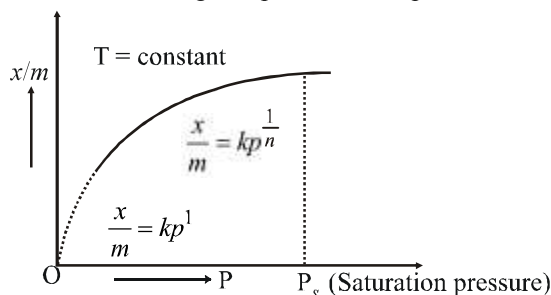
The variation in the amount of gas adsorbed by adsorbent with pressure at constant temperature is expressed with help of **Adsorption Isotherm**.

Freundlich Adsorption Isotherm

A relationship was given by Freundlich which is as follows:

$$\frac{x}{m} = kp^{1/n} \quad (n > 1)$$

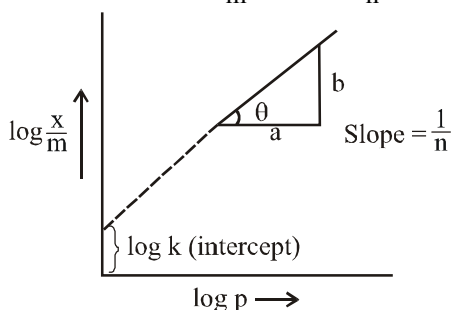
Where $x \rightarrow$ mass of gas adsorbed
 $m \rightarrow$ mass of adsorbent
 $p \rightarrow$ pressure
 $k, n \rightarrow$ Constants which depend on nature of adsorbent and the gas at particular temperature.



- At low pressure :** x/m is directly proportion to pressure i.e. $x/m \propto p$.
- At high pressure :** The extent of adsorption x/m becomes independent of pressure i.e., $x/m \propto p^0$.
- At intermediate pressure :** x/m will depend upon the power of pressure which lies between 0 and 1.

The curves seem to approach saturation at high pressure.

Taking log, we have $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$



Langmuir Adsorption Isotherm

Acc to his theory of adsorption,

- Adsorption could take place on the surface of a solid only till whole of the surface was completely covered with a unimolecular layer of the gas molecules.
 - Adsorption consists of two opposing process, namely condensation of gas molecules on solid surface and evaporation of gas molecules from surface back into gaseous phase.
 - The rate of condensation depends upon the bare surface available for condensation whereas rate of evaporation depends upon the covered surface.
- and, mathematically, the langmuir adsorption isotherm is given as :

$$\frac{x}{m} = \frac{ap}{1 + bp} \quad \dots(1)$$

where $p \rightarrow$ pressure of the gas at any instant and a and b are constants whose values depend upon the nature of the gas adsorbed, the nature of adsorbent and temperature.

The above equation can be written as

$$\frac{x/m}{p} = \frac{a}{1 + bp} \quad \text{or} \quad \frac{p}{x/m} = \frac{1 + bp}{a} = \frac{1}{a} + \frac{b}{a}p$$

Thus a plot of $p/x/m$ vs p is a straight line with slope

$$= \frac{b}{a} \quad \text{and intercept on y-axis} = \frac{1}{a}$$

Application of Adsorption

- Production of high vacuum (by using charcoal)
- Gas masks
- Control of humidity (by using silica and aluminium gels)
- Removal of colouring matter from solutions (using animal charcoal)
- Heterogeneous catalysis
- Separation of inert gases (using coconut charcoal)
- In curing diseases
- In froth floatation process
- Adsorption indicators (Example : Silver halides)
- Chromatographic analysis.

CATALYSIS

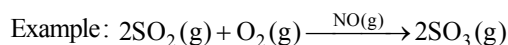
Catalyst is a substance which can change the speed of a chemical reaction without itself undergoing any change in mass and chemical composition at the end of the reaction and the phenomenon is known as catalysis.

Certain substances which enhance the activity of a catalyst are called promoters. Those which lower the activity of the catalyst are called poisons and process is called catalytic poisoning.

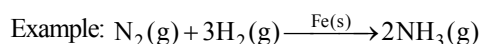
Types of Catalysis

Catalysis is of two types :

- Homogeneous catalysis:** When catalyst, reactants and the products are in same phase the process is called homogeneous catalysis.



- Heterogeneous catalysis :** When the catalyst is in different phase than that of reactants and products the process is known as heterogeneous catalysis.



Classification of Catalysts

Catalysts are divided into four types:

- (i) **Positive catalysts:** The substance which increases the rate of a reaction is known as a positive catalyst. It decreases the energy of activation for the reaction.
- (ii) **Negative catalysts:** The substance which decreases the rate of chemical reaction is called negative catalyst or inhibitor. It increases the activation energy for the reaction.
- (iii) **Autocatalyst:** When one of the products of the reaction begins to act as a catalyst, it is called auto-catalyst.
- (iv) **Induced catalyst:** When a chemical reaction enhances the rate of another chemical reaction, it is called induced catalysis.

General Characteristics of Catalysts:

- (i) A catalyst remains unchanged in mass and chemical composition.
- (ii) Only a very small amount of catalyst is sufficient to catalyze a reaction.
- (iii) A catalyst does not initiate a reaction & does not control a chemical reaction.
- (iv) When a catalyst is a solid, it is usually more efficient when used in finely divided form.
- (v) Generally catalyst does not change the nature of products.
- (vi) A catalysts does not change the equilibrium state of a reversible reaction but helps to timely achieve equilibrium state or position of equilibrium.

Theory of Catalysis:

- (i) Intermediate theory
 - (ii) Adsorption theory
 - (iii) Modern theory
 - (i) **Intermediate theory** - A catalyst combines with one of the reactants and forms the unstable intermediate compound which in turn combines with another reactant and generates the catalyst.
 - (ii) **Adsorption theory** - By the adsorption of the reactants at the surface of a catalyst, their concentrations are increased. The rate being directly proportional to concentration, is increased.
 - (iii) **Modern theory** - It is the combination of intermediate theory and adsorption theory. At the surface of a catalyst there are residual or free valencies and reactant molecules are retained at the surface in distorted or strained positions. These molecules then react vigorously to give products and make space for other reactant molecules. The greater the surface area of the catalyst, the more is its activity. Further catalysts with rough surface, having greater number of corners, peaks,
- (i) **On the basis of physical state of dispersed phase and dispersion medium:**

cracks have more active centres and more effective e.g. finely divided nickel or platinum.

Important Features of Solid Catalysts

- (i) **Activity:** It is the capacity of a catalyst to increase the speed of a chemical reaction.
- (ii) **Selectivity:** It is ability of a catalyst to direct a reaction to yield a particular product.

Shape - Selective Catalysis

The catalytic reaction which depends upon the pore structure of the catalyst and the size of reactant and product molecules is called shape-selective catalysis. **zeolites** are good shape - selective catalyst because of their honeycomb - like structures.

ENZYME CATALYSIS

Many complex chemical reactions like oxidation, reduction or hydrolysis take place in presence of enzymes which are highly complex, nitrogenous non living organic substances. They are highly specific in nature.

Mechanism of Enzyme Catalysed Reactions:

The most accepted mechanism of enzyme catalysed reaction is lock and key mechanism. Enzymes are highly specific in their action due to presence of active sites on their surface. The shape of the active site in any enzyme is like a cavity such that a specific substrate can fit into it in the same way as one key can fit into a particular lock. This binding gives enzyme-substrate complex.

The reaction takes place as:



COLLOIDS

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. Colloidal particles are larger than simple molecules but small enough to remain suspended. Their range of diameter is between 1000 nm (10^{-9} to 10^{-6} m).

Dispersed phase : Discontinuous phase of colloidal system is known as dispersed phase.

Dispersed medium : The continuous phase of colloidal system known as dispersion medium.

Classification of Colloids

Colloids are classified on the basis of following criteria:

- (i) Physical state of dispersed phase and dispersion medium
 - (ii) Nature of interaction between dispersed phase and dispersion medium.
 - (iii) Type of particles of dispersed phase.
- These are discussed as follows:

	Dispersed phase	Dispersion Medium	Type of colloid	Examples
1	Solid	Solid	Solid sol	gem stones alloys
2	Solid	Liquid	Sol	Paints, cell fluids, colloidal gold
3	Solid	Gas	Aerosol	Smoke, dust, occluded gases
4	Liquid	Solid	Gel	Cheese, butter, jellies
5	Liquid	Liquid	Emulsion	Milk, hair cream
6	Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
7	Gas	Solid	Solid sol	Pumice stone, foam rubber
8	Gas	Liquid	Foam	Froth, whipped cream, soap lather

Note: A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular structure.

(ii) Based on the nature of interaction between dispersed phase and dispersed medium

- (a) Lyophilic colloids :** When dispersed phase has certain affinity for the dispersion medium it is known as lyophilic sol.

Characteristics of lyophilic colloids:

1. They can be prepared easily by directly mixing with liquid dispersion medium
2. They are stable and cannot be easily precipitated or coagulated.
3. They are highly hydrated.
4. Their particles carry a characteristics charge either positive or negative.
5. Reversible in nature, i.e., once precipitated can reform the colloidal sol by simply remixing with the dispersion medium. Usually formed by organic substances like starch, gum, proteins, etc.
6. Surface tension is almost same as that of solvent.

- (b) Lyophobic colloids:** When dispersed phase has no affinity for dispersion medium it is known as lyophobic sol.

Characteristics of lyophobic colloids.

1. Prepared by special methods only and gets easily precipitated by addition of a small amount of a suitable electrolyte.
2. Not much hydrated.
3. The particles have little charge or no charge at all.
4. Irreversible in nature i.e., cannot be reformed by simple addition of dispersion medium usually formed by inorganic substances.
5. Like metals, their sulphides, etc.
6. The particles have little or no charge at all.

Note:

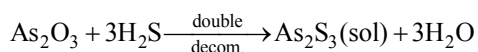
- (i) In associated colloids, micelle formation takes place only above a particular temperature called Kraft temperature (T_K) and above a particular concentration called critical micelle concentration (CMC).
- (ii) **Micelle formation:**
Soap is sodium or potassium salt of a higher fatty acid $\text{RCOO}^- \text{Na}^+$. The RCOO^- ions consist of a long hydrocarbon chain R which is hydrophobic and a polar group COO^- which is hydrophilic. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part is in the oil droplet and hydrophilic part projects out of the grease droplet. Since the polar groups can interact with water, the oil droplet is pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats.

Preparation of Colloids

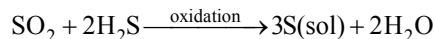
Some important methods for preparation of colloids are:

Chemical methods

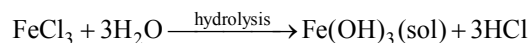
- (i) **Double decomposition:** An arsenic sol is prepared by passing H_2S through cold solution As_2O_3 till yellow colour deepens to its maximum.



- (ii) A sol of sulphur is prepared by passing H_2S into SO_2 solution.



- (iii) Ferric hydroxide sol is prepared by pouring dilute solution of ferric chloride into boiling water



- (iv) Sols of gold, platinum and silver are prepared by reduction of their compounds in H_2O using tannic acid or hydrazine.

Bredig's arc method :

An electric arc is struck between electrodes of the metal immersed in dispersion medium. The intense heat produced vapourises the metal which then condenses to form particles of colloidal size. It is used for metals like Au, Ag, Pt, etc.

Peptization :

It is defined as a process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent.

Note:

The cause of peptization is that during peptization, the ppt adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative on ppt, which ultimately break up into smaller particles of colloidal size.

Purification of Colloidal Solutions

The process used for reducing the amount of impurities to a requisite minimum amount known as purification of colloidal sol. Difference methods of purification of colloidal solutions are :

- (i) **Dialysis:** It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. The membrane used can be animal membrane, or parchment paper or cellophane sheet as colloidal particles cannot pass through them.
A mixture containing colloidal particles and true solution is placed in parchment bag. The bag is hanged in water vessel through which it is continuously flowing. True solution comes out of membrane leaving behind colloidal solution.
- (ii) **Electro-dialysis:** To increase the speed of dialysis process, an electric field is applied (if impurity is an electrolyte) and the process is called electro-dialysis.
In this process vessel is fitted with electrodes which makes the removal of electrolytes fast.
- (iii) **Ultrafiltration:** It is a process of separating the colloidal particles from the solvent and soluble solutes present in colloidal solution by specially prepared filters which are permeable to all substances except colloidal particles.

Properties of Colloidal Solutions

- (i) **Colligative properties:** Values of colligative properties are smaller as compared to true solutions because colloidal particles being bigger aggregates, the no. of particles in the solution are small as compared to true solution.
- (ii) **Tyndall effect:** It is defined as the scattering of light by colloidal particles present in colloidal sol. It is due to this scattering of light that the path of light is illuminated with bluish light when viewed at right angles to the direction of light.

Ex: Tyndall effect is observed during projection of picture in cinema hall due to scattering of light by dust and smoke particles.

- (iii) **Brownian movement:** It is defined as continuous zig-zag movement of colloidal particles in a colloidal sol.
- It does not depend on nature of colloid.
 - It depends on size of particles and viscosity of solution. Smaller the size of particles and lesser the viscosity, faster the movement.
 - It arises due to unbalanced bombardment of particles by particles of dispersion medium.
 - It has a stirring effect which does not allow the particles to settle and is thus responsible for **stability of sols**.
- (iv) **Colour:** The colour of colloidal solution depends upon the wavelength of light scattered by colloidal particles which in turn depends upon size and nature of particles.

- (v) **Charge on colloidal particles:** The **stability of colloidal sol** is due to the fact that the particles are electrically charged, they repel one another and do not coagulate. All particles of dispersed phase carry same charge (which can be either +ve or -ve) while dispersed medium carries equal and opposite charge.

Note :

- The best explanation for the **origin** of electric charge is the **preferential adsorption of ions from solution**. The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions. When two or more ions are present in dispersion medium, preferential adsorption of the ion common to colloidal particles usually takes place.
- Electrical double layer :**
When one type of ions are adsorbed by colloidal particles, a **fixed layer** is formed. It attracts counter ions from the medium forming a second layer which is mobile and is called **diffused layer**. The double layer of opposite charges thus formed is called **Helmholtz electrical double layer**. As a result, a potential exists between fixed and diffused layers and is called **electrokinetic** or **zeta potential**.
- Electrophoresis:** It is the movement of colloidal particles under the influence of an electric field. Positively charged particles move towards cathode (-ve) while negatively charged particles move towards anode (+ve). On reaching the oppositely charged electrode, they get neutralised and coagulated.
It confirms the existence of charge on colloidal particles.
- Electro-osmosis:** It is the phenomenon in which the molecules of dispersion medium are allowed to move under the influence of an electric field whereas colloidal particles are not allowed to move.
- Coagulation or precipitation:** It is a process of aggregating / settling down of colloidal particles is called coagulation or precipitation.
It is done in the following ways:
 - By electrophoresis :** During electrophoresis the charged sol particles migrate towards the electrode of opposite sign. There they deposit their charge and then get coagulated
 - By mixing two oppositely charged sols :** The neutral coagulation of two sols of opposite charge can be effected by mixing them., For eg $\text{Fe}(\text{OH})_3$ (positive sol) and Arsenious sulphide (negative sol) when mixed join and coagulate.

- By boiling :** Sols such as sulphur and silver halides disperse in water, get coagulated when boiled due to increased collisions between sol particles and water molecules which removes the adsorbed charged layer from the sol and therefore the sol particles settle down.
- By addition of electrolytes:** When excess of an electrolyte is added, colloidal particles get precipitated because particles take up ions which are oppositely charged and thus get neutralised.

Coagulation Ion and Coagulating Value

The ion responsible for neutralization of charge on the particles is called **coagulating ion**.

The minimum amount of an electrolyte (in millimoles per litre) required to cause precipitation of a sol in two hours is called **coagulating value** or **flocculation value**. Smaller is the coagulation value of an electrolyte, greater is its coagulating power.

Hardy - Schulze Rule

It states that the precipitating effect of an ion on dispersed phase particles of opposite charge increases with the valence of the ion.

- For precipitation of negatively charged sol the flocculating power of Al^{3+} , Ba^{2+} and Na^+ is in the order: $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$.
- For precipitation of positive sol, flocculating power is in the

$$\text{order: } [\text{Fe}(\text{CN}_6)]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$$

Coagulation of Lyophobic and Lyophilic Colloids:

Lyophilic sols are more stable than lyophobic colloids. This is because stability of **lyophilic** colloids is due to two factors:

- Same charge on all colloidal particles
 - Solvation of colloids
- However, stability of **lyophobic** sol is only due to charge which can be removed by adding electrolyte only. Hence, they can be easily coagulated.
- On the other hand, to coagulate lyophilic colloids, both factors (i) and (ii) have to be removed. This is done by adding
- electrolyte
 - suitable solvent (like alcohol or acetone which causes dehydration of colloidal particles)

Protection of Colloids

Lyophobic sols are readily precipitated by small amounts of electrolytes. However these sols are often stabilized by addition of lyophilic sols.

Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to a lyophobic sol, lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes lyophilic colloids used for this purpose are called protective colloids.

Gold Number

The number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10% sodium chloride solution is known as gold number. The smaller the value of gold number of lyophilic sol, the greater is the protective action.

$$\text{Protection capacity} \propto \frac{1}{\text{Gold number}}$$

Colloids Around us

Examples of colloids are:

- (i) Blue colour of sky
- (ii) Fog, mist and rain
- (iii) Food articles
- (iv) Blood
- (v) Soils
- (vi) Formation of delta

Application of Colloids

- (i) Electrical precipitation of smoke
- (ii) Purification of drinking water
- (iii) Medicines
- (iv) Tanning
- (v) Cleansing action of soaps and detergents
- (vi) Photographic plates and films
- (vii) Rubber industry
- (viii) Industrial products like paints, inks, rubber, cement etc.

EMULSIONS

It is a colloidal dispersion in which both dispersed phase and dispersion medium are liquids (two liquids involved are otherwise immiscible).

They are of two types:

- (i) Oil dispersed in water (O/W type) Ex: milk, vanishing cream
- (ii) Water dispersed in oil (W/O type) Ex: butter, cream.

Emulsions are usually not stable. To stabilise an emulsion, other substances are added called emulsifying agents or emulsifiers.

Examples are: proteins, gums, natural and synthetic soaps (for O/W emulsions) and heavy metal salts of fatty acid, long chain alcohols, lampblack, etc. (for W/O type)

Properties of Emulsions :

- (i) They show Tyndal effect and Brownian movement.
- (ii) They can be demulsified (broken) by heating, adding electrolytes, freezing and centrifuging
- (iii) They can be diluted with dispersion medium.

GELS

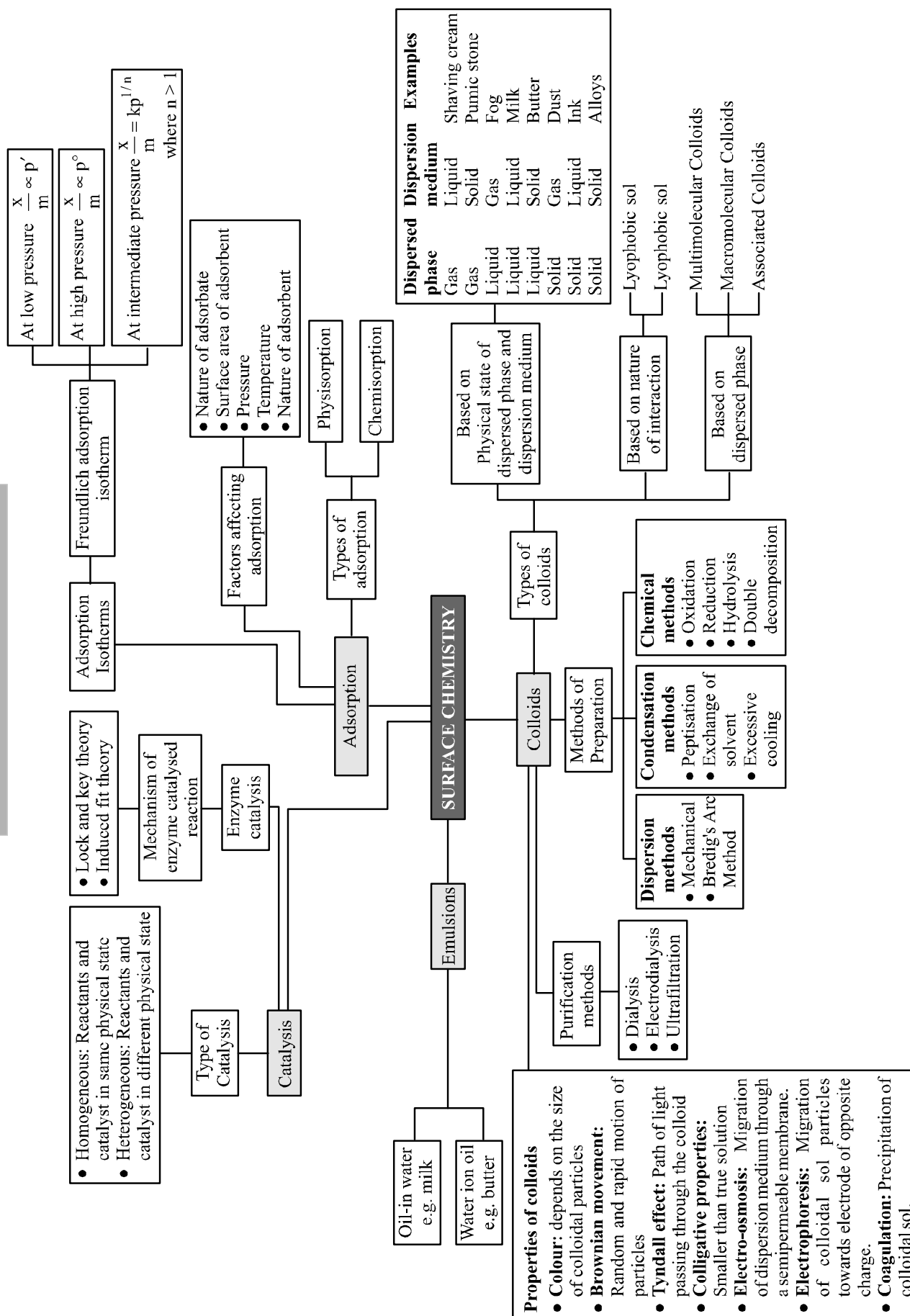
A gel is a jelly like colloidal system in which a liquid is dispersed in solid medium. Gels are of two types:

- (i) **Elastic gels** - They can be temporarily deformed by applying force eg Gelatin, starch and soaps.
- (ii) **Non elastic gels** - They are rigid eg silica gel.

Properties of Gels

- (i) **Syneresis** - Shrinkage of gels on standing by exudation of solvent is known as syneresis
- (ii) **Thixotropy** - Certain gels when shaken form a sol and on standing are converted into the form of gel They are known as thixotropic gels and sol - gel transformation is known as thixotropy.
- (iii) **Swelling or imbibition of gels** - The property of adsorbing definite amount of water and causing the volume of gel to increase is known as swelling or imbibition.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- What is the name given to a phenomenon in which both adsorption and absorption take place?
(a) Chemisorption (b) Physisorption
(c) Desorption (d) Sorption
- The dispersed phase, dispersion medium and nature of colloidal solution (lyophilic or lyophobic) of 'gold sol' respectively, are
(a) solid, solid, lyophobic
(b) liquid, liquid, lyophobic
(c) solid, liquid, lyophobic
(d) solid, liquid, lyophilic
- In Langmuir's model of adsorption of a gas on a solid surface
(a) the mass of gas striking a given area of surface is proportional to the pressure of the gas
(b) the mass of gas striking a given area of surface is independent of the pressure of the gas
(c) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
(d) the adsorption at a single site on the surface may involve multiple molecules at the same time
- Pick out the statement which is not relevant in the discussion of colloids:
(a) Sodium aluminium silicate is used in the softening of hard water
(b) Potash alum is used in shaving rounds and as a styptic in medicine
(c) Artificial rain is caused by throwing electrified sand on the clouds from an aeroplane
(d) Deltas are formed at a place where the river pours its water into the sea
- How many layers are adsorbed in chemical adsorption ?
(a) One (b) Two
(c) Many (d) Zero
- Adsorption due to strong chemical forces is called
(a) Chemisorption (b) Physisorption
(c) Reversible adsorption (d) Both (b) and (c)
- In physical adsorption, gas molecules are bound on the solid surface by
(a) chemical forces (b) electrostatic forces
(c) gravitational forces (d) van der Waal's forces
- Which among the following statements are correct with respect to adsorption of gases on a solid?
(i) The extent of adsorption is equal to kp^n according to Freundlich isotherm
(ii) The extent of adsorption is equal to $kp^{1/n}$ according to Freundlich isotherm
(iii) The extent of adsorption is equal to $(1 + bp)/ap$ according to Langmuir isotherm
(iv) At low pressure x/m is directly proportional to the pressure
(a) (i) and (iii) (b) (i) and (iv)
(c) (ii) and (iii) (d) (ii) and (iv)
- Which of the following statements is not correct ?
(a) Physical adsorption is due to van der Waal's forces
(b) Chemical adsorption first decreases with increase in temperature.
(c) Physical adsorption is reversible
(d) Adsorption energy for a chemical adsorption is generally greater than that of physical adsorption
- The adsorption of a gas on a solid surface varies with pressure of the gas in which of the following manner
(a) Fast $\rightarrow$ slow $\rightarrow$ independent of the pressure
(b) Slow $\rightarrow$ fast $\rightarrow$ independent of the pressure
(c) Independent of the pressure $\rightarrow$ fast $\rightarrow$ slow
(d) Independent of the pressure $\rightarrow$ slow $\rightarrow$ fast
- Adsorption is always
(a) endothermic
(b) exothermic
(c) exothermic in case of physical and endothermic in case of chemical
(d) Either (a) or (b)
- Adsorption of gases on solid surface is exothermic reaction because
(a) free energy increases
(b) enthalpy is positive
(c) entropy increases
(d) enthalpy is negative
- The role of a catalyst in a reversible reaction is to
(a) increase the rate of forward reaction
(b) decrease the rate of backward reaction
(c) alter the equilibrium constant of the reaction
(d) allow the equilibrium to be achieved quickly
- Which of the following kind of catalysis can be explained by the adsorption theory ?
(a) Homogeneous catalysis
(b) Acid - base catalysis
(c) Heterogeneous catalysis
(d) Enzyme catalysis
- "The greater the charge on an ion, the greater its coagulating power" is a statement of :
(a) Tyndall's effect (b) Faraday's law
(c) Mosley's law (d) Hardy-Schulze law
- Catalytic poisons act by :
(a) making the products chemically inactive.
(b) increasing the rate of the backward reaction.
(c) chemical combination with any one of the reactants.
(d) preferential adsorption on the catalyst surface.
- Which one is a colloid?
(a) Sodium chloride (b) Urea
(c) Cane sugar (d) Blood
- The extra stability of lyophilic colloids is due to
(a) Charge on their particles
(b) A layer of medium of dispersion on their particles
(c) The smaller size of their particles
(d) The large size of their particles

19. The action of enzymes in living system is to :
(a) supply energy to tissues
(b) enhance immunity
(c) circulate oxygen
(d) enhance the rate of biochemical reactions.
20. Active charcoal is a good catalyst because it
(a) is made up of carbon atoms.
(b) is very reactive.
(c) has more adsorption power.
(d) has inert nature toward reagents.
21. Which one of the following substances gives a positive charged sol?
(a) Gold (b) A metal sulphide
(c) Ferric hydroxide (d) An acidic dye
22. During dialysis
(a) only solvent molecules can diffuse
(b) solvent molecules, ions and colloidal particles can diffuse
(c) all kinds of particles can diffuse through the semi-permeable membrane
(d) solvent molecules and ions can diffuse
23. At the critical micelle concentration (CMC) the surfactant molecules
(a) decompose
(b) dissociate
(c) associate
(d) become completely soluble
24. The colloidal solution of gelatin is known as
(a) Solvent loving sol (b) Reversible sol
(c) Hydrophilic sol (d) All the above
25. Hardy-Schulze rule explains the effect of electrolytes on the coagulation of colloidal solution. According to this rule, coagulation power of cations follow the order
(a) $\text{Ba}^{+2} > \text{Na}^+ > \text{Al}^{+3}$ (b) $\text{Al}^{+3} > \text{Na}^+ > \text{Ba}^{+2}$
(c) $\text{Al}^{+3} > \text{Ba}^{+2} > \text{Na}^+$ (d) $\text{Ba}^{+2} > \text{Al}^{+3} > \text{Na}^+$
26. Which of the following is used for neutralising charge on colloidal solution?
(a) Electrons
(b) Electrolytes
(c) Positively charged ions
(d) Compounds
27. Which of the following methods is used for the destruction of sol ?
(a) Condensation
(b) Dialysis
(c) Diffusion through animal membrane
(d) Addition of an electrolyte.
28. Colloidal solutions are not purified by
(a) Dialysis (b) Electrodialysis
(c) Ultrafiltration (d) Electrophoresis
29. Pure water can be obtained from sea water by
(a) Centrifugation (b) Plasmolysis
(c) Reverse osmosis (d) Sedimentation
30. How non-polar and polar part in micelle are arranged ?
(a) Polar at outer surface and non-polar at inner surface
(b) Polar at inner surface and non-polar at outer surface
(c) Both polar and non-polar at inner surface
(d) Distributed all over the surface
31. Which of the following forms cationic micelles above certain concentration?
(a) Sodium dodecyl sulphate
(b) Sodium acetate
(c) Urea
(d) Cetyl trimethyl ammonium bromide
32. Which one of the following statements is incorrect in the case of heterogeneous catalysis ?
(a) The catalyst lowers the energy of activation
(b) The catalyst actually forms a compound with the reactant
(c) The surface of the catalyst plays a very important role
(d) There is no change in the energy of activation.
33. The cause of Brownian movement is
(a) heat changes in liquid state
(b) convectional currents
(c) the impact of molecules of the dispersion medium on the colloidal particles.
(d) attractive forces between the colloidal particles and molecules of dispersion medium.
34. Small liquid droplets dispersed in another liquid is called
(a) gel (b) suspension
(c) emulsion (d) true solution
35. Milk is a colloid in which a
(a) liquid is dispersed in a liquid
(b) solid is dispersed in a liquid
(c) gas is dispersed in a liquid
(d) sugar is dispersed in a liquid
36. Butter is a colloid formed when
(a) Fat is dispersed in water
(b) Fat globules are dispersed in water
(c) Water is dispersed in fat
(d) None of the above
37. Commonly used catalyst in the preparation of acrylonitrile from propylene, ammonia and oxygen is
(a) silver (b) bismuth molybdates
(c) caesium chloride (d) nickel
38. Hair cream is an example of
(a) gel (b) sol
(c) aerosol (d) foam
39. Surface tension of lyophilic sols is
(a) lower than that of H_2O
(b) more than that of H_2O
(c) equal to that of H_2O
(d) either less or more than H_2O depending upon the nature of disperse phase
40. Which of the following ions can cause coagulation of proteins ?
(a) Ag^+ (b) Na^+
(c) Mg^{2+} (d) Ca^{2+}
41. Which of the following is a lyophilic colloid ?
(a) Milk (b) Gum
(c) Fog (d) Blood
42. When a strong beam of light is passed through a colloidal solution, the light will
(a) be reflected (b) be scattered
(c) be refracted (d) give a rainbow

43. Adsorption is accompanied by
 (a) decrease in enthalpy and increase in entropy
 (b) increase in enthalpy and increase in entropy
 (c) decrease in enthalpy and decrease in entropy
 (d) increase in enthalpy and decrease in entropy
44. In coagulating the colloidal solution of As_2S_3 which has the minimum coagulating value?
 (a) NaCl (b) KCl
 (c) $BaCl_2$ (d) $AlCl_3$
45. The simplest way to check whether a system is colloidal or not is by
 (a) Tyndall effect (b) Brownian movement
 (c) Electrodialysis (d) Measuring particle size
46. Which of the following is most effective in causing the coagulation of ferric hydroxide sol?
 (a) KCl (b) KNO_3
 (c) K_2SO_4 (d) $K_3[Fe(CN)_6]$
47. The ability of an ion to bring about coagulation of a given colloid depends upon
 (a) its size
 (b) the magnitude of its charge
 (c) the sign of its charge
 (d) both magnitude and sign of its charge
48. The formation of micelles takes place only above
 (a) inversion temperature (b) Boyle temperature
 (c) critical temperature (d) Kraft temperature
49. Gold number is the index for :
 (a) electroplated gold (b) metallic gold
 (c) protective colloid (d) purity of gold
50. Which of the following electrolytes is least effective in coagulating ferric hydroxide solution?
 (a) KBr (b) K_2SO_4
 (c) K_2CrO_4 (d) $K_4[Fe(CN)_6]$
51. An aerosol is a :
 (a) dispersion of a solid or liquid in a gas
 (b) dispersion of a solid in a liquid
 (c) dispersion of a liquid in a liquid
 (d) solid solution
52. Colloidion is a 4% solution of which one of the following in an alcohol-ether mixture?
 (a) nitroglycerine (b) celluloseacetate
 (c) glycoldinitrate (d) nitrocellulose
53. A precipitate is changed to colloidal solution by the following process :
 (a) dialysis (b) ultrafiltration
 (c) peptization (d) electrophoresis
54. The movement of colloidal particles towards their respective electrodes in the presence of an electric field is known as :
 (a) electrolysis (b) Brownian movement
 (c) electrodialysis (d) electrophoresis
55. Which of the following acts as protective colloid?
 (a) Silica gel (b) Gelatin
 (c) Sodium acetate (d) None of these
56. Which of the following is the best protective colloid?
 (a) Gelatin (Gold No. = 0.005)
 (b) Gum arabic (Gold No. = 0.15)
 (c) Egg albumin (Gold No. = 0.08)
 (d) All possess same protective power
57. Which one of the following is correctly matched?
 (a) Emulsion-smoke (b) Gel-butter
 (c) Aerosol-hair cream (d) Sol-whipped cream
58. Which of the following will be most effective in the coagulation of $Al(OH)_3$ sol?
 (a) KCN (b) $BaCl_2$
 (c) NaCl (d) $Mg_3(PO_4)_2$
59. Tyndall effect shown by colloids is due to :
 (a) scattering of light by the particles
 (b) movement of particles
 (c) reflection of light by the particles
 (d) coagulation of particles
60. Alloy is an example of
 (a) gel (b) solidified emulsion
 (c) solid solution (d) sol
61. The separation of colloidal particles from particles of molecular dimensions is known as
 (a) sedimentation (b) dispersion
 (c) pyrolysis (d) dialysis
62. According to Freundlich adsorption isotherm, the amount of gas adsorbed at very high pressure
 (a) reaches a constant limiting value
 (b) goes on increasing with pressure
 (c) goes on decreasing with pressure
 (d) increase first and decreases later with pressure
63. The Langmuir adsorption isotherm is deduced by using the assumption
 (a) the adsorption sites are equivalent in their ability to adsorb the particles
 (b) the heat of adsorption varies with coverage
 (c) the adsorbed molecules interact with each other
 (d) the adsorption takes place in multilayers.
64. If x is amount of adsorbate and m is amount of adsorbent, which of the following relations is not related to adsorption process?
 (a) $x/m = f(p)$ at constant T.
 (b) $x/m = f(T)$ at constant p .
 (c) $p = f(T)$ at constant (x/m) .
 (d) $\frac{x}{m} = p \times T$
65. In Freundlich Adsorption isotherm, the value of $1/n$ is :
 (a) between 0 and 1 in all cases
 (b) between 2 and 4 in all cases
 (c) 1 in case of physical adsorption
 (d) 1 in case of chemisorption
66. Which one of the following, statements is incorrect about enzyme catalysis?
 (a) Enzymes are mostly proteinous in nature.
 (b) Enzyme action is specific.
 (c) Enzymes are denaturated by ultraviolet rays and at high temperature.
 (d) Enzymes are least reactive at optimum temperature.
67. The protecting power of lyophilic colloidal sol is expressed in terms of :
 (a) coagulation value
 (b) gold number
 (c) critical miscelle concentration
 (d) oxidation number
68. Which of the following statements is incorrect regarding physisorptions?
 (a) More easily liquefiable gases are adsorbed readily.
 (b) Under high pressure it results into multimolecular layer on adsorbent surface.
 (c) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is low and positive.
 (d) It occurs because of van der Waal's forces.

69. Bredig arc method cannot be used to prepare colloidal solution of which of the following
 (a) Pt (b) Fe
 (c) Ag (d) Au
70. Which one is an example of multimolecular colloid system
 (a) Soap dispersed in water
 (b) Protein dispersed in water
 (c) Gold dispersed in water
 (d) Gum dispersed in water
71. Metals like Pt and Pd can adsorb large volume of hydrogen under specific conditions. Such adsorbed hydrogen by the metal is known as
 (a) Occluded hydrogen (b) Absorbed hydrogen
 (c) Reactive hydrogen (d) Atomic hydrogen
72. The electrical charge on a colloidal particle is observed by:
 (a) Ultramicroscope (b) Scattering
 (c) Brownian movement (d) Electrophoresis
73. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is
 (a) $D < A < C < B$ (b) $C < B < D < A$
 (c) $A < C < B < D$ (d) $B < D < A < C$
74. Among the electrolytes Na_2SO_4 , CaCl_2 , $\text{Al}_2(\text{SO}_4)_3$ and NH_4Cl , the most effective coagulating agent for Sb_2S_3 sol is
 (a) Na_2SO_4 (b) CaCl_2
 (c) $\text{Al}_2(\text{SO}_4)_3$ (d) NH_4Cl
75. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient condition is :-
 (a) $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
 (b) $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
 (c) $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$
 (d) $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$

EXERCISE - 2

Applied Questions

1. Which one of the following impurities present in colloidal solution cannot be removed by electro dialysis?
 (a) Sodium chloride (b) Potassium sulphate
 (c) Urea (d) Calcium chloride
2. The dispersed phase and dispersion medium in soap lather are respectively
 (a) gas and liquid (b) liquid and gas
 (c) solid and gas (d) solid and liquid
3. Which of the following is most powerful to coagulate the negative colloid?
 (a) ZnSO_4 (b) Na_3PO_4
 (c) AlCl_3 (d) $\text{K}_4[\text{Fe}(\text{CN})_6]$
4. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is NOT correct?
 (a) Coagulation in both sols can be brought about by electrophoresis
 (b) Mixing the sols has no effect
 (c) Sodium sulphate solution causes coagulation in both sols
 (d) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol
5. Alum helps in purifying water by
 (a) forming Si complex with clay particles
 (b) sulphate part which combines with the dirt and removes it
 (c) aluminium which coagulates the mud particles
 (d) making mud water soluble
6. In petrochemical industry alcohols are directly converted to gasoline by passing over heated
 (a) Platinum (b) ZSM-5
 (c) Iron (d) Nickel
7. The function of gum arabic in the preparation of an Indian ink is
 (a) coagulation (b) peptization
 (c) absorption (d) protective action
8. Which is adsorbed in maximum amount by activated charcoal ?
 (a) N_2 (b) CO_2
 (c) Cl_2 (d) O_2
9. A colloidal solution is subjected to an electric field. The particles move towards anode. The coagulation of same sol is studied using NaCl , BaCl_2 and AlCl_3 solutions. The order of their coagulation power should be -
 (a) $\text{NaCl} > \text{BaCl}_2 > \text{AlCl}_3$ (b) $\text{BaCl}_2 > \text{AlCl}_3 > \text{NaCl}$
 (c) $\text{AlCl}_3 > \text{BaCl}_2 > \text{NaCl}$ (d) $\text{BaCl}_2 > \text{NaCl} > \text{AlCl}_3$
10. Associated colloid among the following is
 (a) enzymes (b) proteins
 (c) cellulose (d) sodium stearate
11. Coagulation value of the electrolytes AlCl_3 and NaCl for As_2S_3 sol are 0.093 and 52 respectively. How many times AlCl_3 has greater coagulating power than NaCl ?
 (a) 930 (b) 520
 (c) 560 (d) None of these

12. The density of gold is 19 g/cm^3 . If $1.9 \times 10^{-4} \text{ g}$ of gold is dispersed in one litre of water to give a sol having spherical gold particles of radius 10 nm , then the number of gold particles per mm^3 of the sol will be :
- (a) 1.9×10^{12} (b) 6.3×10^{14}
 (c) 6.3×10^{10} (d) 2.4×10^6
13. The disease kala azar is caused by
 (a) colloidal antimony (b) milk of magnesia
 (c) argyrols (d) colloidal gold
14. Which is correct about physical adsorption?
 (a) High temperature and high pressure favour adsorption
 (b) High temperature and low pressure favour adsorption
 (c) Low temperature and high pressure favour adsorption
 (d) Low temperature and low pressure favour adsorption
15. The rate of oxidation of oxalic acid by acidified KMnO_4 increases as the reaction progresses. It is an example of
 (a) promoter (b) catalytic poison
 (c) autocatalysis (d) inhibitor
16. At the high pressure, Langmuir adsorption isotherm takes the form
 (a) $\frac{x}{m} = \frac{ap}{1+bp}$ (b) $\frac{x}{m} = \frac{a}{b}$
 (c) $\frac{x}{m} = ap$ (d) $\frac{m}{x} = \frac{b}{a} + \frac{1}{ap}$
17. Freundlich equation for adsorption of gases (in amount of $x \text{ g}$) on a solid (in amount of $m \text{ g}$) at constant temperature can be expressed as
 (a) $\log \frac{x}{m} = \log p + \frac{1}{n} \log K$
 (b) $\log \frac{x}{m} = \log K + \frac{1}{n} \log p$
 (c) $\frac{x}{m} \propto p^n$
 (d) $\frac{x}{m} = \log p + \frac{1}{n} \log K$
18. Which one of the following is an example for multimolecular colloid?
 (a) Aqueous starch sol
 (b) Aqueous enzyme sol
 (c) Alcoholic polystyrene sol
 (d) Aqueous sol of sodium laurylsulphate
19. When KClO_3 is heated, it decomposes into $\text{KCl} + \text{O}_2$. If some MnO_2 is added, the reaction goes much faster because
 (a) MnO_2 decomposes to give O_2
 (b) MnO_2 provides heat by reacting
 (c) better contact is provided by MnO_2
 (d) MnO_2 acts as a catalyst
20. According to Langmuir adsorption isotherm, the amount of gas adsorbed at very high pressures
 (a) reaches a constant limiting value
 (b) goes on increasing with pressure
 (c) goes on decreasing with pressure
 (d) increases first and then decreases with pressure
21. The charge on colloidal particles is due to
 (a) presence of electrolyte
 (b) very small size of particles
 (c) adsorption of ions from the solution
 (d) None of these
22. The efficiency of an enzyme in catalysing a reaction is due to its capacity
 (a) to form a strong enzyme-substrate complex
 (b) to decrease the bond energies of substrate molecule
 (c) to change the shape of the substrate molecule
 (d) to lower the activation energy of the reaction
23. Purple of cassius is colloidal solution of :
 (a) Silver (b) Lead
 (c) Gold (d) Mercury
- DIRECTIONS for Qs. 24 and 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation of Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
24. **Statement-1** : The enthalpy of physisorption is greater than chemisorption.
Statement-2 : Molecules of adsorbate and adsorbent are held by van der Waal's forces in physisorption and by chemical bonds in chemisorption.
25. **Statement-1** : According to Freundlich: $\frac{x}{m} = K \cdot p^{1/n}$.
Statement-2 : The isotherm shows variation of the amount of gas adsorbed by the adsorbent with temperature.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Which of the following process does not occur at the interface of phases?
 - Crystallisation
 - Heterogeneous catalysis
 - Homogeneous catalysis
 - Corrosion
- At the equilibrium position in the process of adsorption
 - $\Delta H > 0$
 - $\Delta H = T\Delta S$
 - $\Delta H > T\Delta S$
 - $\Delta H < T\Delta S$
- Which of the following interface cannot be obtained?
 - Liquid-liquid
 - Solid-liquid
 - Liquid-gas
 - Gas-gas
- The term 'sorption' stands for
 - absorption
 - adsorption
 - Both absorption and adsorption
 - desorption
- Extent of physisorption of a gas increases with
 - increase in temperature
 - decrease in temperature
 - decrease in surface area of adsorbent
 - decrease in strength of van der Waal's forces
- Extent of adsorption of adsorbate from solution phase increases with
 - increase in amount of adsorbate in solution
 - decrease in surface area of adsorbate
 - increase in temperature of solution
 - decrease in amount of adsorbate in solution
- Which one of the following is not applicable to the phenomenon of adsorption?
 - $\Delta H > 0$
 - $\Delta G < 0$
 - $\Delta S < 0$
 - $\Delta H < 0$
- Which of the following is not a favourable condition for physical adsorption?
 - High pressure
 - Negative ΔH
 - Higher critical temperature of adsorbate
 - High temperature
- Physical adsorption of a gaseous species may change to chemical adsorption with
 - decrease in temperature
 - increase in temperature
 - increase in surface area of adsorbent
 - decrease in surface area of adsorbent
- In physisorption adsorbent does not show specificity for any particular gas because
 - involved van der Waal's forces are universal
 - gases involved behave like ideal gases
 - enthalpy of adsorption is low
 - it is a reversible process
- Which of the following is an example of absorption?
 - Water on silica gel
 - Water on calcium chloride
 - Hydrogen on finely divided nickel
 - Oxygen on metal surface
- On the basis of data given below predict which of the following gases shows least adsorption on a definite amount of charcoal?

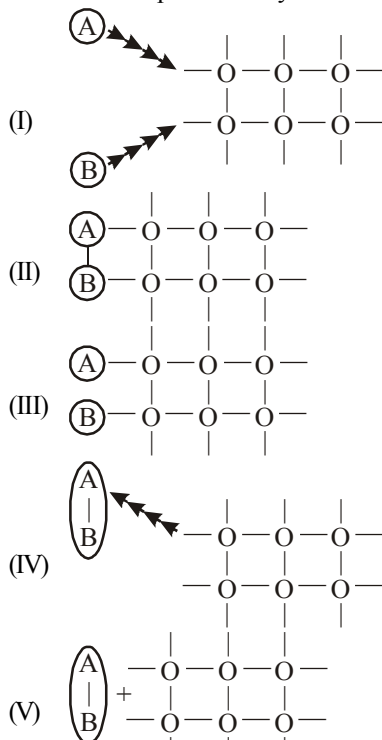
Gas	CO ₂	SO ₂	CH ₄	H ₂
Critical temp./K	304	630	190	33

 - CO₂
 - SO₂
 - CH₄
 - H₂
- In which of the following reactions heterogeneous catalysis is involved?
 - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{\text{NO}(\text{g})} 2\text{SO}_3(\text{g})$
 - $2\text{SO}_2(\text{g}) \xrightarrow{\text{Pt}(\text{s})} 2\text{SO}_3(\text{g})$
 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{\text{Fe}(\text{s})} 2\text{NH}_3(\text{g})$
 - $\text{CH}_3\text{COOCH}_3(\ell) + \text{H}_2\text{O}(\ell) \xrightarrow{\text{HCl}(\ell)} \text{CH}_3\text{COOH}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})$
 - (ii), (iii)
 - (ii), (iii) and (iv)
 - (i), (ii) and (iii)
 - (iv)
- At high concentration of soap in water, soap behaves as
 - molecular colloid
 - associated colloid
 - macromolecular colloid
 - lyophilic colloid
- Which of the following will show Tyndall effect?
 - Aqueous solution of soap below critical micelle concentration
 - Aqueous solution of soap above critical micelle concentration
 - Aqueous solution of sodium chloride
 - Aqueous solution of sugar
- Method by which lyophobic sol can be protected
 - by addition of oppositely charged sol
 - by addition of an electrolyte
 - by addition of lyophilic sol
 - by boiling
- Freshly prepared precipitate sometimes gets converted to colloidal solution by
 - coagulation
 - electrolysis
 - diffusion
 - peptisation
- Which of the following electrolytes will have maximum coagulating value for Ag/Ag⁺ sol?
 - Na₂S
 - Na₃PO₄
 - Na₂SO₄
 - NaCl
- A colloidal system having a solid substance as a dispersed phase and a liquid as a dispersion medium is classified as
 - solid sol
 - gel
 - emulsion
 - sol

20. The values of colligative properties of colloidal solution are of small order in comparison to those shown by true solutions of same concentration because of colloidal particles

- exhibit enormous surface area
- remain suspended in the dispersion medium
- form lyophilic colloids
- are comparatively less in number

21. Arrange the following diagrams in correct sequence of steps involved in the mechanism of catalysis, in accordance with modern adsorption theory.

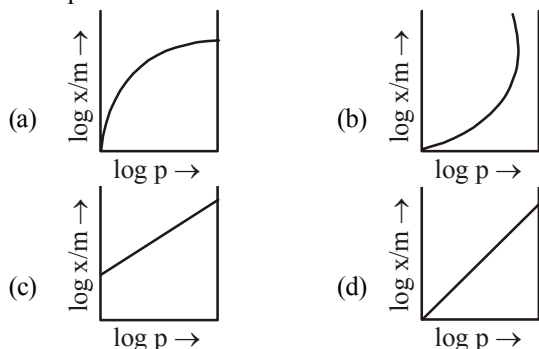


- I $\rightarrow$ II $\rightarrow$ III $\rightarrow$ IV $\rightarrow$ V
- I $\rightarrow$ III $\rightarrow$ II $\rightarrow$ IV $\rightarrow$ V
- I $\rightarrow$ III $\rightarrow$ II $\rightarrow$ V $\rightarrow$ IV
- I $\rightarrow$ II $\rightarrow$ III $\rightarrow$ V $\rightarrow$ IV

22. Which of the following process is responsible for the formation of delta at a place where rivers meet the sea?

- Emulsification
- Colloid formation
- Coagulation
- Peptisation

23. Which of the following curves is in according with Freundlich adsorption isotherm?

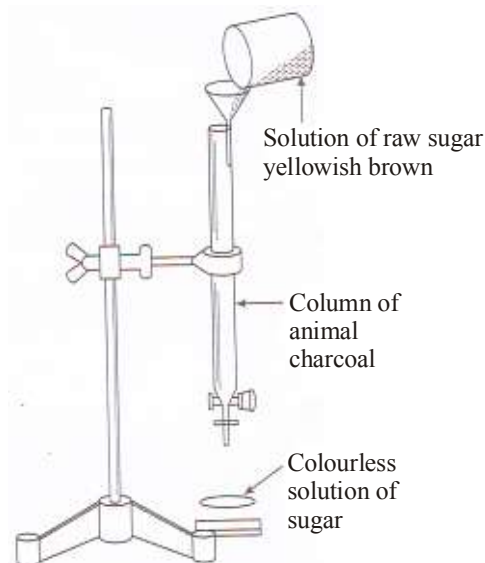


24. Which of the following process is not responsible for the presence of electric charge on the sol particles?

- Electron capture by sol particles
- Adsorption of ionic species from solution

- Formation of Helmholtz electrical double layer
- Absorption of ionic species from solution

25. Which of the following phenomenon is applicable to the process shown in the figure?



- Absorption
- Adsorption
- Coagulation
- Emulsification

NEET/AIPMT (2013-2017) Questions

26. Which of the following statements is correct for the spontaneous adsorption of a gas ? [2014]

- ΔS is negative and, therefore, ΔH should be highly positive
- ΔS is negative and therefore, ΔH should be highly negative
- ΔS is positive and, therefore, ΔH should be negative
- ΔS is positive and, therefore, ΔH should also be highly positive

27. Which property of colloidal solution is independent of charge on the colloidal particles:- [2014, 2015]

- Electrophoresis
- Electro-osmosis
- Tyndall effect
- Coagulation

28. Which one of the following characteristics is associated with adsorption ? [2016]

- ΔG is negative but ΔH and ΔS are positive
- ΔG , ΔH and ΔS all are negative
- ΔG and ΔH are negative but ΔS is positive
- ΔG and ΔS are negative but ΔH is positive

29. Fog is colloidal solution of [2016]

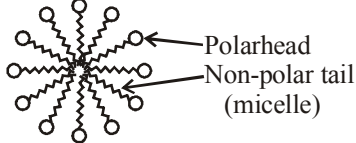
- Liquid in gas
- Gas in liquid
- Solid in gas
- Gas in gas

30. Which one of the following statements is not correct? [2017]

- The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium
- Enzymes catalyse mainly bio-chemical reactions
- Coenzymes increase the catalytic activity of enzyme
- Catalyst does not initiate any reaction

Hints & Solutions

EXERCISE - 1

1. (d) Sorption : Absorption and adsorption occur together.
Absorption : Particles of gas or liquid get uniformly distributed throughout the body of solid and the force of attraction between them is weak vander waal's force of attraction or by some bond formation.
Adsorption → Physical adsorption (vander waal's force of a attraction)
Chemical adsorption (bond formation between adsorbed and adsorbate molecules).
2. (c) In case of **gold sol**, we have
Dispersed phase – **solid**.
Dispersion medium – **liquid**
Gold sol is lyophobic colloid. i.e., (c) is correct.
3. (a) According to Langmuir's model of adsorption of a gas on a solid surface the mass of gas adsorbed (x) per gram of the adsorbent (m) is directly proportional to the pressure of the gas (p) at constant temperature.
4. (a) This statement is not relevant in discussion of colloids as softening of hard water involves removal of salts that cause hardness of water i.e., salts of Ca^{2+} and Mg^{2+} .
5. (a) Chemical adsorption involves formation of monolayer.
6. (a) Chemisorption involves strong chemical forces.
7. (d) In physisorption, gas molecules are held on the solid surface by weak van der Waal's forces.
8. (d) (i) This statement is incorrect.
(ii) At intermediate pressure, $\frac{x}{m} = k \cdot p^{1/n}$, so this statement is correct.
(iii) This statement is incorrect because the correct expression for Langmuir adsorption isotherm is $\frac{x}{m} = \frac{k_1 p}{1 + k_1 p}$, which may also be expressed as $\frac{x}{m} = \frac{ap}{1 + bp}$
(iv) At low pressure $\frac{x}{m} = kp$
These statements (ii) and (iv) are correct and so option (d) is correct.
9. (b)
10. (a) Adsorption of a gas on solid is represented by following equilibria,
Gas (Adsorbate) + solid (Adsorbent) $\rightleftharpoons$ Gas adsorbed on solid + Heat
Initially adsorption increases with increase in pressure at a particular temperature then got slow. After attaining equilibrium adsorption become independent of pressure.
11. (b) Adsorption is an exothermic process.
12. (d) Adsorption is accompanied by evolution of heat as the residual forces acting along the surface of adsorbent decrease i.e., adsorption is accompanied by decrease in enthalpy.
13. (d) For a reaction in equilibrium, the increase in rate of reaction in forward direction by catalyst increases the concentration of product(s) and thus the rate of backward reaction also increases with the same magnitude and allow the equilibrium to be achieved quickly.
14. (c) Adsorption theory is applied to heterogeneous catalysis
15. (d) The above statement is the law proposed by Hardy-Schulze. According to this law, the coagulating power of an ion is directly proportional to the charge it possesses. e.g. $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$
16. (d) The catalytic poisons decrease the activity of the catalyst because they are preferentially adsorbed on the surface of catalyst.
17. (d) Blood is a –vely charged colloidal system. Rest of the compounds, i.e., NaCl, urea & cane sugar form true solution in water.
18. (b) The stability of a lyophilic sol is due to both the charge and solvation of particles, but largely to the latter factor.
19. (d) Enzymes are biological catalysts and enhance the rate of biochemical reactions.
20. (c) Active charcoal has more adsorption power due to greater surface area.
21. (c) $\text{Fe}(\text{OH})_3$ particles absorb Fe^{3+} ions and get peptized to give a positively charged sol.
22. (d) The use of membrane for separating colloidal particles from those of crystalloids is termed as dialysis. Hence it is clear that colloidal particles cannot pass through animal parchment membrane. Hence only solvent molecules and ions (in case of electrodialysis) can diffuse through membrane.
23. (c) The critical micelle concentration is the lowest concentration at which micelle formation appears when surfactants are present above that CMC, they can act as emulsifiers that will solubilise a compound which is normally insoluble in the solvent being used.
24. (d) Gelatin is a lyophilic solution (lyo-liquid philic -love). Lyophilic colloids are also known as reversible colloids since on evaporating the dispersion medium (i.e. water), the residue can again be easily reconverted into colloidal state simply by addition of the liquid i.e. water.
25. (c) According to this law the coagulating effect of an ion on dispersed phase of opposite charge increases with the increase in valency of the ion. The precipitating power of Al^{3+} , Ba^{++} , Na^+ ions is in order $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$.
26. (b) Electrolytes are used for neutralising charge on colloidal particles.
27. (d) Addition of electrolytes causes precipitation (coagulation) of a sol.
28. (d) Colloidal solutions are not purified by electrophoresis. Movement of colloidal particles under the influence of electric field is called electrophoresis. So, it can make easier. Electrophoresis is the property of colloids not the purification method.
29. (c) The osmotic pressure of sea water is 25 atm at 15°C . When pressure greater than 26 atm is applied on sea water separated by a rigid emipermeable membrane, pure water is obtained.
30. (a) 

31. (d) Cetyl trimethyl ammonium bromide, $[C_{16}H_{33}(CH_3)_3 N^+ Br^-]$ is a cationic micelle.
32. (c) The theory of heterogeneous catalysis is based upon the phenomenon of adsorption. The activity of catalyst is due to the presence of free valencies on its surface due to which surface of catalyst has force of attraction.
33. (c) It is due to impact of molecules of dispersion medium on the colloidal particles.
34. (c) When the dispersed phase and dispersion medium both are liquid, the colloidal system is called as an emulsion like milk, vanishing cream etc.
Option (c) is correct.
35. (a) Milk is an emulsion in which liquid is dispersed in liquid.
36. (c) In butter (liquid - solid) water is dispersed in fat.
37. (b) Bismuth cerium molybdate catalysts promoted with alkali metal and other optional ingredients provide high yields of acrylonitrile in the ammoxidation of propylene.
38. (d) Emulsions are liquid-liquid colloidal systems, Generally one of the two liquids is water.
39. (a) Surface tension of lyophilic sols is lower than water (dispersion medium).
40. (a) Proteins are coagulated by some heavy metal ions like Ag^+ , Hg^{2+} and Pb^{2+} .
41. (b) Gum is lyophilic colloid.
42. (b) It is due to Tyndall effect.
43. (c) Adsorption is an exothermic process i.e. ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules becomes restricted i.e. ΔS is negative. Hence adsorption accompanied by decrease in enthalpy as well as decrease in entropy of the system.
44. (d) As_2S_3 is negative sol. For coagulating negative sol Al^{3+} is most effective. It is because higher the magnitude of the charge, the lower is coagulating value.
45. (a) Tyndall effect is the simplest way to check colloidal system since path of light beam becomes visible due to scattering of light.
46. (d) $Fe(OH)_3$ is positive sol. $K_3[Fe(CN)_6]$ will provide $[Fe(CN)_6]^{3-}$ for coagulation having highest magnitude of -ve charge among given options.
47. (d) According to the Hardy Schulze rule the coagulating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion. Therefore more the charge on oppositely charged ion higher is the coagulation value.
48. (d) The formation of micelles takes place only above a particular temperature called Kraft temperature (T_K).
49. (c) Gold number is measure of protective power of lyophilic colloid.
Protective power of colloid $\propto \frac{1}{\text{Gold number}}$
50. (a) Smaller the charge on anion, lesser will be its coagulating power.
 $\therefore$ KBr have Br^- with least charge of -1 on Br thus KBr is least effective in coagulating $Fe(OH)_3$.
51. (a)
52. (d) Colloidion is a flammable, syrupy solution of proxylene (nitrocellulose) in ether and alcohol.
53. (c) 54. (d) 55. (b)
56. (a) Lower is the gold number, higher will be the protective power. Thus, gelatin has maximum protective power.
57. (b) Butter is an example of gel.
58. (d) $Al(OH)_3$ is a positive sol so salt having anion with maximum negative charged (i.e. phosphate ion) will be most effective in coagulation.
59. (a)
60. (c) Alloy is an example of solid solution.
61. (d) The separation of colloidal particles of molecular dimension is known as dialysis. It is a purification method of colloid.
62. (a) According to Freundlich adsorption isotherm
 $\frac{x}{m} = kp^{1/n}$ (where $n > 1$)
At very high pressure $x/m = kp^0$
63. (a) Langmuir adsorption isotherm is based on the assumption that every adsorption site is equivalent and the ability of a particle to bind there is independent of whether nearby sites are occupied or not.
64. (d)
65. (a) According to Freundlich Adsorption isotherm
 $\frac{x}{m} = KP^n$
at low pressure $\frac{1}{n} = 1$
 $\therefore \frac{x}{m} \propto P^1$
at high pressure $\frac{1}{n} = 0$
 $\frac{x}{m} \propto P^0$
i.e., the value of n varies between 0 to 1
66. (d) Enzymes are most reactive at optimum temperature. The optimum temperature for enzyme activity lies between $40^\circ C$ to $60^\circ C$.
67. (b) The lyophobic sols are less stable than lyophilic sols. The lyophilic sols are thus used to protect the lyophobic sols. This property of lyophilic sols is known as protective action of lyophilic sols which is represented by gold number.
68. (c) Adsorption is an exothermic process, hence ΔH will always be negative.
69. (b) Bredig's arc method is suitable for the preparation of colloidal solution of metals like gold, silver, platinum etc. An arc is struck between the metal electrode under the surface of water containing some stabilizing agent such as a trace of KOH. However, Fe does not react with alkalis that is why it is not obtained by Bredig's-arc method.
70. (c) Example of multimolecular colloid system is a gold dispersed in water.
71. (a)
72. (d) The electrical change on a colloidal particle is observed by electrophoresis. Under electric field, charged particles move in a particular direction.
73. (c) For a protective colloid lesser the value of gold number more will be the protective power. Thus the correct order of protective power of A, B, C and D is
 $\Rightarrow$
Gold number $\frac{(A)}{0.50} < \frac{(C)}{0.10} < \frac{(B)}{0.01} < \frac{(D)}{0.005}$

Hence (c) is the correct answer

74. (c) As Sb_2S_3 is a negative sol, so $\text{Al}_2(\text{SO}_4)_3$ will be the most effective coagulant due to higher positive charge on Al (Al^{3+}) – **Hardy-Schulze rule**.
75. (b)

EXERCISE - 2

- (c) Electrodialysis involves movement of ions towards oppositely charged electrodes.
Urea being a covalent compound does not dissociate to give ions and hence it cannot be removed by electrodialysis. However all the other given compounds are ionic which can undergo dissociation to give oppositely charged ions and thus can be separated.
- (a) Soap lather is a colloid containing gas as a dispersed phase and liquid as a dispersion medium.
- (c) According to Hardy-Schulze rule "The amount of electrolyte required to coagulate a fixed amount of a sol depends upon the sign of charge and valency of the flocculating ion."
Thus, the coagulating power vary in the order.
 $\text{Al}^{3+} > \text{Zn}^{++} > \text{Na}^+$
- (b) When oppositely charged sols are mixed their charges are neutralised. Both sols may be partially or completely precipitated.
- (c) Alum coagulates mud particles and helps in purifying water.
- (b) ZSM-5 is a shape selective catalyst. Zeolites are good shape selective catalysts because of the honey comb like structure.
- (d) Gum arabic has protective power.
- (b) The gases having higher values for critical temperature are easily liquified and are adsorbed to the greater extent. CO_2 has highest critical temperature of 304K.
- (c) As colloidal particles move towards anode so these particles are negatively charged and coagulated by cations of electrolyte.
According to Hardy Schulze rule,
Coagulation power $\propto$ charge of ion
 $\therefore$ Order of coagulation power is $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$
- (d) Sodium stearate is a soap. Soaps and detergents are surface agents which when dissolved in a medium, forms aggregated particles, called associated colloids.
- (c)
$$\frac{\text{Coagulation power of AlCl}_3}{\text{Coagulation power of NaCl}} = \frac{\text{Coagulation value of NaCl}}{\text{Coagulation value of AlCl}_3}$$
$$= \frac{52}{0.093} = 559.13 \approx 560$$
- (d) Volume of gold dispersed in 1 L water
$$= \frac{\text{mass}}{\text{density}} = \frac{1.9 \times 10^{-4} \text{ g}}{19 \text{ gm cm}^{-3}} = 1 \times 10^{-5} \text{ cm}^3$$

Radius of gold sol particle
 $= 10 \text{ nm} = 10 \times 10^{-7} \text{ cm} = 10^{-6} \text{ cm}$
Volume of gol sol particle $= \frac{4}{3} \pi r^3$
$$= \frac{4}{3} \times \frac{22}{7} \times (10^{-6})^3 = 4.19 \times 10^{-18} \text{ cm}^3$$

 $\therefore$ No. of gold sol particles in $1 \times 10^{-5} \text{ cm}^3$

$$= \frac{1 \times 10^{-5}}{4.19 \times 10^{-18}} = 2.38 \times 10^{12}$$

$$\therefore \text{No. of gold sol particles in one mm}^3$$

$$= \frac{2.38 \times 10^{12}}{10^6} = 2.38 \times 10^6$$

- (a) Colloidal antimony is used in curing kala-azar.
- (c) Physical adsorption involves weak forces, physical in nature with small heat of adsorption. Thus low temperature and high pressure favours physical adsorption.
- (c) Since the rate of oxidation of oxalic acid by acidified KMnO_4 increases with the progress of the reaction so the reaction is catalysed by one of the products of reaction
$$2 \text{MnO}_4^- + 5 \text{C}_2\text{O}_4^{2-} + 16 \text{H}^+ \longrightarrow 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$$

The Mn^{2+} ion formed acts as catalyst.
- (b) Langmuir adsorption isotherm, is
$$\frac{x}{m} = \frac{ap}{1 + bp}$$

At high pressure, $1 + bp = bp$
or
$$\frac{x}{m} = \frac{ap}{bp} = \frac{a}{b}$$
- (b) According to Freundlich equation.
$$\frac{x}{m} \propto p^{1/n} \text{ or } \frac{x}{m} = Kp^{1/n}$$

or
$$\log \frac{x}{m} = \log Kp^{1/n} \text{ or } \log \frac{x}{m} = \log K + \frac{1}{n} \log p$$
- (a) Multimolecular colloids consist of aggregates of atoms or small molecules. Sulphur sol is an example of multimolecular colloids
- (d)
$$2 \text{KClO}_3 \xrightarrow{\text{MnO}_2} 2 \text{KCl} + 3 \text{O}_2$$
- (a) According to Langmuir Adsorption isotherm the amount of gas adsorbed at very high pressure reaches a constant limiting volume.
- (c)
- (d) Efficiency of catalysing property of a catalyst is inversely proportional to activation energy.
- (c) Purple of cassius is colloidal solution of gold.
- (d) Statement - 1 is false but Statement - 2 is true. The enthalpy of chemisorption is of the order of 40 - 400 kJmol^{-1} while for physical adsorption it is of the order of 20 - 40 kJmol^{-1} .
- (c) Statement - 1 is true but Statement - 2 is false.
Freundlich adsorption isotherm gives an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

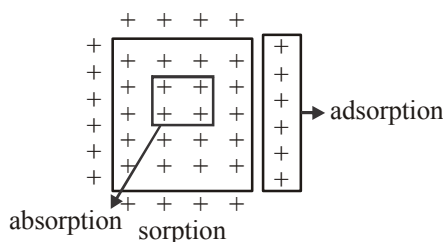
EXERCISE - 3

Exemplar Questions

- (c) In homogeneous catalysis reactant and catalyst have same phase so homogeneous catalysis can not occur at the interface of phases
- (b) Equilibrium $\Delta G = 0$
$$\Delta H - T\Delta S = 0$$

$$\Delta H = T\Delta S$$

3. (d) Gas-gas interface can not be obtained as gases are completely miscible in nature.
4. (c) When both absorption and adsorption occur it is called sorption



5. (b) In physisorption particles are attached to the surface by weak van der Waal's force of attraction so on increasing temperature they get desorbed.
6. (a) When amount of adsorbate increases the interaction of adsorbate adsorbent increases which lead to increase in adsorption.
7. (a) Enthalpy change during adsorption is negative. As in adsorption, there is decrease in residual forces of the surface which result in decrease in surface energy in form of heat.
8. (d) Adsorbate get adsorbed on the adsorbent surface by weak van der Waal's force of attraction in physisorption. Rise in temperature will break the interaction between adsorbate and adsorbent so adsorbate particles get desorbed.
9. (b) With increase in temperature physisorption changes to chemisorption, because energy of activation of adsorbate particles increases which lead to formation of chemical bond.
10. (a) The extent of van der Waal's interaction between adsorbate and adsorbent is constant for all gases.
11. (b) Absorption is a bulk phenomena in which particles goes to the bulk instead of residing only to surface.
12. (d) Critical temperature of gases is directly proportional to the extent of adsorption.
13. (a) Reaction in which catalyst and reactant/product is in different phase then it is known as heterogeneous catalysis.
14. (b) At high concentration of soap in water, soap particles present in the solution get associated and it leads to the formation of associated colloid.
15. (b) Tyndall effect is a characteristic of colloidal solution, as aqueous solution of soap above cmc form a colloidal solution.
16. (c) Lyophobic sol can be protected by addition of lyophilic sol as lyophobic sols are readily precipitated on addition of small amount of electrolytes or shaking, or heating hence they are made stable by adding lyophilic sol which stabilises the lyophobic sols.

17. (d) Peptisation is a process in which by addition of a suitable peptising agent precipitate gets converted into colloidal solution.
18. (b) According to Hardy-Schulze law, greater the charge on anion greater will be its coagulating power.

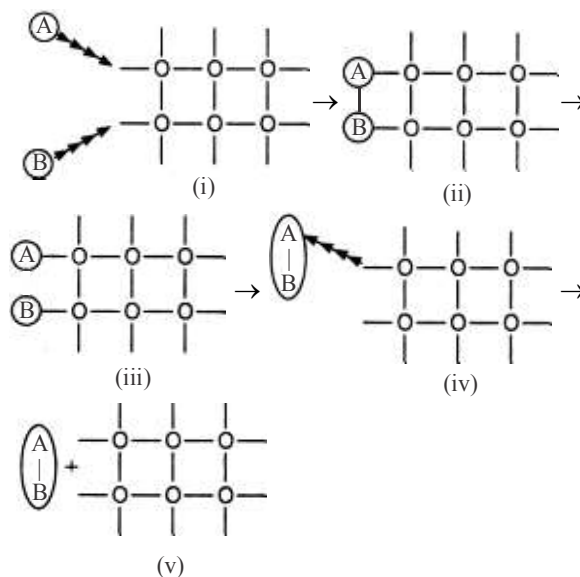
Electrolytes	Anionic part	Charge on anion
Na_2S	S^{2-}	2
Na_3PO_4	PO_4^{3-}	3
Na_2SO_4	SO_4^{2-}	2
NaCl	Cl^-	1

Here PO_4^{3-} have highest charge. Hence, PO_4^{3-} have highest coagulating power.

19. (d) Sol is a colloidal system in which solid substance is a dispersed phase and a liquid is a dispersion medium e.g., paint, cell fluids etc.

In paints solid colouring particles are dissolved in liquid dispersion medium.

20. (b) The value of colligative properties of colloidal solution are of small order in comparison to those of true solutions of same concentration because colloidal particles are comparatively less in number.
21. (b) The Correct sequence of steps is I $\rightarrow$ III $\rightarrow$ II $\rightarrow$ IV $\rightarrow$ V
Each step represents a meaningful process as follows
I $\rightarrow$ adsorption of A and B on surface
III $\rightarrow$ II interaction between A and B to form intermediate
III $\rightarrow$ IV starting desorption of A-B
IV $\rightarrow$ V complete desorption



22. (c) River water is a colloidal solution of clay and sea. Water contains various electrolytes. When river water comes in contact with sea water, then the electrolytes present

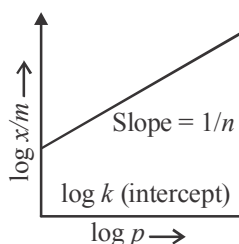
in sea water coagulate the suspended colloidal particles which ultimately settle down at the point of contact.

23. (c) According to the Freundlich adsorption isotherm

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

Taking log on both side $\log \frac{x}{m} = \left(\frac{1}{n}\right) \log p + \log k$

This equation is comparable with straight line equation, $y = mx + c$, where m represents slope of the line and c represents intercept on y axis.



24. (d) Absorption of ionic species from solution is not responsible for the presence of electric charge on the sol particles. Charge on the sol particles is due to
- electrons capture by sol particles during electro dispersion of metal.
 - preferential adsorption of ionic species from solution.
 - formation of Helmholtz electrical double layer.
25. (b) Above figure represent adsorption of yellowish brown colour of raw sugar by animal charcoal.

Here, aqueous solution of raw sugar is filtered by using animal charcoal. Yellowish brown colour of raw sugar is adsorbed and filtrate is colourless which gives white colour on crystallisation. Hence, this phenomenon is adsorption.

NEET/AIPMT (2013-2017) Questions

26. (b) For adsorption $\Delta S < 0$ and for a spontaneous change $\Delta G = -ve$
hence ΔH should be highly negative which is clear from the equation

$$\Delta G = \Delta H - T\Delta S$$

$$= -\Delta H - T(-\Delta S) = -\Delta H + T\Delta S$$
 So if ΔH is highly negative ΔG will also be $(-ve)$
27. (c) Tyndall effect is an optical property, and it is independent of charge on colloidal particles.
28. (b) Adsorption is spontaneous process, therefore change in the free energy (ΔG) for the process is negative.
According to Gibbs's Helmholtz eqn.

$$\Delta G = \Delta H - T\Delta S$$
 ΔS is negative because adhering of gas molecules to the surface lowers the randomness.
 $\therefore \Delta G$ can be $-ve$ only when ΔH is $-ve$.
29. (a) Fog is a colloidal system having dispersed phase as liquid and dispersion medium as gas.
30. (a) A catalyst speeds up both forward and backward reaction with the same rate.
So, equilibrium constant is not affected by the presence of a catalyst at any given temperature.

Chapter 20 General Principles and Processes of Isolation of Elements

OCCURENCE OF METALS

All naturally occurring chemical substances in the earth crust are called minerals. Minerals from which metal can be extracted profitably are called ores. Thus, all ores are minerals but all minerals are not ores.

Elements vary in abundance. Among metals, Al is the most abundant. Fe is the second most abundant metal in the earth's crust. The principal ores of some metals are given in the table below :

Metals	Ores	Composition
Aluminium	(i) Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
	(ii) Kaolinite	$[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5]$
Iron	(i) Haemetite	Fe_2O_3
	(ii) Magnetite	Fe_3O_4
	(iii) Siderite	FeCO_3
	(iv) Iron pyrites	FeS
Copper	(i) Copper pyrites	CuFeS_2
	(ii) Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	(iii) Cuprite	Cu_2O
	(iv) Copper glance	Cu_2S
Zinc	(i) Zinc blende	ZnS
	(ii) Calamine	ZnCO_3
	(iii) Zincite	ZnO

METALLURGICAL PROCESSES

The ore is contaminated with earthly or undesired materials known as gangue. The extraction and isolation of metals from ores involve the following steps:

- Concentration of ore
- Isolation of metal from concentrated ore
- Purification of metal

The entire scientific and technological process used for isolation of the metal from its ore is known as metallurgy.

Concentration of ores

Removal of unwanted materials from the ore is known as concentration, dressing or beneficiation. It involves various steps which depend upon the differences in the physical properties of the compound of the metal present and that of the gangue.

Some important procedures are following :

- Hydraulic Washing :** It is a type of gravity separation. It is based on the differences in gravities of the ore and gangue particles.

In this process, a stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ore particles are left behind. Oxide ores of Fe, Sn and native ores of Au, Ag etc. are concentrated by this method.

- Magnetic Separation :** It is based on the differences in the magnetic properties of the ore components. It is carried out if either the ore or the gangue is magnetic in nature. The finely powdered ore is dropped over electromagnetic rollers with conveyor belt. As the belt moves the magnetic particles of the ore are attracted by the magnetic roller and fall nearer to the roller while non-magnetic impurities fall away from the roller, giving rise to two heaps, one having magnetic particles and other with non-magnetic particles. For example, chromite $[\text{Fe}(\text{CrO}_2)_2]$ being magnetic is separated from silicious impurities by this method.

- Froth floatation method :** It is used for sulphide ores. In this process, a suspension of powdered ore is made with water. To it, collectors and froth stabilizers are added. The mineral particles are wetted by oil while the gangue particles got wet with water. The mixture is then violently agitated by passing a current of compressed air. As a result, froth is formed which carries the mineral particles. The froth is light and skimmed off. It is then dried for recovery of the ore particles.

The role of collectors is to enhance the non-wettability of mineral particles. Examples : pine oils, fatty acids, xanthates, etc. The role of froth stabilisers is to stabilise the froth. Examples : cresols, aniline

It is possible to separate two sulphide ores by adjusting the proportion of oil to water or by using 'depressants'. For example in an ore containing ZnS and PbS, NaCN is used as a depressant. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

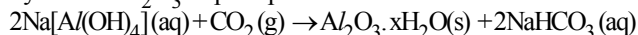
(iv) **Leaching** : It is used if the ore is soluble in a suitable solvent.

(a) Leaching of alumina from bauxite:

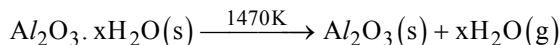
Bauxite contains SiO_2 , iron oxide and TiO_2 as impurities. The powdered ore is digested with conc. NaOH solution at 473–523 K and 35–36 bar pressure Al_2O_3 is leached out as sodium aluminate (SiO_2 as sodium silicate) leaving the impurities behind.



The solution is then neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated out.

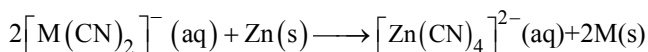
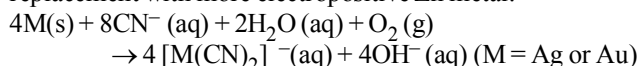


Sodium silicate remains in the solution and hydrated Al_2O_3 is filtered, dried and heated to give back pure Al_2O_3 .



(b) Leaching of Au and Ag:

In metallurgy of Ag and Au, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) to form soluble cyanide complex while impurities remains unaffected. The metal is later obtained by its replacement with more electropositive Zn metal.

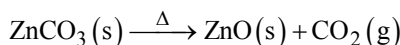
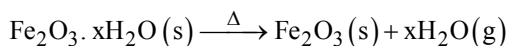


Extraction of crude Metal from concentrated ore

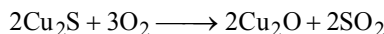
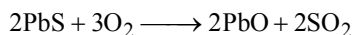
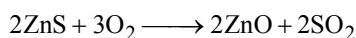
It involves two major steps:

(i) Conversion to oxide

(a) Calcination : It involves heating in absence or limited supply of air. Thus the volatile matter (moisture, S, As, P etc.) escapes leaving behind metal oxide. This method is commonly used to convert metal carbonates and hydroxides to their respective oxides.



(b) Roasting: The ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. This process is commonly used for sulphide ores. In this process moisture organic matter and non-metallic impurities got removed.

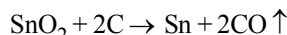


(ii) Reduction of oxide to the metal : It involves heating the metal oxide with some reducing agent (C or CO or other metal). The reducing agent (ex: C) combines with oxygen of the metal oxide.

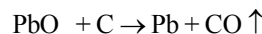


Some metals are easily reduced while some are reduced with difficulty.

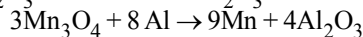
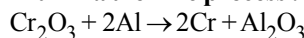
(a) Carbon reduction method : Smelting



Tin oxide Tin



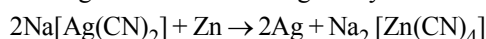
(b) Alumina thermic process :



(c) Precipitation method :



Silver glance Sodium argentocyanide



(d) Electrolytic method : If metal oxides, chlorides or hydroxides in fused state are electrolysed, the metal deposits at cathode. The reduction of active elements such as alkali metals, alkaline earth metals and the oxides of Al with carbon is difficult because these form carbides with carbon at high temperature. For these metals, electrolytic method is used.

THERMODYNAMIC PRINCIPLES OF METALLURGY

Some concepts of thermodynamics, like Gibbs free energy (G) help in understanding metallurgical transformations.

The change in Gibbs energy is given by:

$$\Delta G = \Delta H - T\Delta S$$

Also, $\Delta G = -RT \ln K$

For a reaction to be spontaneous, ΔG should be negative.

If on coupling the two reactions, sum of their ΔG comes out to be negative, then the overall reaction will occur.

H.J.T. Ellingham diagram (plots of ΔG Vs T) provides a sound basis for considering the choice of reducing agent in the reduction of oxides.

The reducing agent forms its oxide when the metal oxide is reduced.

The role of reducing agent is to provide ΔG negative and large enough to make the sum of ΔG° of the two reactions negative.

The temperature is chosen such that the sum of ΔG° in the two combined redox process is negative.

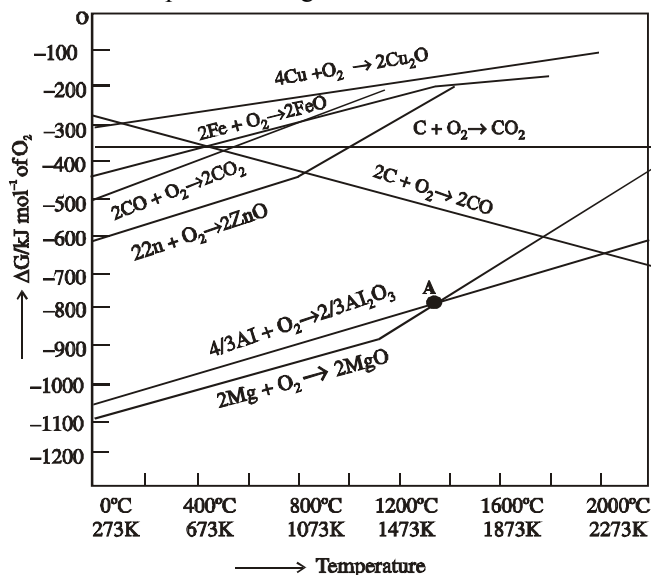
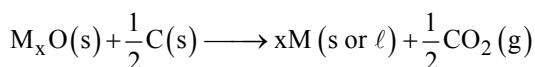
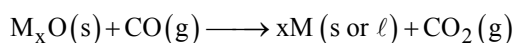
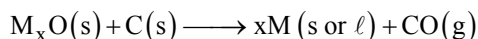


Fig. Gibbs energy (ΔG°) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

In ΔG° vs T plots, this is indicated by the point of intersection of the two curves. After that point, ΔG value becomes more negative for the combined process including the reduction of M_xO .

The difference in the two ΔG° values after that point determines whether reductions of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier.

The reduction of metal oxide can be accomplished with the help of the following reaction



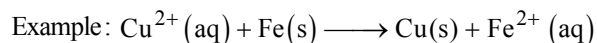
ELECTROCHEMICAL PRINCIPLES OF METALLURGY

Reduction of metal in the molten state or in solution state is carried out by using electrolysis or by adding suitable reducing agent. The equation used is $\Delta G^\circ = -nFE^\circ$

where $n \rightarrow$ no. of electrons

$E^\circ \rightarrow$ electrode potential of the redox couple

If the difference of two E° values is positive, ΔG becomes -ve and thus, a less reactive metal will be displaced by a more reactive metal. The less reactive metal will come out of the solution and the more reactive will go to the solution.

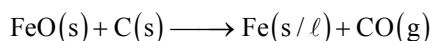


In electrolysis, M^{n+} ions are discharged at the cathode (-ve electrode). Sometimes a flux is added to make the molten mass more conducting.

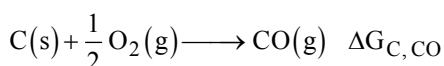
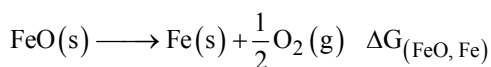
EXTRACTION OF SOME METALS FROM THEIR ORES

(a) Extraction of Iron From its Oxides:

Iron ores are concentrated by magnetic separation method. Iron oxide is reduced by using coke in a blast furnace. One of the main reduction step is:



This reaction can be written as:



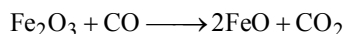
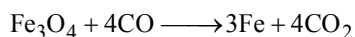
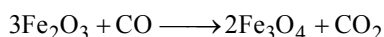
The net Gibbs energy change becomes:

$$\Delta G_{(C, CO)} + \Delta G_{(FeO, Fe)} = \Delta_r G$$

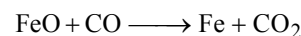
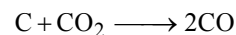
From Ellingham diagram, it is found that at temperatures above 1073 K (approx), coke reduces FeO and itself gets oxidised to CO.

In Blast furnace, reduction of iron oxide takes place at different temperature ranges.

At 500 – 800 K, the reactions taking place are:

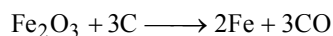


At 900 – 1500 K, the reactions are:



Limestone is decomposed to CaO which removes silicate impurity as slag. The slag is in the molten state and separates out from iron. The iron obtained is called pig iron and contain about 4% carbon and many impurities in smaller amount.

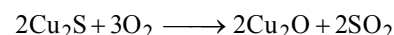
- Cast iron has slightly lower C-content and is very hard and brittle.
- Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace.



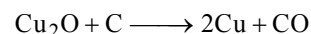
(b) Extraction of Copper From Cuprous Oxide

The ore is concentrated by froth flotation method.

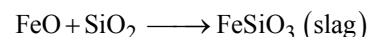
The oxide ores of Cu are easily reduced to the metal by heating with coke. However, most of the ores are sulphide and may also contain iron. The sulphide ore is first roasted / smelted to give oxide:



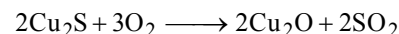
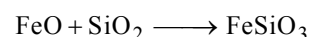
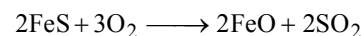
The oxide can then be easily reduced to metallic copper using coke:



The ore is heated in a reverberatory furnace after mixing with silica. Iron oxide 'slags off' as iron silicate and copper is produced in the form of copper matte. This contains Cu_2S and FeS .

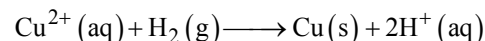


Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS , FeO to $FeSiO_3$ and Cu_2S , Cu_2O to metallic copper. Following reactions take place:



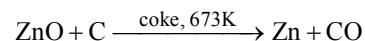
The solidified copper obtained has blistered appearance due to evolution of SO_2 and is also called blister copper.

Copper from low grade ores and scraps : Cu is extracted by hydrometallurgy from low grade ores. It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2 .



(c) Extraction of Zinc from Zinc Oxide

The reduction is done by using coke. For the purpose of heating, the oxide is made into brickettes with coke and clay.

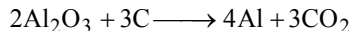


The metal is distilled off and collected by rapid chilling

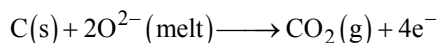
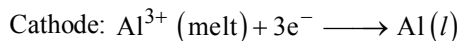
(d) Extraction of Aluminium from Alumina

Al is obtained from alumina by the process of electrolysis which is known as Hall-Heroult process. Steel cathode and graphite anode are used. Alumina is mixed with Na_3AlF_6 or CaF_2 (they lower the melting point of the mix and brings conductivity). The fused matrix is electrolysed.

The overall reaction can be written as:



The oxygen liberated at anode reacts with C of anode to produce CO and CO_2 . For each kg of Al produced, about 0.5 kg of C anode is burnt away. The reactions are:

**REFINING**

Some methods of purifying the metals are:

(i) Distillation:

It is useful for low boiling metals like Zn and Hg. The impure metal is evaporated to obtain the pure metal as distillate.

(ii) Liquation:

In this, low melting metal like Sn is made to flow on a sloping surface. Being low melting, the metal melts and flows down the slope while the higher melting impurities stay behind.

(iii) Electrolytic Refining

Many metals are purified electrolytically. The metal salt is taken as electrolyte, impure metal rod as anode and thin pure metal rod or strip as cathode. On electrolysis pure metal is deposited at cathode. Cu, Ag, Al, Zn, Cr etc. metals are purified by this method.

(iv) Zone Refining

It is based on the principle that impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, pure metal crystallises out of the melt and impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved

in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for producing semi-conductor and other metals of very high purity.

Ex. Ge, Si, B, Ga and In.

(v) Vapour Phase Refining

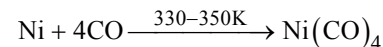
In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal.

Two requirements are :

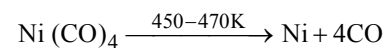
- Metal should form a volatile compound with an available reagent.
- The volatile compound should be easily decomposable, so that the recovery is easy.

Mond process for refining nickel:

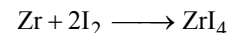
Ni is heated in a stream of CO to form volatile $\text{Ni}(\text{CO})_4$:



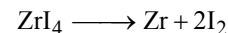
The carbonyl compound is subjected to higher temperature so that it is decomposed giving pure metal:

**Van Arkel method for refining Zr or Ti:**

The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:



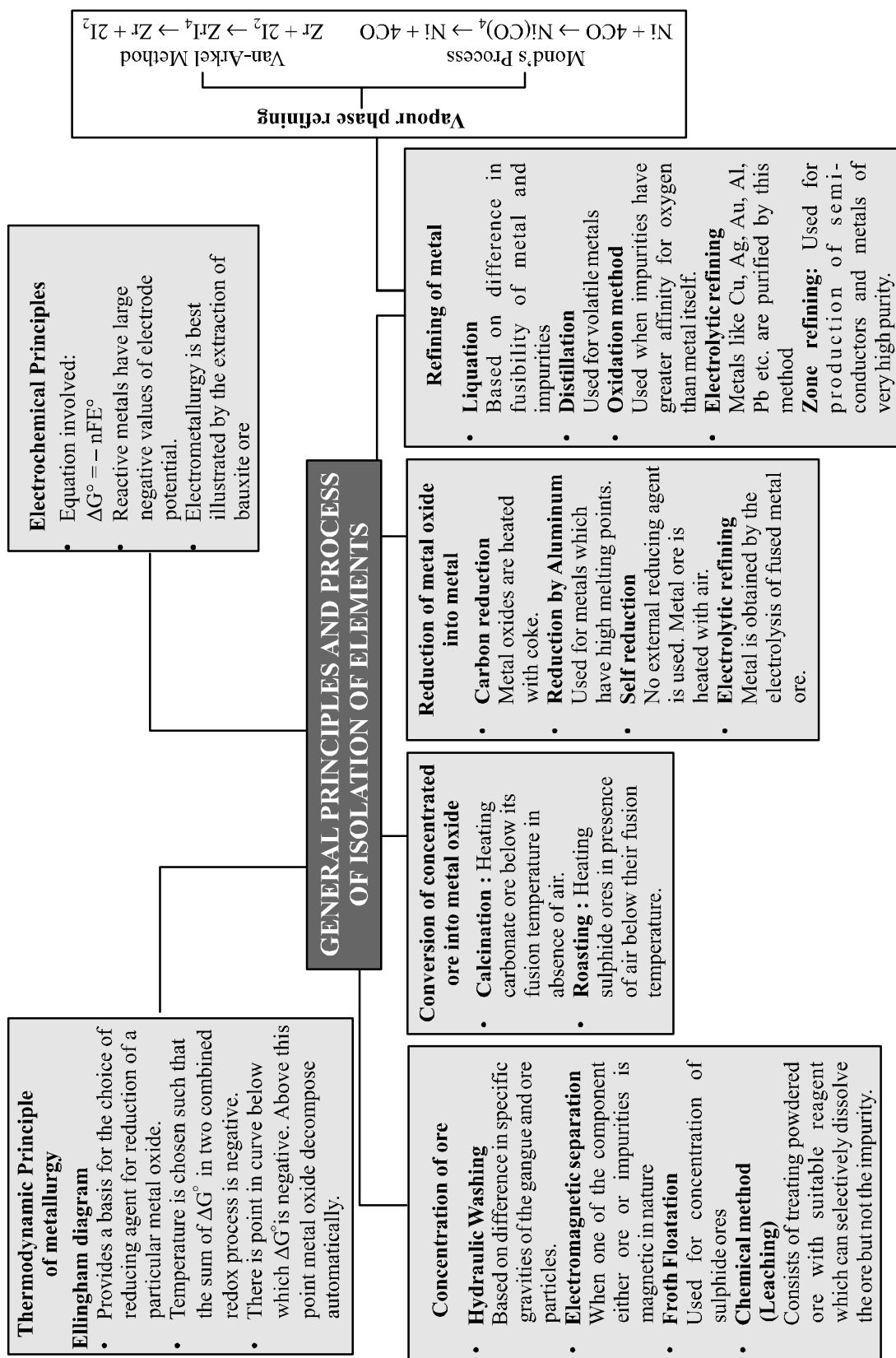
The metal iodide is decomposed on a tungsten filament, when electrically heated to about 1800 K. The pure metal is thus deposited on the filament:

**(vi) Chromatographic Methods**

It is based on the principle that different components of a mixture are differently adsorbed on the adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.

Different components are adsorbed at different levels on the column. Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method is given the name.

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

- Which one of the following is an ore of silver ?
(a) Argentite (b) Stibnite
(c) Haematite (d) Bauxite
- Leaching is a process of
(a) reduction (b) concentration
(c) refining (d) oxidation
- Copper can be extracted from
(a) Kupfernickel (b) Dolomite
(c) Malachite (d) Galena
- Autoreduction is employed in the metallurgy is
(a) Hg (b) Al (c) Ti (d) Zn
- The most abundant metal on the surface of the earth is
(a) Fe (b) Al (c) Ca (d) Na
- Which of the following is an ore of tin ?
(a) Carborundum (b) Epsomite
(c) Cassiterite (d) Spodumene
- Which of the following is chalcopyrite?
(a) CuFeS_2 (b) FeS_2
(c) $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ (d) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
- Which one of the following does not occur as sulphide ore?
(a) Zn (b) Cr (c) Ag (d) Fe
- Which of the following metal is correctly matched with its ore?

Metal	Ore
(a) Zinc	Calamine
(b) Silver	Ilmenite
(c) Magnesium	Cassiterite
(d) Tin	Azurite
- Composition of azurite mineral is
(a) $\text{CuCO}_3 \cdot \text{CuO}$ (b) $\text{Cu}(\text{HCO}_3)_2 \cdot \text{Cu}(\text{OH})_2$
(c) $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (d) $\text{CuCO}_3 \cdot 2\text{Cu}(\text{OH})_2$
- Which one of the following ores is best concentrated by froth-flotation method ?
(a) Galena (b) Cassiterite
(c) Magnetite (d) Malachite
- Germanium of very high purity is obtained by
(a) liquation (b) vapour phase refining
(c) distillation (d) zone refining
- Iron is obtained on large scale from Fe_2O_3 by
(a) reduction with Na (b) reduction with Al
(c) reduction with CO (d) passing H_2
- Cassiterite is concentrated by
(a) levigation
(b) electromagnetic separation
(c) floatation
(d) liquefaction
- Among of the following statements the correct one is
(a) zinc blende and iron pyrites are sulphides
(b) calamine and siderite are carbonates
(c) malachite and azurite are ores of copper
(d) argentite and cuprite are oxides
- Calcination is used in metallurgy for removal of
(a) moisture (b) water and CO_2
(c) CO_2 and H_2S (d) H_2O and H_2S
- Which one of the following is not a sulphide ore?
(a) Magnetite (b) Iron pyrites
(c) Copper glance (d) Sphalerite
(e) Galena
- Roasting is generally done in case of the
(a) oxide ores (b) silicate ores
(c) sulphide ores (d) carbonate ores
- Heating of pyrites in air for oxidation of sulphur is called
(a) roasting (b) calcination
(c) smelting (d) slagging
- Pyrolusite is an ore of
(a) polonium (b) manganese
(c) tin (d) lead
- Which one of the furnaces among the following can produce the highest temperature?
(a) muffle furnace (b) blast furnace
(c) reverberatory furnace (d) electric furnace
- The role of calcination in metallurgical operations is
(a) to remove moisture
(b) to decompose carbonates
(c) to drive off organic matter
(d) to decompose carbonates and drive off moisture and organic matter
- Solder is an alloy of lead with :
(a) copper (b) zinc (c) nickel (d) tin
- General method for the extraction of metal from oxide ore is
(a) carbon reduction (b) reduction by aluminium
(c) reduction by hydrogen (d) electrolytic reduction
- Aluminothermic process is used for the extraction of metals, whose oxides are
(a) fusible
(b) not easily reduced by carbon
(c) not easily reduced by hydrogen
(d) strongly basic
- In the blast furnace iron oxide is reduced by
(a) Silica (b) CO
(c) carbon (d) Limestone
- Which of the following is the chief ore of copper?
(a) Cu_2S (b) Cu_2S
(c) CuFeS_2 (d) $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- Furnaces are lined with calcium oxide because
(a) it gives off oxygen on heating
(b) it gives strong light on heating
(c) it is refractory and basic
(d) it is not affected by acids
- The substance used in the thermite process of reducing metal ores is
(a) aluminium (b) thorium
(c) heated Pt gauge (d) carbon

30. Which of the following is not an ore of magnesium?
 (a) Carnallite (b) Magnesite
 (c) Dolomite (d) Gypsum
31. Process followed before reduction of carbonate ore is –
 (a) calcination (b) roasting
 (c) liquation (d) polling
32. Which of the following set of equations represent correct mode of obtaining Pb from PbS by self-reduction process?
- (A) $\text{PbS} \xrightarrow[\Delta]{\text{Air}} \text{PbO} + \text{SO}_2$
- $\downarrow \text{2PbS}$
 $\text{2Pb} + \text{SO}_2$
- (B) $\text{PbS} \xrightarrow[\Delta]{\text{Air}} \text{PbO} + \text{SO}_2$
- $\downarrow \text{C}$
 $\text{Pb} + \text{CO}_2$
- (a) (A) (b) (B)
 (c) Both (A) and (B) (d) Neither (A) nor (B)
33. Which of the following species has the highest electron affinity?
 (a) F (b) O (c) O^- (d) Na^+
34. Flux is used to :
 (a) remove silica
 (b) remove silica and undesirable metal oxides
 (c) remove all impurities from ores
 (d) reduce metal oxide
35. Thermite process is used in reduction of
 (a) Cr_2O_3 (b) Al_2O_3 (c) PbO_2 (d) CuO
36. Which of the following reactions represents calcination?
 (a) $2\text{Ag} + 2\text{HCl} + [\text{O}] \rightarrow 2\text{AgCl} + \text{H}_2\text{O}$
 (b) $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$
 (c) $2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2$
 (d) $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$
37. The electrolytic method of reduction is employed for the preparation of metals that
 (a) are weakly electropositive
 (b) are moderately electropositive
 (c) are strongly electropositive
 (d) form oxides
38. Froth floatation process is used for the concentration of
 (a) Chloride ore (b) Amalgams
 (c) Oxide ore (d) Sulphide ore
39. The cryolite is represented by
 (a) BaSO_4 (b) Al_2O_3
 (c) CuFeS_2 (d) Na_3AlF_6
40. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are
 (a) Fe and Ni (b) Ag and Au
 (c) Pb and Zn (d) Sn and Ag
41. Van Arkel method of purification of metals involves converting the metal to a
 (a) volatile stable compound
 (b) volatile unstable compound
 (c) non volatile stable compound
 (d) None of the above
42. A metal which is refined by poling is
 (a) sodium (b) blister copper
 (c) zinc (d) silver
43. In the extraction of Cu, the metal is formed in the bessemer converter due to the reaction :
 (a) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{Cu} + \text{SO}_2$
 (b) $\text{Cu}_2\text{S} \longrightarrow 2\text{Cu} + \text{S}$
 (c) $\text{Fe} + \text{Cu}_2\text{O} \longrightarrow 2\text{Cu} + \text{FeO}$
 (d) $2\text{Cu}_2\text{O} \longrightarrow 4\text{Cu} + \text{O}_2$
44. If the impurities in a metal has a greater affinity for oxygen and is more easily oxidised than the metal, then the purification of metal may be carried out by
 (a) distillation (b) zone refining
 (c) electrolytic refining (d) cupellation
45. The sulphide ore of copper is concentrated by
 (a) chemical method (b) froth floatation method
 (c) magnetic method (d) none of these
46. In order to refine "blister copper" it is melted in a furnace and is stirred with green logs of wood. The purpose is
 (a) to expel the dissolved gases in blister copper.
 (b) to bring the impurities to surface and oxidize them.
 (c) to increase the carbon content of copper.
 (d) to reduce the metallic oxide impurities with hydrocarbon gases liberated from the wood.
47. Hydro-metallurgical process of extraction of metals is based on
 (a) complex formation (b) hydrolysis
 (c) dehydration (d) dehydrogenation
48. In Hall's process, the main reagent is mixed with :
 (a) NaF (b) Na_3AlF_6
 (c) AlF_3 (d) none of these
49. Match List I with List II and select the correct answer using the codes given below the list
- | List I | List II |
|------------------------|------------------------|
| 1. Ti | A. Bauxite |
| 2. Si | B. Cerussite |
| 3. Al | C. Van-Arkel method |
| 4. Pb | D. Zone refining |
| (a) 1-B, 2-A, 3-C, 4-D | (b) 1-B, 2-C, 3-A, 4-B |
| (c) 1-C, 2-A, 3-B, 4-D | (d) 1-C, 2-D, 3-A, 4-B |
50. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true?
 (a) The ΔG_f° of the sulphide is greater than those for CS_2 and H_2S .
 (b) The ΔG_f° is negative for roasting of sulphide ore to oxide.
 (c) Roasting of the sulphide to the oxide is thermodynamically feasible.
 (d) Carbon and hydrogen are suitable reducing agents for reduction of metal sulphides.

EXERCISE - 2

Applied Questions

- The elements present in the core of earth are collectively known as
 - lithophiles
 - nucleophiles
 - chalcophiles
 - siderophiles
- Method used for obtaining highly pure silicon which is used as a semiconductor material, is
 - oxidation
 - electrochemical
 - crystallization
 - zone refining
- Refractory metals are used in construction of furnaces because
 - they can withstand high temperature
 - they are chemically inert
 - their melting point is high
 - None of these
- In electro-refining of metal the impure metal is used to make the anode and a strip of pure metal as the cathode, during the electrolysis of an aqueous solution of a complex metal salt. This method cannot be used for refining of
 - Silver
 - Copper
 - Aluminium
 - Sodium
- According to Ellingham diagram, the oxidation reaction of carbon to carbon monoxide may be used to reduce which one of the following oxides at the lowest temperature ?
 - Al_2O_3
 - Cu_2O
 - MgO
 - ZnO
- While extracting an element from its ore, the ore is grounded and leached with dil. potassium cyanide solution to form the soluble product potassium argento cyanide. The element is
 - Lead
 - Chromium
 - Manganese
 - Silver
- Calcination is the process in which :
 - ore is heated above its melting point to expel H_2O or CO_2 or SO_2
 - ore is heated below its melting point to expel volatile impurities
 - ore is heated above its melting point to remove S, As and Sb as SO_2 , As_2O_3 and Sb_2O_3 respectively
 - ore is heated below its melting point to expel H_2O or CO_2
- When CuSO_4 is electrolysed using platinum electrodes,
 - copper is liberated at cathode, sulphur at anode
 - copper is liberated at cathode, oxygen at anode
 - sulphur is liberated at cathode, oxygen at anode
 - oxygen is liberated at cathode, copper at anode
- Consider the following statements –
 - In the Aluminothermite process, aluminium acts as reducing agent.
 - The process of extraction of gold involves the formation of $[\text{Au}(\text{CN})_2]^-$ and $[\text{Zn}(\text{CN})_4]^{2-}$.
 - In the extractive metallurgy of zinc, partial fusion of ZnO with coke is called sintering and reduction of ore to the molten metal is called smelting.
 - Extractive metallurgy of silver from its ore argentite involves complex formation and displacement by more electropositive metal.
 Choose the correct options –
 - A and B
 - B and C
 - A, B and C
 - A, B, C and D
- In Goldschmidt aluminothermic process which of the following reducing agents is used :
 - calcium
 - coke
 - Al-powder
 - sodium
- Which statement is correct ?
 - Gangues are carefully chosen to combine with the slag present in the ore to produce easily fusible flux to carry away the impurities
 - Slags are carefully chosen to combine with the flux present in the ore to produce easily fusible gangue to carry away the impurities
 - Gangues are carefully chosen to combine with the flux present in the ore to produce easily fusible slag to carry away the impurities
 - Fluxes are carefully chosen to combine with the gangue present in the ore to produce easily fusible slag to carry away the impurities
- Sulfide ores are common for the metals
 - Ag, Cu and Pb
 - Ag, Mg and Pb
 - Ag, Cu and Sn
 - Al, Cu and Pb
- Bauxite ore is made up of $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{TiO}_2 + \text{Fe}_2\text{O}_3$. This ore is treated with conc. NaOH solution at 500 K and 35 bar pressure for few hours and filtered hot. In the filtrate the species present, is/are
 - $\text{NaAl}(\text{OH})_4$ only
 - $\text{Na}_2\text{Ti}(\text{OH})_6$ only
 - $\text{NaAl}(\text{OH})_4$ and Na_2SiO_3
 - Na_2SiO_3 only
- Which is not a basic flux ?
 - CaCO_3
 - Lime
 - SiO_2
 - CaO
- The compound that can work both as an oxidising agent and a reducing agent is
 - KMnO_4
 - H_2S
 - BaO_2
 - H_2O_2

16. Aluminium is prepared in large quantities by
 (a) heating cryolite in a limited quantity of air
 (b) reducing aluminium oxide with coke
 (c) reducing aluminium oxide with sodium
 (d) electrolysis of aluminium oxide dissolved in fused electrolyte
17. Duraluminium is an alloy of
 (a) Al and Mg (b) Al, Mg and Ni
 (c) Al, Mg, Mn and Cu (d) Al and Ni.
18. Which of the following factors is of *no significance* for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?
 (a) Metal sulphides are thermodynamically more stable than CS_2
 (b) CO_2 is thermodynamically more stable than CS_2
 (c) Metal sulphides are less stable than the corresponding oxides
 (d) CO_2 is more volatile than CS_2
19. Pb and Sn are extracted from their chief ore by
 (a) carbon reduction and self reduction.
 (b) self reduction and carbon reduction.
 (c) electrolysis and self reduction.
 (d) self reduction and electrolysis.
20. Extraction of zinc from zinc blende is achieved by
 (a) electrolytic reduction
 (b) roasting followed by reduction with carbon
 (c) roasting followed by reduction with another metal
 (d) roasting followed by self-reduction

DIRECTIONS for Qs. 21 to 25: These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
21. **Statement-1** Zinc can be used while copper cannot be used in the recovery of Ag from the complex $[\text{Ag}(\text{CN})_2]^-$.
Statement-2 Zinc is a powerful reducing agent than copper.
22. **Statement-1** Coke and flux are used in smelting.
Statement-2 The phenomenon in which ore is mixed with suitable flux and coke is heated to fusion is known as smelting.
23. **Statement-1** Leaching is a process of reduction.
Statement-2 Leaching involves treatment of the ore with a suitable reagent so as to make it soluble while impurities remains insoluble.
24. **Statement-1** Lead, tin and bismuth are purified by liquation method.
Statement-2 Lead, tin and bismuth have low m.p. as compared to impurities.
25. **Statement-1** Levigation is used for the separation of oxide ores from impurities.
Statement-2 Ore particles are removed by washing in a current of water.

EXERCISE - 3

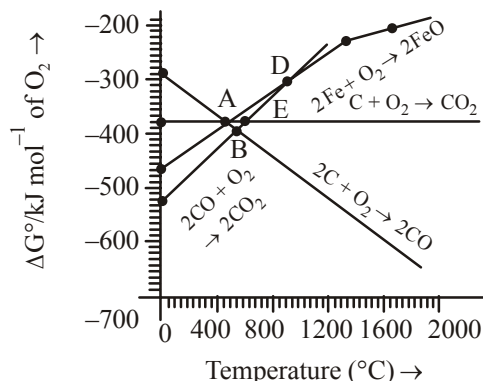
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. In the extraction of chlorine by electrolysis of brine
 (a) oxidation of Cl^- ion to chlorine gas occurs
 (b) reduction of Cl^- ion to chlorine gas occurs
 (c) for overall reaction ΔG° has negative value
 (d) a displacement reaction takes place
2. When copper ore is mixed with silica in a reverberatory furnace copper matte is produced. The copper matte contains
 (a) sulphides of copper (II) and iron (II)
 (b) sulphides of copper (II) and iron (III)
 (c) sulphides of copper (I) and iron (II)
 (d) sulphides of copper (I) and iron (III)
3. Which of the following reactions is an example of auto-reduction?
 (a) $\text{Fe}_3\text{O}_4 + 4\text{CO} \longrightarrow 3\text{Fe} + 4\text{CO}_2$
 (b) $\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$
 (c) $\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$
 (d) $\text{Cu}_2\text{O} + \frac{1}{2}\text{Cu}_2\text{S} \longrightarrow 3\text{Cu} + \frac{1}{2}\text{SO}_2$
4. A number of elements are available in earth's crust but most abundant elements are
- (a) Al and Fe (b) Al and Cu
 (c) Fe and Cu (d) Cu and Ag
5. Zone refining is based on the principle that
 (a) impurities of low boiling metals can be separated by distillation.
 (b) impurities are more soluble in molten metal than in solid metal.
 (c) different components of a mixture are differently adsorbed on an adsorbent.
 (d) vapours of volatile compound can be decomposed in pure metal.
6. In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu_2O with
 (a) FeS (b) CO
 (c) Cu_2S (d) SO_2
7. Brine is electrolysed by using inert electrodes. The reaction at anode is
 (a) $\text{Cl}^-(\text{aq}) \longrightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^-$; $E^\circ_{\text{cell}} = 1.36 \text{ V}$
 (b) $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$; $E^\circ_{\text{cell}} = 1.23 \text{ V}$
 (c) $\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$; $E^\circ_{\text{cell}} = 2.71 \text{ V}$
 (d) $\text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \frac{1}{2}\text{H}_2(\text{g})$; $E^\circ_{\text{cell}} = 0.00 \text{ V}$

8. In the metallurgy of aluminium
- Al^{3+} is oxidised to $\text{Al}(\text{s})$.
 - graphite anode is oxidised to carbon monoxide and carbon dioxide.
 - oxidation state of oxygen changes in the reaction at anode.
 - oxidation state of oxygen changes in the overall reaction involved in the process.
9. Electrolytic refining is used to purify which of the following metals?
- Cu and Zn
 - Ge and Si
 - Zr and Ti
 - Zn and Hg
10. Extraction of gold and silver involves leaching the metal with CN^- ion. The metal is recovered by
- displacement of metal by some other metal from the complex ion.
 - roasting of metal complex.
 - calcination followed by roasting.
 - thermal decomposition of metal complex.

Direction (Q. No. 11-13) Answer the questions on the basis of figure.



11. Choose the correct option of temperature at which carbon reduces FeO to iron and produces CO .
- Below temperature at point A
 - Approximately at the temperature corresponding to point A
 - Above temperature at point A but below temperature at point D
 - Above temperature at point A
12. Below point 'A' FeO can
- be reduced by carbon monoxide only.
 - be reduced by both carbon monoxide and carbon.
 - be reduced by carbon only.
 - not be reduced by both carbon and carbon monoxide.
13. For the reduction of FeO at the temperature corresponding to point D, which of the following statements is correct?
- ΔG value for the overall reduction reaction with carbon monoxide is zero.

- ΔG value for the overall reduction reaction with a mixture of 1 mol carbon and 1 mol oxygen is positive.
- ΔG value for the overall reduction reaction with a mixture of 2 mol carbon and 1 mol oxygen will be positive.
- ΔG value for the overall reduction reaction with carbon monoxide is negative.

NEET/AIPMT (2013-2017) Questions

14. The metal oxide which cannot be reduced to metal by carbon is
[NEET Kar. 2013]
- Fe_2O_3
 - Al_2O_3
 - PbO
 - ZnO
15. "Metals are usually not found as nitrates in their ores". Out of the following two ((i) and (ii)) reasons which is/are true for the above observation?
[2015]
- Metal nitrates are highly unstable.
 - Metal nitrates are highly soluble in water.
- (i) and (ii) are false
 - (i) is false but (ii) is true
 - (i) is true but (ii) is false
 - (i) and (ii) are true
16. In the extraction of copper from its sulphide ore, the metal finally obtained by the reduction of cuprous oxide with :
[2015 RS]
- iron (II) sulphide
 - carbon monoxide
 - copper (I) sulphide
 - sulphur dioxide
17. Match items of Column I with the items of Column II and assign the correct code :
[2016]
- | Column-I | Column-II |
|-----------------------------|-------------------------------|
| (A) Cyanide process | (i) Ultrapure Ge |
| (B) Froth flotation process | (ii) Dressing of ZnS |
| (C) Electrolytic reduction | (iii) Extraction of Al |
| (D) Zone refining | (iv) Extraction of Au |
| | (v) Purification of Ni |
- Code :**
- | | | | |
|-----------|-------|-------|------|
| (a) | (b) | (c) | (d) |
| (a) (iv) | (ii) | (iii) | (i) |
| (b) (ii) | (iii) | (i) | (v) |
| (c) (i) | (ii) | (iii) | (iv) |
| (d) (iii) | (iv) | (v) | (i) |
18. Extraction of gold and silver involves leaching with CN^- ion. Silver is later recovered by
[2017]
- distillation
 - zone refining
 - displacement with Zn
 - liquation

Hints & Solutions

EXERCISE - 1

1. (a) Argentite or silver glance (Ag_2S) is an ore of Ag.
2. (b) Leaching is a process used for concentration of ore. In this process, a powdered ore is treated with a suitable reagent (such as acids, bases or other chemicals) which can selectively dissolve the ore, but not the impurities.
3. (c) Malachite is $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ it is ore of copper.
4. (a) Autoreduction or self reduction is mainly used for sulphide ores of less electropositive metals like Hg, Pb, Cu, etc.

$$2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$$

$$2\text{PbO} + \text{PbS} \longrightarrow 3\text{Pb} + 2\text{SO}_2$$
5. (b) Al is most abundant metal on the surface of the earth.
6. (c) Carborundum - SiC
 Epsomite or Epsom salt - $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
 Cassiterite - SnO_2
 Spodumene - Ore of lithium
7. (a) Chalcopyrite : CuFeS_2
 Fool's gold : FeS_2
 Carnalite : $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$
 Bauxite : $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
8. (b) Except chromium all the given metals exists as their sulphides.
 Zn exists as zinc blende ZnS .
 Silver exists as silver glance Ag_2S .
 Iron exists as iron pyrites FeS_2 .
9. (a) (a) Zinc Calamine is ZnCO_3
 (b) Silver Ilmenite is FeTiO_3
 (c) Magnesium Cassiterite is SnO_2
 (d) Tin Azurite is $[\text{2CuCO}_3 \cdot \text{Cu}(\text{OH})_2]$
10. (c) Azurite is a basic carbonate ore of copper.
 $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
11. (a) Galena is PbS and thus purified by froth floatation method.
 Froth floatation method is used to concentrate sulphide ores. This method is based on the fact that the surface of sulphide ores is preferentially wetted by oils while that of gangue is preferentially wetted by water.
12. (d) Metals of high purity are obtained by zone refining e.g., silicon, germanium, boron, gallium, indium.
13. (c) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ (in blast furnace)
14. (b) Cassiterite contains the magnetic impurities of FeSO_4 and thus concentrated by electromagnetic separation.
15. (a) Zinc blende is ZnS and iron pyrite is FeS .
16. (b) Calcination is used for removal of volatile impurities and decompose carbonates into their respective oxides.

$$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}$$
 Bauxite Alumina

$$\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$$
 Limestone Calcium oxide
17. (a) The formula of magnetite is Fe_3O_4 .
18. (c) In this process sulphide ores are converted into oxide ores.

$$2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2 \uparrow$$
19. (a)
20. (b) Pyrolusite is MnO_2 . So, it is an ore of manganese. It is used in making dry batteries and also in brick industry.
21. (d)
22. (d)
23. (d) Solder is an alloy of lead (Pb) with tin (Sn). It contains about 30% Sn and 70% Pb.
24. (a) Carbon reduction, $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
25. (b) Aluminothermite process involves reduction of oxides which are not satisfactorily reduced by carbon such as Fe_2O_3 , Mn_3O_4 , Cr_2O_3 , etc. to metals with aluminium.

$$\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr} \quad \Delta H = -ve$$
26. (b) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
27. (c) The most common ore of copper is CuFeS_2 which is commonly known as chalcopyrite.
28. (c)
29. (a) A mixture of Al powder and metallic oxide (Cr_2O_3 , Mn_3O_4 etc.) is called thermite.
30. (d) Gypsum which is chemically represented as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is not an ore of magnesium among the given choices.
 Note: Carnallite is $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, magnesite is MgCO_3 and dolomite is $\text{MgCO}_3 \cdot \text{CaCO}_3$.
31. (a) Calcination is heating ore in absence of air to remove moisture and volatile impurities. Carbonate ores decomposed to corresponding oxides as a result of calcination.
32. (a) PbS reduces PbO to Pb and SO_2 is liberated. This is called as self-reduction.
33. (a) Fluorine is the most electronegative element. Hence its electron affinity is highest. By gaining one electron it completes its octet. Whereas oxygen needs electrons, O^- is already a negatively charged species hence have some repulsion for the incoming electron. Na^+ , will again loose its octet by gaining electron.
34. (b) Flux is used during metallurgy to remove silica and undesirable metal oxides.
35. (a) Due to high affinity for oxygen aluminium reduces several metallic oxides like Fe_2O_3 , Cr_2O_3 , Mn_2O_3 etc.

$$\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr} + \text{Heat}$$
 This process is known as thermite process.
36. (c)
37. (d) Calcination is a process of heating the ore in a limited supply of air below its melting point.

$$\text{MgCO}_3 \xrightarrow{\Delta} \text{MgO} + \text{CO}_2$$
38. (d) Froth floatation process is used for sulphide ores in which ore particles are accumulated in froth and the impurities remain in solution.
39. (d) Na_3AlF_6 (cryolite) is used to decrease the melting point of Al_2O_3 prior to electrolysis to get pure aluminium.

40. (b) During the process of electrolytic refining of copper Ag and Au are obtained as anode mud.
41. (a)
$$\text{Ti} + 2\text{I}_2 \xrightarrow{523\text{K}} \underset{\substack{\text{Volatile} \\ \text{Stable compound}}}{\text{TiI}_4} \xrightarrow{1700\text{K}} \underset{\text{Pure metal}}{\text{Ti}} + 2\text{I}_2$$
42. (b) Poling is used for purification of metal which contain their own oxide as impurity e.g., Cu_2O in Cu, SnO_2 in Sn etc.
43. (d) Decomposition of carbonates and hydrated oxides.
44. (d)
45. (b) Froth floatation process is used for the concentration of lighter ores (sulphides) like CuFeS_2 (copper pyrite).
46. (d)
$$2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$$

$$3\text{Cu}_2\text{O} + \underset{\substack{\text{(From green} \\ \text{logs of wood)}}}{\text{CH}_4} \rightarrow 6\text{Cu} + 2\text{H}_2\text{O} + \text{CO}$$
47. (a) For example, Ag_2S is converted into $\text{Na}[\text{Ag}(\text{CN})_2]$. When Zn is added, Ag is displaced.
48. (b) $\text{Na}_3\text{AlF}_6 \rightarrow \text{Cryolite}$
 Al_2O_3 is mixed with cryolite.
 Cryolite improves the electrical conductivity of the cell as Al_2O_3 is a poor conductor. In addition, the cryolite serves as an added impurity and lowers the melting point of the mixture to about 950°C .
49. (d) Ti – van-Arkel method
 Si – Zone refining method
 Al – Bauxite (Al_2O_3)
 Pb – Cerussite (PbCO_3)
50. (d) The sulphide ore is roasted to oxide before reduction because the ΔG_f° of most of the sulphides are greater than those of CS_2 and H_2S , therefore neither C nor H can reduce metal sulphide to metal. Further, the standard free energies of formation of oxide are much less than those of SO_2 . Hence oxidation of metal sulphides to metal oxide is thermodynamically favourable.
7. (d) Calcination is a process of heating a substance to a high temperature but below the melting or fusion point, causing loss of moisture, reduction or oxidation and dissociation into simpler substances.
8. (b)
$$\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$$

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

 At cathode : $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 At anode : $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$
9. (d) (A)
$$\text{Cr}_2\text{O}_3 + 2\text{Al} \xrightarrow{+3} \text{Al}_2\text{O}_3 + 2\text{Cr}$$

 (B)
$$\text{Au} + 2\text{CN}^- + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \longrightarrow [\text{Au}(\text{CN})_2]^- + 2\text{OH}^-$$

$$2[\text{Au}(\text{CN})_2]^- + \text{Zn} \rightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Au}$$

 (C) Statement is true
 (D)
$$\text{Ag}_2\text{S} + 4\text{NaCN} \xrightarrow{\text{O}_2} 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$$

$$2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}$$
10. (c) Reduction by powdered aluminium is known as Gold-Schmidt aluminothermic process. This process is employed in cases where metals have very high m.p. and are to be extracted from their oxides.
11. (d)
12. (a) Silver, copper and lead are commonly found in earth's crust as Ag_2S (silver glance), CuFeS_2 (copper pyrites) and PbS (galena)
13. (a) In bauxite ore, only Al_2O_3 reacts with conc. NaOH and formed sodium meta aluminate. This, further dissolves in water.

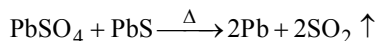
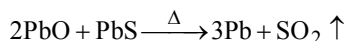
EXERCISE - 2

1. (d)
2. (d) Si obtained by reduction of SiCl_4 with H_2 is further purified by zone refining method to get Si of very high purity. Silicon is purified by zone-refining process because the impurities present in it are more soluble in the liquid phase than in the solid phase.
3. (a) Refractory metals are used in the construction of furnaces because they can withstand high temperature e.g. silica, flint, lime, etc.
 Option (a) is correct.
4. (d) Na reacts vigorously with water (exothermic process)
5. (b) In the graph of $\Delta_f G^\circ$ vs T for formation of oxides, the Cu_2O line is almost at the top. So, it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke both the lines of C, CO and C, CO_2 are at much lower temperature (500 - 600 K).

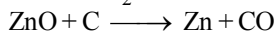
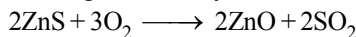
$$\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$$
6. (d) Cyanide process is used in the metallurgy of Ag

$$2\text{Ag}_2\text{S} + 8\text{NaCN} + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{Na}[\text{Ag}(\text{CN})_2] + 4\text{NaOH} + 2\text{S}$$
14. (c) SiO_2 is an acidic flux.
15. (b) In froth floatation process, ore particles float because their surface is hydrophobic i.e., not easily wetted by oil.
16. (d)
17. (c) Duraluminium alloy contains Al (95%), Cu (3%), Mn (1%), Mg (1%).
18. (c) The reduction of metal sulphides by carbon reduction process is not spontaneous because ΔG for such a process is positive. The reduction of metal oxide by carbon reduction process is spontaneous as ΔG for such a process is negative. From this we find that on thermodynamic considerations CO_2 is more stable than CS_2 and the metal sulphides are more stable than corresponding oxides.
 In view of above the factor listed in choice (c) is incorrect and so is of no significance.
19. (b) PbO & PbSO_4 get reduced by PbS itself which is already present in mixture so because the reduction took place

by itself, hence is known as self reduction.



20. (b) Extraction of Zn from ZnS (Zinc blende) is achieved by roasting followed by reduction with carbon.



21. (a)
22. (b) Both statement-1 and statement-2 are true but statement-2 is not the correct explanation of statement-1. Non fusible mass present in ore in mixing with suitable flux are fused which are then reduced by coke to give free metal.
23. (d) Statement-1 is false but statement-2 is true. Leaching is a process of concentration.
24. (a)
25. (c) Statement-1 is true but Statement-2 is false. Oxide ores being heavier than the earthy or rocky gangue particles, settle down while lighter impurities are washed away.

EXERCISE - 3

Exemplar Questions

1. (a) Chlorine extraction by electrolysis can be represented as :-

$$2\text{H}_2\text{O}(\text{l}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) + 2\text{OH}^-(\text{aq})$$
 So, the oxidation of Cl^- to Cl_2 occurs.
2. (c) Copper matte contains sulphide of copper (I) and iron (II).
3. (d)
$$\text{Cu}_2\text{O} + \frac{1}{2}\text{Cu}_2\text{S} \longrightarrow 3\text{Cu} + \frac{1}{2}\text{SO}_2$$
 In this given reaction, copper is reduced by itself hence it is known as auto-reduction.
4. (a) The most abundant elements are aluminium (8.3% by weight) and iron (4.2% by weight).
5. (b) The principle behind zone refining is that the impurities are more soluble in molten state than in solid state of the metal.
6. (c) In the extraction of copper from its sulphide ore, the metal is formed according to the reaction given :

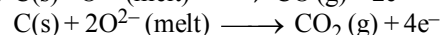
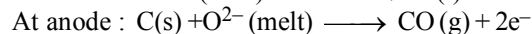
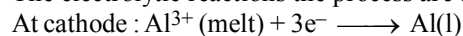
$$\text{Cu}_2\text{O} + \frac{1}{2}\text{Cu}_2\text{S} \longrightarrow 3\text{Cu} + \frac{1}{2}\text{SO}_2$$
7. (a) Possible reactions occurring at anode are :
 (i)
$$\text{Cl}^-(\text{aq}) \longrightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^-; E_{\text{cell}}^\ominus = 1.36 \text{ V}$$

 (ii)
$$2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-; E_{\text{cell}}^\ominus = 1.23 \text{ V}$$
 The reaction at anode with lower value of $E^\ominus$ is preferred and therefore water should get oxidised in preference to $\text{Cl}^-(\text{aq})$. However, Cl_2 is produced instead of O_2 . This unexpected result is explained on the basis of the fact that water needs greater voltage for oxidation

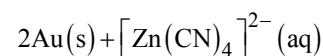
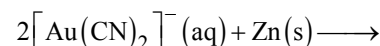
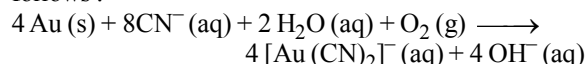
to O_2 than that needed for oxidation of Cl^- ions to Cl_2 . So reaction (i) is taking place at anode.

8. (b) In metallurgy of aluminium, graphite anode is oxidised to CO and CO_2 and this process is known as Hall-Heroult process.

The electrolytic reactions the process are :



9. (a) Two metals which are generally purified by using electrolytic refining are copper and zinc.
10. (a) In the process of extraction of Ag and Au involving leaching with cyanide ion, the metal can be recovered by displacement of Ag/Au by some other metal in the complex ion. Reactions involved in the process are as follows :



11. (d) Above point A : $\Delta_f G^\ominus_{(\text{C}, \text{CO})} < \Delta_f G^\ominus_{(\text{Fe}, \text{FeO})}$
 Therefore, reduction of FeO by carbon occurs above point A.
12. (a) Gibbs free energy change for the formation of CO_2 from CO has lesser value than Gibbs free energy change for the formation of FeO (below point A). As a result, FeO will be reduced by CO below point A.
13. (a) ΔG curve for the formation of CO_2 and FeO intersect each other at point D thus, net reduction of FeO with CO is zero.

NEET/AIPMT (2013-2017) Questions

14. (b) Al_2O_3 cannot be reduced by carbon.
15. (b) Metal nitrates are highly soluble in water and are very stable for e.g. NaNO_3 and KNO_3 .
16. (c)
$$2\text{Cu}_2\text{S}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Cu}_2\text{O}(\text{s}) + 2\text{SO}_2(\text{g})$$
 The unchanged Cu_2S , mixed with Cu_2O and heated strongly in absence of air

$$2\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$$

17. (a) Highly electropositive metals like Al, K, Na etc. are extracted by the electrolytic reduction.
 • zone refining method is used for obtaining metals of high purity e.g. Ge
 • Froth flotation process is suitable for sulphide ores
 • Cyanide process is used for the extraction of gold.
18. (c) Zn being more reactive than Ag and Au, displaces them.

$$4\text{Ag} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_2 \xrightarrow{\text{Leaching}} 4\text{Na}[\text{Ag}(\text{CN})_2] + 4\text{NaOH}$$
 Soluble Sodium dicyanoargentate (I)
 Soluble cyanide compound can be treated with Zn to give metal by displacement.

$$2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \xrightarrow{\text{Displacement}} \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag} \downarrow$$

Chapter 21 The p-Block Elements (Group 15, 16, 17 and 18)

GROUP 15 ELEMENTS

It includes

Nitrogen (N)	]	Non-metals
Phosphorus (P)		
Arsenic (As)	]	Metalloids
Antimony (Sb)		
Bismuth (Bi)		Metal

Elements of this group are called **pinacogen**

Atomic Properties

- Electronic Configuration:** Their valence shell electronic configuration is $ns^2 np^3$. Due to half-filled p-orbitals, they are extra stable.
- Atomic and Ionic radii:** Covalent and ionic radius increases down the group. Increase in covalent radii from As to Bi is very small. This is due to poor shielding of the valence e^- s by d- and f- orbitals in heavier members.
- Ionisation enthalpy:** Down the group, IE decreases due to increase in size. The IE of group 15 is much greater than group 14 in corresponding periods. This is because of extra stable filled p-orbital configuration and smaller size.
- Electronegativity :** With increase in size down the group, electronegativity decreases.

Physical Properties

- All the elements are polyatomic
- N_2 is a gas while other elements are solids
- Metallic character increases down the group due to decrease in IE and increase in atomic size.
- Except nitrogen, all elements show allotropy.

Chemical Properties

- Oxidation states:** Common oxidation states are -3, +3, and +5. The stability of +5 oxidation state decreases down the group while that of +3 oxidation state increases down the group. This is due to inert pair effect. For N, +1 to +4 oxidation states disproportionate in acid solution.
Ex: $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$
For P, all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.
Example: $4\text{H}_3\overset{+3}{\text{P}}\text{O}_3 \xrightarrow{\Delta} 3\text{H}_3\overset{+5}{\text{P}}\text{O}_4 + \overset{-3}{\text{PH}_3}$
From As to Bi tendency to undergo disproportionation decreases.

N shows a maximum covalency of 4 since only four orbitals are available for bonding. The heavier elements show higher covalency due to availability of vacant d-orbitals. ex: PF_6^- .

(ii) Reactivity towards hydrogen:

They form hydrides of the type EH_3 where $\text{E} = \text{N} \setminus \text{P} \setminus \text{As} \setminus \text{Sb} \setminus \text{Bi}$. The stability of hydrides decreases from NH_3 to BiH_3 . This is because with increase in bond length from N to Bi, bond strength decreases due to which reducing character of hydrides increases down the group.

Hydrides are formed by the action of water or dilute acids on compounds: Mg_3N_2 , Ca_3P_2 , Zn_3As_2 , Mg_3Sb_2 and Mg_3Bi_2 .

All hydrides are coloured gases. The order of basicity of hydrides is $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$.

This is because EH_3 has a lone pair of e^- s on E which is available for donation. As the e^- density of NH_3 is high due to smaller size of N, thus availability of lone pair of electrons for donation is more and hence, basicity of NH_3 is more compared to other hydrides of the group.

Trends from NH_3 to BiH_3

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Basic character decreases $\longrightarrow$				
Thermal stability decreases $\longrightarrow$				
Reducing nature increases $\longrightarrow$				
Dipole moment decreases $\longrightarrow$				
Bond angle decreases $\longrightarrow$				

(iii) Reactivity towards oxygen:

Nitrogen forms five oxides with oxidation states ranging from +1 to +5 while other elements form oxides in +3 and +5 oxidation states.

The oxide in higher oxidation state of the element is more acidic than that of lower oxidation state. The oxides of the type E_2O_3 of N and P are purely acidic, that of As and Sb are amphoteric and those of Bi are predominantly basic.

(iv) Reactivity towards halogens:

They form two series of halides: EX_3 and EX_5 . N does not form pentahalide due to non-availability of d-orbitals in its valence shell. All trihalides except those of N are stable. In case of N, only NF_3 is known to be stable. The reason assigned to unstable nature of NCl_3 , NBr_3 , NI_3 is the weakness of the N-X bond due to large difference in the size of nitrogen and halogen atom.

Pentahalides are more covalent than trihalides. This is because it is very difficult to form E^{5+} due to very high I.E. Bi does not form pentahalides due to inert pair effect

Note :

- Pentahalides are thermally less stable than trihalides down the group stability of +5 oxidation state decreases due to inert pair effect.
 - As the size of the halogen increases from F to I strength E–X of bond decreases and steric hinderance increases.
- (v) **Reactivity towards metals:**
All these elements react with metals to form binary compounds exhibiting –3 oxidation state such as Ca_3N_2 , Ca_3P_2 , Na_3As_2 , Zn_3Sb_2 and Mg_3Bi_2 .

Anomalous properties of nitrogen

Nitrogen shows different behaviour from rest of the members of the group due to its:

- smaller size
- high electronegativity
- high IE
- non-availability of d-orbitals.

Thus, the properties of N which are different from other elements of the group are:

- N can form $p\pi - p\pi$ multiple bonds with itself and other elements of small size and high electronegativity. As a result, N exists as a diatomic molecule with a triple bond between the two atoms. On the other hand, P, As and Sb form single bonds as P–P, As–As, Sb–Sb.
- Due to non-availability of d-orbitals, N cannot form $d\pi-p\pi$ bond while other elements can. Thus, $R_3P=O$ exists but $R_3N=O$ cannot.
- Due to small size and high electronegativity, nitrogen forms nitride ion (N^{3-}). Phosphorus to some extent also gives phosphide ion (P^{3-}) in some compounds. This tendency is absent in rest of the elements.

NITROGEN AND SOME OF ITS IMPORTANT COMPOUNDS

Dinitrogen, N_2

Preparation:

- $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$
- $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$
- $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$ (give very pure N_2)
- $2NaN_3 \longrightarrow 2Na + 3N_2$
Commercially, it is produced by liquefaction and fractional distillation of air. Liquid N_2 distils out first leaving behind liquid oxygen.

Physical Properties:

- It is colourless, odourless, tasteless and non-toxic gas.
- It has two stable isotopes ^{14}N and ^{15}N .
- It is inert at room temperature due to high bond energy of $N \equiv N$ bond.
- At higher temp, it becomes reactive

Chemical properties :

- Li, Mg, Ca, Al form nitrides
 $3Ca + N_2 \xrightarrow{\Delta} Ca_3N_2$
- $N_2 + O_2 \rightleftharpoons 2NO$ (electric arc) – 43.2 kcal
This reaction forms the basis for the manufacture of HNO_3 by **Birkland and Eyde process**.
- $CaC_2 + N_2 \xrightarrow{1273K} Ca(CN)_2 + C$
calcium carbide calcium cyanamide
 $Ca(CN)_2$ gives ammonia on reaction with water, therefore $[Ca(CN)_2 + C]$ is used as fertilizer under the name nitrolim.
- Combination with hydrogen to form NH_3 (**Haber's process**) under pressure 100 – 1000 atmospheres.
$$N_2 + 3H_2 \xrightleftharpoons{Fe+Mo; 400-550^\circ C} 2NH_3$$

Uses :

- Used for the manufacture of NH_3 , HNO_3 , $Ca(CN)_2$ etc.
- To provide inert atmosphere N_2 gas is used in metallurgical processes.
- It is used in filling electric bulbs.

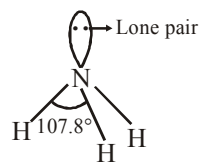
Ammonia, NH_3

Preparation:

- $NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$
urea
- $2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$
- $(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$
- Haber's process:
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 $\Delta_f H^\circ = -46.1 \text{ kJ mol}^{-1}$
Optimum conditions for this reaction are high pressure ($200 \times 10^5 \text{ Pa}$) and temperature ($\sim 700 \text{ K}$) and use of catalyst like iron oxide with small amounts of K_2O and Al_2O_3 .

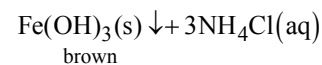
Physical Properties:

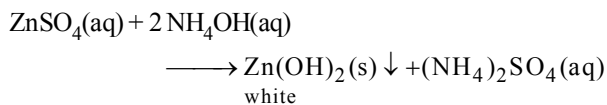
- It is a colourless gas with pungent odour.
- In solid and liquid states, it is associated through H-bonds which results in its high M.Pt and B.Pt.
- It is trigonal pyramidal, i.e.,



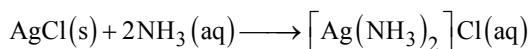
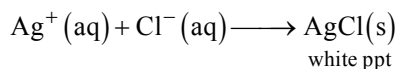
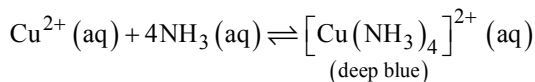
Chemical properties :

- Its aqueous solution is weakly basic due to formation of OH^- ions:
 $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
- It forms ammonium salts with acids and being a weak base, precipitates the hydroxides of many metals from their salt solutions. For ex:

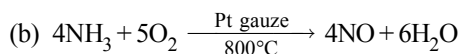
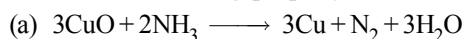




- (iii) It acts as a Lewis base due to presence of lone pair of e^- s on N and combines with Lewis acids ex:



- (iv) **Oxidation** (reducing property) :



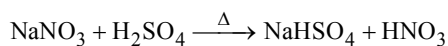
Oxides of nitrogen these are tabulated below :

Name of oxide	Formula	O.S. of N	Common methods of preparation	Physical appearance and chemical nature
(1) Dinitrogen oxide	N_2O	+1	$\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	colourless gas, neutral
(2) Nitrogen monoxide	NO	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	colourless gas, neutral
(3) Dinitrogen trioxide	N_2O_3	+3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$	blue solid, acidic
(4) Nitrogen dioxide	NO_2	+4	$2\text{Pb}(\text{NO}_3)_2 \rightarrow 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	brown gas, acidic
(5) Dinitrogen tetraoxide	N_2O_4	+4	$2\text{NO}_2 \xrightleftharpoons[\text{heat}]{\text{cool}} \text{N}_2\text{O}_4$	colourless solid, liquid, acidic
(6) Dinitrogen pentaoxide	N_2O_5	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic

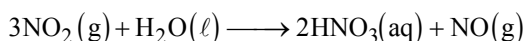
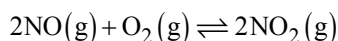
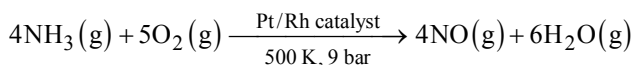
Nitric acid, HNO_3 .

Preparation:

- (i) Lab method:

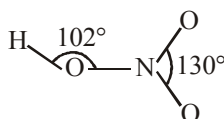


- (ii) Ostwald's process:

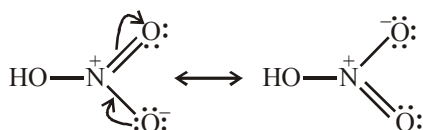


Properties:

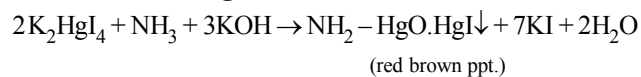
- (i) In gaseous state, it exists as a planar molecule as shown below:



It is a resonance hybrid of the following structures :

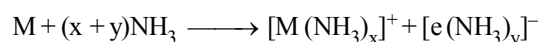


- (v) **With Nessler's reagent :**

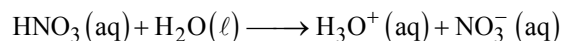


Uses

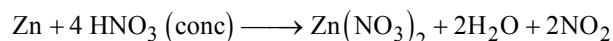
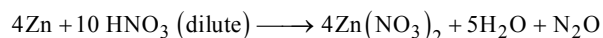
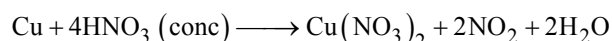
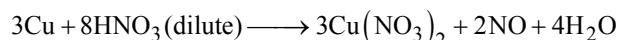
- Due to lone pair of electrons it acts as a Lewis base.
- Preparation of fertilizers.
- In making artificial silk.
- As a laboratory reagent.
- In refrigeration.
- In making HNO_3 , $(\text{NH}_4)_2\text{CO}_3$, Na_2CO_3 etc.
- Liquid NH_3 is a good solvent for the alkali and alkaline earth metals. The solution is conducting and blue in color. The electrical conductivity is due to ammoniated cations as well as electrons.



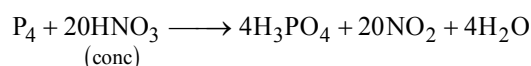
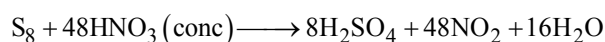
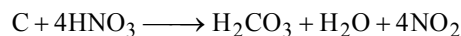
- (ii) In aqueous solution, it behaves as a strong acid.



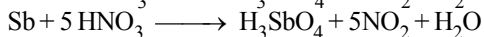
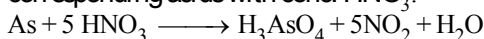
- (iii) It is a strong oxidising agent.



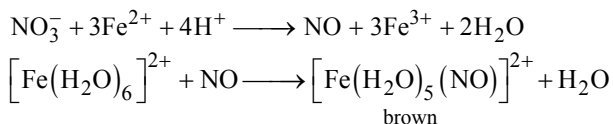
- (iv) It oxidises non-metals and their compounds. ex:



- (v) Semi metals or metalloids such as As and Sb are oxidised to corresponding acids with conc. HNO_3 .



Brown ring test: It is for the detection of NO_3^- ions in a salt. In this test, dilute FeSO_4 is added to an aqueous solution of NO_3^- ions and then conc H_2SO_4 is added along the sides of test-tube. A brown ring at the interface indicates NO_3^- ion.



ALLOTROPES OF PHOSPHORUS

Phosphorous exists in many allotropic forms, important ones being white, red and black.

(i) White P:

It is translucent waxy solid, poisonous, insoluble in H_2O but soluble in CS_2 and shows chemiluminescence (glowing in dark). In white phosphorus P_4 molecules are held by weak Van der Waal's forces. Therefore it is low melting and low boiling in nature. It readily catches fire in air give dense fumes of P_4O_{10} .

Reaction with aqueous alkalis:



(white)

White phosphorus acts as a strong reducing agent. It reduces HNO_3 to NO_2 , H_2SO_4 to SO_2 and CuSO_4 to Cu and itself oxidised to H_3PO_4 .

(ii) Red Phosphorus

It is obtained by heating white phosphorus in an inert atmosphere for several days.

- (a) It possesses iron grey lustre.
- (b) It is odourless, non-poisonous, insoluble in H_2O as well as CS_2 .
- (c) Chemically, it is less reactive than white phosphorus.
- (d) Red phosphorus does not react with caustic alkalis.
- (e) Red phosphorus react at ordinary temp. and on heating respectively with chlorine giving PCl_3 and PCl_5 .

(iii) Black Phosphorus

It has two forms: α - and β - α -black phosphorus is formed by heating red phosphorus. It has opaque monoclinic or rhombohedral crystals. It does not oxidise in air.

β -black phosphorus is prepared by heating white phosphorus under high pressure. It does not burn in air upto 673 K.

SOME IMPORTANT COMPOUND OF PHOSPHORUS

Phosphine [PH_3]

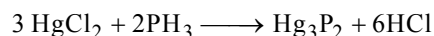
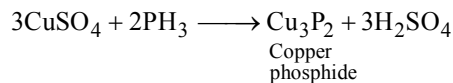
Preparation

- (i) $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
 $\text{Ca}_3\text{P}_2 + 6\text{HCl} \longrightarrow 3\text{CaCl}_2 + 2\text{PH}_3$
- (ii) $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$

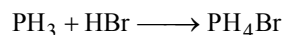
Properties (Physical and Chemical) :

- (i) It is colourless gas and is highly poisonous.
- (ii) It explodes in contact with oxidising agents like HNO_3 , Cl_2 and Br_2 vapours.
- (iii) In water, it decomposes in presence of light to give red P and H_2 .

- (iv) Reaction with aqueous metallic salts:



- (v) It is weakly basic and gives phosphonium compounds with acids. ex:



Uses :

- (i) It is used in smoke screens.
- (ii) Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal. These are called Holme's signals.

Phosphorus Halides

P forms two types of halides, PX_3 and PX_5 .

(X = F, Cl, Br, I)

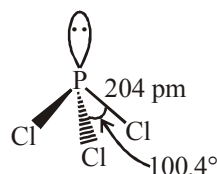
Phosphorus Trichloride (PCl_3)

Preparation:

- (i) $\text{P}_4 + 6\text{Cl}_2 \longrightarrow 4\text{PCl}_3$
(white)
- (ii) $\text{P}_4 + 8\text{SOCl}_2 \longrightarrow 4\text{PCl}_3 + 4\text{SO}_2 + 2\text{S}_2\text{Cl}_2$

Properties:

- (i) Reaction with H_2O :
 $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
- (ii) Reaction with organic compounds:
 $\text{PCl}_3 + 3\text{CH}_3\text{COOH} \longrightarrow 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3$
 $\text{PCl}_3 + 3\text{CH}_3\text{CH}_2\text{OH} \longrightarrow 3\text{C}_2\text{H}_5\text{Cl} + \text{H}_3\text{PO}_3$
- (iii) It has a pyramidal shape in which P is sp^3 -hybridised



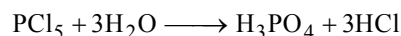
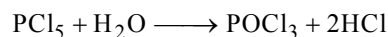
Phosphorus Pentachloride (PCl_5)

Preparation:

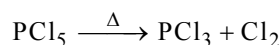
- (i) $\text{P}_4 + 10\text{Cl}_2 \longrightarrow 4\text{PCl}_5$
(white) (excess)
- (ii) $\text{P}_4 + 10\text{SO}_2\text{Cl}_2 \longrightarrow 4\text{PCl}_5 + 10\text{SO}_2$

Properties:

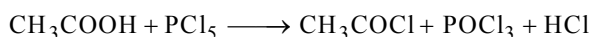
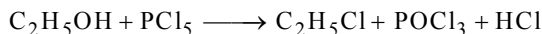
- (i) In moist air, it hydrolyses to POCl_3 and finally gets converted to phosphoric acid.



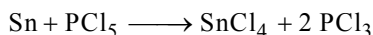
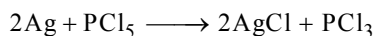
- (ii) On heating, it sublimes and decomposes on stronger heating.



(iii) It reacts with organic compounds

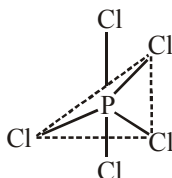


(iv) Finely divided metals on heating with PCl_5 give corresponding chlorides.



(v) In gaseous and liquid phases, it has trigonal bipyramidal structure as shown :

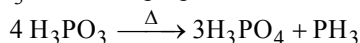
The two axial bonds are longer than equatorial bonds. This is because axial bond pairs suffer more repulsion than equatorial bond pairs.



(vi) In solid state, it exists as an ionic solid, $[\text{PCl}_4]^+ [\text{PCl}_6]^-$ in which $[\text{PCl}_4]^+$ is tetrahedral and $[\text{PCl}_6]^-$ is octahedral.

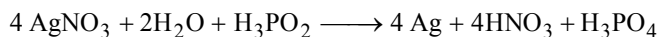
Oxoacids of Phosphorus

Phosphorus forms two types of oxoacids namely phosphorus and phosphoric acids. In oxoacids, P is tetrahedrally surrounded by other atoms. These acids contain one $\text{P}=\text{O}$ and at least one $\text{P}-\text{OH}$ bond. The acids in +3 oxidation state of P, ex: $\text{H}_4\text{P}_2\text{O}_6$, H_3PO_2 , H_3PO_3 , tend to disproportionate. ex:

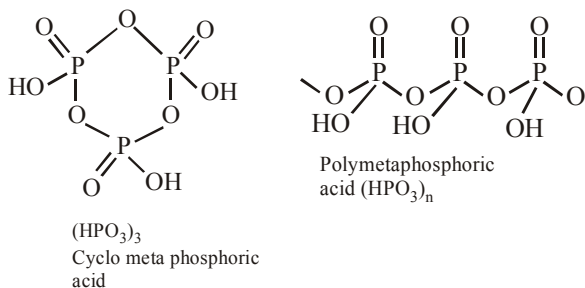
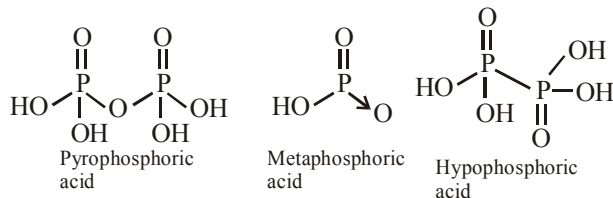
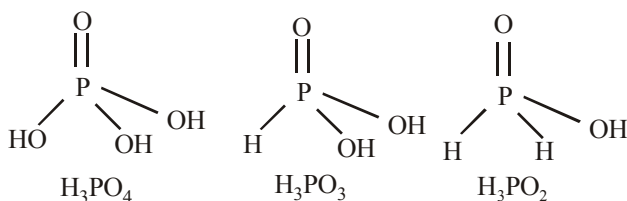


The hydrogen atoms in $\text{P}-\text{OH}$ bonds are ionisable and are therefore acidic. However these are not ionisable in $\text{P}-\text{H}$ bonds and are responsible for the reducing properties of acids.

Ex: H_3PO_2 reduces AgNO_3 to Ag (it has two $\text{P}-\text{H}$ bonds)



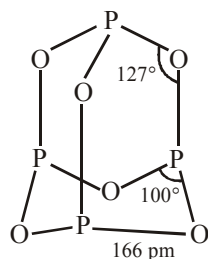
Structures of some oxoacids are:



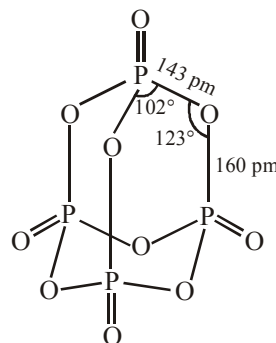
The $\text{P}-\text{H}$ bonds are not ionisable to give H^+ and do not play any role in basicity. The H -atoms attached to O in $\text{P}-\text{OH}$ are ionisable and cause basicity. Thus, H_3PO_4 is tribasic (three- OH bonds) H_3PO_3 is dibasic (2- OH bonds) while H_3PO_2 is monobasic (one- OH bond)

Oxides of Phosphorus

(i) Phosphorus trioxide (P_4O_6)



(ii) Phosphorus pentoxide (P_4O_{10})



GROUP 16 ELEMENTS

It includes

Oxygen (O)	}	Non-metals
Sulphur (S)		
Selenium (Se)	}	Metalloids
Tellurium (Te)		
Polonium (Po)	}	Metal

They are also called chalcogens (ore forming elements) because these are involved in chemical formulas of the ores such as oxides, sulphides, tellurides etc.

Atomic Properties

- Electronic Configuration:**
Their general electronic configuration is $ns^2 np^4$.
- Atomic and Ionic radii.**
Atomic and ionic radii increases down the group. The size of O is exceptionally small.
- Ionisation enthalpy :**
Down the group, IE decreases due to increase in size. IE values of group 16 elements are much lower than those of group 15 elements. This is because group 15 elements have extra stable half-filled p-orbital electronic configuration
- Electron gain enthalpy:**
They have high tendency to accept two e^- s to become stable and hence have large negative electron gain enthalpies. Electron gain enthalpy of oxygen is least negative in this group due to its small size resulting in large $e^- - e^-$ repulsions in 2p-subshell due to which the incoming e^- s are not accepted with ease.
- Electronegativity :**
 - Electronegativity value decreases down the group with increase in size. Oxygen is the second most electronegative element in the periodic table. This is due to its very small size and urge to take up two electrons to acquire a ns^2 configuration.

Physical Properties :

- O exists as a diatomic molecule while other elements exist as octaatomic solids.
- O forms $p\pi-p\pi$ double bonds while other elements do not.
- S has stronger tendency for catenation than O (due to stronger S-S bonds compared to O-O bonds)
- All elements of this group show allotropy
- M.pts. and B.pts. increases down the group with increase in atomic number.

Chemical Properties**(i) Oxidation states:**

They show both negative and positive oxidation states. The stability of -2 O.S. decreases down the group. Due to high electronegativity of O it shows only negative O.S. of -2 except in OF_2 and O_2F_2 where it shows $+2$ and $+1$ oxidation states respectively. In peroxides like H_2O_2 , O has -1 oxidation states and in O_2 , it has zero oxidation states. Other elements show $+2$, $+4$, $+6$ oxidation states. S, Se, Te show $+4$ oxidation states with O and $+6$ with F. Due to inert pair effect, stability of $+6$ oxidation state decreases down the group while that of $+4$ oxidation states increases. Bonding in higher oxidation states, i.e. $+4$ and $+6$, is primarily covalent.

(ii) Reactivity with hydrogen :

They form hydrides of the type H_2E . Bond angle decreases from H_2O to H_2Te . This is because as electronegativity decreases from O to Te, electron density also decreases i.e. electron pair repulsion in electron pairs around the central metal atom decreases bond angle also decreases. Their acidic character increases from H_2O to H_2Te . This is due to decrease in bond dissociation energy down the group. For the same reason, thermal stability of hydrides decreases from H_2O to H_2Po . All hydrides except H_2O possess reducing property and this character increases from H_2S to H_2Te . This is due to decrease in bond dissociation energy due to increase in bond length value.

(iii) Reactivity with oxygen:

Ozone is considered as oxide of oxygen O. Oxides of other elements are as follows

Element	Mono Oxide	Dioxide	Tri Oxide
S	SO	SO_2	SO_3
Se	-	SeO_2	SeO_3
Te	TeO	TeO_2	TeO_3
Po	PoO	PoO_2	-

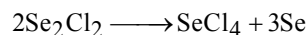
O_3 and SO_2 are gases while SeO_3 is solid. Reducing property of dioxides decreases from SO_2 to TeO_2 , SO_2 is reducing while TeO_2 is an oxidising agent.

(iv) Reactivity towards halogens:

They form a large number of halides of the type EX_6 , EX_4 , EX_2 . The stability of halides decreases in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

Among hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature and have octahedral structure. SF_6 is exceptionally stable due to steric reasons. Among tetrafluorides, SF_4 is a gas, SeF_4 is a liquid and TeF_4 a solid. They have sp^3d hybridisation and see-saw geometry (with a lone pair at one of equatorial positions).

All elements except Se form dichlorides and dibromides which have sp^3 hybridisation and tetrahedral structure. Monohalides are dimeric in nature and undergo disproportionation. Examples are S_2F_2 , S_2Cl_2 , S_2Br_2 , Se_2Cl_2 , Se_2Br_2 .

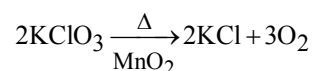
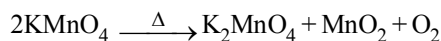
**Anomalous Behaviour of Oxygen**

The anomalous behaviour of oxygen is due to:

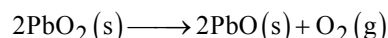
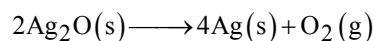
- its small size
- high electronegativity
- absence of d-orbitals (which limits its covalency to 4)

OXYGEN AND SOME OF ITS IMPORTANT COMPOUNDS**Dioxygen, O_2** **Preparation :**

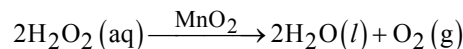
- By heating oxygen containing salts like chlorates, nitrates and permanganates.



- By thermal decomposition of oxides of metals low in the electrochemical series and higher oxides of some metals.



- By catalytic decomposition of H_2O_2

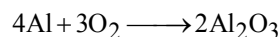
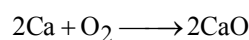


- On large scale, electrolysis of water leads to release of hydrogen at cathode and oxygen at anode.
- By liquefaction of air followed by its fractional distillation where N_2 distills off at 77K and O_2 remains as liquid.

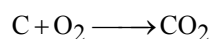
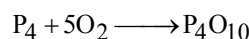
Properties

- It has three stable isotopes, ^{16}O , ^{17}O and ^{18}O
- O_2 is paramagnetic inspite of having even number of e^- s. This is due to unpaired e^- s in anti-bonding orbitals.
- The reaction of O_2 with other elements is highly exothermic which sustains the reaction. As the bond dissociation enthalpy of $\text{O}=\text{O}$ is high, some external heating is required to initiate the reaction.

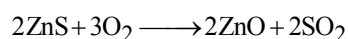
- Reaction with metals:



- Reaction with non-metals:



- Reaction with metal sulphides:



- Reaction with hydrocarbons:



Uses:

- (i) In respiration and combustion processes.
- (ii) In oxyacetylene welding and manufacture of steel.
- (iii) As oxygen cylinders in hospitals, high altitude flying and in mountaineering.

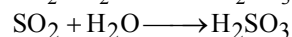
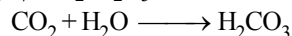
Oxides

A binary compound of oxygen with other element is called oxide.

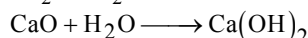
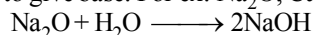
Simple oxides

Simple oxides are classified on the basis of their acidic, basic or amphoteric character. An acidic oxide combines with H_2O to give an acid.

Example: $SO_2, Cl_2O_7, CO_2, N_2O_5$.

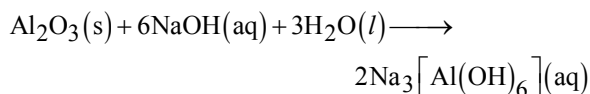
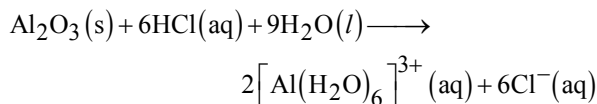


These acidic oxides react with bases to form salts and water. Non-metal oxides and oxides of some metals in high oxidation state (ex: Mn_2O_7, CrO_3, V_2O_5) have acidic character. A basic oxide combines with H_2O to give base. For ex: Na_2O, CaO, BaO



Basic oxides form salts and water with acids. Metallic oxides are basic.

Some oxides show characteristics of acidic as well as basic oxides. They are called amphoteric oxides. For ex: Al_2O_3, ZnO, PbO and SnO . It reacts with acids as well as alkalis.



Some oxides are neither acidic nor basic. They are called neutral oxides. For ex: CO, NO and N_2O .

Polyoxides - These contain more oxygen than normal oxidation number of M and M – O and O – O bonds. They are further classified as

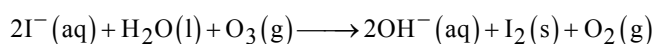
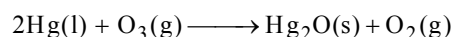
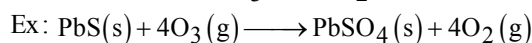
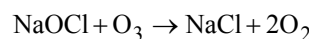
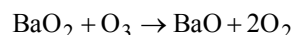
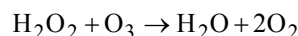
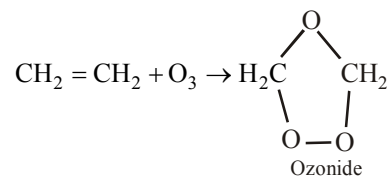
- (i) **Peroxides** - They contain O_2^{2-} ion, produce hydrogen peroxide with dil. acids and O_2 with concentrated acids eg BaO_2, Na_2O_2
- (ii) **Super oxides** - They contain O_2^- ion. With water they give hydrogen peroxide and oxygen
- (iii) **Dioxides** - They give chlorine with conc HCl and oxygen with Conc H_2SO_4 eg MnO_2, PbO_2 etc.
- (iv) **Suboxides** - They contain lower percentage of oxygen eg N_2O, C_3O_2 . They have M – M and M – O bonds. For example: $O=C=C=C=O$ (carbon suboxide)
- (v) **Mixed oxides** - Formed by the combination of two simple oxides eg Red lead, Pb_3O_4 ($PbO_2 \cdot 2PbO$), Fe_3O_4 ($FeO \cdot Fe_2O_3$)

Ozone, O_3 **Preparation:**

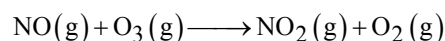
When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of O_2 to O_3 occurs.

**Properties :**

- (i) It is a pale blue gas, dark blue liquid and violet-black solid.
- (ii) In small concentrations, it is harmless. If concentration rises above 100 ppm, breathing becomes uncomfortable resulting in headache and nausea.
- (iii) It is thermodynamically unstable with w.r.t O_2 (as its decomposition into O_2 results in liberation of heat (i.e., negative ΔH) and increase in entropy (i.e. $+\Delta S$), resulting in negative ΔG (i.e. spontaneous process)
- (iv) O_3 is diamagnetic while O_2 is paramagnetic.
- (v) It is powerful oxidising agent as it readily releases atoms of nascent oxygen i.e., $O_3 \longrightarrow O_2 + O$

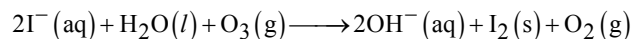
**(vi) Reducing action****(vii) Addition reactions****Note :**

- (i) Nitrogen oxides react with O_3 rapidly and result in depletion of O_3 in upper atmosphere.

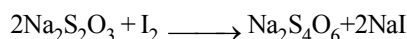


- (ii) O_3 can be quantitatively estimated using KI and $Na_2S_2O_3$ solutions as follows:

When O_3 is treated with excess of KI solution buffered with borate buffer (pH 9.2), I_2 is liberated quantitatively.



The I_2 thus liberated is titrated against a standard solution of $Na_2S_2O_3$ using starch as an indicator.

**SULPHUR-ALLOTROPIC FORMS**

The yellow rhombic (α – sulphur) and monoclinic (β – sulphur) allotropes of sulphur are the most important. At room temperature, the stable form is rhombic sulphur which when heated above 369 K, transforms to monoclinic sulphur. Conversely, α -sulphur is stable below 369 K and transforms into β -sulphur above this. At 369 K, both the forms are stable. This temperature is called transition temperature.

SULPHUR AND SOME OF ITS IMPORTANT COMPOUNDS

Sulphur

Preparation :

- Main source of sulphur are : Sicily and Louisiana the processes employed are called : Sicilian process and Louisiana (or Frasch) process
- Sulphur is also obtained from alkali wastes, spent oxides of coal gas and iron pyrites :
- Flowers of sulphur** : In the purification process, vapours of boiling sulphur (444°C) are condensed on the cold walls of the vessel as a light yellow powder called flowers of sulphur. Both the forms have S_8 molecules. The S_8 ring in both the forms is puckered and has a crown shape. In vapour state, S partly exist as S_2 molecule which has two unpaired e^{-1} s in the antibonding π^* orbitals like O_2 , and hence, exhibits paramagnetism.

Sulphur Dioxide, SO_2

Preparation

- $\text{S}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g})$
- Lab method** : By heating Cu with conc H_2SO_4
 $\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
- From iron pyrite :
 $4\text{FeS}_2(\text{s}) + 11\text{O}_2(\text{g}) \longrightarrow 2\text{Fe}_2\text{O}_3(\text{s}) + 8\text{SO}_2(\text{g})$
 (Industrial method)

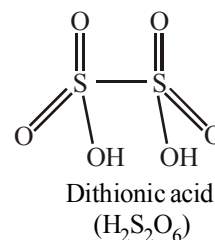
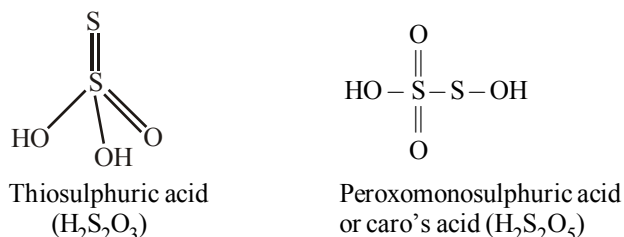
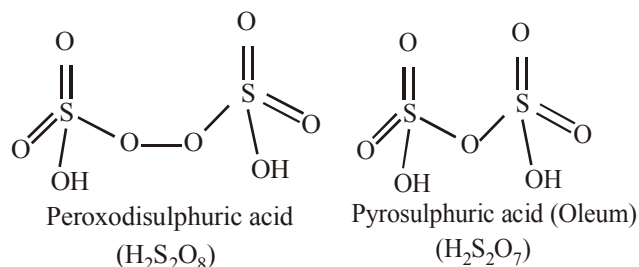
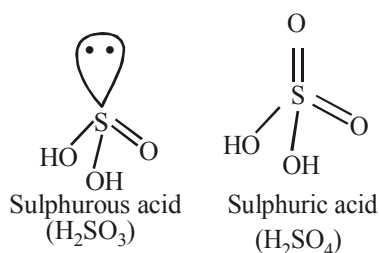
Properties

- As oxidising agent**
 $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S} \downarrow$
 $\text{SO}_2 + 2\text{Mg}(\text{burning}) \rightarrow 2\text{MgO} + \text{S} \downarrow$
- Burning of potassium** - Potassium burns in SO_2 giving sulphate and thiosulphate
 $4\text{K} + 3\text{SO}_2 \rightarrow \text{K}_2\text{SO}_3 + \text{K}_2\text{S}_2\text{O}_3$
- Bleaching action** - Its bleaching action is due to reduction
 $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}$
- When moist, it behaves as a reducing agent. For ex:
 (a) $2\text{Fe}^{3+} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Fe}^{2+} + \text{SO}_4^{2-} + 4\text{H}^+$
 (b) $5\text{SO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \longrightarrow 5\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{Mn}^{2+}$

Oxoacids of Sulphur

S forms a number of oxoacids such as H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$, $\text{H}_2\text{S}_2\text{O}_4$, $\text{H}_2\text{S}_2\text{O}_5$, $\text{H}_2\text{S}_x\text{O}_6$ ($x = 2$ to 5), H_2SO_4 , $\text{H}_2\text{S}_2\text{O}_7$, H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$.

Structure of some important oxoacids are:



Sulphuric acid, H_2SO_4

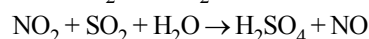
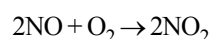
Manufacture:

- By contact process**
 It involves the following steps:
 (a) Production of SO_2 by burning sulphur or roasting iron pyrites.
 $\text{S}_8 + 8\text{O}_2 \longrightarrow 8\text{SO}_2$
 $4\text{FeS}_2 + 11\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$
- Catalytic oxidation of SO_2 by air to give SO_3 .
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H = -196.6 \text{ kJ mol}^{-1}$
 According to Le Chatelier's principle, the yield of SO_2 is increased with high P, low T and use of catalyst like Pt or V_2O_5 .
- Absorption of SO_3 in 98% H_2SO_4 to form oleum.
 $\text{SO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S}_2\text{O}_7$ (oleum)
 Dilution of oleum give H_2SO_4 of desired concentration.
 $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{SO}_4$

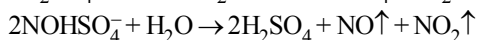
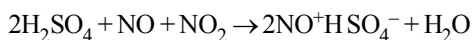
Lead chamber process : Here oxidation of SO_2 is affected catalytically by means of oxides of nitrogen in the presence of water.



Mechanism may be described as :



The unreacted gases (NO , NO_2 , O_2 and N_2) are absorbed in H_2SO_4 and nitrosyl sulphuric acid. The product on decomposition gives H_2SO_4 .

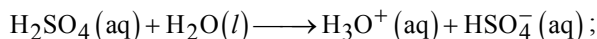
**Physical properties :**

- (i) It is colourless, dense, oily liquid with a specific gravity of 1.84.
- (ii) It dissolves in H_2O with the evolution of lot of heat.

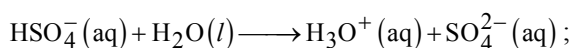
Chemical properties :

The chemical reactions of H_2SO_4 are due to its (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent.

- (i) In aqueous solution, H_2SO_4 ionises in two steps:



$$K_{a1} = 1 \times 10^3$$

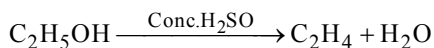
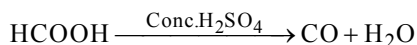
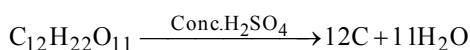


$$K_{a2} = 1.2 \times 10^{-2}$$

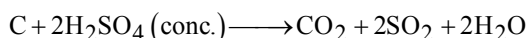
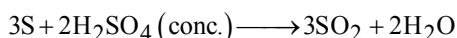
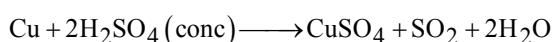
Large value of K_a shows that H_2SO_4 is a strong acid.

- (ii) $2\text{MX} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{HX} + \text{M}_2\text{SO}_4$ ($\text{X} = \text{F}, \text{Cl}, \text{NO}_3$)
($\text{M} = \text{metal}$)

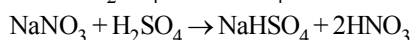
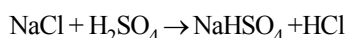
- (iii) It is a strong dehydrating agent. Ex.



- (iv) It is a strong oxidising agent and oxidises both metals and non-metals
Exs:



- (v) **Displaces more volatile acids :**

**GROUP 17 ELEMENTS**

It includes

Fluorine (F)
Chlorine (Cl)
Bromine (Br)
Iodine (I)
Astatine (At)

They are collectively known as halogens.

Atomic Properties

- (i) **Electronic configuration**

Their general electronic configuration is ns^2np^5 .

- (ii) **Atomic and Ionic radii:**

They have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. Down the group, atomic and ionic radii increases

- (iii) **Ionisation enthalpy**

They have very high IE as they have little tendency to loose. electron(s) IE decreases down the group with increase in atomic size.

- (iv) **Electron gain enthalpy:**

As they need only one e^- to become stable, halogens show a high tendency to accept e^- s and hence they have large negative values of electron gain enthalpy.

Down the group, electron gain enthalpy becomes less negative. However, electron gain enthalpy of F is less than that of Cl. This is due to small size of F atom resulting in strong interelectronic repulsion in the relatively small 2p-orbitals of F.

- (v) **Electronegativity**

They have high electronegativity. F is the most electronegative element in the periodic table.

Physical properties

- (i) F_2 and Cl_2 are gases, Br_2 is a liquid and I_2 is a solid.
- (ii) All the halogens are coloured. F_2 is yellow, Cl_2 greenish yellow, Br_2 is red and I_2 is violet. The colour arises due to excitation of outer e^- s to higher energy levels by absorbing radiations in visible region.
- (iii) In halogen molecules, the bond dissociation enthalpies are expected to decrease with the increase in bond length values.
- (iv) F_2 has smaller bond dissociation enthalpy as compared to Cl_2 . This is due to large $e^- - e^-$ repulsion among the lone pairs in F_2 molecule.

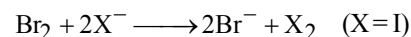
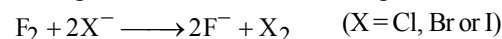
Chemical Properties

- (i) **Oxidation states:**

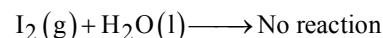
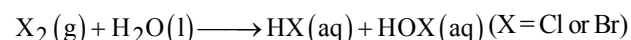
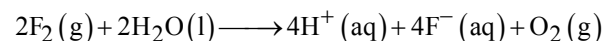
All halogens exhibit -1 oxidation state Cl, Br and I exhibit $+1$, $+3$, $+5$ and $+7$ oxidation state also. F exhibits only -1 oxidation state being the most electronegative element in the table. Halogens are highly reactive and react with metals and non-metals to form halides.

- (ii) **Oxidising nature :**

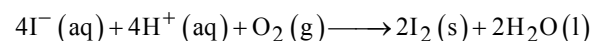
Halogens are strong oxidising agents due to their tendency to accept e^- s. F_2 is the strongest oxidising agent. In general, a halogen oxidises halide ions of higher atomic number.



- (iii) **Reaction with water.**



Instead, I^- ions can be oxidised by oxygen in acidic medium.



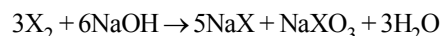
- (iv) **Reaction with alkalis :**

Cl_2 , Br_2 and I_2 behave similarly when treated with alkali (They undergo disproportionation reaction)

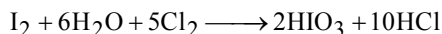
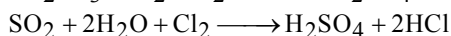
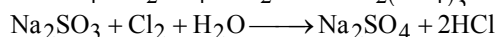
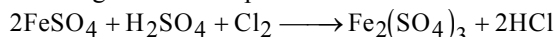
- (a) **Cold and dilute alkali :**



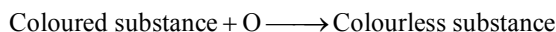
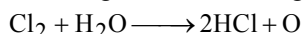
- (b) **Hot and concentrated alkali :**



(ix) Oxidising action: Examples.



(x) Bleaching action: Bleaching action is due to oxidation.



The bleaching by Cl_2 is permanent. The colour of bleached articles cannot be restored.

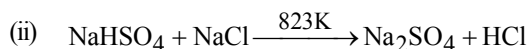
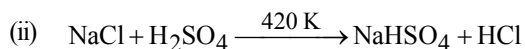
Notes : On standing, Cl_2 water loses its yellow colour due to formation of HCl and HOCl . HOCl so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

Uses:

- For bleaching pulp, cotton and textiles.
- Extraction of Au and Pt.
- Manufacture of dyes, drugs and organic compounds like CCl_4 , CHCl_3 , DDT, refrigerants, etc.
- Sterilising drinking water.

Hydrogen Chloride, HCl

Preparation:



Properties :

- It is soluble in water and ionises as:

$$\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad K_a = 10^7$$
- The aqueous solution of HCl is called hydrochloric acid. It is a strong acid as indicated by high value of K_a .
- Action with NH_3 :

$$\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$$
- Aqua regia (3 parts conc. HCl + 1 part conc HNO_3) is used to dissolve noble metals, ex: gold, platinum

$$\text{Au} + 4\text{H}^+ + \text{NO}_3^- + 4\text{Cl}^- \longrightarrow \text{AuCl}_4^- + \text{NO} + 2\text{H}_2\text{O}$$

$$3\text{Pt} + 16\text{H}^+ + 4\text{NO}_3^- + 18\text{Cl}^- \longrightarrow 3\text{PtCl}_6^{2-} + 4\text{NO} + 8\text{H}_2\text{O}$$
- It decomposes salts of weaker acids, examples

$$\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

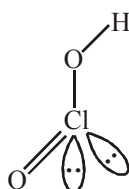
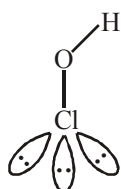
$$\text{NaHCO}_3 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{Na}_2\text{SO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2$$

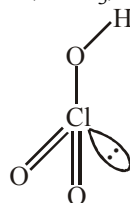
Oxoacids of Halogens

F forms only one oxoacids, HOF (due to high electronegativity and small size of F). Cl, Br and I form four series of oxoacids with formula HOX , HOXO , HOXO_2 and HOXO_3 . Structures of oxoacids of chlorine are given below:

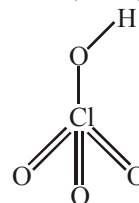
- (a) Hypochlorous acid (HOCl) (b) Chlorous acid (HClO_2)



- (c) Chloric acid (HClO_3)



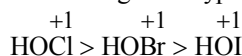
- (d) Perchloric acid (HClO_4)



Perchloric acid (no lp on Cl)

- (i) Acid strength and oxidising power

(a) Acid strength of hypohalous acids:



As electronegativity of halogens decreases electron density on O increases and thus, O–H bond polarity decreases thereby decreasing the acid strength.

(b) Oxidising power of hypohalous acids:



As size of halogen increases thermal stability of O–X bond also increases thereby decreasing the oxidising power.

- (ii) (a) Acid strength of perhalic acids



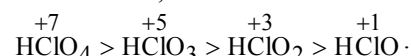
As electronegativity of halogen decreases, tendency of XO_3 to withdraw e^- s of O–H bond towards itself decreases thereby decreasing the acid strength.

(b) Oxidising power of perhalates



It is on the basis of their electrode potential values.

- (iii) Acid strength of oxoacids of same halogen in different oxidation states. It increases with increase in oxidation number of X-atom i.e.,



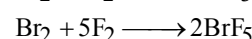
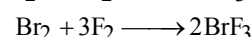
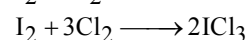
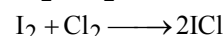
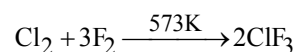
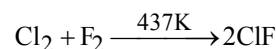
It is on the basis of the stability of the anion formed after the removal of proton. Greater the no. of O-atoms in the anion, greater is the dispersal of negative charge and hence, greater is the stability of the anion.

Interhalogen Compounds

They are compounds of two different halogens. They have compositions like XX' , XX'_3 , XX'_5 and XX'_7 where X is the halogen of larger size and X' is halogen of smaller size and X is more electropositive than X' .

Fluorine being smallest and most electronegative element forms the maximum number of interhalogen compounds.

Preparation:



Note: The less electronegative halogen is always written first.

Properties:

- They are covalent and diamagnetic in nature.
- Except ClF which is a gas, rest all are volatile solids or liquids.

- (iii) They are more reactive than halogens (except F_2) because the $X-X'$ bond is weaker than $X-X$ bond.
- (iv) $XX' + H_2O \longrightarrow HX' + HOX$
- (v) The XX'_3 compounds have bent T-shape, XX'_5 compounds square pyramidal and XX'_7 has pentagonal bipyramidal structure.

GROUP 18 ELEMENTS

It includes :

Helium (He)
Neon (Ne)
Argon (Ar)
Krypton (Kr)
Xenon (Xe)
Radon (Rn)

Because of their inert nature, they are termed noble gases.

Some **atomic, physical and chemical** properties are discussed as follows:

Atomic Properties

(i) Electronic configuration

Their general electronic configuration is ns^2np^6 . He has configuration of $1s^2$

(ii) Ionisation enthalpy

Due to stable electronic configuration, they have very high ionisation enthalpy. Ionisation enthalpy decreases down the group with increase in atomic size.

(iii) Atomic radii

The atomic radii are the largest in their respective periods. This is because they have van der waal's radii while others have covalent radii and van der waal's radii are larger than covalent radii. Down the group, atomic radii increases due to increase in number of shells.

(iv) Electron gain enthalpy

Due to their stable electronic configurations, they have no tendency to accept e^- and thus, they have large positive values of electron gain enthalpy.

Physical properties:

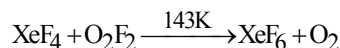
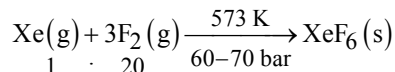
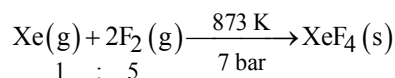
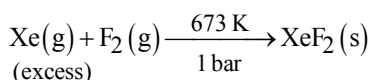
- (i) Due to their stable outer electronic configuration noble gases are monoatomic
- (ii) They are colourless, odourless and tasteless.
- (iii) Due to weak dispersion forces holding the atoms together noble gases have low M. pts. and B.pts. (He has the lowest b.pt of any known substance)
- (iv) Due to weak van der Waal's forces holding the atoms together noble gases cannot be liquefied easily. Down the group, ease of liquifaction increases.
- (v) They are sparingly soluble in water.

Chemical properties :

- (i) Noble gases are least reactive due to:
(a) stable outer shell electronic configuration.
(b) high ionisation energy and more positive electron gain enthalpy.
- (ii) The first compound of noble gases was prepared by Neil Bartlett by mixing PtF_6 and Xe. The compound formed was $Xe^+[PtF_6]^-$ (red colour).

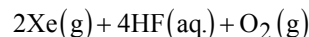
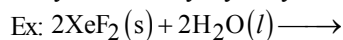
XENON-FLUORINE COMPOUNDS:

Preparation:

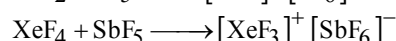
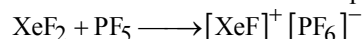


Properties

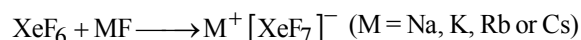
- (i) XeF_2 , XeF_4 and XeF_6 are colourless crystalline solids and powerful fluorinating agents.
- (ii) They are readily hydrolysed even with traces of water.



- (iii) Reactions with fluoride ion acceptors



- (iv) Reactions with fluoride ion donors



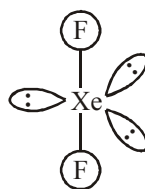
Structures of fluorides of Xe:

XeF_2 is linear, XeF_4 is square planar and XeF_6 is distorted octahedral as shown below:

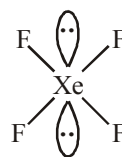
(a) XeF_2

(b) XeF_4

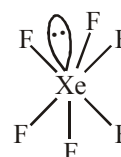
(c) XeF_6



Linear



Square planar



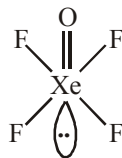
Distorted octahedral

Xenon-Oxygen Compounds

Preparation :

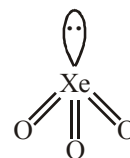
- (i) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
- (ii) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
- (iii) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$
- (iv) $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

Structures :



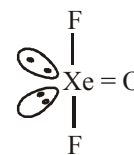
$XeOF_4$

Square pyramidal
(sp^3d^2)



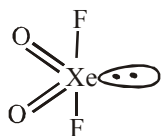
XeO_3

trigonal pyramidal
(sp^3)

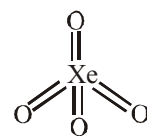


$XeOF_2$

T-shaped
(sp^3d)



XeO_2F_2
See-Saw
(sp^3d)



XeO_4
Tetrahedral
(sp^3)

CONCEPT MAP

THE p-BLOCK ELEMENTS (GROUP 15, 16, 17 AND 18)

Group 15 Elements

- **Elements** : N, P, As, Sb and Bi
- **Electronic configuration** : $ns^2 np^3$
- **Oxidation states** : Common oxidation states are -3, +3 and +5
- **Hydrides** : Form hydrides of type MH_3 , NH_3 , PH_3 , AsH_3 , SbH_3 and BiH_3
- Basic character decreases
Thermal stability decreases
Reducing nature increases
Bond angle decreases
- **Oxides** : Form oxides of type M_2O_3 , M_2O_4 and M_2O_5 . Acidic character of oxides decreases down the group
- **Halides** : Form halides of type EX_3 and EX_5

Group 16 Elements

- **Elements** : O, S, Se, Te and Po
- **Electronic configuration** : $ns^2 np^4$
- **Oxidation states** : Oxygen shows commonly -2 and also shows +2 and +1 in OF_2 and O_2F_2 respectively. S, Se, Te and Po show +2, +4 and +6 O.S.
- 1^{st} IE of group 16 elements is lower than that of group 15 elements.
- **Hydrides** : Form Hydrides of type H_2X
- * Bond angle of hydrides decreases from H_2O to H_2Po
- * The volatility of hydrides increases from H_2O to H_2S
- * Acidic strength increases from H_2O to H_2Te
- * Covalent character increases from O to Po
- **Oxides** : Form oxides of type EO_2 and EO_3
- Acidic property increases from S to Te oxides
- **Halides** : Form halides of type EX_2 , EX_4 , EX_6 and E_2X_2
- Stability of halides decreases in order $F > Cl > Br > I$

Group 17 Elements

- **Elements** : F, Cl, Br, I, At
- **Electronic configuration** : $ns^2 np^5$
- **Oxidation states** : Fluorine show 1, 0, 5 other shows +1, +3, +5 and +7
- **Reaction with metals** :
Ionic character : $MF > MCl > MBr > MI$
- **Displacement reaction** :
F replaces Cl, Br and I, Cl replaces Br and I
- **Oxo-acids of halogens** :
* Acid-character of oxo-acids of same halogen increases with increase in O.S.
* Oxidising power : $HOCl > HOBr > HOI$
* Thermal stability
 $HOCl < HClO_2 < HClO_3 < HClO_4$
- **Interhalogen compounds** :
* Compounds of halogens with themselves.
* These are covalent compounds
* More reactive than halogens except F due to weaker A-X bond than X-X bond.

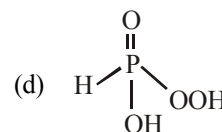
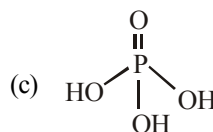
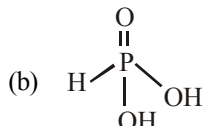
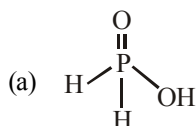
Group 18 Elements

- **Elements** : He, Ne, Ar, Kr, Xe and Rn
- **Electronic configuration** : $ns^2 np^6$ except He ($1s^2$)
- Least reactive due to stable inert gas configuration and due to high I.E. and more positive electron gain enthalpy.
- Xe Forms 3 binary fluorides XeF_2 , XeF_4 and XeF_6 . These are powerful fluorinating agents.
- The only oxide of Xe is XeO_3

EXERCISE - 1

Conceptual Questions

- The gas used in air ships is :
(a) He (b) Ne (c) Ar (d) Xe
- When orthophosphoric acid is heated to 600°C , the product formed is
(a) PH_3 (b) P_2O_5 (c) H_3PO_3 (d) HPO_3
- Which one has the lowest boiling point ?
(a) NH_3 (b) PH_3 (c) AsH_3 (d) SbH_3
- Least stable oxide of chlorine is :
(a) Cl_2O (b) ClO_2 (c) Cl_2O_7 (d) ClO_3
- Which of the following statements is not correct for nitrogen?
(a) Its electronegativity is very high
(b) d -orbitals are available for bonding
(c) It is a typical non-metal
(d) Its molecular size is small
- P_2O_5 is heated with water to give
(a) hypophosphorous acid (b) phosphorous acid
(c) hypophosphoric acid (d) orthophosphoric acid
- The gas not absorbed by coconut charcoal is :
(a) He (b) Ne (c) Ar (d) Kr
- PCl_3 reacts with water to form
(a) PH_3 (b) H_3PO_4 and HCl
(c) POCl_3 (d) H_3PO_4
- $\text{PH}_4\text{I} + \text{NaOH}$ forms
(a) PH_3 (b) NH_3 (c) P_4O_6 (d) P_4O_{10}
- Pure nitrogen is prepared in the laboratory by heating a mixture of
(a) $\text{NH}_4\text{OH} + \text{NaCl}$ (b) $\text{NH}_4\text{NO}_3 + \text{NaCl}$
(c) $\text{NH}_4\text{Cl} + \text{NaOH}$ (d) $\text{NH}_4\text{Cl} + \text{NaNO}_2$
- Sugarcane on reaction with nitric acid gives
(a) CO_2 and SO_2 (b) $(\text{COOH})_2$
(c) HCOOH (d) No reaction occurs
- The acid which cannot be kept in glass bottles is :
(a) HCl (b) HBr (c) HF (d) HI
- Nitrogen is relatively inactive element because
(a) its atom has a stable electronic configuration
(b) it has low atomic radius
(c) its electronegativity is fairly high
(d) dissociation energy of its molecule is fairly high
- H_3PO_2 is the molecular formula of an acid of phosphorus. Its name and basicity respectively are
(a) phosphorus acid and two
(b) hypophosphorous acid and two
(c) hypophosphorous acid and one
(d) hypophosphoric acid and two
- As compared to nitrogen, oxygen is
(a) less electronegative and less reactive
(b) more electronegative and less reactive
(c) more electronegative and more reactive
(d) less electronegative and more reactive
- The structural formula of hypophosphorous acid is



- With which of the given pairs CO_2 resembles?
(a) $\text{HgCl}_2, \text{C}_2\text{H}_2$ (b) $\text{HgCl}_2, \text{SnCl}_4$
(c) $\text{C}_2\text{H}_2, \text{NO}_2$ (d) N_2O and NO_2
- The number of hydrogen atom(s) attached to phosphorus atom in hypophosphorous acid is
(a) three (b) one (c) two (d) zero
- Nitrogen dioxide cannot be obtained by heating :
(a) KNO_3 (b) $\text{Pb}(\text{NO}_3)_2$ (c) $\text{Cu}(\text{NO}_3)_2$ (d) AgNO_3
- Which of the following has the highest $p\pi - p\pi$ bonding tendency ?
(a) N (b) P (c) As (d) Sb
- Concentrated sulphuric acid is always diluted by adding
(a) water to acid
(b) alcohol to acid
(c) acid to water
(d) distilled water to acid
- Most acidic oxide among the following is –
(a) N_2O_5 (b) P_2O_5 (c) N_2O_4 (d) As_2O_3
- Nitrogen reacts with calcium and carbon to give –
(a) calcium nitride (b) calcium cyanide
(c) calcium cyanamide (d) calcium nitrate
- The most efficient agent for the absorption of SO_3 is :
(a) 80% H_2SO_4 (b) 98% H_2SO_4
(c) 50% H_2SO_4 (d) 20% $\text{H}_2\text{S}_2\text{O}_7$
- $\text{NH}_4\text{ClO}_4 + \text{HNO}_3 (\text{dil.}) \longrightarrow \text{HClO}_4 + [\text{X}]$
 $[\text{X}] \xrightarrow{\Delta} \text{Y}(\text{g})$
 $[\text{X}]$ and $[\text{Y}]$ are respectively –
(a) NH_4NO_3 & N_2O (b) NH_4NO_2 & N_2
(c) HNO_4 & O_2 (d) None of these
- NH_3 gas can be dried by ?
(a) conc. H_2SO_4 (b) P_2O_5
(c) CaO (d) CaCl_2
- In Haber's process for the manufacture of NH_3 :
(a) finely divided nickel is used as a catalyst
(b) finely divided iron is used as a catalyst
(c) finely divided molybdenum is used as a catalyst
(d) no catalyst is necessary
- Chlorine upon reaction with NaOH in cold yields:
(a) $\text{NaCl}, \text{NaClO}, \text{H}_2\text{O}$ (b) $\text{NaCl}, \text{NaClO}_3, \text{H}_2\text{O}$
(c) $\text{NaClO}, \text{NaClO}_3, \text{H}_2\text{O}$ (d) $\text{NaCl}, \text{H}_2\text{O}$
- Ammonia on reaction with hypochlorite anion can form :
(a) NO (b) N_2H_4
(c) NH_4Cl (d) Both (b) and (c)
- How many bonding electron pairs are there in white phosphorus ?
(a) 2 (b) 4 (c) 3 (d) 5
- Nitrogen is obtained when NaNO_2 reacts with :
(a) NH_4Cl (b) NH_4NO_3
(c) $(\text{NH}_4)_2\text{CO}_3$ (d) NH_4OH

32. The sides of safety matches contains :
 (a) red phosphorous + sand powder
 (b) P_4S_3
 (c) $Ca_3(PO_4)_2$ + glass pieces
 (d) $KClO_3$, KNO_3 , sulphur + antimony
33. One mole of magnesium nitride on reaction with an excess of water gives
 (a) one mole of NH_3 (b) two moles of NH_3
 (c) one mole of HNO_3 (d) two moles of HNO_3
34. The bonds present in N_2O_5 are :
 (a) only ionic (b) covalent and coordinate
 (c) only covalent (d) covalent and ionic
35. Which of the following oxides of nitrogen is a coloured gas?
 (a) N_2O (b) NO (c) N_2O_5 (d) NO_2
36. One mole of calcium phosphide on reaction with excess water gives
 (a) one mole of phosphine
 (b) two moles of phosphoric acid
 (c) two moles of phosphine
 (d) one mole of phosphorus pentoxide
37. Which of the following is not a chalcogen :
 (a) Se (b) O (c) S (d) Na
38. The number of P – O – P bonds in cyclic metaphosphoric acid is
 (a) zero (b) two (c) three (d) four
39. Nitrogen is obtained by the thermal decomposition of :
 (a) NH_4NO_2 (b) NH_4NO_3
 (c) $AgNO_3$ (d) $Pb(NO_3)_2$
40. The gases respectively absorbed by alkaline pyrogallol and oil of cinnamon are
 (a) O_3 and CH_4 (b) O_2 and O_3
 (c) SO_2 and CH_4 (d) N_2O and O_3
41. It is possible to obtain oxygen from air by fractional distillation because
 (a) oxygen is in a different group of the periodic table from nitrogen
 (b) oxygen is more reactive than nitrogen
 (c) oxygen has higher b.p. than nitrogen
 (d) oxygen has a lower density than nitrogen.
42. Which would quickly absorb oxygen ?
 (a) Alkaline solution of pyrogallol
 (b) Conc. H_2SO_4
 (c) Lime water
 (d) Alkaline solution of $CuSO_4$
43. Which one of the following is a correct statement :
 (a) all metal nitrates are insoluble in water
 (b) solubility depends on temperature
 (c) all metal nitrates are soluble in water
 (d) all metal nitrates are soluble in alcohol
44. Polyanion formation is maximum in
 (a) nitrogen (b) oxygen
 (c) sulphur (d) boron
45. The acid which has a peroxy linkage is
 (a) sulphurous acid (b) pyrosulphuric acid
 (c) dithionic acid (d) caro's acid
46. By passing H_2S gas in acidified $KMnO_4$ solution, we get
 (a) S (b) K_2S (c) MnO_2 (d) K_2SO_3
47. In the manufacture of bromine from sea water, the mother liquor containing bromides is treated with
 (a) CO_2 (b) I_2 (c) Cl_2 (d) H_2O
48. Oxidation of thiosulphate by iodine gives
 (a) tetrathionate ion (b) sulphide ion
 (c) sulphate ion (d) sulphite ion
49. When PbO_2 reacts with conc. HNO_3 the gas evolved is
 (a) NO_2 (b) O_2 (c) N_2 (d) N_2O
50. The compound which gives off oxygen on moderate heating is :
 (a) cupric oxide (b) mercuric oxide
 (c) zinc oxide (d) aluminium oxide
51. The oxide which form dimer is :
 (a) N_2O_5 (b) N_2O (c) NO_2 (d) N_2O_3
52. On electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be
 (a) hydrogen (b) oxygen
 (c) hydrogen sulphide (d) sulphur dioxide.
53. Which compound is used in photography?
 (a) Na_2SO_5 (b) $Na_2S_2O_8$
 (c) $Na_2S_2O_6$ (d) $Na_2S_2O_3$
54. Which among the following is strongest acid?
 (a) $H(ClO)O_2$ (b) $H(ClO)O_3$
 (c) $H(ClO)O^-$ (d) $H(ClO)$
55. Sodium thiosulphate is a
 (a) reducing agent (b) oxidising agent
 (c) complexing agent (d) bleaching agent
56. A gas that cannot be collected over water is :
 (a) N_2 (b) O_2 (c) SO_2 (d) PH_3
57. Sodium thiosulphate is prepared by
 (a) reducing Na_2SO_4 solution with H_2S
 (b) boiling Na_2SO_3 solution with S in alkaline medium
 (c) neutralising $H_2S_2O_3$ solution with NaOH
 (d) boiling Na_2SO_3 solution with S in acidic medium
58. Which of the following is not oxidized by O_3 ?
 (a) KI (b) $FeSO_4$ (c) $KMnO_4$ (d) K_2MnO_4
59. Laughing gas is prepared by heating :
 (a) $NH_4Cl + NaNO_3$ (b) NH_4Cl
 (c) $(NH_4)_2SO_4$ (d) NH_4NO_2
60. $4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + X$ In the above reaction, the product X is
 (a) NO_2 (b) N_2O_3 (c) N_2O_4 (d) N_2O_5
61. In the manufacture of bromine from sea water, the mother liquor containing bromides is treated with
 (a) carbon dioxide (b) chlorine
 (c) iodine (d) sulphur dioxide
62. Which of the following species has four lone pairs of electrons?
 (a) I (b) O^- (c) Cl^- (d) He
63. A solution of potassium bromide is treated with each of the following. Which one would liberate bromine ?
 (a) Hydrogen iodide (b) Sulphur dioxide
 (c) Chlorine (d) Iodine
64. Which one of the following oxides of chlorine is obtained by passing dry chlorine over silver chlorate at $90^\circ C$?
 (a) Cl_2O (b) ClO_3 (c) ClO_2 (d) ClO_4
65. Ammonia and sodium hypochlorite reacts to produce
 (a) NH_2OH (b) NH_2NH_2
 (c) N_2 (d) NO

66. Which one is the correct order of the size of iodine species?
 (a) $I > I^+ > I^-$ (b) $I > I^- > I^+$
 (c) $I^+ > I^- > I$ (d) $I^- > I > I^+$
67. A one litre flask is full of brown bromine vapours. The intensity of brown colour of vapours will not decrease appreciably on adding to the flask some
 (a) pieces of marble (b) animal charcoal powder
 (c) carbon tetrachloride (d) carbon disulphide
68. Which of the following is the best description for the behaviour of bromine in the reaction given below?
 $H_2O + Br_2 \rightarrow HOBr + HBr$
 (a) Proton acceptor only
 (b) Both oxidized and reduced
 (c) Oxidized only
 (d) Reduced only
69. P_2O_5 is an anhydride of
 (a) HPO_3 (b) H_3PO_4
 (c) H_3PO_3 (d) $H_2P_2O_7$
70. The correct order of the thermal stability of hydrogen halides (H-X) is
 (a) $HI > HCl < HF > HBr$ (b) $HCl < HF > HBr < HI$
 (c) $HF > HCl > HBr > HI$ (d) $HI < HBr > HCl < HF$
71. Cl_2 reacts with hot and conc. NaOH to give –
 (a) NaClO (b) NaClO₃ (c) NaClO₂ (d) NaClO₄
72. Oleum is a mixture of
 (a) $H_2SO_4 + SO_2$ (b) $H_2SO_4 + SO_3$
 (c) $H_2S_2O_3 + SO_3$ (d) $H_2S_2O_3 + SO_2$
73. Conc. HNO_3 reacts with I_2 to form :
 (a) HI (b) HOI (c) HIO₂ (d) HIO₃
74. For a given alcohol the order of reactivity of halogen acids is:
 (a) $HI > HBr > HCl$ (b) $HCl > HBr < HI$
 (c) $HI < HBr < HCl$ (d) $HCl < HI < HBr$
75. Which of the following has maximum bond energy?
 (a) Cl_2 (b) F_2 (c) Br_2 (d) I_2
76. Which of the following product is formed by the reaction of sulphur dioxide with chlorine in presence of sunlight :
 (a) SO_2Cl (b) SO_2Cl_2 (c) $SOCl_2$ (d) SO_3Cl
77. Fluorine exhibits an oxidation state of only –1 because
 (a) it can readily accept an electron
 (b) it is very strongly electronegative
 (c) it is a non-metal
 (d) it belongs to halogen family
78. In XeF_2 , XeF_4 , XeF_6 the number of lone pairs on Xe are respectively
 (a) 2, 3, 1 (b) 1, 2, 3 (c) 4, 1, 2 (d) 3, 2, 1.
79. Formula for tear gas is :
 (a) $COCl_2$ (b) CCl_3NO_2
 (c) N_2O (d) none of these
80. Which of the following is least polarisable ?
 (a) Ne (b) He (c) Xe (d) Kr
81. End-product of the hydrolysis of XeF_6 is
 (a) XeF_4O (b) XeF_2O_2 (c) XeO_3 (d) XeO_3^-
82. For advertisement, the coloured discharge tubes contain :
 (a) He (b) Ne (c) Ar (d) Kr
83. Noble gases do not react with other elements because
 (a) they have completely filled valence shell (ns^2np^6)
 (b) the sizes of their atoms are very small
 (c) they are not found in abundance
 (d) they are monoatomic
84. Hydrolysis of NCl_3 gives NH_3 and X. Which of the following is X ?
 (a) $HClO_4$ (b) $HClO_3$ (c) $HOCl$ (d) $HClO_2$
85. Which one of the following noble gases is not found in the atmosphere
 (a) Rn (b) Kr (c) Ne (d) Ar
86. Noble gases are group of elements which exhibit
 (a) high chemical activity
 (b) low chemical activity
 (c) minimum electronegativity
 (d) paramagnetic properties
87. PbO_2 on reaction with conc. HNO_3 gives
 (a) $PbNO_2 + O_2$
 (b) $Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2$
 (c) $Pb + N_2 + H_2O$
 (d) $Pb(OH)_2 + N_2O$
88. In nitrogen family, the H-M-H bond angle in the hydrides gradually becomes closer to 90° on going from N to Sb. This shows that gradually
 (a) The basic strength of the hydrides increases
 (b) Almost pure p-orbitals are used for M-H bonding
 (c) The bond energies of M-H bonds increase
 (d) The bond pairs of electrons become nearer to the central atom
89. Perdisulphuric acid has the following bond
 (a) $O \leftarrow O = O$ (b) $\leftarrow O = O \rightarrow$
 (c) $> O \rightarrow O <$ (d) $-O-O-$
90. Which one of the following statements regarding helium is incorrect ?
 (a) It is used to produce and sustain powerful superconducting magnets.
 (b) It is used as a cryogenic agent for carrying out experiments at low temperatures.
 (c) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable.
 (d) It is used in gas-cooled nuclear reactors.
91. The formation of $O_2^+[PtF_6]^-$ is the basis for the formation of xenon fluorides. This is because
 (a) O_2 and Xe have comparable sizes
 (b) both O_2 and Xe are gases
 (c) O_2 and Xe have comparable ionisation energies
 (d) Both (a) and (c)
92. The species not containing peroxide ions is :
 (a) H_2O_2 (b) PbO_2 (c) SrO_2 (d) BaO_2
93. Which one of the following orders correctly represents the increasing acid strengths of the given acids?
 (a) $HOClO < HOCl < HOClO_3 < HOClO_2$
 (b) $HOClO_2 < HOClO_3 < HOClO < HOCl$
 (c) $HOClO_3 < HOClO_2 < HOClO < HOCl$
 (d) $HOCl < HOClO < HOClO_2 < HOClO_3$
94. Which one of the following arrangements does not give the correct picture of the trends indicated against it ?
 (a) $F_2 > Cl_2 > Br_2 > I_2$: Oxidizing power
 (b) $F_2 > Cl_2 > Br_2 > I_2$: Electron gain enthalpy
 (c) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
 (d) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity.

95. In the case of alkali metals, the covalent character decreases in the order:
 (a) $MF > MCl > MBr > MI$
 (b) $MF > MCl > MI > MBr$
 (c) $MI > MBr > MCl > MF$
 (d) $MCl > MI > MBr > MF$
96. Among the following which is the strongest oxidising agent?
 (a) Br_2 (b) I_2 (c) Cl_2 (d) F_2
97. The correct order of increasing bond angles in the following species are :
 (a) $Cl_2O < ClO_2 < ClO_2^-$ (b) $ClO_2 < Cl_2O < ClO_2^-$
 (c) $Cl_2O < ClO_2^- < ClO_2$ (d) $ClO_2^- < Cl_2O < ClO_2$
98. Oxidation states of P in $H_4P_2O_5$, $H_4P_2O_6$, and $H_4P_2O_7$, are respectively:
 (a) +3, +5, +4 (b) +5, +3, +4
 (c) +5, +4, +3 (d) +3, +4, +5
99. Which one of the following compounds is a peroxide ?
 (a) KO_2 (b) BaO_2 (c) MnO_2 (d) NO_2
100. How many bridging oxygen atoms are present in P_4O_{10} ?
 (a) 5 (b) 6 (c) 4 (d) 2

EXERCISE - 2

Applied Questions

1. In which of the following, NH_4OH is not used?
 (a) Tollen's reagent
 (b) Nessler's reagent
 (c) Group reagent for the analysis of IV group basic radicals
 (d) Group reagent for the analysis of III group basic radicals
2. Which of the following oxides will be the least acidic?
 (a) As_4O_6 (b) As_4O_{10}
 (c) P_4O_{10} (d) P_4O_6
3. Noble gases are used in discharge tubes to give different colours. Reddish orange glow is due to
 (a) Ar (b) Ne (c) Xe (d) Kr
4. Which of the following species has the highest dipole moment?
 (a) NH_3 (b) PH_3
 (c) AsH_3 (d) SbH_3
5. Which of the following bonds will be most polar?
 (a) N-Cl (b) O-F
 (c) N-F (d) N-N
6. When Br_2 is treated with aqueous solutions of NaF, NaCl and NaI separately
 (a) F_2 , Cl_2 and I_2 are liberated
 (b) only F_2 and Cl_2 are liberated
 (c) only I_2 is liberated
 (d) only Cl_2 is liberated
7. Regarding F^- and Cl^- which of the following statements is/are correct?
 (i) Cl^- can give up an electron more easily than F^-
 (ii) Cl^- is a better reducing agent than F^-
 (iii) Cl^- is smaller in size than F^-
 (iv) F^- can be oxidized more readily than Cl^-
 (a) (i) and (ii) (b) (i), (ii) and (iv)
 (c) (iii) and (iv) (d) Only (i)
8. The p-block element that forms predominantly basic oxide is
 (a) N (b) P (c) As (d) Bi
9. In case of nitrogen, NCl_3 is possible but not NCl_5 while in case of phosphorus, PCl_3 as well as PCl_5 are possible. It is due to
 (a) availability of vacant d orbitals in P but not in N
 (b) lower electronegativity of P than N
 (c) lower tendency of H-bond formation in P than N
 (d) occurrence of P in solid while N in gaseous state at room temperature.
10. In which one of the following oxides of nitrogen, one nitrogen atom is not directly linked to oxygen?
 (a) NO (b) N_2O_4 (c) N_2O (d) N_2O_3
11. The ease of liquefaction of noble gases increases in the order
 (a) $He < Ne < Ar < Kr < Xe$ (b) $Xe < Kr < Ne < Ar < He$
 (c) $Kr < Xe < He < Ne < Ar$ (d) $Ar < Kr < Xe < Ne < He$
12. Which of the following represents correct sequence of decreasing acidic character of oxides?
 (a) $N_2O_5 > NO > N_2O$ (b) $MnO > MnO_2 > MnO_4^-$
 (c) $Cr_2O_3 > CrO_4^{2-}$ (d) $Fe_2O_3 > FeO > Fe_3O_4$
13. The solubility of silver bromide in hypo solution is due to the formation of :
 (a) Ag_2SO_3 (b) $Ag_2S_2O_3$
 (c) Ag^+ (d) NH_4^+
14. The correct decreasing order of basic strength is:
 (a) $AsH_3 > SbH_3 > PH_3 > NH_3$
 (b) $SbH_3 > AsH_3 > PH_3 > NH_3$
 (c) $NH_3 > PH_3 > AsH_3 > SbH_3$
 (d) $PH_3 > AsH_3 > SbH_3 > NH_3$
15. Oxygen and sulphur both are the members of the same group in periodic table but H_2O is liquid while H_2S is gas because
 (a) molecular weight of water is more
 (b) electronegativity of sulphur is more
 (c) H_2S is weak acid
 (d) water molecules are having weak hydrogen bonds between them
16. Euchlorine is a mixture of
 (a) Cl_2 and SO_2 (b) Cl_2 and ClO_2
 (c) Cl_2 and CO (d) None of these
17. The correct order of heat of formation of halogen acids is
 (a) $HI > HBr > HCl > HF$ (b) $HF > HCl > HBr > HI$
 (c) $HCl > HF > HBr > HI$ (d) $HCl > HBr > HF > HI$
18. Which of the following acts as pickling agent?
 (a) HNO_3 (b) HCl (c) H_2SO_4 (d) HNO_2
19. KF combines with HF to form KHF_2 . The compound contains the species.
 (a) K^+ , F^- and H^+ (b) K^+ , F^- and HF
 (c) K^+ and $[HF_2]^-$ (d) $[KHF]^{+}$ and F^-
20. Which of the following iodide is least stable and has doubtful existence?
 (a) Cl_4 (b) GeI_4 (c) SnI_4 (d) PbI_4
21. In the preparation of sulphuric acid, V_2O_5 is used in the reaction, which is
 (a) $S + O_2 \longrightarrow SO_2$ (b) $SO_2 + H_2O \longrightarrow H_2SO_4$
 (c) $2SO_2 + O_2 \longrightarrow 2SO_3$ (d) $N_2 + 3H_2 \longrightarrow 2NH_3$

22. In compounds of type ECl_3 , where $\text{E} = \text{B}, \text{P}, \text{As}$ or Bi , the angles $\text{Cl} - \text{E} - \text{Cl}$ for different E are in the order
 (a) $\text{B} > \text{P} = \text{As} = \text{Bi}$ (b) $\text{B} > \text{P} > \text{As} > \text{Bi}$
 (c) $\text{B} < \text{P} = \text{As} = \text{Bi}$ (d) $\text{B} < \text{P} < \text{As} < \text{Bi}$
23. Match List - I (substances) with List - II (processes) employed in the manufacture of the substances and select the correct option.
- | List - I
Substances | List - II
Processes |
|------------------------|-------------------------|
| (A) Sulphuric acid | (i) Haber's process |
| (B) Steel | (ii) Bessemer's process |
| (C) Sodium hydroxide | (iii) Leblanc process |
| (D) Ammonia | (iv) Contact process |
- Options:**
- | | | | |
|----------|-------|-------|-------|
| (A) | (B) | (C) | (D) |
| (a) (iv) | (ii) | (iii) | (i) |
| (b) (i) | (iv) | (ii) | (iii) |
| (c) (i) | (ii) | (iii) | (iv) |
| (d) (iv) | (iii) | (ii) | (i) |
24. Which of the following statements is not valid for oxoacids of phosphorus?
 (a) Orthophosphoric acid is used in the manufacture of triple superphosphate.
 (b) Hypophosphorous acid is a diprotic acid.
 (c) All oxoacids contain tetrahedral four coordinated phosphorus.
 (d) All oxoacids contain atleast one $\text{P} = \text{O}$ and one $\text{P} - \text{OH}$ group.
25. Sulphur trioxide can be obtained by which of the following reaction :
 (a) $\text{CaSO}_4 + \text{C} \xrightarrow{\Delta}$ (b) $\text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\Delta}$
 (c) $\text{S} + \text{H}_2\text{SO}_4 \xrightarrow{\Delta}$ (d) $\text{H}_2\text{SO}_4 + \text{PCl}_5 \xrightarrow{\Delta}$
26. Which one of the following reactions of xenon compounds is not feasible?
 (a) $3\text{XeF}_4 + 6\text{H}_2\text{O} \longrightarrow 2\text{Xe} + \text{XeO}_3 + 12\text{HF} + 1.5\text{O}_2$
 (b) $2\text{XeF}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Xe} + 4\text{HF} + \text{O}_2$
 (c) $\text{XeF}_6 + \text{RbF} \longrightarrow \text{Rb}[\text{XeF}_7]$
 (d) $\text{XeO}_3 + 6\text{HF} \longrightarrow \text{XeF}_6 + 3\text{H}_2\text{O}$
27. Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 gives –
 (a) $\text{Na}_2\text{S}_4\text{O}_6$ (b) NaHSO_4
 (c) NaCl (d) NaOH
28. The reaction of P_4 with X leads selectively to P_4O_6 . The X is
 (a) Dry O_2
 (b) A mixture of O_2 and N_2
 (c) Moist O_2
 (d) O_2 in the presence of aqueous NaOH
29. Extra pure N_2 can be obtained by heating
 (a) NH_3 with CuO (b) NH_4NO_3
 (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (d) $\text{Ba}(\text{N}_3)_2$
30. The shape of XeO_2F_2 molecule is
 (a) trigonal bipyramidal (b) square planar
 (c) tetrahedral (d) see-saw
31. Which of the following oxide is amphoteric ?
 (a) SnO_2 (b) CaO (c) SiO_2 (d) CO_2
32. In which of the following compounds, nitrogen exhibits highest oxidation state ?
 (a) N_2H_4 (b) NH_3 (c) N_3H (d) NH_2OH
33. Identify the incorrect statement among the following.
 (a) Br_2 reacts with hot and strong NaOH solution to give NaBr and H_2O .
 (b) Ozone reacts with SO_2 to give SO_3 .
 (c) Silicon reacts with $\text{NaOH}(\text{aq})$ in the presence of air to give Na_2SiO_3 and H_2O .
 (d) Cl_2 reacts with excess of NH_3 to give N_2 and HCl .
34. Regular use of which of the the following fertilizers increases the acidity of soil?
 (a) Ammonium sulphate (b) Potassium nitrate
 (c) Urea (d) Superphosphate of lime.
35. Which of the following has maximum number of lone pairs associated with Xe ?
 (a) XeF_4 (b) XeF_6 (c) XeF_2 (d) XeO_3
36. Which of the following statements regarding sulphur is incorrect?
 (a) S_2 molecule is paramagnetic.
 (b) The vapours at 200°C consists mostly of S_8 rings.
 (c) At 600°C the gas mainly consists of S_2 molecules.
 (d) The oxidation state of sulphur is never less than +4 in its compounds.
37. In nitrogen family, the $\text{H}-\text{M}-\text{H}$ bond angle in the hydrides gradually becomes closer to 90° on going from N to Sb . This shows that gradually
 (a) The basic strength of the hydrides increases
 (b) Almost pure p-orbitals are used for $\text{M}-\text{H}$ bonding
 (c) The bond energies of $\text{M}-\text{H}$ bonds increase
 (d) The bond pairs of electrons become nearer to the central atom
38. Which acid has $\text{P} - \text{P}$ linkage ?
 (a) Hypophosphoric acid
 (b) Pyrophosphoric acid
 (c) Metaphosphoric acid
 (d) Orthophosphoric acid
39. The no. of $\text{S}-\text{O}-\text{S}$ bonds in cyclic SO_3 is
 (a) 1 (b) 2
 (c) 3 (d) None of these
40. Which of the following fluorides does not exist?
 (a) NF_5 (b) PF_5
 (c) AsF_5 (d) SbF_5
41. Which of the following shows nitrogen with its increasing order of oxidation number?
 (a) $\text{NO} < \text{N}_2\text{O} < \text{NO}_2 < \text{NO}_3^- < \text{NH}_4^+$
 (b) $\text{NH}_4^+ < \text{N}_2\text{O} < \text{NO}_2 < \text{NO}_3^- < \text{NO}$
 (c) $\text{NH}_4^+ < \text{N}_2\text{O} < \text{NO} < \text{NO}_2 < \text{NO}_3^-$
 (d) $\text{NH}_4^+ < \text{NO} < \text{N}_2\text{O} < \text{NO}_2 < \text{NO}_3^-$
42. When Br_2 is treated with aqueous solutions of NaF , NaCl and NaI separately
 (a) F_2 , Cl_2 and I_2 are liberated
 (b) only F_2 and Cl_2 are liberated
 (c) only I_2 is liberated
 (d) only Cl_2 is liberated
43. In which one of the following oxides of nitrogen, one nitrogen atom is not directly linked to oxygen?
 (a) NO (b) N_2O_4
 (c) N_2O (d) N_2O_3
44. In which of the following, NH_4OH is not used?
 (a) Tollen's reagent
 (b) Nessler's reagent
 (c) Group reagent for the analysis of IV group basic radicals
 (d) Group reagent for the analysis of III group basic radicals
45. The geometry of XeF_6 is
 (a) planar hexagon
 (b) regular octahedron
 (c) distorted octahedron
 (d) square bipyramid

46. Noble gases are used in discharge tubes to give different colours. Reddish orange glow is due to
 (a) Ar (b) Ne
 (c) Xe (d) Kr
47. The oxidation state of phosphorus in cyclotrimetaphosphoric acid is
 (a) +3 (b) +5
 (c) -3 (d) +2
- DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these questions contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
- (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- (c) Statement-1 is True, Statement-2 is False
- (d) Statement-1 is False, Statement-2 is True
48. **Statement-1** : White phosphorus is more reactive than red phosphorus.
Statement-2 : Red phosphorus consists of P_4 tetrahedral units linked to one another to form linear chains.
49. **Statement-1** : When a metal is treated with conc. HNO_3 it generally yields a nitrate, NO_2 and H_2O .
Statement-2 : Conc. HNO_3 reacts with metal and first produces a metal nitrate and nascent hydrogen. The nascent hydrogen then further reduces HNO_3 to NO_2 .
50. **Statement-1** : Bond angle of H_2S is smaller than H_2O .
Statement-2 : Electronegativity of the central atom increases, bond angle decreases.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because
 (a) H_2SO_4 reduces HI to I_2 (b) HI is of violet colour
 (c) HI gets oxidised to I_2 (d) HI changes to HIO_3
 - In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dil. HCl, a black precipitate is obtained. On boiling the precipitate with dil. HNO_3 , it forms a solution of blue colour. Addition of excess of aqueous solution of ammonia to this solution gives
 (a) deep blue precipitate of $Cu(OH)_2$
 (b) deep blue solution of $[Cu(NH_3)_4]^{2+}$
 (c) deep blue solution of $Cu(NO_3)_2$
 (d) deep blue solution of $Cu(OH)_2 \cdot Cu(NO_3)_2$
 - In a cyclotrimetaphosphoric acid molecule, how many single and double bonds are present?
 (a) 3 double bonds; 9 single bonds
 (b) 6 double bonds; 6 single bonds
 (c) 3 double bonds; 12 single bonds
 (d) Zero double bond; 12 single bonds
 - Which of the following elements can be involved in $p\pi - d\pi$ bonding?
 (a) Carbon (b) Nitrogen
 (c) Phosphorus (d) Boron
 - Which of the following pairs of ions are isoelectronic and isostructural?
 (a) CO_3^{2-} , NO_3^- (b) ClO_3^- , CO_3^{2-}
 (c) SO_3^{2-} , NO_3^- (d) ClO_3^- , SO_3^{2-}
 - Affinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?
 (a) HF (b) HCl
 (c) HBr (d) HI
 - Bond dissociation enthalpy of $E - H$ ($E = \text{element}$) bonds is given below. Which of the following compounds will act as the strongest reducing agent?
- | Compound | NH_3 | PH_3 | AsH_3 | SbH_3 |
|---------------------------------------|--------|--------|---------|---------|
| $\Delta_{diss} (E - H) / kJ mol^{-1}$ | 389 | 322 | 297 | 255 |
- (a) NH_3 (b) PH_3
 (c) AsH_3 (d) SbH_3
 - On heating with concentrated NaOH solution in an inert atmosphere of CO_2 , white phosphorus gives a gas. Which of the following statements is incorrect about the gas?
 (a) It is highly poisonous and has smell like rotten fish
 (b) Its solution in water decomposes in the presence of light
 (c) It is more basic than NH_3
 (d) It is less basic than NH_3
 - Which of the following acids forms three series of salts?
 (a) H_3PO_2 (b) H_3BO_3
 (c) H_3PO_4 (d) H_3PO_3
 - Strong reducing behaviour of H_3PO_2 is due to
 (a) low oxidation state of phosphorus
 (b) presence of two $-OH$ groups and one $P - H$ bond
 (c) presence of one $-OH$ group and two $P - H$ bonds
 (d) high electron gain enthalpy of phosphorus
 - On heating lead nitrate forms oxides of nitrogen and lead. The oxides formed are
 (a) N_2O , PbO (b) NO_2 , PbO
 (c) NO , PbO (d) NO , PbO_2
 - Which of the following elements does not show allotropy?
 (a) Nitrogen (b) Bismuth
 (c) Antimony (d) Arsenic
 - Maximum covalency of nitrogen is
 (a) 3 (b) 5
 (c) 4 (d) 6
 - Which of the following statements is wrong?
 (a) Single $N - N$ bond is stronger than the single $P - P$ bond.
 (b) PH_3 can act as a ligand in the formation of coordination compounds with transition elements.
 (c) NO_2 is paramagnetic in nature.
 (d) Covalency of nitrogen in N_2O_3 is four.

15. A brown ring is formed in the ring test for NO_3^- ion. It is due to the formation of
 (a) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ (b) $\text{FeSO}_4 \cdot \text{NO}_2$
 (c) $[\text{Fe}(\text{H}_2\text{O})_4(\text{NO})_2]^{2+}$ (d) $\text{FeSO}_4 \cdot \text{HNO}_3$
16. Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterised compound in +5 oxidation state. The compound is
 (a) Bi_2O_5 (b) BiF_5
 (c) BiCl_5 (d) Bi_2S_5
17. On heating ammonium dichromate and barium azide separately we get
 (a) N_2 in both the cases
 (b) N_2 with ammonium dichromate and NO with barium azide
 (c) N_2O with ammonium dichromate and N_2 with barium azide
 (d) N_2O with ammonium dichromate and NO_2 with barium azide
18. In the preparation of HNO_3 , we get NO gas by catalytic oxidation of ammonia. The moles of NO produced by the oxidation of two moles of NH_3 will be
 (a) 2 (b) 3
 (c) 4 (d) 6
19. The oxidation state of central atom in the anion of compound NaH_2PO_2 will be
 (a) +3 (b) +5
 (c) +1 (d) -3
20. Which of the following is not tetrahedral in shape?
 (a) NH_4^+ (b) SiCl_4
 (c) SF_4 (d) SO_4^{2-}
21. Which of the following are peroxoacids of sulphur?
 (a) H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_8$ (b) H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_7$
 (c) $\text{H}_2\text{S}_2\text{O}_7$ and $\text{H}_2\text{S}_2\text{O}_8$ (d) $\text{H}_2\text{S}_2\text{O}_6$ and $\text{H}_2\text{S}_2\text{O}_7$
22. Hot conc. H_2SO_4 acts as moderately strong oxidising agent. It oxidises both metals and non-metals. Which of the following element is oxidised by conc. H_2SO_4 into two gaseous products?
 (a) Cu (b) S
 (c) C (d) Zn
23. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from
 (a) -3 to +3 (b) -3 to 0
 (c) -3 to +5 (d) 0 to -3
24. In the preparation of compounds of Xe, Bartlett had taken $\text{O}_2^+ \text{PtF}_6^-$ as a base compound. This is because
 (a) both O_2 and Xe have same size.
 (b) both O_2 and Xe have same electron gain enthalpy.
 (c) both O_2 and Xe have almost same ionisation enthalpy.
 (d) both Xe and O_2 are gases.
25. In solid state PCl_5 is a
 (a) covalent solid
 (b) octahedral structure
 (c) ionic solid with $[\text{PCl}_6]^+$ octahedral and $[\text{PCl}_4]^-$ tetrahedral
 (d) ionic solid with $[\text{PCl}_4]^+$ tetrahedral and $[\text{PCl}_6]^-$ octahedral
26. Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.
- | Ion | ClO_4^- | IO_4^- | BrO_4^- |
|--|--------------------------|--------------------------|--------------------------|
| Reduction potential E° / V | $E^\circ = 1.19\text{V}$ | $E^\circ = 1.65\text{V}$ | $E^\circ = 1.74\text{V}$ |
- (a) $\text{ClO}_4^- > \text{IO}_4^- < \text{BrO}_4^-$ (b) $\text{IO}_4^- > \text{BrO}_4^- < \text{ClO}_4^-$
 (c) $\text{BrO}_4^- > \text{IO}_4^- < \text{ClO}_4^-$ (d) $\text{BrO}_4^- > \text{ClO}_4^- < \text{IO}_4^-$
27. Which of the following is isoelectronic pair?
 (a) $\text{ICl}_2, \text{ClO}_2$ (b) $\text{BrO}_2^-, \text{BrF}_2^+$
 (c) ClO_2, BrF (d) CN^-, O_3

NEET/AIPMT (2013-2017) Questions

28. Which is the strongest acid in the following : [2013]
 (a) HClO_3 (b) HClO_4
 (c) H_2SO_3 (d) H_2SO_4
29. Which of the following does not give oxygen on heating? [2013]
 (a) $\text{Zn}(\text{ClO}_3)_2$ (b) $\text{K}_2\text{Cr}_2\text{O}_7$
 (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (d) KClO_3
30. Identify the incorrect statement, regarding the molecule XeO_4 : [NEET Kar. 2013]
 (a) XeO_4 molecule is tetrahedral
 (b) XeO_4 molecule is square planar
 (c) There are four $p\pi - d\pi$ bonds
 (d) There are four $sp^3 - p, \sigma$ bonds
31. Acidity of diprotic acids in aqueous solutions increases in the order : [2014]
 (a) $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$ (b) $\text{H}_2\text{Se} < \text{H}_2\text{S} < \text{H}_2\text{Te}$
 (c) $\text{H}_2\text{Te} < \text{H}_2\text{S} < \text{H}_2\text{Se}$ (d) $\text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{S}$
32. Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by one of these compounds, but not by the other? [2015]
 (a) is a reducing agent
 (b) is soluble in water
 (c) is used as a food-preservative
 (d) forms 'acid-rain'
33. Which of the statements given below is incorrect? [2015 RS]
 (a) Cl_2O_7 is an anhydride of perchloric acid
 (b) O_3 molecule is bent
 (c) ONF is isoelectronic with O_2N^- .
 (d) OF_2 is an oxide of fluorine
34. The variation of the boiling point of the hydrogen halides is in the order $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$. [2015 RS]
 What explains the higher boiling point of hydrogen fluoride?
 (a) The electronegativity of fluorine is much higher than for other elements in the group.
 (b) There is strong hydrogen bonding between HF molecules
 (c) The bond energy of HF molecules is greater than in other hydrogen halides.
 (d) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule.

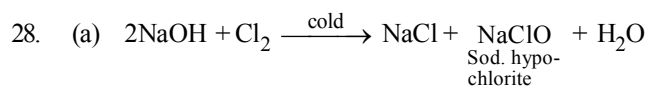
35. Strong reducing behaviour of H_3PO_2 is due to [2015 RS]
 (a) presence of one $-\text{OH}$ group and two $\text{P}-\text{H}$ bonds
 (b) high electron gain enthalpy of phosphorus
 (c) high oxidation state of phosphorus
 (d) presence of two $-\text{OH}$ groups and one $\text{P}-\text{H}$ bond.
36. Among the following, the correct order of acidity is [2016]
 (a) $\text{HClO}_3 < \text{HClO}_4 < \text{HClO}_2 < \text{HClO}$
 (b) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
 (c) $\text{HClO}_2 < \text{HClO} < \text{HClO}_3 < \text{HClO}_4$
 (d) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO} < \text{HClO}_3$
37. Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules? [2016]
 (a) $\text{I}_2 > \text{Br}_2 > \text{Cl}_2 > \text{F}_2$ (b) $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$
 (c) $\text{Br}_2 > \text{I}_2 > \text{F}_2 > \text{Cl}_2$ (d) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
38. Match the compounds given in column I with the hybridisation and shape given in column II and mark the correct option. [2016]
- | Column-I | | Column-II | |
|--------------------|--|--------------------------|--|
| 1. XeF_6 | | (i) Distorted octahedral | |
| 2. XeO_3 | | (ii) Square planar | |
| 3. XeOF_4 | | (iii) Pyramidal | |
| 4. XeF_4 | | (iv) Square pyramidal | |
- Code :
- | | 1 | 2 | 3 | 4 |
|-----|------|-------|------|-------|
| (a) | (i) | (iii) | (iv) | (ii) |
| (b) | (i) | (ii) | (iv) | (iii) |
| (c) | (iv) | (iii) | (i) | (ii) |
| (d) | (iv) | (i) | (ii) | (iii) |
39. Which is the correct statement for the given acids? [2016]
 (a) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid
 (b) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid
 (c) Both are triprotic acids
 (d) Both are diprotic acids
40. The product obtained as a result of a reaction of nitrogen with CaC_2 is [2016]
 (a) $\text{Ca}(\text{CN})_2$ (b) CaCN
 (c) CaCN_3 (d) Ca_2CN
41. Match the interhalogen compounds of column-I with the geometry in column II and assign the correct code. [2017]
- | Column-I | Column-II |
|-------------------|-----------------------------|
| 1. XX' | (i) T-shape |
| 2. XX'_3 | (ii) Pentagonal bipyramidal |
| 3. XX'_5 | (iii) Linear |
| 4. XX'_7 | (iv) Square-pyramidal |
| | (v) Tetrahedral |
- Code :
- | | 1 | 2 | 3 | 4 |
|-----|-------|-------|-------|------|
| (a) | (iii) | (i) | (iv) | (ii) |
| (b) | (v) | (iv) | (iii) | (ii) |
| (c) | (iv) | (iii) | (ii) | (i) |
| (d) | (iii) | (iv) | (i) | (ii) |
42. In which pair of ions both the species contain S – S bond?
 (a) $\text{S}_4\text{O}_6^{2-}$, $\text{S}_2\text{O}_3^{2-}$ (b) $\text{S}_2\text{O}_7^{2-}$, $\text{S}_2\text{O}_8^{2-}$ [2017]
 (c) $\text{S}_4\text{O}_6^{2-}$, $\text{S}_2\text{O}_7^{2-}$ (d) $\text{S}_2\text{O}_7^{2-}$, $\text{S}_2\text{O}_3^{2-}$

Hints & Solutions

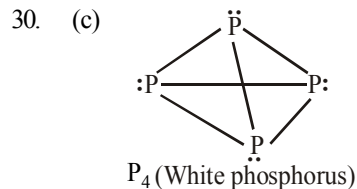
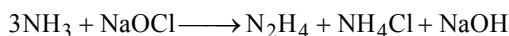
EXERCISE - 1

- (a) Hydrogen is lighter than helium but still helium is used in ballons because hydrogen is highly explosive and reactive gas. It may lead to accident.
- (d) $2\text{H}_3\text{PO}_4 \xrightarrow[-2\text{H}_2\text{O}]{600^\circ\text{C}} 2\text{HPO}_3$
- (b) The order of boiling points of the group 15 hydrides is : $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
- (b) ClO_2 is least stable. The order of stability is $\text{Cl}_2\text{O} < \text{ClO}_2 < \text{ClO}_3 < \text{Cl}_2\text{O}_7$
The higher the oxygen atom involved the greater the stability. The oxygen atom being electro-negative does not allow electron of chlorine atom to be showed with others in the formation of compound. So Cl_2O_7 is most inactive or highly stable.
- (b) In case of nitrogen, d-orbitals are not available.
- (d) $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{H}_3\text{PO}_4$
- (a) He being the smallest sized atom, can not be absorbed by coconut charcoal.
- (b) $\text{PCl}_3 + \text{H}_2\text{O} \longrightarrow \text{POCl}_3 + 2\text{HCl}$
 $\text{POCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 3\text{HCl}$
- (a) $\text{PH}_4\text{I} + \text{NaOH} \rightarrow \text{NaI} + \text{PH}_3 + \text{H}_2\text{O}$
- (d) $\text{NH}_4\text{Cl} + \text{NaNO}_2 \xrightarrow[-\text{NaCl}]{\text{Heat}} \text{NH}_4\text{NO}_2$
 $\xrightarrow{\text{Heat}} \text{N}_2 + 2\text{H}_2\text{O}$
- (b) $\text{C}_{12}\text{H}_{22}\text{O}_{11} + 18[\text{O}] \longrightarrow 6(\text{COOH})_2 + 5\text{H}_2\text{O}$
Cane sugar From HNO_3 Oxalic acid
- (c) HF (Hydrofluoric acid or Hydrogen flouride) is the acid which cannot be kept in glass because it reacts with glass
 $6\text{HF} + \text{SiO}_2 \longrightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$
- (d) N_2 molecule contains triple bond between N atoms having very high dissociation energy (946 kJ mol^{-1}) due to which it is relatively inactive.
- (c) H_3PO_2 is named as hypophosphorous acid. It is monobasic as it contains only one P – OH bond, its basicity is one.
$$\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{P}-\text{OH} \\ | \\ \text{H} \end{array}$$
- (c) As compared to nitrogen, oxygen is more electronegative and more reactive because as we go from left to right in a group electronegativity increases and reactivity decreases. So, nitrogen should be more reactive than oxygen but in nitrogen p-orbitals are exactly half filled which make it stable and less reactive as compared to oxygen.
- (a) We know that empirical formula of hypophosphorus acid is H_3PO_2 . In this only one ionisable hydrogen atom is present i.e. it is monobasic. Therefore option (a) is correct structural formula of it.
- (d) CO_2 is oxide of non-metal. Both N_2O and NO_2 are also oxide of non-metal. They form acids on dissolution in water. In this way CO_2 resembles N_2O and NO_2 . Option (d) is the answer.
- (c) Structure of hypophosphorous acid
$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{O}-\text{P} \rightarrow \text{O} \\ | \\ \text{H} \end{array}$$

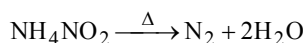
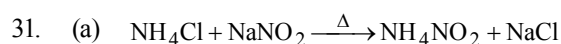
Two H-atoms are attached to P atom.
- (a) Only nitrates of heavy metals and lithium decompose on heating to produce NO_2 .
- (a) Nitrogen due to small size is able to show $p\pi-p\pi$ lateral overlap forming $\text{N} \equiv \text{N}$, rest elements due to bigger size are not able to show $p\pi-p\pi$ lateral overlap.
- (c) concentrated sulphuric acid is always diluted by adding acid to water because the process of mixing generates a lot of heat. If we add water to acid due to generation of large amount of heat acid may spill over to its surroundings.
- (a) Oxide in which central atom has higher charge and more electronegativity is more acidic, i.e.
 $\text{N}_2\text{O}_5 > \text{N}_2\text{O}_4 > \text{P}_2\text{O}_5 > \text{As}_2\text{O}_3$.
- (c) $\text{Ca} + 2\text{C} \longrightarrow \text{CaC}_2$
 $\text{CaC}_2 + \text{N}_2 \xrightarrow{1273\text{K}} \text{CaCN}_2 + \text{C}$
Calcium cyanamide
- (b) Most efficient agent for the absorption of SO_3 is 98% H_2SO_4 . They form oleum.
 $\text{SO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S}_2\text{O}_7$ (oleum)
Sulphur trioxide is not directly absorbed in water to form sulphuric acid because it forms dense fog of sulphuric acid.
- (a) $\text{NH}_4\text{ClO}_4 + \text{HNO}_3 \rightarrow \text{HClO}_4 + \text{NH}_4\text{NO}_3$
 $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
- (c) NH_3 gas can be dried by CaO (calcium oxide or quick lime).
- (b) In Haber's process for manufacture of NH_3 , finely divided iron is used as catalyst and molybdenum is used as catalytic promoter
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow[800\text{K, High P}]{\text{Fe+Mo}} 2\text{NH}_3(\text{g})$$



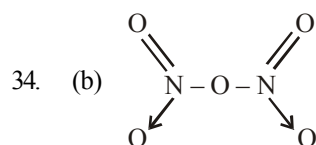
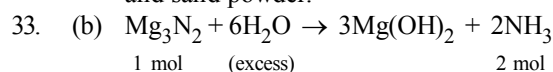
29. (d) N_2H_4 and NH_4Cl are obtained by reaction of ammonia with hypochlorite anion.



$\therefore$ Each P-atom forms 3 bonds. Thus it has 3 bond pairs of electrons.

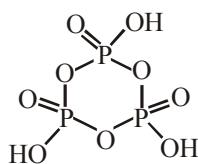


32. (a) The sides of safety matches contain red phosphorus and sand powder.

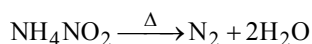


The structure clearly shows the presence of covalent and co-ordinate bonds.

35. (d) NO_2 is reddish brown coloured gas. Rest of the oxides are colourless.
36. (c) $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$; i.e 2 moles of phosphine are produced from one mole of calcium phosphide.
37. (d) Group 16, elements are known as Chalcogens Na is not group 16 element. So it is not Chalcogen.
38. (c) In cyclic metaphosphoric acid number of P–O–P bonds is three.



39. (a) Nitrogen is obtained by the thermal decomposition of NH_4NO_2

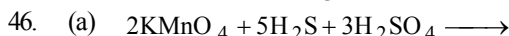
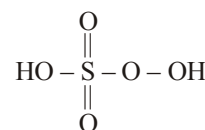


40. (b) Alkaline pyrogallol absorbs O_2 and oil of cinnamon absorbs O_3 .

41. (c) Air is liquified by making use of the joule-Thompson effect (cooling by expansion of the gas) Water vapour and CO_2 are removed by solidification. The remaining

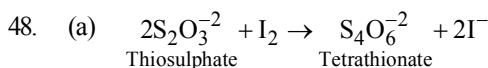
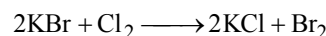
major constituents of liquid air i.e., liquid oxygen and liquid nitrogen are separated by means of fractional distillation (b.p. of $\text{O}_2 = -183^\circ\text{C}$; b. P. of $\text{N}_2 = -195.8^\circ\text{C}$)

42. (a) Alkaline solution of pyrogallol absorbs oxygen quickly.
43. (b) Solubility depends upon temperature. In most cases it increases with rise in temperature but in those cases where the process of dissolution is exothermic, solubility decreases with rise in temperature.
44. (c) Due to greater tendency for catenation, sulphur shows property of polyanion formation to a greater extent. For example, in polysulphides such as S_3^{2-} , S_4^{2-} , S_5^{2-}
45. (d) Caro's acid is H_2SO_5 which contains one S–O–OH peroxy linkage. It is also known as permonosulphuric acid.

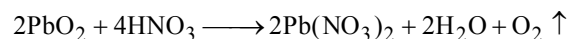


Thus in this reaction S^{2-} is oxidised to S.

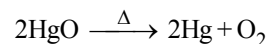
47. (c) In the manufacture of bromine from sea water, the mother liquor which contains bromides is treated with chlorine which oxidises bromide ion to bromine



49. (b) PbO_2 is a powerful oxidizing agent and liberate O_2 when treated with acids.



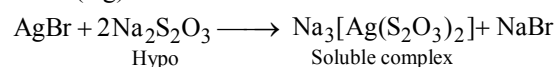
50. (b) Oxygen can be prepared by heating oxides of Hg, Pb, Ag, Mn and Ba.



51. (c) NO_2 is the compound which forms dimer N_2O_4 . NO_2 has one unpaired electron. So, it dimerises to form paired electrons.

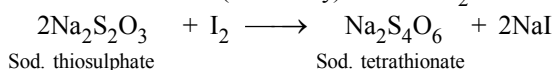


53. (d) Hypo ($\text{Na}_2\text{S}_2\text{O}_3$) is used in photography. It is used during fixing of image. It dissolves AgBr that has not been affected by light during exposure leaving metallic silver (Ag) as such



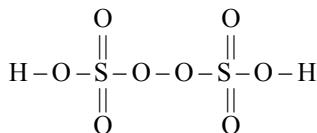
54. (b) HClO_4 is the strongest acid.

55. (a) Sodium thiosulphate is a reducing agent. It is used in volumetric titration (Iodimetry) to reduce I_2 to I^- .



56. (c) SO_2 is highly soluble in water and therefore cannot be collected over water.
57. (b) $\text{Na}_2\text{SO}_3 + \text{S} \xrightarrow[\text{medium}]{\text{In alkaline}} \text{Na}_2\text{S}_2\text{O}_3$
58. (c) In KMnO_4 manganese is already present in its highest possible oxidation state i.e. +7. So no further oxidation is possible.
59. (a) Laughing gas (N_2O) is prepared by heating mixture of NH_4Cl and NaNO_3
- $$\text{NH}_4\text{Cl} + \text{NaNO}_3 \xrightarrow{\Delta} \text{NH}_4\text{NO}_3 + \text{NaCl}$$
- $$\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$$
60. (d) N_2O_5 is colourless deliquescent solid. It is highly reactive, a strong oxidizing agent and is light sensitive. It is anhydride of HNO_3 .
61. (b) Bromide in the mother liquor is oxidised to Br_2 by Cl_2 which is a stronger oxidising agent.
- $$2\text{Br}^- + \text{Cl}_2 \rightarrow \text{Br}_2 + 2\text{Cl}^-$$
62. (c) Outer electronic configuration of Cl atom
- $$= 3s^2 3p_x^2 3p_y^2 3p_z^1$$
- Outer electronic configuration of Cl^- ion = $3s^2 3p_x^2 3p_y^2 3p_z^2$
- Hence Cl^- has 4 unshared pair of electrons.
63. (a) A stronger oxidising agent (Cl_2) displaces a weaker oxidising agent (Br_2) from its salt solution.
- $$2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2$$
64. (c) $2\text{AgClO}_3 + \text{Cl}_2(\text{dry}) \xrightarrow{90^\circ\text{C}} 2\text{AgCl} + 2\text{ClO}_2 + \text{O}_2$
65. (b) $\text{NH}_3 + \text{NaOCl} \xrightarrow{\text{fast}} \text{NH}_2\text{Cl} + \text{NaOH}$
- $$2\text{NH}_3 + \text{NH}_2\text{Cl} \longrightarrow \text{NH}_2\text{NH}_2 + \text{NH}_4\text{Cl}$$
66. (d) We know that positive ion is always smaller and negative ion is always larger than the corresponding atom. Therefore the correct order of the size is $\text{I}^- > \text{I} > \text{I}^+$
67. (a) Due to absence of reaction between marble and bromine.
68. (b) $\text{H}_2\text{O} + \text{Br}_2 \xrightarrow{\quad} \text{HOBr} + \text{HBr}$
- Thus here oxidation number of Br increases from 0 to +1 and also decreases from 0 to -1. Thus it is oxidised as well as reduced.
69. (b) H_3PO_4
- P_2O_5 exists as dimer (P_4O_{10})
- $$\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_4$$
70. (c) The H-X bond strength decreases from HF to HI. i.e. $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$. Thus HF is most stable while HI is least stable. The decreasing stability of the hydrogen halide is also reflected in the values of dissociation energy of the H-X bond
- | | | | |
|----------------------------|----------------------------|---------------------------|---------------------------|
| H - F | H - Cl | H - Br | H - I |
| 135 kcal mol ⁻¹ | 103 kcal mol ⁻¹ | 87 kcal mol ⁻¹ | 71 kcal mol ⁻¹ |
71. (b) $\text{Cl}_2 + 2\text{NaOH} \xrightarrow{\text{(cold \& dil)}} \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$
- $$3\text{Cl}_2 + 6\text{NaOH} \xrightarrow{\text{(hot \& conc.)}} 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$$
72. (b) $\text{H}_2\text{SO}_4 + \text{SO}_3 \longrightarrow \text{H}_2\text{S}_2\text{O}_7$
Oleum
73. (d) $\text{I}_2 + 10\text{HNO}_3 \xrightarrow{\text{(Conc)}} 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$
Periodic acid
74. (a) Longer bond length means weaker bond energy i.e. less bond dissociation energy or more reactivity. Larger the size of anion more will be bond length thus the order of reactivity is $\text{HI} > \text{HBr} > \text{HCl}$.
75. (a) The order of bond energy is $\text{Cl}-\text{Cl} > \text{F}-\text{F} > \text{Br}-\text{Br} > \text{I}-\text{I}$
- The small value of bond energy in F_2 than Cl_2 (anomaly) is due to smaller size of F atom which leads to inter-electronic repulsions.
76. (b)
77. (b) $\text{SO}_2 + \text{Cl}_2 \xrightarrow{\text{Sun light}} \text{SO}_2\text{Cl}_2$ (Sulphuryl chloride)
78. (d)
79. (b) CCl_3NO_2
80. (b) Polarizability of noble gases increases down the group because of increase of distance of electrons from nucleus. Thus He (first member of group) is least polarized.
81. (c) $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 6\text{HF}$
- $\therefore$ Complete hydrolysis of XeF_6 gives XeO_3 (an explosive).
82. (b)
83. (a)
84. (c) Completing the reaction, we get
- $$\text{NCl}_3 + 3\text{H}_2\text{O} \longrightarrow 3\text{HClO} + \text{NH}_3$$
85. (a) Rn because it is radioactive element obtained by the disintegration of radium
- $${}_{88}\text{Ra}^{226} \rightarrow {}_{86}\text{Rn}^{222} + {}_2\text{He}^4$$
86. (b)
87. (b) PbO_2 is a strong oxidising agent. It reacts with conc. HNO_3 as shown:
- $$\text{PbO}_2 + 2\text{HNO}_3 \longrightarrow \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$$
88. (b) With the decrease in the electronegativity of central atom the bond angle decreases

89. (d) Perdisulphuric acid is represented as



So, it contains a peroxo linkage – O – O –

90. (c) Helium is twice as heavy as hydrogen it is inflammable but not lighter than hydrogen. Helium has the lowest melting and boiling point of any element which makes liquid helium an ideal coolant for many extremely low temperature application such as super conducting magnet and cryogenic research where temperature close to absolute zero are needed. He is used in gas cooled atomic reactors as a heat transfer agent.

91. (d) (i) The first ionization energy of xenon ($1,170 \text{ kJ mol}^{-1}$) is quite close to that of dioxygen ($1,180 \text{ kJ mol}^{-1}$).
(ii) The molecular diameters of xenon and dioxygen are almost identical.

Based on the above similarities Barlett (who prepared $\text{O}_2^+[\text{PtF}_6]^-$ compound) suggested that since oxygen combines with PtF_6 , so xenon should also form similar compound with PtF_6 .

92. (b) PbO_2 does not contain peroxide ion. It is lead dioxide.

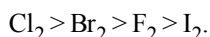
93. (d) $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$
 $\quad \quad \quad +1 \quad \quad +3 \quad \quad +5 \quad \quad +7$

In case of oxyacids of similar element as the oxidation number of the central atom increases, strength of acid also increases.

94. (b, c) From the given options we find option (a) is correct. The oxidising power of halogens follow the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. Option (b) is incorrect because it is not the correct order of electron gain enthalpy of halogens.

The correct order is $\text{Cl}_2 > \text{F}_2 > \text{Br}_2 > \text{I}_2$. The low value of F_2 than Cl_2 is due to its small size.

Option (c) is incorrect. The correct order of bond dissociation energies of halogens is

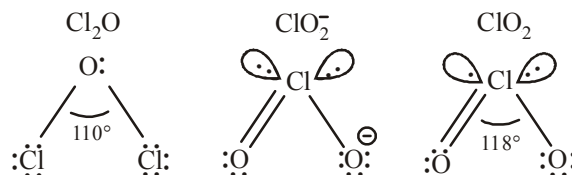


Option (d) is correct. It is the correct order of electronegativity values of halogens. Thus option (b) and (c) are incorrect.

95. (c) $\text{MI} > \text{MBr} > \text{MCl} > \text{MF}$. As the size of the anion decreases covalent character also decreases.

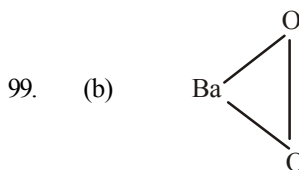
96. (d) Since all the halogens have a strong tendency to accept electrons. Therefore halogens act as strong oxidising agents and their oxidising power decreases from fluorine to iodine.

97. (c) The correct order of increasing bond angle is
 $\text{Cl}_2\text{O} < \text{ClO}_2^- < \text{ClO}_2$



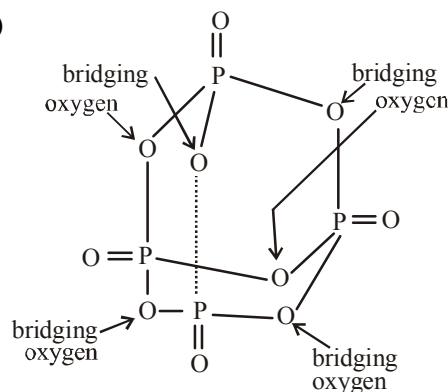
* In ClO_2^- there are 2 lone pairs of electrons present on the central chlorine atom. Therefore the bond angle in ClO_2^- is less than 118° which is the bond angle in ClO_2 which has less number of electrons on central chlorine atom.

98. (d)



99. (b)

100. (b)



∴ Correct choice : (b)

EXERCISE - 2

- (b) Potassium tetraiodo mercurate (II) (K_2HgI_4) dissolves in KOH solution to give Nessler's reagent. Nessler's reagent is used to test NH_4^+ ions.
- (a) Acidic strength of oxyacids increases with increase in oxidation number and on moving from top to bottom in a group acidic strength of oxides also decrease due to decrease in electronegativity down the group.
 $\text{P}_4\text{O}_{10} > \text{P}_4\text{O}_6 > \text{As}_4\text{O}_{10} > \text{As}_4\text{O}_6$
- (b) Neon gives a distinct reddish glow when used in either low-voltage neon glow lamps or in high voltage discharge tube.
- (a) Order of dipole moment
 $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$
 (Based upon electronegativity)
- (c) Polarity of the bond depends upon the electronegativity difference of the two atoms forming the bond. Greater

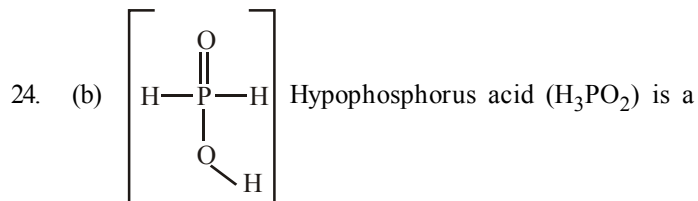
the electronegativity difference, more is the polarity of the bond.

N-Cl	O-F	N-F	N-N
3.0-3.0	3.5-4.0	3.0-4.0	3.0-3.0

6. (c) Br_2 reacts with NaI only to get I_2 .
 $2\text{NaI} + \text{Br}_2 \rightarrow 2\text{NaBr} + \text{I}_2$
7. (d)
8. (d) Bi forms basic oxides whereas N and P form acidic and As and Sb form amphoteric oxides.
9. (a) ${}_7\text{N} = 1s^2 2s^2 2p^3$; ${}_{15}\text{P} = 1s^2 2s^2 2p^6 3s^2 3p^3$
 In phosphorous the $3d$ - orbitals are available. Hence phosphorus can form pentahalides also but nitrogen cannot form pentahalide due to absence of d -orbitals
10. (c) In N_2O (nitrous oxide) two N atoms are covalently bonded through triple bond
 $[\text{N} \equiv \text{N} \longrightarrow \text{O}]$
11. (a) As size increases, van der Waal's forces of attraction between noble gas atoms also increases. Consequently, ease of their liquefaction increases.
12. (a) For oxides of same element higher the oxidation state, more will be acidic character.
 $\begin{matrix} +5 & +2 & +1 \\ \text{N}_2\text{O}_5 & > & \text{NO} > \text{N}_2\text{O} \end{matrix}$
13. (b) Hypo solution is $\text{Na}_2\text{S}_2\text{O}_3$ solution which is used in photography for fixing films & prints. Photographic emulsions are made of AgBr. After developing, the film is put into hypo solution. This forms soluble complex with Ag.
 $\text{Na}_2\text{S}_2\text{O}_3 + \text{Ag Br} \rightarrow \text{Ag}_2\text{S}_2\text{O}_3$
 $\xrightarrow{\text{Na}_2\text{S}_2\text{O}_3} \text{Na}_5[\text{Ag}(\text{S}_2\text{O}_3)_3]$
14. (c) As the size of central atom increases the lone pair of electrons occupies a larger volume. In other words electron density on the central atom decreases and consequently its tendency to donate a pair of electrons decreases along with basic character from NH_3 to BiH_3 .
15. (d) H_2O is liquid but H_2S is a gas. This can be attributed to the presence of intermolecular hydrogen bonding in case of H_2O .
16. (b) Mixture of Cl_2 and ClO_2 acts as a bleaching agent and is called euechlorine.
17. (b) On moving from top to bottom of halogen group the bond dissociation energy of hydrogen halides decreases and so the heat of formation of halogen acids also decreases.
18. (c) Pickling agent is H_2SO_4 . Pickling is cleaning the surface of metals before enameling, electroplating and galvanising.
19. (c) $\text{KF} + \text{HF} \rightleftharpoons \text{KHF}_2 \rightleftharpoons \text{K}^+ + [\text{HF}_2]^-$
20. (d) Due to inert pair effect.
21. (c) $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} 2\text{SO}_3$
22. (b) In BCl_3 , $H = \frac{1}{2}(3+3+0-0) = 3$; sp^2 hybridization
 (bond angle = 120°) similarly PCl_3 , AsCl_3 and BiCl_3 are found to have sp^3 hybridized central atom with one lone pair of electrons on the central atom. The bond

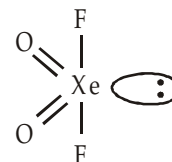
angle $\leq 109^\circ 28'$, since the central atoms belong to the same group, the bond angle of the chlorides decreases as we go down the group. Thus the order of bond angle is, $\text{BCl}_3 > \text{PCl}_3 > \text{AsCl}_3 > \text{BiCl}_3$.

23. (a)
- | | |
|----------------------|-------------------------|
| (A) Sulphuric acid | (iv) Contact process |
| (B) Steel | (ii) Bessemer's process |
| (C) Sodium hydroxide | (iii) Leblanc process |
| (D) Ammonia | (i) Haber's process |



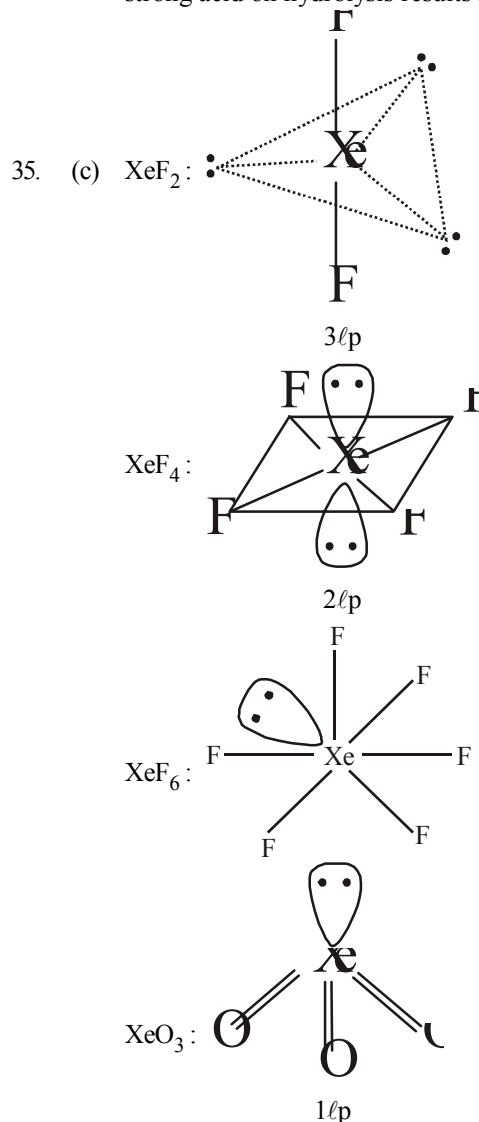
monobasic acid. i.e., it has only one ionisable hydrogen atom or one OH is present.

25. (b) $\text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 3\text{SO}_3$
26. (d) The products of the concerned reaction react each other forming back the reactants.
 $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 6\text{HF}$
27. (b) The following reaction occurs
 $\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} \longrightarrow 2\text{NaHSO}_4 + 8\text{HCl}$
28. (b) $\text{P}_4 + 3\text{O}_2 \xrightarrow{\text{In presence of N}_2} \text{P}_4\text{O}_6$
 Here N_2 acts as a diluent and thus retards further oxidation. Reaction of P_4 under other three conditions.
- (a) $\text{P}_4 + 3\text{O}_2 \longrightarrow \text{P}_4\text{O}_6 \xrightarrow{2\text{O}_2} \text{P}_4\text{O}_{10}$
- (c) In moist air, P_4O_6 is hydrolysed to form H_3PO_3
 $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_3$
- (d) In presence of NaOH,
 $\text{P}_4 + 3\text{OH}^- + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{H}_2\text{PO}_2^-$
29. (d) Very pure N_2 can be obtained by thermal decomposition of sodium or barium azide. $\text{Ba}(\text{N}_3)_2 \longrightarrow \text{Ba} + 3\text{N}_2$
30. (d) XeO_2F_2 has trigonal bipyramidal geometry, but due to presence of lone pair of electrons on equatorial position, its actual shape is *see-saw*.

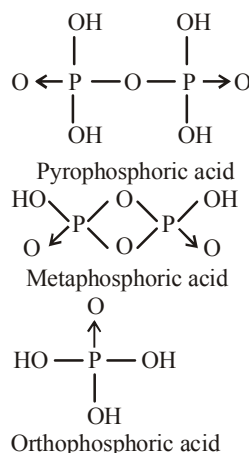
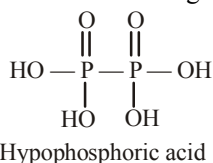


31. (a) SnO_2 is an amphoteric oxide because it reacts with acids as well as with bases to form corresponding salts.
 $\text{SnO}_2 + 2\text{H}_2\text{SO}_4(\text{conc}) \longrightarrow \text{Sn}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$
 $\text{SnO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O}$

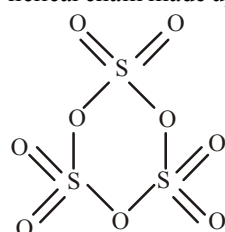
32. (c) Compound Oxidation number of nitrogen
 N_2H_4 = -2
 NH_3 = -3
 N_3H = -1/3
 NH_2OH = -1
33. (d) Chlorine reacts with excess of ammonia to produce ammonium chloride and nitrogen.
 $3\text{Cl}_2 + 8\text{NH}_3 (\text{excess}) \longrightarrow 6\text{NH}_4\text{Cl} + \text{N}_2$
34. (a) $(\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{SO}_4 + \text{NH}_4\text{OH}$
 H_2SO_4 being strong acid increases the acidity of soil. In case of potassium nitrate and superphosphate of lime on hydrolysis strong base also form along with strong acid on hydrolysis results into neutralisation.



- Hence XeF_2 has maximum no. of lone pairs of electrons.
36. (d) Oxidation state of sulphur varies from -2 to +6 in its various compounds.
37. (b) With the decrease in the electronegativity of central atom the bond angle decreases
38. (a)



39. (c) The structure of solid sulphur trioxide is complex, it possesses either cyclic trimer structure or an infinite helical chain made up of linked SO_4 tetrahedron.



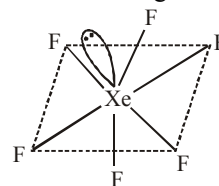
total no of S - O - S bonds = 3

40. (a) NF_5 does not exist because N does not form pentahalides due to the absence of d-orbital in its valence shell. While P, As and Sb form pentahalides of the general formula MX_5 (where, M = P, As and Sb) due to the presence of vacant d-orbitals in their respective valence shell.
41. (c) Compound O.S. of N
 N_2O +1
 NO +2
 NO_2 +4
 NO_3^- +5
 NH_4^+ -3

Therefore increasing order of oxidation state of N is:



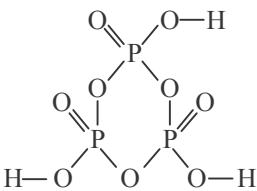
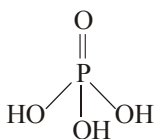
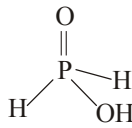
42. (c) Br_2 reacts with NaI only to get I_2 .
 $2\text{NaI} + \text{Br}_2 \rightarrow 2\text{NaBr} + \text{I}_2$
43. (c) In N_2O (nitrous oxide) two N atoms are covalently bonded through triple bond
 $[\text{N} \equiv \text{N} \longrightarrow \text{O}]$
44. (b) Potassium tetraiodo mercurate (II) (K_2HgI_4) dissolves in KOH solution to give Nessler's reagent. Nessler's reagent is used to test NH_4^+ ions.
45. (c) The geometry of XeF_6 is distorted octahedral in which all the six positions are occupied by fluorine atoms and the lone pair of electrons of Xe atom is present at the corner of one of the triangular faces.



46. (b) Neon gives a distinct reddish glow when used in either low-voltage neon glow lamps or in high voltage discharge tube.
47. (b) Formula of cyclotrimetaphosphoric acid is $(\text{HPO}_3)_3$
Oxidation state of 'P' is $3(+1 + x + 3(-2)) = 0$
 $x + -6 + 1 = 0 \Rightarrow x = +5$
48. (b) White phosphorus exists as P_4 tetrahedral molecule having P-P-P bond angle 60° . Hence the molecule is under strain and more reactive. On the other hand red phosphorus exists as P_4 tetrahedra which are joined together through covalent bonds giving polymeric structure.
49. (a) Both assertion and reason are true and reason is the correct explanation of assertion.
- $$\begin{array}{ccccccc} \text{M} & + & \text{HNO}_3 & \longrightarrow & \text{MNO}_3 & + & \text{H} \\ \text{(metal)} & & \text{(conc.)} & & \text{(metal nitrate)} & & \text{(nascent hydrogen)} \end{array}$$
- $$2\text{HNO}_3 + \text{(nascent hydrogen)} \longrightarrow 2\text{NO}_2 + 2\text{H}_2\text{O}$$
50. (c) Bond angle of H_2S (92°) < H_2O ($104^\circ 31'$). As the electronegativity of the central atom decreases, bond angle decreases. In the present case, S is less electronegative than oxygen. Thus bond pairs in H_2S are more away from the central atom than in H_2O and thus repulsive forces between bond pairs are smaller producing smaller bond angle.

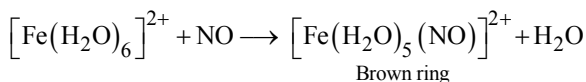
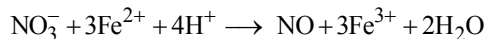
EXERCISE - 3

Exemplar Questions

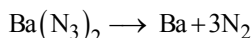
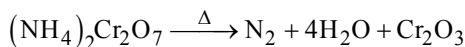
1. (c) Hydrogen iodide (HI) is stronger reducing agent than H_2SO_4 . Hence, it reduces H_2SO_4 to SO_2 and itself oxidises to I_2 .
- $$\text{H}_2\text{SO}_4 + 2\text{HI} \longrightarrow \text{SO}_2 + \underset{\text{(Violet colour)}}{\text{I}_2} + 2\text{H}_2\text{O}$$
2. (b) When H_2S gas is passed through an aqueous solution of copper sulphate acidified with dil. HCl a black ppt. of CuS is obtained.
- $$\text{CuSO}_4 + \text{H}_2\text{S} \xrightarrow[\text{black ppt}]{\text{dil. HCl}} \text{CuS} + \text{H}_2\text{SO}_4$$
- On boiling CuS with dil. HNO_3 it forms a blue coloured solution and the following reactions occur
- $$3\text{CuS} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$$
- $$\text{Cu}_{(\text{aq})}^{2+} + 4\text{NH}_3(\text{aq}) \longrightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$$
- (Deep blue solution)
3. (c)
- 
- i.e., 3 double and 12 single Bonds
4. (c) Among carbon, nitrogen, phosphorus and boron only phosphorus has vacant d -orbital hence only phosphorus has the ability to form $p\pi - d\pi$ bonding.
5. (a) Both CO_3^{2-} and NO_3^- have same number of electrons.
- $$\text{CO}_3^{2-} = 6 + 8 \times 3 + 2 = 32$$
- $$\text{NO}_3^- = 7 + 8 \times 3 + 1 = 32$$
- Hence, CO_3^{2-} and NO_3^- are isoelectronic. Also, both have same type of hybridization (sp^2) and have trigonal planar structure. Hence, they are also isostructural.
6. (a) On moving down the group size of halogen atom increases hence the H-X bond length increases. As a result, bond dissociation enthalpy decreases. Hence, the correct order of bond enthalpy is : $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$.
7. (d) On moving down the group size of central atom increases thus bond length of E-H bond increases and bond dissociation energy decreases. Hence, reducing nature increases in the order : $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$
8. (c) White phosphorus on reaction with NaOH solution in the presence of inert atmosphere of CO_2 produces phosphine gas which is less basic than NH_3 .
- $$\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$$
- (Sodium hypophosphite)
9. (c) Structure of H_3PO_4 is
- 
- H_3PO_4 has 3 -OH groups i.e., three ionisable H-atoms and hence it forms three series of salts: NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4
10. (c) The acids which contain P-H bond have strong reducing properties. Thus, H_3PO_2 is a strong reducing agent due to the presence of two P-H bonds and one -OH group
- 
- Hypophosphorous acid
11. (b) On heating, lead nitrate produces brown coloured nitrogen dioxide (NO_2) and lead (II) oxide.
- $$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$$
12. (a) Nitrogen does not show allotropy due to its small size and high electronegativity. The N-N bond is weak due to high inter-electronic repulsions among non-bonding electrons due to the small bond distance. Hence it does not show allotropy.
13. (c) Maximum covalency of nitrogen is 4 in which one electron is from s -orbital and 3 electrons are from p -orbitals. Hence, total four electrons are available for bonding.

14. (a) The single N — N bond is weaker than the single P — P bond. This is why phosphorus show allotropy but nitrogen does not.

15. (a) When freshly prepared solution of FeSO_4 is added to an aqueous solution containing NO_3^- ion, it leads to the formation of a brown coloured complex. This is known as brown ring test for nitrate ion.



16. (b) The only well characterised compound having + 5 oxidation state of Bi is BiF_5 . It is due to smaller size and high electronegativity of fluorine.
17. (a) On heating ammonium dichromate and barium azide both produces N_2 gas separately.

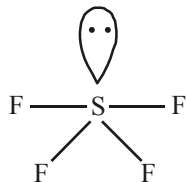


18. (a) $4\text{NH}_3 + 5\text{O}_2 \xrightarrow[500\text{K}, 9\text{ bar}]{\text{Pt/Rh gauge catalyst}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
 $\therefore$ Two moles of NH_3 will produce 2 moles of NO on catalytic oxidation.

19. (c) Let oxidation state of P in NaH_2PO_2 is x.

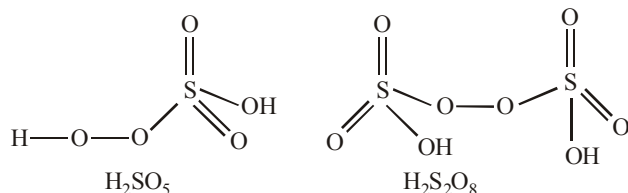
$$\begin{aligned} 1 + 2 \times 1 + x + 2 \times -2 &= 0 \\ 1 + 2 + x - 4 &= 0 \\ +x - 1 &= 0 \\ x &= +1 \end{aligned}$$

20. (c) SF_4 has sea-saw shape as shown below:

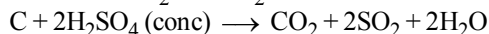


It has trigonal bipyramidal geometry having sp^3d hybridisation.

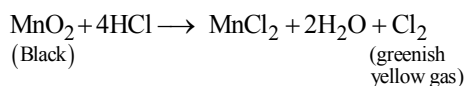
21. (a) Peroxoacids of sulphur must contain one — O — O — bond as shown below:



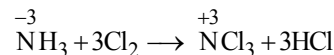
22. (c) Carbon on oxidation with H_2SO_4 produces two types of oxides CO_2 and SO_2 .



23. (a) MnO_2 reacts with HCl to produce greenish yellow coloured gas of Cl_2 .

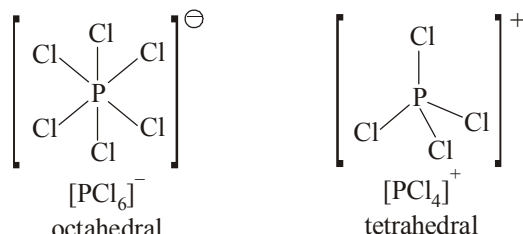


Cl_2 on further treatment with NH_3 produces NCl_3 .



Hence, NH_3 (− 3) changes to NCl_3 (+ 3).

24. (c) Bertlett had taken $\text{O}_2^+ \text{Pt F}_6^-$ as a base compound because O_2 and Xe both have almost same ionisation enthalpy.
25. (d) In solid state PCl_5 exists as an ionic solid with the cation $[\text{PCl}_4]^+$ (tetrahedral) and the anion $[\text{PCl}_6]^-$ (octahedral).



26. (c) Greater the SRP value, higher will be the oxidising power. Hence the correct order of oxidising power is:



27. (b) Isoelectronic pair have same number of electrons
 Total number of electrons for the given compounds :

$$= \frac{\text{BrO}_2^-}{35 + 2 \times 8 + 1} = 52 = \frac{\text{BrF}_2^+}{35 + 9 \times 2 - 1} = 52$$

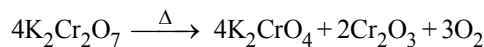
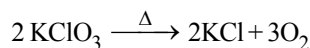
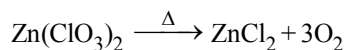
$$\begin{array}{ccc} \text{ICl}_2 & \text{ClO}_2 & \text{BrF} \\ 53 + 2 \times 17 = 87 & 17 + 16 = 33 & 35 + 9 = 44 \end{array}$$

$$\begin{array}{ccc} \text{CN}^- & \text{O}_3 \\ 6 + 7 + 1 = 14 & 8 \times 3 = 24 \end{array}$$

NEET/AIPMT (2013-2017) Questions

28. (b) HClO_4 is the strongest acid amongst all because the oxidation state of Cl is maximum (+7).

29. (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$



30. (b) (Tetrahedral sp^3)

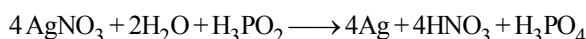
31. (a) The weakening of M—H bond with increase in size of M (where M = S, Se, Te) explains the acid character of hydrides. Since on moving down the group atomic size increases hence bond length increases and hence removal tendency of H also increases.

32. (c) SO_2 is widely used in food and drinks industries for its property as a preservative and antioxidant while NO_2 is not used as food preservative.

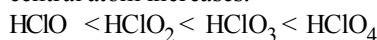
33. (d) OF_2 ; among the following O and F, F is more electronegative than oxygen.

So OF_2 cannot be called oxide because in that case fluorine is in +1 oxidation state which is not possible, so OF_2 is called oxygen difluoride.

34. (b) The H-bonding is present in HF due to high electronegativity of fluorine atom. While H-bonding is not present in HI, HBr and HCl.
35. (a) The acids which contain P-H bond have strong reducing properties. Thus H_3PO_2 acid is good reducing agent as it contains two P-H bonds and reduces, for example, AgNO_3 to metallic silver.



36. (b) Acidic strength increases as the oxidation number of central atom increases.

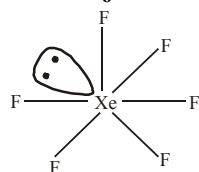


37. (b) Bond dissociation enthalpy decreases as the bond distance increases from F_2 to I_2 . This is due to increase in the size of the atom, on moving from F to I.

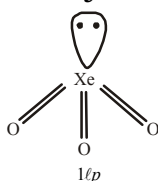
F-F bond dissociation enthalpy is smaller than Cl-Cl and even smaller than Br-Br. This is because F atom is very small and hence the three lone pairs of electrons on each F atom repel the bond pair holding the F-atoms in F_2 molecules.

The increasing order of bond dissociation enthalpy is $\text{I}_2 < \text{F}_2 < \text{Br}_2 < \text{Cl}_2$

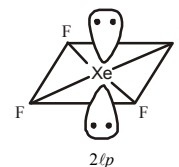
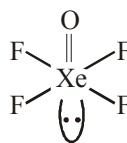
38. (a) XeF_6



distorted octahedral
 XeOF_4



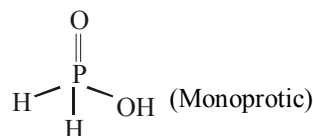
Pyramidal
 XeF_4



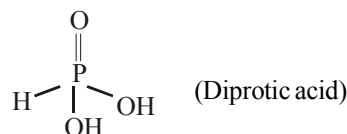
Square pyramidal

Square planar

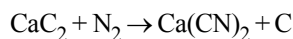
39. (b) Phosphinic acid as shown in structure below has one P-OH bond thus it is monobasic or monoprotic



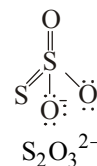
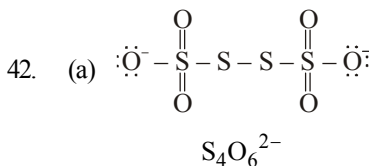
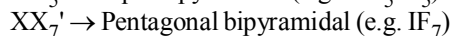
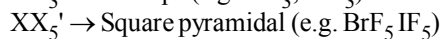
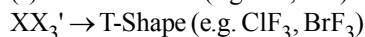
Phosphonic acid as shown in structure has two P-OH bonds thus it is dibasic or diprotic



40. (a) (Bonus)



41. (a) $\text{XX}' \rightarrow$ Linear (e.g. ClF , BrF)



Chapter 22

The *d*- and *f*-Block Elements

THE TRANSITION ELEMENTS (*d*-BLOCK)

Position in the Periodic Table

The elements which lie in between *s* and *p* - block elements are called transition elements. They are called *d* - block elements since in them, 3*d*, 4*d*, 5*d* and 6*d* sub - shells are incomplete and the last electrons enters the $(n - 1)$ *d* subshell. A transition element is defined as an element whose atoms in ground state or ions in one of the common oxidation states, has incomplete *d* - subshell.

Classification of *d*-Block Elements

Transition elements consist of the following four series

- (i) 3*d* series $_{21}\text{Sc}$ to $_{30}\text{Zn}$ $3d^{1-10} 4s^{1-2}$
- (ii) 4*d* series $_{39}\text{Y}$ to $_{48}\text{Cd}$ $4d^{1-10} 5s^{0-2}$
- (iii) 5*d* series $_{57}\text{La}$ $_{72}\text{Hf}$ to $_{80}\text{Hg}$ $5d^{1-10} 6s^{1-2}$
- (iv) 6*d* series $_{89}\text{Ac}$ $_{104}\text{Rf}$ to $_{111}\text{Rg}$

Electronic Configuration of *d*-Block Elements

General electronic configuration of these elements is $(n - 1) d^{1-10} ns^{1-2}$.

The last shell electronic configuration of Cr and Cu are $3d^5 4s^1$ (instead of $3d^4 4s^2$) and $3d^{10} 4s^1$ (instead of $3d^9 4s^2$). This is because of extra stability associated with half and completely filled orbitals.

The electronic configurations of Zn, Cd and Hg are represented by general formula $(n - 1) d^{10} ns^2$. The orbitals in these elements, in ground as well as in common oxidation state, are completely filled and hence, they are not regarded as transition elements but they show properties of transition elements to appreciable extent.

General Properties of Transition Elements

Since only penultimate shell i.e., $(n - 1)$ is expanding, they have resemblance in their physical and chemical properties.

(i) All the *d*-block elements behave as metals.

They are hard, malleable and ductile. i.e., Cu, Ag and Au are most ductile. They are good conductors of heat and electricity (due to free electrons).

Explanation :

The electronic configuration of these elements reveals that they have one or more unpaired electrons present in either *ns* or $(n - 1)$ *d*-orbitals which are available for bond formation. In general, greater the number of such electrons available, more will be the chances of their mutual combination and more will be strength of the metallic bond.

(ii) Melting and boiling points :

Strong metallic bonds between the atoms of these elements are responsible for the high melting and boiling points. This is clear from their high **enthalpies of atomization**. (i.e., *heat required to break the metal lattice to get free atoms*)

Metals of 4*d* and 5*d* series have greater enthalpies of atomisation than 3*d* series due to much more frequent metal-metal bonding in their compounds. Greater is the number of unpaired *d*-electrons stronger will be metallic bonding. Thus in a particular series metallic strength increased up to middle and then decreases.

Note : In Zn, Cd, and Hg there is no unpaired electron present in *d*-orbital, so the metallic bond is weak and their m.pt. and b.pt. are very low. (Volatile metals Zn, Cd, Hg)

(iii) Density

The atomic volume of the transition elements are low compared with *s*-block, so their density is comparatively high.

There is a normal increase in density from 3*d* to 4*d* series. However from 4*d* to 5*d*, it becomes almost double due to lanthanoid contraction.

In 3*d* series

Sc → Cr density increases

Cu → Zn decreases

(iv) Atomic and ionic sizes

They lie between those of *s* - and *p* - block elements. Atomic radii in a series decreases with increase in atomic number but the decrease is small after mid-way. This is because in the beginning, the nuclear charge increases but screening effect of *d*-electron is less. After mid-way screening effect of *d*-electrons increases which counter balances increased nuclear charge and hence increase in size is not much.

At the end of period, there is a slight increase in atomic radii. This is because near the end of series, the increased $e^- - e^-$ repulsions between added electrons in same orbital are greater than attractive forces due to increased nuclear charge.

Amongst the dipositive ions of 3*d* series, Cu^{2+} is the smallest in size.

The elements of 4*d* and 5*d* series have almost similar atomic radii. This is due to Lanthanoid contraction. E.g. atomic radii of Zr ≈ Hf; Tc ≈ Re; Nb ≈ Ta; Ru ≈ Os etc.

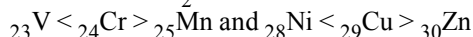
(v) Ionisation enthalpies

The IE increases with increase in atomic number due to increased nuclear charge. However, some irregularities are observed. This is because removal of an electron alters the relative energies of 4s and 3d orbitals. Thus, there is a **reorganisation energy** accompanying ionisation. This results into the release of exchange energy which increases as the number of electrons increases in the d^n configuration and also from the transference of s-electrons into d-orbitals.

Difference between IE of any two successive d-block elements is very less as compared to s or p-block elements. It is because addition of d electrons in last but one $[(n-1) \text{ or penultimate}]$ shell with increase in atomic number provides a screening effect and thus shields the outer s electrons from inward nuclear pull.

The 1st IE of Zn, Cd and Hg are very high due to fully filled $(n-1)d^{10}ns^2$ configuration.

The order for IE_2 for 1st series is:



This is because after removal of one e^- , Cr and Cu acquire stable configuration (d^5 and d^{10}), so removal of 2nd e^- becomes difficult.

Third IE of Mn ($25, 3d^5 4s^2$) is very high as the third e^- has to be removed from stable half-filled 3d-orbital.

Third IE for change from Fe^{2+} to Fe^{3+} (${}_{26}\text{Fe}, 3d^6 4s^2$) is small because loss of third e^- gives stable configuration of $3d^5$.

The high values of third IE for Cu, Zn and Ni explain why they have a maximum O.S. of +2.

The first IE's of 5d elements are higher as compared to those of 3d and 4d elements. This is because of the weak shielding effect of electrons present in 4f-orbitals which results in greater effective nuclear charge. Thus in 5d elements outer valence electrons are more tightly held.

The lower the electrode potential, i.e., more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal ion in aqueous medium.

Element $\rightarrow$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^\circ(\text{M}^{2+} / \text{M})$ in volts (V)	-1.63	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
$E^\circ(\text{M}^{3+} / \text{M}^{2+})$ in volts (V)	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	—	—	—

The irregular trend is due to variation in ionization energies and sublimation energies. E° values along the series becomes less negative generally it is due to increase in sum of IE_1 and IE_2 .

Cu has a +ve value of $E^\circ(\text{M}^{2+} / \text{M})$. As a result, it does not liberate H_2 gas from acids.

The $E^\circ(\text{M}^{2+} / \text{M})$ values for Mn, Ni and Zn are more -ve than expected. This is due to greater stability of half-filled 3d-orbital in Mn^{2+} (d^5) completely filled 3d-orbital in Zn^{2+} (d^{10}) and exceptional behaviour of Ni is due to high -ve enthalpy of hydration for Ni^{2+} .

A very low $E^\circ(\text{Sc}^{3+} / \text{Sc}^{2+})$ value reflects the stability of Sc^{3+} which has noble gas configuration. The highest $E^\circ(\text{M}^{3+} / \text{M}^{2+})$ for Zn is due to high stability of Zn^{2+} with d^{10} configuration. Comparitively high value of

(vi) Oxidation states

Transition metals exhibit a large no. of O.S. This is because there is little difference in energies of $(n-1)d$ and ns orbitals and hence, both the levels can be used for bond formation.

Most common O.S. of first row transition metals is +2 due to loss of two ns^2 electrons (exception: Sc, it has +3). In +2 and +3 O.S., ionic bonds are formed. In higher O.S., bonds formed are covalent as they are formed by sharing of d-electrons. The elements which show maximum no. of O.S. occur in or near middle of series. For ex: $\text{Mn} \rightarrow +2 \text{ to } +7$. Highest O.S. is +8 (shown by osmium). In a group, higher O.S. are more stable for heavier elements. For ex: in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). This is why Cr(VI) in $\text{Cr}_2\text{O}_7^{2-}$ is a stronger oxidizing agent in acidic medium whereas MoO_3 and WO_3 are not.

Low O.S. are found when a complex compound has ligands capable of π -acceptor character in addition to σ -bonding. The compounds of metals with F and O exhibit highest O.S. as F and O are small in size and highly electronegative. O stabilizes the highest O.S. even more than F. This is due to the ability of O to form multiple bonds with metal atoms. Usually transition metal ions in their lower oxidation state behave as reducing agents and in higher oxidation state, they behave as oxidising agents.

E.g. : Ti^{+2} , V^{+2} , Fe^{+2} , Co^{+2} etc are reducing agents

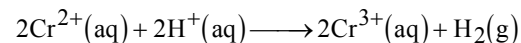
Cr^{+6} , Mn^{+7} , Mn^{+4} , Mn^{+5} , Mn^{+6} etc are oxidising agents.

(vii) Standard electrode potentials (E°) and chemical reactivity

Thermodynamic stability of compound of transition metals can be evaluated in terms of its IE. Smaller the IE of metal, stabler is its compound. In solution, the stability of the compounds depends upon electrode potentials which depends on $\Delta_{\text{sub}}H$, IE and $\Delta_{\text{hyd}}H$.

$E^\circ(\text{Mn}^{3+} / \text{Mn}^{2+})$ is due to stable d^5 configuration of Mn^{2+} . Low value of $E^\circ(\text{Fe}^{3+} / \text{Fe}^{2+})$ is due to extra stability of Fe^{3+} (d^5). Low value for V is due to stability of V^{2+} due to its

half filled t_{2g}^3 configuration. E° values for the redox couple $\text{M}^{3+} / \text{M}^{2+}$ indicate that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solution whereas Ti^{2+} , V^{2+} and Cr^{2+} are the strongest reducing agents and can liberate hydrogen from a dilute acid, Ex :

**(viii) Magnetic properties**

Transition metals contain unpaired electrons in $(n-1)d$ orbitals and hence most of transition metal ions and their compounds are paramagnetic.

Transition metals which have paired electrons are diamagnetic. Magnetic moment of transition metal ions is calculated by using 'spin - only' formula given as: $\mu = \sqrt{n(n+2)}$ B. M. where 'n' is the no. of unpaired electrons. As the number of unpaired electrons increases the magnetic moment also increases. Ions with d^5 configuration have maximum magnetic moment.

(ix) Coloured ions

Most transition metal compounds are coloured both in solid and in aqueous solution. Colour is due to presence of incomplete d - subshell. The d - orbitals split into two sets, one with lower energy and other with higher energy. The e^- absorbs energy and gets excited to higher energy level. When this excited e^- falls back to the ground state, it emits radiation which falls in the visible range of spectrum.

Thus, colour of transition metals is due to d-d transitions. Sc^{3+} and Ti^{4+} have empty d - orbitals and are colourless. Cu^+ , Ag^+ , Au^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} have completely filled d-orbitals, there are no vacant d - orbitals for promotion of electrons, hence they are also colourless.

(x) Complex formation

Transition metal ions form a large no. of complex compounds because:

- of comparatively smaller size of their metal ions.
- of their high positive charge.
- of availability of vacant d - orbitals so that they can accept lone pair of e^- s donated by ligands.

(xi) Catalytic properties

Transition metals act as catalysts due to following reasons:

- presence of unpaired electrons in their incomplete d-orbitals and posses the capacity to absorb and re-emit wide range of energies.
- Transition metals exhibit variable oxidation states and may form intermediate compounds with one of reactants providing a new path with lower activation energy.
- Transition metals provides a suitable large surface are with free valencies on which reactants are adsorbed.

Note : When transition elements and their compounds are in powdered state, their catalytic behaviour increases. This is due to greater surface area available in the powdered state.

(xii) Interstitial compounds

Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc. The smaller sized atoms get entrapped in between the interstitial spaces of the metal lattices. These interstitial compounds are non stoichiometric in nature and hence cannot be given any definite formula.

Some important characteristics of these compounds are:

- they have high m. pts. higher than those of pure metals.
- they are very hard and rigid.
- they show conductivity like that of pure metal.
- they are chemically inert.

(xiii) Alloy formation

Alloys are homogeneous solid solutions of two or more metals obtained by melting the components and then cooling the melt.

Transition metals have similar atomic radii and other characteristics, hence they form alloys readily. Alloys are generally harder, have higher m. pts. and more resistant to corrosion than individual metals.

Some important alloy :

- Bronze – Cu (75 - 90 %) + Sn (10 - 25 %)
- Brass – Cu (60 - 80 %) + Zn (20 - 40 %)
- Gun metal – (Cu + Zn + Sn) (87 : 3 : 10)
- German Silver – Cu + Zn + Ni (2 : 1 : 1)
- Bell metal – Cu (80%) + Sn (20%)
- Nichrome – (Ni + Cr + Fe)

Some Important Compounds of Transition Metals

Oxides and oxoanions

Oxides are formed by reaction of O_2 with metals at high temperatures. They are formed in O.S. from +1 to +7 As oxidation number of metal increases, ionic character decreases.

e.g., MnO , Mn_3O_4 , Mn_2O_3 , MnO_2 , Mn_2O_7
 $+2 \quad +8/3 \quad +3 \quad +4 \quad +7$

Ionic character decreases

The oxides in lower OS of metals are basic and in higher OS they are acidic whereas in intermediate OS, they are amphoteric.

For ex:

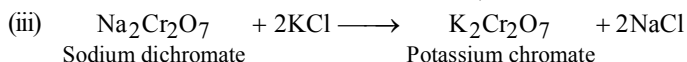
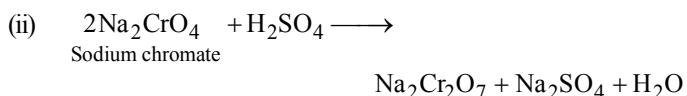
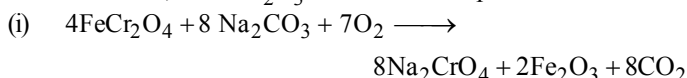
(i) MnO Mn_3O_4 Mn_2O_3 MnO_2 Mn_2O_7
 Basic Amphoteric Amphoteric Amphoteric Acidic
 ($\therefore Mn_2O_7 + H_2O$)
 $HMnO_4$

(ii) V_2O_3 V_2O_4 V_2O_5
 basic less basic amphoteric (mainly acidic)
 ($\therefore V_2O_5$ reacts with alkalis and acids to give VO_4^{3-} and VO_4^+)

(iii) CrO Cr_2O_3 CrO_3
 basic amphoteric acidic
 (CrO_3 dissolves in water to give the acids H_2CrO_4 and $H_2Cr_2O_7$)

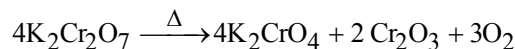
Potassium dichromate ($K_2Cr_2O_7$)

Preparation : It is prepared from ore called chromite or ferrochrome or chrome iron, $FeO \cdot Cr_2O_3$. The various steps involved are:

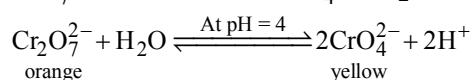
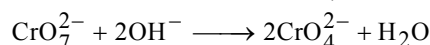
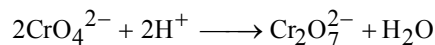


Properties:

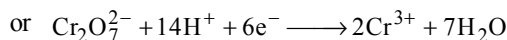
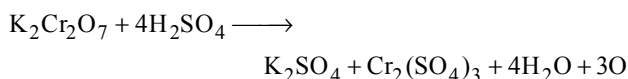
- It forms orange crystals which melt at 669 K.
- It is moderately soluble in cold water and freely soluble in hot water.
- When heated, it decomposes with the evolution of oxygen.



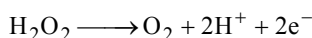
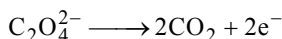
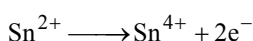
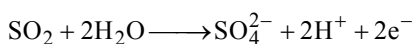
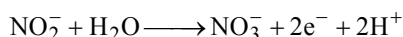
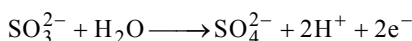
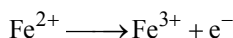
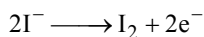
- The chromates and dichromates are interconvertible in aqueous solution depending on pH of the solution.



- (v) $\text{Na}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$ are strong oxidising agents. In acidic medium, it furnishes 3 atoms of available oxygen as shown by the equation :



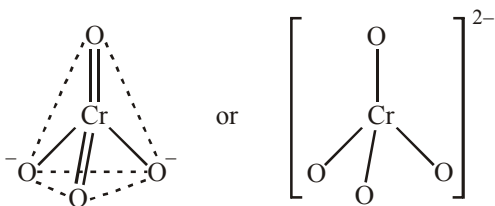
It oxidises



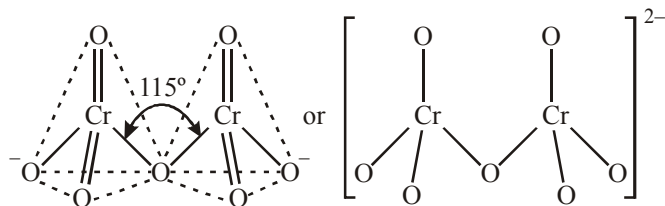
Uses -

- In chrome tanning,
- In dyeing-calico printing,
- In photography
- Chromic acid (mixture of $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$) used as cleaning agent,
- In preparation of compounds such as $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_2 \cdot 24\text{H}_2\text{O}$, CrO_2Cl_2 etc.

Structures of chromate and dichromate ions :



Chromate ion – Tetrahedral structure



Dichromate ion – Two tetrahedra showing one oxygen atom at one corner

Note :

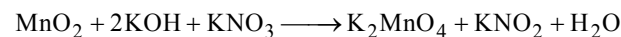
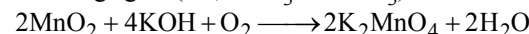
- OS of Cr in chromate and dichromate is same, i.e., +6.
- It is used in the detection of Cl^- in qualitative analysis in the chromyl chloride test.
- $\text{Na}_2\text{Cr}_2\text{O}_7$ is more soluble in water than $\text{K}_2\text{Cr}_2\text{O}_7$.
- $\text{Na}_2\text{Cr}_2\text{O}_7$ is not used in volumetric analysis as it is deliquescent

Potassium permanganate (KMnO_4)

Preparation

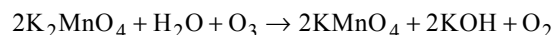
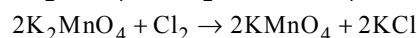
- (i) **Conversion of MnO_2 into potassium manganate :**

Pyrolusite is fused with KOH or K_2CO_3 in presence of air or oxidising agent (i.e., KNO_3 or KClO_3)

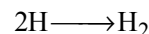
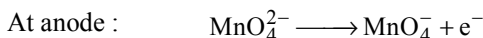
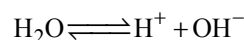
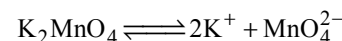


Oxidation of K_2MnO_4 to KMnO_4 :

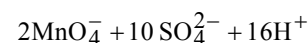
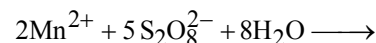
- (a) **Chemical oxidation :**



- (b) **Electrolytic oxidation :** The alkaline manganate solution is electrolysed between iron electrodes :

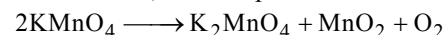


- (ii) **Laboratory method :**

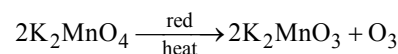


Properties

- It exists as deep purple black prisms with greenish lustre which become dull in air due to superficial reduction.
- It is moderately soluble in H_2O at room temperature.
- When heated, it decomposes at 513 K

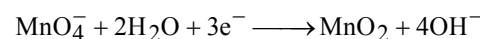


At red heat.

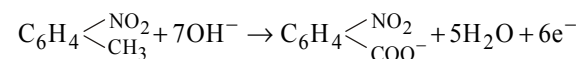
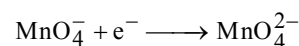


- (iv) It is a powerful oxidising agent (in neutral, alkaline and acidic medium)

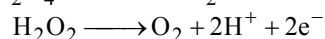
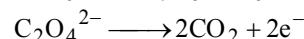
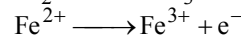
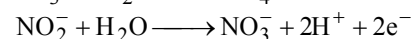
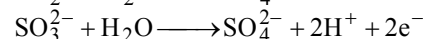
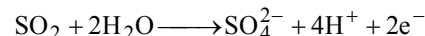
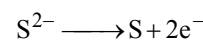
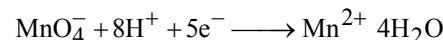
In **neutral** medium, the reaction is



In **alkaline** medium:



In **acidic** medium :



Note : Volumetric titrations involving KMnO_4 are carried out only in presence of H_2SO_4 not HCl or HNO_3 . This is because oxygen produced from $\text{KMnO}_4 + \text{dil. H}_2\text{SO}_4$ is used only for oxidising the reducing agent. Moreover, H_2SO_4 does not give any oxygen of its own to oxidize the reducing. In case HCl is used, the oxygen produced from $\text{KMnO}_4 + \text{HCl}$ is partly used up to oxidise HCl to chlorine and in case HNO_3 is used, it itself acts as oxidising agent and partly oxidizes the reducing agent.

THE INNER TRANSITION ELEMENTS (f-BLOCK)

The elements in which the last e^- enters the anti - penultimate energy level, i.e., $(n-2)$ f-orbitals are called f - block elements. They are also called inner transition elements.

Their general electronic configuration is :

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2.$$

The f - block consists of two series, lanthanoids and actinoids.

The Lanthanoids (Ln)

Electronic configurations

They have electronic configuration with $6s^2$ common but with variable occupancy of 4 f-level. The electronic configuration of their tripositive ions are of the form $4f^n$.

Atomic and ionic sizes

In lanthanoids with increasing atomic number, there is a progressive decrease in the atomic as well as ionic radii. This regular decrease in size with increasing atomic number is called **lanthanoid contraction**. It arises due to imperfect shielding of the electrons by the f - subshell.

In the lanthanoid series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from La^{+3} to Lu^{+3} . This contraction in size is known as lanthanoid contraction.

Cause of lanthanoid contraction :

As we move along lanthanoid series, the nuclear charge increases by one unit at each element and is added into same sub-shell ($4f$). Due to shape of f-orbitals, there is imperfect shielding of one electron by another. This imperfect shielding is unable to counterbalance the effect of increased nuclear charge, thus resulting in contraction in size.

Consequences of lanthanoid contraction

- Difficulty in the separation of lanthanoids due to very small change in their atomic radii
- Similarity in size of elements belonging to same group of second and third transition series.
- As the size decreases from La^{3+} to Lu^{3+} , covalent character of hydroxides increases and hence, the basic strength decreases. Thus $\text{La}(\text{OH})_3$ is most basic while $\text{Lu}(\text{OH})_3$ is least basic..

Oxidation states

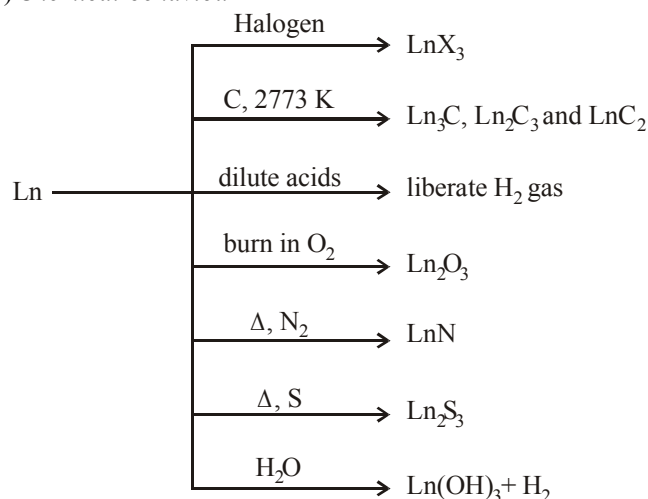
The typical OS of Ln is +3. Oxidation states + 2 and +4 occur particularly when they lead to :

- A noble gas configuration e.g. Ce^{4+} (f^0)
- A half filled 'f' orbital e.g. Eu^{2+} , Tb^{4+} , (f^7)
- A completely filled 'f' orbital e.g. Yb^{2+} (f^{14})

They show limited OS due to large energy gap between 4f and 5d subshells.

General characteristics

- They are silvery white soft metals and tarnish rapidly in air.
- They have high densities and melting points.
- They have typical metallic structure and are good conductors of heat and electricity.
- The lanthanoid ions have unpaired electrons in their incomplete 4f orbitals. Thus these electrons absorb energy in visible region of light and undergo f-f transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. Lanthanoid ions having $4f^0$, $4f^7$ and $4f^{14}$ are colourless.
- Their ions [except La^{3+} (f^0) and Lu^{3+} (f^{14})] show paramagnetism due to unpaired electrons in 4f - subshell.
- They have low IE and are highly electropositive. They readily lose e^- s and are thus good reducing agents.
- Because of their large size and low charge density they do not have much tendency to form complexes.
- Chemical behaviour*



Uses of lanthanoids

- Lanthanoids are used in production of alloy steels for plates and pipes. Ex: misch metal (Ln metal (95%), iron (5%) and traces of S, C, Ca and Al. Misch metal is used in making magnesium based alloys, bullets, shells and lighter flints.
- Their oxides are used in glass industry, for polishing glass and for making coloured glasses for goggles as they give protection against UV light.
- Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.
- Lanthanoid compounds like cerium molybdate, cerium tungstate are used as paints and dyes.

The Actinoids (Ac)

Electronic configurations

The general configuration of actinoids may be given as $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$. They have common $7s^2$ configuration and variable occupancy of 5f and 6d subshells. Though 4f and 5f orbitals have similar shapes but 5f is less deeply buried than 4f. Hence, 5f electrons can participate in bonding to a far greater extent

Ionic sizes

They show a general trend of decrease in size like lanthanoids. This is referred to as actinoid contraction. The contraction is greater from element to element resulting from poor shielding by 5f - electrons.

This is on account of the reason that the 5f orbitals are more diffused than the orbitals present in 4f sub-shell. Consequently, the shielding by 5f electrons is much less than by 4f electrons in lanthanoids. The magnitude of actinoid contraction is more than that of lanthanoid contraction.

Oxidation states

They show larger no. of OS due to small energy gap between 5f, 6d and 7s subshells. General OS is +3. They also show OS of +4. Compounds with +3 and +4 oxidation state tend to hydrolyse.

General characteristics

- (i) Actinoid metals have silvery appearance.
- (ii) Actinoid cations are coloured due to f - f transitions. Cations with f^0 , f^7 and f^{14} configurations are colourless.
- (iii) They have high m.pt and b.pt., high densities, low IE and are highly electropositive.
- (iv) They are strongly paramagnetic, strong reducing agents and are radioactive.

Note : The actinoids have lower ionization enthalpies than lanthanoids because 5f is less penetrating than 4f.

Comparison of lanthanoids and actinoids

Similarities:

- (i) Both show an OS of +3

- (ii) Both are electropositive and highly reactive.
- (iii) Both exhibit magnetic and spectral properties.

Differences:

Lanthanoids		Actinoids	
1	Besides +3 OS, they show +2 and +4 OS in few cases.	1	Besides +3 OS, they show higher OS of +4, +5, +6, +7 also.
2	Most of their ions are colourless.	2	Most of their ions are coloured.
3	They have less tendency to form complexes.	3	They have greater tendency to form complexes.
4	Lanthanoid compounds are less basic.	4	Actinoid compounds are more basic
5	Non-radioactive, except promethium	5	Radioactive
6	Their magnetic properties can be explained easily.	6	Their magnetic properties cannot be explained easily.

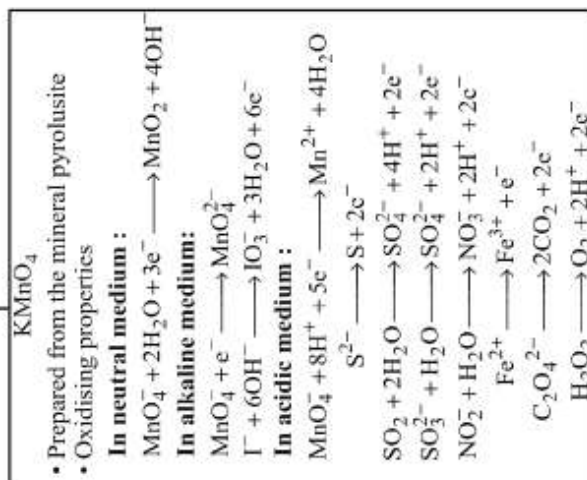
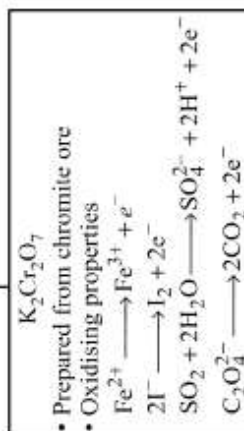
CONCEPT MAP

THE d- & f-BLOCK ELEMENTS

The d-Block Elements

- **Four transition series:**
 - (a) 3d series : From Se(21) to Zn (30)
 - (b) 4d series : From Y (39) to Cd (48)
 - (c) 5d series : 57 (La), 72 (Hf) to Hg 80
 - (d) 6d series : 89 (Ac), 104 (Ku) to (Uub) 112
- **Electronic configuration:** $(n-d)^m n-s^2$
- **Oxidation state:** Shows variable oxidation states
- **Magnetic property:** Transition elements and many of their compounds are paramagnetic.
- **Coloured compounds:** Forms coloured compounds due to $d-d$ transition.
- **Forms complexes:** Due to small highly charged ions and vacant d-orbitals
- **Forms interstitial compounds:** As they are able to entrap atoms of elements having small atomic size like H, C, N, B etc.
- **Oxides:** Oxides in lower oxidation states are basic, whereas those with higher oxidation state are acidic or amphoteric

Some important d-block elements compound



The f-Block Elements

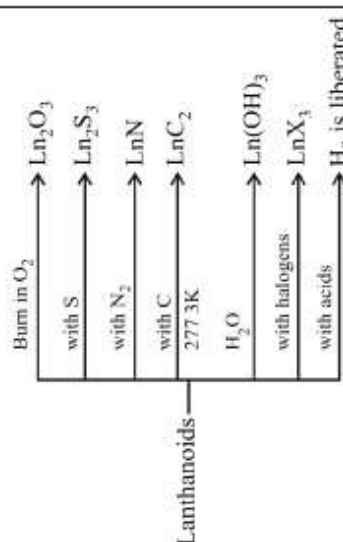
Lanthanoids

- 14 elements from Ce to Lu
- General E.C: $6s^2 5d^0 4f^{1-14}$
- Shows lanthanoid contraction due to poor shielding effect of 4f electrons.
- Most stable O.S. is +3

Actinoids

- General E.C: $[Rn] 5f^{1-14} 6d^{0-1} 7s^2$
- Most stable O.S. is +3. Also shows O.S like +4, +5, +6 and +7
- These are mostly radioactive
- Have much greater tendency to form complexes than lanthanides.

Chemical properties



EXERCISE - 1

Conceptual Questions

- The oxides, CrO_3 , MoO_3 , and WO_3 are strongly
 - neutral
 - acidic
 - basic
 - none of these
- $4\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{heat}} 4\text{K}_2\text{CrO}_4 + 3\text{O}_2 + \text{X}$. In the above reaction X is:
 - Cr_2O_3
 - Cr_2O_7
 - Cr_2O_5
 - CrO_5
- Which one of the following ionic species will impart colour to an aqueous solution?
 - Ti^{4+}
 - Cu^{+}
 - Zn^{2+}
 - Cr^{3+}
- The aqueous solution containing which one of the following ions will be colourless? (Atomic number: Sc = 21, Fe = 26, Ti = 22, Mn = 25)
 - Sc^{3+}
 - Fe^{2+}
 - Ti^{3+}
 - Mn^{2+}
- When tin is treated with concentrated nitric acid:
 - it is converted into stannous nitrate
 - it is converted into stannic nitrate
 - it is converted into metastannic acid
 - it becomes passive
- In which of the following pairs both the ions are coloured in aqueous solutions?
 - Sc^{3+} , Ti^{3+}
 - Sc^{3+} , Co^{2+}
 - Ni^{2+} , Cu^{+}
 - Ni^{2+} , Ti^{3+}
 (At. no. : Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)
- Which of the following ions has the maximum magnetic moment?
 - Mn^{+2}
 - Fe^{+2}
 - Ti^{3+}
 - Cr^{+2}
- For the ions Zn^{2+} , Ni^{2+} and Cr^{3+} which among the following statements is correct? (atomic number of Zn = 30, Ni = 28 and Cr = 24)
 - All these are colourless
 - All these are coloured
 - Only Ni^{2+} is coloured and Zn^{2+} and Cr^{3+} are colourless
 - Only Zn^{2+} is colourless and Ni^{2+} and Cr^{3+} are coloured
- Copper and con. H_2SO_4 react to produce
 - Cu
 - SO_2
 - H_2
 - O_2
- The volatile metal is :
 - Fe
 - Zn
 - Cu
 - Ag
- Which of the following metal ions is not coloured?
 - Ti^{3+}
 - Fe^{3+}
 - V^{2+}
 - Cu^{+}
- The transition metal with least atomic number is :
 - Os
 - Zr
 - Pt
 - Ru
- Which of the following element is not a member of transition elements?
 - Zn
 - Pt
 - Ce
 - Mo
- Which of the following configuration is correct for iron?
 - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4$
 - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6 4s^2$
 - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2$
 - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2 4s^2$
- Percentage of silver in German silver is :
 - 0%
 - 1%
 - 5%
 - none of these
- In first transition series, the melting point of Mn is low because
 - due to d^{10} configuration, metallic bonds are strong
 - due to d^7 configuration, metallic bonds are weak
 - due to d^5 configuration, metallic bonds are weak
 - None of these
- The number of unpaired electrons in gaseous species of Mn^{3+} , Cr^{3+} and V^{3+} respectively are.
 - 4, 3 and 2
 - 3, 3 and 2
 - 4, 3 and 2
 - 3, 3 and 3
- The liquified metal expanding on solidification is
 - Ga
 - Al
 - Zn
 - Cu
- In which of the following metallic bond is strongest?
 - Fe
 - Sc
 - V
 - Cr
- Stainless steel contains iron and
 - Cr + Ni
 - Cr + Zn
 - Zn + Pb
 - C + Cr + Ni
- Among the following, the compound that is both paramagnetic and coloured, is
 - KMnO_4
 - CuF_2
 - $\text{K}_2\text{Cr}_2\text{O}_7$
 - All are coloured
- Which of the following elements shows maximum number of different oxidation states in its compounds?
 - Eu
 - La
 - Gd
 - Am
- $\text{K}_2\text{Cr}_2\text{O}_7$ on heating with aqueous NaOH gives
 - CrO_4^{2-}
 - $\text{Cr}(\text{OH})_3$
 - $\text{Cr}_2\text{O}_7^{2-}$
 - $\text{Cr}(\text{OH})_2$
- CrO_3 dissolves in aqueous NaOH to give
 - $\text{Cr}_2\text{O}_7^{2-}$
 - CrO_4^{2-}
 - $\text{Cr}(\text{OH})_3$
 - $\text{Cr}(\text{OH})_2$
- To prevent corrosion, iron pipes carrying drinking water are covered with zinc. The process involved is
 - alloy formation
 - electroplating
 - galvanising
 - soldering
- When KMnO_4 acts as an oxidising agent and ultimately forms $[\text{MnO}_4]^{-2}$, MnO_2 , Mn_2O_3 , Mn^{+2} then the number of electrons transferred in each case respectively is
 - 4, 3, 1, 5
 - 1, 5, 3, 7
 - 1, 3, 4, 5
 - 3, 5, 7, 1.

27. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is:
 (a) +3 (b) +2
 (c) +6 (d) +4
28. When the same amount of zinc is treated separately with excess of H_2SO_4 and excess of NaOH, the ratio of volumes of H_2 evolved is
 (a) 1 : 1 (b) 1 : 2
 (c) 2 : 1 (d) 9 : 4
29. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives
 (a) HgO (b) Hg_2O
 (c) $\text{NH}_2 - \text{Hg} - \text{Hg} - \text{Cl}$ (d) $\text{Hg}_2\text{NH}_2\text{Cl}$
30. Copper becomes green when exposed to moist air for longer period –
 (a) because of the formation of a layer of cupric oxide on the surface of copper
 (b) because of the formation of a layer of basic carbonate of copper on the surface of copper
 (c) because of the formation of a layer of cupric hydroxide on the surface of copper
 (d) because of the formation of a layer of cupric acetate on the surface of copper
31. Copper displaces which of the metal from their salt solutions?
 (a) AgNO_3 (b) ZnSO_4
 (c) FeSO_4 (d) All of the above
32. Gun metal is an alloy of:
 (a) Cu and Al (b) Cu and Sn
 (c) Cu, Zn and Sn (d) Cu, Zn and Ni
33. Which of the following has lowest percentage of carbon?
 (a) Cast iron
 (b) Wrought iron
 (c) Steel iron
 (d) All have same percentage.
34. Black jack is an ore of:
 (a) Cr (b) Sn
 (c) Zn (d) Ni
35. Which one of the following is coinage metal?
 (a) Zn (b) Cu
 (c) Sn (d) Pb.
36. When excess of SnCl_2 is added to a solution of HgCl_2 , a white precipitate turning to grey is obtained. This grey colour is due to the formation of
 (a) Hg_2Cl_2 (b) SnCl_4
 (c) Sn (d) Hg.
37. Bronze is an alloy of:
 (a) Pb + Sn + Zn (b) Cu + Sn
 (c) Pb + Zn (d) Cu + Zn
38. The treatment of Cu with dilute HNO_3 gives:
 (a) N_2O (b) NO
 (c) NH_4^+ (d) NO_2
39. White vitriol has the formula:
 (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (c) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (d) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
40. Addition of iron fillings to CuSO_4 solution caused precipitation of Cu owing to the
 (a) Reduction of Cu^{2+} (b) Oxidation of Cu^{2+}
 (c) Reduction of Fe (d) Reduction of Fe^{3+}
41. The final products formed on the addition of KI to copper sulphate solution are:
 (a) K_2SO_4 , CuI_2 and I_2 (b) K_2SO_4 , Cu_2I_2 and I_2
 (c) K_2SO_4 and Cu_2O (d) K_2SO_4 , CuO and I_2
42. KMnO_4 (acidic/alkaline) is not decolourised by
 (a) mohr salt (b) oxalic acid
 (c) benzene (d) propene
43. Bessemer converter is used in the manufacture of
 (a) Pig iron (b) Steel
 (c) Wrought (d) Cast iron.
44. Among the lanthanoides the one obtained by synthetic method is
 (a) Lu (b) Pm
 (c) Pr (d) Gd
45. Both acid and base may react with which of the following oxides?
 (a) CaO (b) Na_2O_2
 (c) ZnO (d) Mn_3O_4 .
46. The lanthanoid contraction is responsible for the fact that
 (a) Zr and Y have about the same radius
 (b) Zr and Nb have similar oxidation state
 (c) Zr and Hf have about the same radius
 (d) Zr and Zn have the same oxidation state
 (Atomic numbers: Zr = 40, Y = 39, Nb = 41, Hf = 72, Zn = 30)
47. Which one of the following elements shows maximum number of different oxidation states in its compounds?
 (a) Eu (b) La
 (c) Gd (d) Am
48. Among the following which is used as an electrolyte in electroplating a base metal with gold?
 (a) NH_4Cl (b) $\text{K}[\text{Au}(\text{CN})_2]$
 (c) HgCN (d) AgCN
49. Cuprous chloride is used in gas analysis to absorb?
 (a) CO_2 (b) CO
 (c) H_2 (d) CH_4
50. Lanthanoids are
 (a) 14 elements in the sixth period (atomic no. = 90 to 103) that are filling 4f sublevel
 (b) 14 elements in the seventh period (atomic no. = 90 to 103) that are filling 5f sublevel
 (c) 14 elements in the sixth period (atomic no. = 58 to 71) that are filling 4f sublevel
 (d) 14 elements in the seventh period (atomic no. = 58 to 71) that are filling 4f sublevel
51. Aufbau principle does not give the correct arrangement of filling up of atomic orbitals in:
 (a) Cu and Zn (b) Co and Zn
 (c) Mn and Cr (d) Cu and Cr
52. The radius of La^{3+} (Atomic number of La = 57) is 1.06 Å. Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71)?
 (a) 1.40 Å (b) 1.06 Å
 (c) 0.85 Å (d) 1.60 Å

53. Which of the following compounds is formed when a mixture of $K_2Cr_2O_7$ and $NaCl$ is heated with conc. H_2SO_4 ?
 (a) CrO_2Cl_2 (b) $CrCl_3$
 (c) $Cr_2(SO_4)_3$ (d) Na_2CrO_4
54. Which of the following factors may be regarded as the main cause of lanthanoid contraction?
 (a) Greater shielding of $5d$ electrons by $4f$ electrons
 (b) Poorer shielding of $5d$ electrons by $4f$ electrons
 (c) Effective shielding of one of $4f$ electrons by another in the subshell
 (d) Poor shielding of one of $4f$ electron by another in the subshell
55. For making Ag from $AgNO_3$, which of the following is used
 (a) PH_3 (b) phosphonium iodide
 (c) Na_2CO_3 (d) NH_3
56. The titanium (atomic number 22) compound that does not exist is
 (a) TiO (b) TiO_2
 (c) K_2TiF_6 (d) K_2TiO_4
57. The Ce ($Z = 58$) belongs to IIIrd group of periodic table. If it furnish one α particle to form an element 'X', then X belongs to
 (a) IIIrd group (b) IInd group
 (c) Ist group (d) zero group
58. Lanthanum is grouped with f-block elements because
 (a) it has partially filled f-orbitals
 (b) it is just before Ce in the periodic table
 (c) it has both partially filled f and d-orbitals
 (d) properties of lanthanum are very similar to the elements of f-block
59. The approximate percentage of iron in mischmetal is
 (a) 10 (b) 20
 (c) 50 (d) 5
60. Which of the following is not an actinide ?
 (a) Curium (b) Californium
 (c) Uranium (d) Terbium
61. A reduction in atomic size with increase in atomic number is a characteristic of elements of
 (a) high atomic masses (b) d-block
 (c) f-block (d) Radioactive series
62. Identify the product and its colour when MnO_2 is fused with solid KOH in the presence of O_2 .
 (a) $KMnO_4$, purple (b) K_2MnO_4 , dark green
 (c) MnO , colourless (d) Mn_2O_3 , brown
63. Which one of the following ions is the most stable in aqueous solution?
 (a) V^{3+} (b) Ti^{3+}
 (c) Mn^{3+} (d) Cr^{3+}
 (At.No. $Ti = 22$, $V = 23$, $Cr = 24$, $Mn = 25$)
64. Identify the incorrect statement among the following :
 (a) Lanthanoid contraction is the accumulation of successive shrinkages.
 (b) As a result of lanthanoid contraction, the properties of 4d series of the transition elements have no similarities with the 5d series of elements.
- (c) Shielding power of $4f$ electrons is quite weak.
 (d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.
65. The correct order of decreasing second ionisation enthalpy of Ti (22), V (23), Cr (24) and Mn (25) is :
 (a) $Cr > Mn > V > Ti$ (b) $V > Mn > Cr > Ti$
 (c) $Mn > Cr > Ti > V$ (d) $Ti > V > Cr > Mn$
66. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states?
 (a) $3d^5 4s^1$ (b) $3d^5 4s^2$
 (c) $3d^2 4s^2$ (d) $3d^3 4s^2$
67. Which one of the following ions has electronic configuration $[Ar] 3d^6$?
 (a) Ni^{3+} (b) Mn^{3+}
 (c) Fe^{3+} (d) Co^{3+}
 (At. Nos. $Mn = 25$, $Fe = 26$, $Co = 27$, $Ni = 28$)
68. Which of the following pairs has the same size?
 (a) Fe^{2+} , Ni^{2+} (b) Zr^{4+} , Ti^{4+}
 (c) Zr^{4+} , Hf^{4+} (d) Zn^{2+} , Hf^{4+}
69. Which of the following oxidation states is the most common among the lanthanoids?
 (a) 3 (b) 4
 (c) 2 (d) 5
70. For the four successive transition elements (Cr , Mn , Fe and Co), the stability of +2 oxidation state will be there in which of the following order?
 (a) $Mn > Fe > Cr > Co$ (b) $Fe > Mn > Co > Cr$
 (c) $Co > Mn > Fe > Cr$ (d) $Cr > Mn > Co > Fe$
71. Acidified $K_2Cr_2O_7$ solution turns green when Na_2SO_3 is added to it. This is due to the formation of :
 (a) $Cr_2(SO_4)_3$ (b) CrO_4^{2-}
 (c) $Cr_2(SO_3)_3$ (d) $CrSO_4$
72. Which of the statements is not true?
 (a) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed.
 (b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis.
 (c) $K_2Cr_2O_7$ solution in acidic medium is orange.
 (d) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7.
73. Which one of the following does not correctly represent the correct order of the property indicated against it?
 (a) $Ti < V < Cr < Mn$: increasing number of oxidation states
 (b) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$: increasing magnetic moment
 (c) $Ti < V < Cr < Mn$: increasing melting points
 (d) $Ti < V < Mn < Cr$: increasing 2nd ionization enthalpy
74. The catalytic activity of transition metals and their compounds is mainly due to :
 (a) their magnetic behaviour
 (b) their unfilled d-orbitals
 (c) their ability to adopt variable oxidation state
 (d) their chemical reactivity
75. Which of the following exhibit only + 3 oxidation state ?
 (a) U (b) Th (c) Ac (d) Pa

EXERCISE - 2

Applied Questions

- To an aqueous solution containing anions a few drops of acidified KMnO_4 are added. Which one of the following anions, if present will not decolourise the KMnO_4 solution?
 - I^-
 - CO_3^{2-}
 - S^{2-}
 - NO_2^-
- Consider the following statements
 - $\text{La}(\text{OH})_3$ is the least basic among hydroxides of lanthanides.
 - Zr^{4+} and Hf^{4+} possess almost the same ionic radii.
 - Ce^{4+} can act as an oxidizing agent.
 Which of the above is/are true?
 - (I) and (III)
 - (II) and (III)
 - (II) only
 - (I) and (II)
- The basic character of the transition metal monoxides follows the order
(Atomic Nos., Ti = 22, V = 23, Cr = 24, Fe = 26)
 - TiO > VO > CrO > FeO
 - VO > CrO > TiO > FeO
 - CrO > VO > FeO > TiO
 - TiO > FeO > VO > CrO
- The correct order of ionic radii of Y^{3+} , La^{3+} , Eu^{3+} and Lu^{3+} is
 - $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$
 - $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$
 - $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$
 - $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$
 (Atomic nos. Y = 39, La = 57, Eu = 63, Lu = 71)
- Which one of the following metals has a different lattice from those of the others?
 - Fe
 - Co
 - Ni
 - Cu
- Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is
(At. nos. Ti = 22; V = 23; Cr = 24; Mn = 25)
 - Ti^{3+} , V^{2+} , Cr^{3+} , Mn^{4+}
 - Ti^+ , V^{4+} , Cr^{6+} , Mn^{7+}
 - Ti^{4+} , V^{3+} , Cr^{2+} , Mn^{3+}
 - Ti^{2+} , V^{3+} , Cr^{4+} , Mn^{5+}
- A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is
 - HgI_2
 - HgO
 - Pb_3O_4
 - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown-red vapours of:
 - CrO_3
 - CrCl_3
 - CrO_2Cl_2
 - Cr_2O_3
- Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them?
 - $(n-1)d^3 ns^2$
 - $(n-1)d^5 ns^1$
 - $(n-1)d^8 ns^2$
 - $(n-1)d^5 ns^2$
- When a small amount of KMnO_4 is added to concentrated H_2SO_4 , a green oily compound is obtained which is highly explosive in nature. Compound may be:
 - MnSO_4
 - Mn_2O_7
 - MnO_2
 - Mn_2O_3
- For d block elements the first ionization potential is of the order:
 - $\text{Zn} > \text{Fe} > \text{Cu} > \text{Cr}$
 - $\text{Sc} = \text{Ti} < \text{V} = \text{Cr}$
 - $\text{Zn} < \text{Cu} < \text{Ni} < \text{Co}$
 - $\text{V} > \text{Cr} > \text{Mn} > \text{Fe}$
- A blue colouration is not obtained when
 - ammonium hydroxide dissolves in copper sulphate
 - copper sulphate solution reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$
 - ferric chloride reacts with sod. ferrocyanide
 - anhydrous CuSO_4 is dissolved in water
- Which of the following combines with Fe (II) ions to form a brown complex?
 - NO
 - N_2O
 - N_2O_3
 - N_2O_5
- Oxidation states of the metal in the minerals haematite and magnetite, respectively, are
 - II, III in haematite and III in magnetite
 - II, III in haematite and II in magnetite
 - II in haematite and II, III in magnetite
 - III in haematite and II, III in magnetite
- A solution of sodium thiosulphate on addition of few drops of ferric chloride gives violet colour due to the formation of
 - $\text{Na}_2\text{S}_4\text{O}_6$
 - $\text{Fe}_2(\text{SO}_4)_3$
 - $\text{Fe}_2(\text{S}_2\text{O}_3)_3$
 - $\text{Fe}_2(\text{S}_2\text{O}_3)_2$
- Precipitate of AgCl is soluble in liquid NH_3 , the compound forms
 - $\text{Ag}(\text{NH}_4)_2\text{OH}$
 - $\text{Ag}(\text{NH}_4)_2\text{Cl}$
 - $\text{Ag}(\text{NH}_3)_2\text{OH}$
 - $\text{Ag}(\text{NH}_3)_2\text{Cl}$
- Philosopher's wool is:
 - ZnCl_2
 - ZnS
 - $\text{Zn}(\text{NO}_3)_2$
 - ZnO
- Zinc and mercury do not show variable valency like d -block elements because
 - they are soft
 - their d -shells are complete
 - they have only two electrons in the outermost subshell
 - their d -shells are incomplete
- Silver nitrate produces a black stain on skin due to
 - being a strong reducing agent
 - its corrosive action
 - formation of complex compound
 - its reduction to metallic silver
- KI and CuSO_4 solutions on mixing produce:
 - $\text{Cu}_2\text{I}_2 + \text{K}_2\text{SO}_4$
 - $\text{Cu}_2\text{I}_2 + \text{I}_2 + \text{K}_2\text{SO}_4$
 - $\text{CuI}_2 + \text{K}_2\text{SO}_4$
 - $\text{CuI}_2 + \text{I}_2 + \text{K}_2\text{SO}_4$
- Which one is most acidic?
 - Cr_2O_3
 - V_2O_5
 - Mn_2O_7
 - Fe_2O_3

22. Which of the following statement is incorrect ?
 (a) Across a period from Sc to Cu the densities increase with increasing atomic number.
 (b) The melting point of transition elements rise to a maximum from Sc to Cr and then decreases from Fe to Zn.
 (c) Transition elements have high enthalpies of atomization and in 3d series increase regularly from Sc to Cu.
 (d) On going down a group from 3d to 6d series the stability of higher oxidation state increases with increasing atomic number.
23. Lithopone is a mixture of :
 (a) $\text{ZnCO}_3, \text{BaCO}_3$ (b) $\text{ZnS}, \text{Na}_2\text{SO}_4$
 (c) $\text{ZnSO}_4, \text{BaSO}_4$ (d) $\text{ZnS}, \text{BaSO}_4$
24. Out of TiF_6^{2-} , CoF_6^{3-} , Cu_2Cl_2 and NiCl_4^{2-} (Z of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are:
 (a) Cu_2Cl_2 and NiCl_4^{2-} (b) TiF_6^{2-} and Cu_2Cl_2
 (c) CoF_6^{3-} and NiCl_4^{2-} (d) TiF_6^{2-} and CoF_6^{3-}
25. Which of the following ions will exhibit colour in aqueous solutions?
 (a) La^{3+} (Z = 57) (b) Ti^{3+} (Z = 22)
 (c) Lu^{3+} (Z = 71) (d) Sc^{3+} (Z = 21)
26. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are
 (a) II, III in haematite and III in magnetite
 (b) II, III in haematite and II in magnetite
 (c) II in haematite and II, III in magnetite
 (d) III in haematite and II, III in magnetite
27. Which of the following arrangements does not represent the correct order of the property stated against it ?
 (a) $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: paramagnetic behaviour
 (b) $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: ionic size
 (c) $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: stability in aqueous solution
 (d) $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: number of oxidation states
28. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{\text{M}^{3+}/\text{M}^{2+}}$ value ?
 (a) Cr (Z = 24) (b) Mn (Z = 25)
 (c) Fe (Z = 26) (d) Co (Z = 27)
29. Identify the incorrect statement among the following:
 (a) 4f and 5f orbitals are equally shielded.
 (b) d-Block elements show irregular and erratic chemical properties among themselves.
 (c) La and Lu have partially filled d-orbitals and no other partially filled orbitals.
 (d) The chemistry of various lanthanoids is very similar.
30. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being
 (a) 4f orbitals more diffused than the 5f orbitals
 (b) lesser energy difference between 5f and 6d than between 4f and 5d orbitals
 (c) more energy difference between 5f and 6d than between 4f and 5d orbitals
 (d) more reactive nature of the actinoids than the lanthanoids
31. Amount of oxalic acid present in a solution can be determined by its titration with KMnO_4 solution in the presence of H_2SO_4 . The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl
 (a) gets oxidised by oxalic acid to chlorine
 (b) furnishes H^+ ions in addition to those from oxalic acid
 (c) reduces permanganate to Mn^{2+}
 (d) oxidises oxalic acid to carbon dioxide and water
32. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect?
 (a) The ionic size of Ln (III) decrease in general with increasing atomic number
 (b) Ln (III) compounds are generally colourless.
 (c) Ln (III) hydroxide are mainly basic in character.
 (d) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
33. In context of the lanthanoids, which of the following statements is not correct?
 (a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
 (b) All the members exhibit +3 oxidation state.
 (c) Because of similar properties the separation of lanthanoids is not easy.
 (d) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.
34. The outer electron configuration of Gd (Atomic No. : 64) is :
 (a) $4f^3 5d^5 6s^2$ (b) $4f^8 5d^0 6s^2$
 (c) $4f^4 5d^4 6s^2$ (d) $4f^7 5d^1 6s^2$
35. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect ?
 (a) Ferrous oxide is more basic in nature than the ferric oxide.
 (b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
 (c) Ferrous compounds are less volatile than the corresponding ferric compounds.
 (d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.
36. Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential $\left(E^\circ_{\text{M}^{2+}/\text{M}}\right)$ value has a positive sign?
 (a) Co (Z = 27) (b) Ni (Z = 28)
 (c) Cu (Z = 29) (d) Fe (Z = 26)
37. Which of the following species is/are paramagnetic?
 Fe^{2+} , Zn^0 , Hg^{2+} , Ti^{4+}
 (a) Fe^{2+} only (b) Zn^0 and Ti^{4+}
 (c) Fe^{2+} and Hg^{2+} (d) Zn^0 and Hg^{2+}
38. The titanium (atomic number 22) compound that does not exist is
 (a) TiO (b) TiO_2
 (c) K_2TiF_6 (d) K_2TiO_4

39. The colour of the following ions V^{2+} , V^{3+} , V^{4+} , Fe^{2+} , Fe^{3+} are respectively
 (a) green, violet, blue, green, yellow
 (b) yellow, green, violet, green, blue
 (c) violet, green, yellow, green, blue
 (d) yellow, green, blue, green, violet
40. Which of the following is not a characteristic of interstitial compounds of transition elements?
 (a) The formulae of these compounds do not correspond to any normal oxidation state
 (b) They have melting points higher than those of pure elements
 (c) They are very hard and some compounds approach diamond in hardness
 (d) They are insulators in contrast to the transition metals
41. In the following salts the lowest value of magnetic moment is observed in
 (a) $MnSO_4 \cdot 4H_2O$ (b) $CuSO_4 \cdot 5H_2O$
 (c) $FeSO_4 \cdot 6H_2O$ (d) $ZnSO_4 \cdot 7H_2O$
42. Which one of the following transition elements does not exhibit variable oxidation state?
 (a) Ni (b) Cu
 (c) Fe (d) Sc
43. Identify the product and its colour when MnO_2 is fused with solid KOH in the presence of O_2 .
 (a) $KMnO_4$, purple (b) K_2MnO_4 , dark green
 (c) MnO , colourless (d) Mn_2O_3 , brown
44. Which one of the following ions has the maximum magnetic moment?
 (a) Sc^{3+} (b) Ti^{3+}
 (c) Cr^{3+} (d) Fe^{3+}

DIRECTIONS for Qs. 45 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
45. **Statement-1 :** Magnetic moment values of actinides are lesser than the theoretically predicted values.
Statement-2 : Actinide elements are strongly paramagnetic.
46. **Statement-1 :** Cu^{2+} and Cd^{2+} are separated from each other by first adding KCN solution and then passing H_2S gas.
Statement-2 : KCN reduces Cu^{2+} to Cu^+ and forms a complex with it.
47. **Statement-1 :** Cuprous ion (Cu^+) has unpaired electrons while cupric ion (Cu^{++}) does not.
Statement-2 : Cuprous ion (Cu^+) is colourless whereas cupric ion (Cu^{++}) is blue in the aqueous solution
48. **Statement-1 :** Transition metals show variable valency.
Statement-2 : Transition metals have a large energy difference between the ns^2 and $(n-1)d$ electrons.
49. **Statement-1 :** Transition metals are good catalysts.
Statement-2 : V_2O_5 or Pt is used in the preparation of H_2SO_4 by contact process.
50. **Statement-1 :** Magnetic moment values of actinides are lesser than the theoretically predicted values.
Statement-2 : Actinide elements are strongly paramagnetic.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Electronic configuration of a transition element X in +3 oxidation state is $[Ar]3d^5$. What is its atomic number?
 (a) 25 (b) 26
 (c) 27 (d) 24
2. The electronic configuration of $Cu(II)$ is $3d^9$ whereas that of $Cu(I)$ is $3d^{10}$. Which of the following is correct.
 (a) $Cu(II)$ is more stable
 (b) $Cu(II)$ is less stable
 (c) $Cu(I)$ and $Cu(II)$ are equally stable
 (d) Stability of $Cu(I)$ and $Cu(II)$ depends on nature of copper salts
3. Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

- (a) Fe (b) Ni
 (c) Co (d) Cu

4. Generally, transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?
 (a) Ag_2SO_4 (b) CuF_2
 (c) ZnF_2 (d) Cu_2Cl_2
5. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4 , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.
 (a) Mn_2O_7 (b) MnO_2
 (c) $MnSO_4$ (d) Mn_2O_3
6. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.
 (a) $3d^7$ (b) $3d^5$
 (c) $3d^8$ (d) $3d^2$
7. Which of the following oxidation state is common for all lanthanoids?
 (a) +2 (b) +3
 (c) +4 (d) +5

8. Which of the following reactions are disproportionation reactions?
- $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$
 - $3\text{MnO}_4^- + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
 - $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
 - $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$
- (i)
 - (i), (ii) and (iii)
 - (ii), (iii) and (iv)
 - (i) and (iv)
9. When KMnO_4 solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because
- CO_2 is formed as the product
 - reaction is exothermic
 - MnO_4^- catalyses the reaction
 - Mn^{2+} acts as autocatalyst
10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?
- U
 - Np
 - Tm
 - Fm
11. KMnO_4 acts as an oxidising agent in acidic medium. The number of moles of KMnO_4 that will be needed to react with one mole of sulphide ions in acidic solution is
- $\frac{2}{5}$
 - $\frac{3}{5}$
 - $\frac{4}{5}$
 - $\frac{1}{5}$
12. Which of the following oxides are amphoteric?
- $\text{Mn}_2\text{O}_7, \text{CrO}_3, \text{Cr}_2\text{O}_3, \text{CrO}, \text{V}_2\text{O}_5, \text{V}_2\text{O}_4$
- $\text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3$
 - $\text{Mn}_2\text{O}_7, \text{CrO}_3$
 - $\text{CrO}, \text{V}_2\text{O}_5$
 - $\text{V}_2\text{O}_5, \text{V}_2\text{O}_4$
13. Gadolinium belongs to 4f series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?
- $[\text{Xe}]4f^7 5d^1 6s^2$
 - $[\text{Xe}]4f^6 5d^2 6s^2$
 - $[\text{Xe}]4f^8 6d^2$
 - $[\text{Xe}]4f^9 5s^1$
14. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?
- They have high melting points in comparison to pure metals
 - They are very hard
 - They retain metallic conductivity
 - They are chemically very reactive
15. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is
- 2.87 BM
 - 3.87 BM
 - 3.47 BM
 - 3.57 BM
16. KMnO_4 acts as an oxidising agent in alkaline medium. When alkaline KMnO_4 is treated with KI, iodide ion is oxidised to
- I_2
 - IO^-
 - IO_3^-
 - IO_4^-
17. Which of the following statements is not correct?
- Copper liberates hydrogen from acids
 - In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine
 - Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution
 - Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution
18. When acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added to Sn^{2+} salt then Sn^{2+} changes to
- Sn
 - Sn^{3+}
 - Sn^{4+}
 - Sn^+
19. Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because
- fluorine is more electronegative than oxygen
 - fluorine does not possess d-orbitals
 - fluorine stabilises lower oxidation state
 - in covalent compounds, fluorine can form single bond only while oxygen forms double bond
20. Although zirconium belongs to 4d transition series and hafnium to 5d transition series even then they show similar physical and chemical properties because
- both belong to d-block
 - both have same number of electrons
 - both have similar atomic radius
 - both belong to the same group of the periodic table
21. Why is HCl not used to make the medium acidic in oxidation reactions of KMnO_4 in acidic medium?
- Both HCl and KMnO_4 act as oxidising agents
 - KMnO_4 oxidises HCl into Cl_2 which is also an oxidising agent
 - KMnO_4 is a weaker oxidising agent than HCl
 - KMnO_4 acts as a reducing agent in the presence of HCl

NEET/AIPMT (2013-2017) Questions

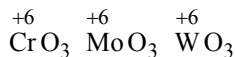
22. Which of the following lanthanoid ions is diamagnetic? (At nos. Ce = 58, Sm = 62, Eu = 63, Yb = 70) [2013]
- Sm^{2+}
 - Eu^{2+}
 - Yb^{2+}
 - Ce^{2+}
23. KMnO_4 can be prepared from K_2MnO_4 as per the reaction:
- $$3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^{2-} + \text{MnO}_2 + 4\text{OH}^-$$
- The reaction can go to completion by removing OH^- ions by adding. [2013]
- KOH
 - CO_2
 - SO_2
 - HCl
24. The outer electronic configuration of Gd (At. No. 64) is: [1997, NEET Kar. 2013]
- $4f^4 5d^5 6s^1$
 - $4f^5 5d^4 6s^1$
 - $4f^7 5d^1 6s^2$
 - $4f^3 5d^5 6s^2$
25. Sc (Z = 21) is a transition element but Zn (Z = 30) is not because [NEET Kar. 2013]
- both Sc and Zn do not exhibit variable oxidation states
 - both Sc^{3+} and Zn^{2+} ions are colourless and form white compounds

- (c) in case of Sc, $3d$ orbitals are partially filled but in Zn these are completely filled
 (d) last electron is assumed to be added to $4s$ level in case of Zn
26. The pair of compounds that can exist together is: [2014]
 (a) $\text{FeCl}_3, \text{SnCl}_2$ (b) $\text{HgCl}_2, \text{SnCl}_2$
 (c) $\text{FeCl}_2, \text{SnCl}_2$ (d) FeCl_3, KI
27. In acidic medium, H_2O_2 changes $\text{Cr}_2\text{O}_7^{2-}$ to CrO_5 which has two ($-\text{O}-\text{O}$) bonds. Oxidation state of Cr in CrO_5 is:- [2014]
 (a) +5 (b) +3
 (c) +6 (d) -10
28. The reaction of aqueous KMnO_4 with H_2O_2 in acidic conditions gives: [2014]
 (a) Mn^{4+} and O_2 (b) Mn^{2+} and O_2
 (c) Mn^{2+} and O_3 (d) Mn^{4+} and MnO_2
29. Magnetic moment 2.83 BM is given by which of the following ions? [2014]
 (At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28):-
 (a) Ti^{3+} (b) Ni^{2+}
 (c) Cr^{3+} (d) Mn^{2+}
30. Reason of lanthanoid contraction is:- [2014]
 (a) Negligible screening effect of ' f ' orbitals
 (b) Increasing nuclear charge
 (c) Decreasing nuclear charge
 (d) Decreasing screening effect
31. Magnetic moment 2.84 B.M. is given by :- [2015]
 (At. nos. Ni = 28, Ti = 22, Cr = 24, Co = 27)
 (a) Ti^{3+} (b) Cr^{2+}
 (c) Co^{2+} (d) Ni^{2+}
32. The number of d -electrons in Fe^{2+} ($Z = 26$) is not equal to the number of electrons in which one of the following? [2015]
 (a) p -electrons in Cl ($Z = 17$)
 (b) d -electrons in Fe ($Z = 26$)
 (c) p -electrons in Ne ($Z = 10$)
 (d) s -electrons in Mg ($Z = 12$)
33. Which of the following processes does not involve oxidation of iron? [2015]
 (a) Decolourization of blue CuSO_4 solution by iron
 (b) Formation of $\text{Fe}(\text{CO})_5$ from Fe
 (c) Liberation of H_2 from steam by iron at high temperature
 (d) Rusting of iron sheets
34. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Numbers in the parenthesis are atomic numbers). [2015]
 (a) Zr (40) and Nb (41) (b) Zr (40) and Hf (72)
 (c) Zr (40) and Ta (73) (d) Ti (22) and Zr (40)
35. The angular momentum of electron in ' d ' orbital is equal to: [2015]
 (a) $\sqrt{2} \hbar$ (b) $2\sqrt{3} \hbar$
 (c) $0\hbar$ (d) $\sqrt{6} \hbar$
36. Assuming complete ionization, same moles of which of the following compounds will require the least amount of acidified KMnO_4 for complete oxidation [2015 RS]
 (a) FeSO_4 (b) FeSO_3
 (c) FeC_2O_4 (d) $\text{Fe}(\text{NO}_2)_2$
37. Gadolinium belongs to $4f$ series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? [2015 RS]
 (a) $[\text{Xe}]4f^8 6d^2$ (b) $[\text{Xe}]4f^9 5s^1$
 (c) $[\text{Xe}]4f^7 5d^1 6s^2$ (d) $[\text{Xe}]4f^6 5d^2 6s^2$
38. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium? [2015 RS]
 (a) $3s 4s 3p 3d$ (b) $4s 3s 3p 3d$
 (c) $3s 3p 3d 4s$ (d) $3s 3p 4s 3d$
39. Which one of the following statements is correct when SO_2 is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution? [2016]
 (a) The solution turns blue
 (b) The solution is decolourized
 (c) SO_2 is reduced
 (d) Green $\text{Cr}_2(\text{SO}_4)_3$ is formed
40. The electronic configurations of Eu (Atomic No. 63), Gd (Atomic No. 64) and Tb (Atomic No. 65) are [2016]
 (a) $[\text{Xe}]4f^7 6s^2$, $[\text{Xe}]4f^8 6s^2$ and $[\text{Xe}]4f^8 5d^1 6s^2$
 (b) $[\text{Xe}]4f^7 5d^1 6s^2$, $[\text{Xe}]4f^7 5d^1 6s^2$ and $[\text{Xe}]4f^9 6s^2$
 (c) $[\text{Xe}]4f^6 5d^1 6s^2$, $[\text{Xe}]4f^7 5d^1 6s^2$ and $[\text{Xe}]4f^8 5d^1 6s^2$
 (d) $[\text{Xe}]4f^7 6s^2$, $[\text{Xe}]4f^7 5d^1 6s^2$ and $[\text{Xe}]4f^9 6s^2$
41. Which copper is heated with conc. HNO_3 it produces [2016]
 (a) $\text{Cu}(\text{NO}_3)_2$ and NO_2
 (b) $\text{Cu}(\text{NO}_3)_2$ and NO
 (c) $\text{Cu}(\text{NO}_3)_2$, NO and NO_2
 (d) $\text{Cu}(\text{NO}_3)_2$ and N_2O
42. Name the gas that can readily decolourise acidified KMnO_4 solution: [2017]
 (a) SO_2 (b) NO_2
 (c) P_2O_5 (d) CO_2
43. The reason for greater range of oxidation states in actinoids is attributed to :- [2017]
 (a) actinoid contraction
 (b) $5f$, $6d$ and $7s$ levels having comparable energies
 (c) $4f$ and $5d$ levels being close in energies
 (d) the radioactive nature of actinoids

Hints & Solutions

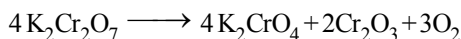
EXERCISE - 1

1. (b) The transition metal oxides in which metal is in lower oxidation states are basic and in which metal is in higher oxidation states are acidic while with intermediate oxidation states are amphoteric.



So, the given transition metal oxides are acidic in nature.

2. (c) Potassium dichromate dissociates with evolution of O_2 on heating.



So, X is Cr_2O_3 .

3. (d)
4. (a) $\text{Sc}^{3+} \rightarrow 3d^0 4s^0$

- $\text{Fe}^{2+} \rightarrow 3d^6 4s^0$

↑↓	↑	↑	↑	↑

- $\text{Ti}^{3+} \rightarrow 3d^1 4s^0$

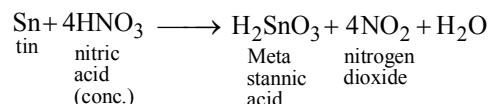
↑				

- $\text{Mn}^{2+} \rightarrow 3d^5 4s^0$

↑	↑	↑	↑	↑

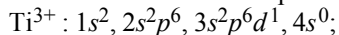
In Sc^{3+} there is/are no unpaired electrons. So the aqueous solution of Sc^{3+} will be colourless.

5. (c) Tin on reaction with conc. HNO_3 to form meta stannic acid and nitrogen dioxide.

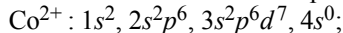


6. (d) $\text{Sc}^{3+} : 1s^2, 2s^2p^6, 3s^2p^6d^0, 4s^0$; no unpaired electron.
 $\text{Cu}^+ : 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^0$; no unpaired electron.
 $\text{Ni}^{2+} : 1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^0$;

unpaired electrons are present.



unpaired electron is present



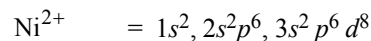
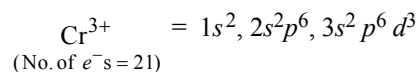
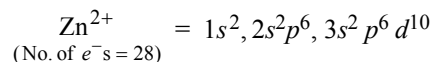
unpaired electrons are present

So from the given options the only correct combination is Ni^{2+} and Ti^{3+} .

7. (a) Mn^{++} – 5 unpaired electrons
 Fe^{++} – 4 unpaired electrons
 Ti^{++} – 2 unpaired electrons
 Cr^{++} – 4 unpaired electrons
Hence maximum no. of unpaired electron is present in Mn^{++} .

Magnetic moment $\propto$ number of unpaired electrons

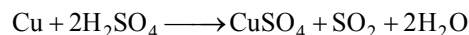
8. (d) The ions with unpaired electrons are coloured and those with paired electrons are colourless.



(No. of e^- s = 26)

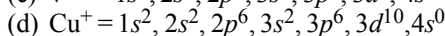
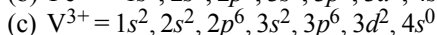
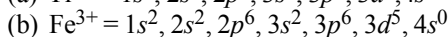
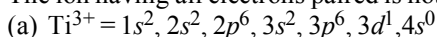
Thus Zn^{2+} , Cr^{3+} and Ni^{2+} have zero, 3 and 2 unpaired electrons respectively.

9. (b) Copper reacts with H_2SO_4 to produce SO_2



But Cu does not displace H_2 from dilute H_2SO_4 as it is less reactive than H_2 (comes below H_2 in electrochemical series)

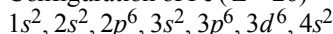
10. (b) Zn is volatile metal
11. (d) The ion having all electrons paired is not coloured.



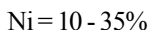
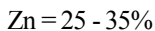
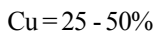
$\therefore$ Only Cu^+ does not have any unpaired electron, it is not coloured.

12. (b) Zirconium ($Z = 40$).
13. (c) Cerium (Ce) belongs to lanthanide series and is member of inner-transition metals.

14. (b) Configuration of Fe ($Z = 26$)



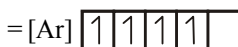
15. (a) German silver is



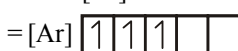
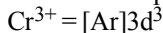
Used as utensils, resistance wire.

16. (c) Due to d^5 configuration, Mn has exactly half filled d-orbitals. As a result the electronic configuration is stable means 3d electrons are more tightly held by the nucleus and this reduces the delocalization of electrons resulting in weaker metallic bonding.

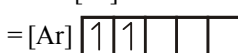
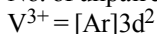
17. (c) $\text{Mn}^{3+} = [\text{Ar}]3d^4$



Number of unpaired electrons = 4



No. of unpaired electrons = 3

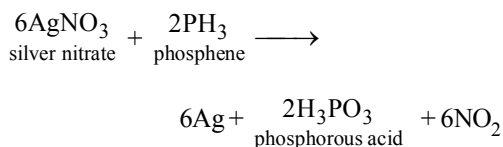


No. of unpaired electrons = 2

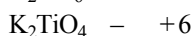
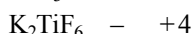
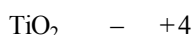
18. (a) Among the given options Ga is the only liquid metal which expands on solidification. It has an unusual structure. Each metal atom has one close neighbour at a distance of $2.43\text{\AA}$, and six more neighbours at distances within range of $2.70\text{\AA}$ to $2.79\text{\AA}$. Due to this structure it exists as discrete diatomic molecules rather than a metallic structure in crystal form which is less dense than its liquid form. As its solid form is heated to 30°C , due to weak metallic bonds this unusual structure no longer exists and melts to liquid. This property is unique to Ga, Ge and Bi.

19. (d) Strength of metallic bond directly depends on the number of unpaired electrons. More is number of unpaired electrons stronger is metallic bond. Hence, metallic bond is strongest in Cr having maximum of 6 unpaired electrons among the given options, i.e., Sc (1 unpaired electron), V (3 unpaired electrons) and Fe (4 unpaired electrons).
20. (d)
21. (b) CuF_2 is both paramagnetic and coloured.
22. (d)
- | | Eu | La | Gd | Am |
|-------|--------|----|----|----------------|
| O.S = | +2, +3 | +3 | +3 | +3, +4, +5, +6 |
23. (a) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
Hence CrO_4^{2-} ion is obtained.
24. (b) $\text{CrO}_3 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CrO}_4 + \text{H}_2\text{O}$
25. (c) Galvanisation is the process of deposition of zinc metal on the surface of Fe to prevent corrosion.
26. (c)
- $$\begin{array}{c}
 \begin{array}{c}
 \xrightarrow{+3} \text{Mn}_2\text{O}_3 \xleftarrow{-4e^-} \xrightarrow{+7} [\text{KMnO}_4] \xrightarrow{-e^-} \xrightarrow{+6} [\text{MnO}_4]^{-2} \\
 \swarrow -5e^- \quad \searrow -3e^- \\
 \text{Mn}^{2+} \quad \text{MnO}_2
 \end{array}
 \end{array}$$
27. (a) $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \longrightarrow 3\text{I}_2 + 7\text{H}_2\text{O} + 2\text{Cr}^{3+}$
oxidation state of Cr is +3.
28. (a) $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
 $\text{Zn} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$
1 mole atom of zinc produces the same amount of H_2 (2 g) in each case.
29. (d) $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \longrightarrow \text{Hg}_2\text{NH}_2\text{Cl} + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$
30. (b) $2\text{Cu} + \text{H}_2\text{O} + \text{CO}_2 + \text{O}_2 \longrightarrow \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
(green coloured basic carbonate of copper is formed)
31. (a) Cu is more electropositive than Ag therefore, it displaces Ag from their salt solution AgNO_3 .
 $\text{Cu} + 2\text{AgNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$
32. (c) Gun metal is an alloy of Cu, Zn and Sn. It contains 88% Cu, 10% Sn and 2% Zn.
33. (b) Wrought iron is the purest form of iron containing lowest percentage of C (0.2-0.5%).
34. (c) Black jack or Zinc blende is ZnS . It is ore of Zn.
35. (b) Cu, Ag and Au are called coinage metals.
36. (d) $2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{HgCl}_2 + \text{SnCl}_4$
White ppt
 $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} + \text{SnCl}_4$
grey
37. (b) Bronze is an alloy of Cu and Sn.
38. (b) $3\text{Cu} + (\text{dil}) 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
39. (c) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is White vitriol
 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is Green vitriol
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is Blue vitriol
40. (a) Addition of iron filling to CuSO_4 solution caused ppt. of Cu owing to the reduction of Cu^{2+} e.g.
 $\text{CuSO}_4 + \text{Fe} \longrightarrow \text{FeSO}_4 + \text{Cu}$
(reduction of copper).
41. (b) $2\text{CuSO}_4 + 4\text{KI} \longrightarrow 2\text{K}_2\text{SO}_4 + \text{Cu}_2\text{I}_2 + \text{I}_2$
42. (c) Benzene does not decolourise KMnO_4 (acidic/alkaline). It is due to the delocalization of π -electron in benzene. Mohr's salt and oxalic acid gives redox reaction with KMnO_4 . Propene decolorises KMnO_4 due to presence of C = C bond.
43. (b) Bessemer converter is used in the manufacture of steel.
44. (b) Pm is obtained by synthetic method.
45. (c) ZnO is amphoteric and dissolves in both acids and bases
 $\text{ZnO} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$
 $\text{ZnO} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$
46. (c) A regular decrease in the size of the atoms and ions in lanthanoid series from La^{3+} to Lu^{3+} is called lanthanide contraction. The similarity in size of the atoms of Zr and Hf is due to the lanthanide contraction.
47. (d) We know that lanthanides La, Gd shows +3, oxidation state, while Eu shows oxidation state of +2 and +3. Am shows +3, +4, +5 and +6 oxidation states. Therefore Americium (Am) has maximum number of oxidation states.
48. (b) Complex soluble salts of the metal to be deposited are usually employed as electrolytes in electroplating. Hence $\text{K}[\text{Au}(\text{CN})_2]$ is used as an electrolyte in gold plating.
49. (b) A solution of CuCl in NH_4OH is often used to measure the amount of CO in gas samples, by measuring the change in volume of the gas.
50. (c) Lanthanides are 4f-series elements starting from cerium ($Z = 58$) to lutetium ($Z = 71$). These are placed in the sixth period and in third group.
51. (d) Electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ because this gives it a stable half filled d^5 configuration. Similarly, electronic configuration of Cu is $[\text{Ar}] 3d^{10} 4s^1$. This filling of electrons is not in accordance with Aufbau principle.
52. (c) Ionic radii $\propto \frac{1}{z}$
Thus, $\frac{z_2}{z_1} \Rightarrow \frac{1.06}{(\text{Ionic radii of } \text{Lu}^{3+})} = \frac{71}{57}$
 $\Rightarrow$ Ionic radii of $\text{Lu}^{3+} = 0.85 \text{ \AA}$
53. (a) $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{KCl} + 6\text{H}_2\text{SO}_4 \xrightarrow{\text{Heat}} 2\text{CrO}_2\text{Cl}_2 + 6\text{KHSO}_4 + 3\text{H}_2\text{O}$
54. (b) In lanthanides, there is poorer shielding of 5d electrons by 4f electrons resulting in greater attraction of the nucleus over 5d electrons and contraction of the atomic radii.

55. (a) When AgNO_3 reacts with PH_3 , then Ag is obtained.



56. (d) Oxidation state of Ti in the given compounds, as follows:



The oxidation states exhibited by Ti is +2, +3, +4. So K_2TiO_4 does not exist.

57. (b) $_{58}\text{Ce}$ is lanthanide. Lanthanides are from 57 to 71 all present in IIIrd group. Hence $_{58}\text{Ce}$ forms $_{56}\text{X}$ element on emission of one α particle with belongs to IInd group.

58. (d)

59. (d) Mischmetal is an alloy which contains rare earth elements (94-95%), iron (5%) and traces of sulphur, carbon, silicon, calcium and aluminium. It is used in gas lighters, tracer bullets and shells.

60. (d) Terbium is lanthanide as it belongs to 4f-series having configuration $[\text{Xe}]4s^2 6s^2$. However the remaining members belong to 5f-series (actinides).

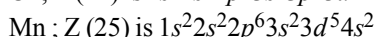
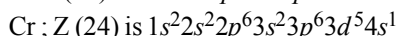
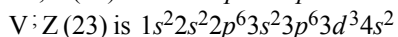
61. (c) Lanthanide contraction results into decrease in atomic and ionic radii.

62. (b) $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
dark green

63. (d) For chromium ion +3 oxidation state is most stable.

64. (b) As a result of lanthanoid contraction change in ionic radii on going from elements of 4d to 5d transition series is very small. Thus chemical properties of 4d and 5d series of transition elements are similar.

65. (a) Ti ; Z (22) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$



The second electron in all the cases (except Cr) has to be removed from 4s-orbital and for Cr it has to be removed from completely half filled 3d-orbital which have extra stability thus I.E₂ is highest for Cr. Now among rest elements more will be the nuclear charge more will be the value of I.E₂. As nuclear charge depends upon atomic number. Therefore correct order of I.E₂ is $\text{Mn} > \text{V} > \text{Ti}$.

i.e. $\text{Cr} > \text{Mn} > \text{V} > \text{Ti}$. So correct answer is (a).

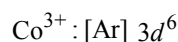
66. (b) Mn - $3d^5 4s^2$

1	1	1	1	1

1

The no. of various oxidation states possible are +2, +3, +4, +5, +6 and +7.

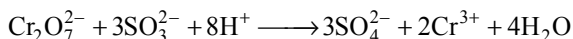
67. (d) $\text{Ni}^{3+} : [\text{Ar}] 3d^7$



68. (c) Due to lanthanide contraction, the size of Zr and Hf (atom and ions) become nearly similar

69. (a) 70. (a)

71. (a) The green colour appears due to the formation of Cr^{+++} ion



72. (b) $\text{Na}_2\text{Cr}_2\text{O}_7$ is hygroscopic.

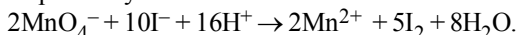
73. (c) The melting points of the transition element first rise to a maximum and then fall as the atomic number increases manganese have abnormally low melting point.

74. (c) The transition metals and their compounds are used as catalysts. Because of the variable oxidation states they may form intermediate compound with one of the reactants. These intermediate provides a new path with low activation energy. $\text{V}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{V}_2\text{O}_4 + \text{SO}_3$
 $2\text{V}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{V}_2\text{O}_5$

75. (c) $\text{Ac} (89) = [\text{Rn}] [6d^1] [7s^2]$

EXERCISE - 2

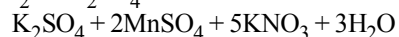
1. (b) Thus they decolourise the KMnO_4 solution. Except CO_3^{2-} all other ions I^- , S^{2-} , NO_2^- , Cl^- are oxidised by acidified KMnO_4 forming I_2 , S, NO_3^- and Cl_2 respectively.



S^{2-} is oxidised to S in presence of KMnO_4



Nitrites are oxidised to nitrates



Chloride is oxidised to chlorine



CO_3^{2-} is not oxidised by KMnO_4 because in CO_3^{2-} , C is already in its highest +4 oxidation state. Thus CO_3^{2-} does not decolourise KMnO_4 solution.

2. (b) As a result of lanthanide contraction Zr^{4+} and Hf^{4+} possess almost the same ionic radii. Ce^{4+} is an oxidising agent. Ce^{4+} gains electron to acquire more stable Ce^{3+} state. $\text{La}(\text{OH})_3$ is the most basic among lanthanide hydroxides.

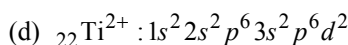
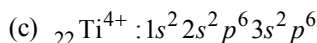
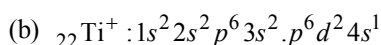
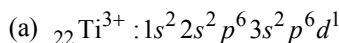
3. (a) The order of basic character of the transition metal monoxide is $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$ because basic character of oxides decreases with increase in atomic number.

4. (c) In lanthanide series there is a regular decrease in the atomic as well as ionic radii of trivalent ions (M^{3+}) as the atomic number increases. Although the atomic radii

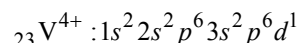
do show some irregularities but ionic radii decreases from La (103 pm) to Lu (86 pm). Y^{3+} belong to second transition series therefore have greater ionic radii than other ions of third transition series.

5. (a) Fe has hcp lattice while all other given metals have ccp lattice.

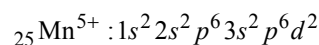
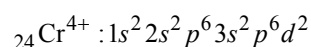
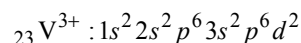
6. (d) The electronic configuration of different species given in the question are :



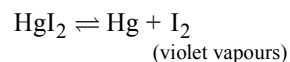
Thus options (a) and (c) are discarded; now let us observe the second point of difference.



Thus option (b) is discarded



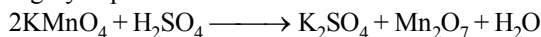
7. (a) $\text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2[\text{HgI}_4]$
 red, solid (insoluble) (soluble)



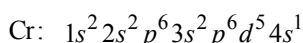
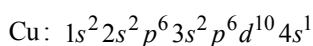
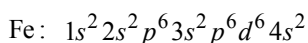
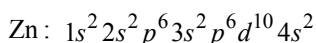
8. (c) Solid potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride gives orange red vapours of a volatile oily liquid CrO_2Cl_2
 $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{NaCl} + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + 4\text{NaHSO}_4 + 2\text{CrO}_2\text{Cl}_2$
 chromyl chloride

9. (d) $(n-1)d^5 ns^2$ attains the maximum O.S. of +7.

10. (b) KMnO_4 reacts with H_2SO_4 to form Mn_2O_7 which is highly explosive substance.



11. (a) The ionisation energies increase with increase in atomic number. However, the trend is some irregular among d -block elements. On the basis of electronic configuration, the



IE_1 follows the order : $\text{Zn} > \text{Fe} > \text{Cu} > \text{Cr}$

12. (b) $2\text{CuSO}_4 + \text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] + 2\text{K}_2\text{SO}_4$
 Chocolate ppt.

13. (a) We know that when nitrogen oxide (NO) combines with Fe (II) ions, a brown complex is formed. This reaction is called brown ring test.

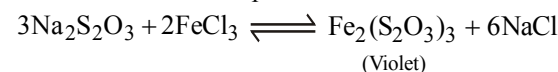
14. (d) (i) Haematite is Fe_2O_3 in which Fe is present in III oxidation state.

- (ii) Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3 .

Oxidation state of Fe in FeO is II.

Oxidation state of Fe in Fe_2O_3 is III.

15. (c) The reaction can be represented as

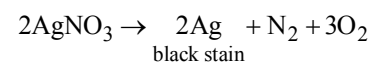


16. (d) $\text{AgCl} + 2\text{NH}_3 \longrightarrow \text{Ag}(\text{NH}_3)_2\text{Cl}$
 diammine silver (I) chloride

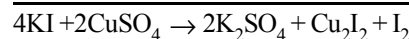
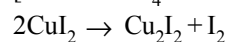
17. (d) Philosopher's wool is ZnO

18. (b) ${}_{30}\text{Zn}$ and ${}_{80}\text{Hg}$ have their d orbitals completely filled so they do not show any variable valency.

19. (d) Its reduction to metallic silver.



20. (b) $[2\text{KI} + \text{CuSO}_4 \rightarrow \text{CuI}_2 + \text{K}_2\text{SO}_4] \times 2$



21. (c) As the oxidation state of metal associated with oxygen increases, the acidic character of oxide increases. So Mn_2O_7 is most acidic as it has highest +7, oxidation state.

22. (c) (a), (b) and (d) are correct statements.

(c) There is drop in enthalpy of atomization at manganese because of half filled stable electronic configuration leading to less mobilisation of electrons. This results in weaker metallic bonds.

23. (d) Lithopone is a mixture of $\text{ZnS} + \text{BaSO}_4$ which is a white paint.

24. (b) The colour exhibited by transition metal ions is due to the presence of unpaired electrons in d -orbitals which permits the $d-d$ excitation of electrons.

In TiF_6^{2-} - Ti is in +4 O.S. ; $3d^0$ = colourless

In CoF_6^{3-} - Co is in +3 O.S. ; $3d^5$ = coloured

In Cu_2Cl_2 - Cu is in +1 O.S. ; $3d^{10}$ - colourless

In NiCl_4^{2-} - Ni is in +2 O.S. ; $3d^8$ - coloured

25. (b) $\text{La}^{3+} : 54 e^- = [\text{Xe}]$

$\text{Ti}^{3+} : 19 e^- = [\text{Ar}] 3d^1$ (Coloured)

$\text{Lu}^{3+} : 68 e^- = [\text{Xe}] 4f^{14}$

$\text{Sc}^{3+} : 18 e^- = [\text{Ar}]$

26. (d) (i) Haematite is Fe_2O_3 in which Fe is present in III oxidation state.

- (ii) Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3 .
Oxidation state of Fe in FeO is II.
Oxidation state of Fe in Fe_2O_3 is III.
27. (a) $\text{V} = 3d^3 4s^2$; $\text{V}^{2+} = 3d^3 = 3$ unpaired electrons
 $\text{Cr} = 3d^5 4s^1$; $\text{Cr}^{2+} = 3d^4 = 4$ unpaired electrons
 $\text{Mn} = 3d^5 4s^2$; $\text{Mn}^{2+} = 3d^5 = 5$ unpaired electrons
 $\text{Fe} = 3d^6 4s^2$; $\text{Fe}^{2+} = 3d^6 = 4$ unpaired electrons
Hence the correct order of paramagnetic behaviour
 $\text{V}^{2+} < \text{Cr}^{2+} = \text{Fe}^{2+} < \text{Mn}^{2+}$
- (b) For the same oxidation state, the ionic radii generally decreases as the atomic number increases in a particular transition series. hence the order is
 $\text{Mn}^{++} > \text{Fe}^{++} > \text{Co}^{++} > \text{Ni}^{++}$
- (c) In solution, the stability of the compound depends upon electrode potentials, SEP of the transition metal ions are given as
 $\text{Co}^{3+}/\text{Co} = +1.97$, $\text{Fe}^{3+}/\text{Fe} = +0.77$;
 $\text{Cr}^{3+}/\text{Cr}^{2+} = -0.41$, Sc^{3+} is highly stable as it does not show +2 O.S.
- (d) $\text{Sc} - (+2), (+3)$
 $\text{Ti} - (+2), (+3), (+4)$
 $\text{Cr} - (+1), (+2), (+3), (+4), (+5), (+6)$
 $\text{Mn} - (+2), (+3), (+4), (+5), (+6), (+7)$
i.e. $\text{Sc} < \text{Ti} < \text{Cr} = \text{Mn}$
28. (d) $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -0.41 \text{ V}$ $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$
 $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} = +1.57 \text{ V}$, $E^\circ_{\text{Co}^{3+}/\text{Co}^{2+}} = +1.97 \text{ V}$
29. (a) $4f$ orbital is nearer to nucleus as compared to $5f$ orbital therefore, shielding of $4f$ is more than $5f$.
30. (b) The main reason for exhibiting larger number of oxidation states by actinoids as compared to lanthanoids is lesser energy difference between $5f$ and $6d$ orbitals as compared to that between $4f$ and $5d$ orbitals.
In case of actinoids we can remove electrons from $5f$ as well as from d and due to this actinoids exhibit larger number of oxidation state than lanthanoids. Thus the correct answer is option (b)
31. (c) The titration of oxalic acid with KMnO_4 in presence of HCl gives unsatisfactory result because of the fact that KMnO_4 can also oxidise HCl along with oxalic acid. HCl on oxidation gives Cl_2 and HCl reduces KMnO_4 to Mn^{2+}
32. (b) Most of the Ln^{3+} compounds except La^{3+} and Lu^{3+} are coloured due to the presence of f -electrons.
33. (d)
34. (d) The configuration of Gd is $[\text{Xe}] 4f^7 5d^1 6s^2$.
35. (d) Fe^{3+} is easily hydrolysed than Fe^{2+} due to more positive charge.
36. (c) $E^\circ_{\text{Cu}^{+2}/\text{Cu}} = 0.34 \text{ V}$
other has -ve $E^\circ_{\text{R.P.}}$
 $E^\circ_{\text{Co}^{++}/\text{Co}} = -0.28 \text{ V}$
- $E^\circ_{\text{Ni}^{++}/\text{Ni}} = -0.25 \text{ V}$
 $E^\circ_{\text{Fe}^{++}/\text{Fe}} = -0.44 \text{ V}$
37. (a) The outermost electronic configuration of Fe is
 $\text{Fe} = [\text{Ar}] 3d^6 4s^2$
 $\text{Fe}^{2+} = [\text{Ar}] 3d^6 4s^0$
- | | | | | |
|----------------------|------------|------------|------------|------------|
| $\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ |
|----------------------|------------|------------|------------|------------|
- Since Fe^{2+} has 4 unpaired electrons it is paramagnetic in nature.
 $\text{Zn} = [\text{Ar}] 3d^{10} 4s^2$ — no unpaired e^-
 $\text{Hg}^{2+} = [\text{Ar}] 4f^{14} 5d^{10}$ — no unpaired e^-
 $\text{Ti}^{4+} = [\text{Ar}] 3d^0 4s^0$ — no unpaired e^-
38. (d) Oxidation state of Ti in the given compounds, as follows:
- | | | |
|--------------------------|---|----|
| TiO | — | +2 |
| TiO_2 | — | +4 |
| TiCl_3 | — | +3 |
| K_2TiF_6 | — | +4 |
| K_2TiO_4 | — | +6 |
- The oxidation states exhibited by Ti is +2, +3, +4. So K_2TiO_4 does not exist.
39. (d) V^{2+} — violet, V^{3+} — green V^{4+} — blue
 Fe^{2+} — green Fe^{3+} — yellow
40. (d) Interstitial compounds of transition metal exhibit metallic conductivity.
41. (a) $\text{Mn}^{++} = 3d^5$ i.e. no. of unpaired $e^- = 5$
 $\text{Cu}^{++} = 3d^9$ i.e. no. of unpaired $e^- = 1$
 $\text{Fe}^{++} = 3d^6$ i.e. no. of unpaired $e^- = 4$
 $\text{Zn}^{++} = 3d^{10}$ i.e. no. of unpaired $e^- = 0$
 $\text{Ni}^{++} = 3d^8$ i.e. no. of unpaired $e^- = 3$
Higher the number of unpaired electrons higher will be the magnetic moment. Hence Mn^{++} having maximum unpaired electrons will have the maximum magnetic moment.
42. (d) Sc does not show variable valency.
43. (b) $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
dark green
44. (d) $\text{Fe}^{3+}(d^5)$ has 5 unpaired electrons therefore magnetic moment $= \sqrt{n(n+2)} = \sqrt{5(5+2)} = 5.91$ which is maximum among given options. As Sc^{3+} , Ti^{3+} , Cr^{3+} , V^{3+} contains 0, 1, 3, and 2 number of unpaired electrons respectively.
45. (b) The magnetic moments are lesser than the theoretically predicted values. This is due to the fact that $5f$ electrons of actinides are less effectively shielded which result in quenching of orbital contribution.
46. (b) KCN forms complexes with Cu^+ and Cd^{2+} as $\text{K}_3[\text{Cu}(\text{CN})_4]$ and $\text{K}_2[\text{Cd}(\text{CN})_4]$ respectively. On passing H_2S , only Cd^{2+} complex is decomposed to give yellow CdS precipitate.
47. (d)
48. (c) The statement-1 is correct but the statement-2 is false. Actually transition metal show variable valency due to very small difference between the ns^2 and $(n-1)d$ electrons.

49. (b) Due to larger surface area and variable valencies to form intermediate absorbed complex easily, transition metals are used as catalysts.
50. (b) The magnetic moments are lesser than the fact that 5f electrons of actinides are less effectively shielded which results in quenching of orbital contribution.

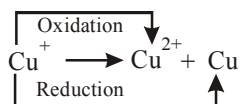
EXERCISE - 3

Exemplar Questions

- (b) Electronic configuration of X^{3+} is $[Ar]3d^5$
Atomic number of $X = 18 + 5 + 3 = 26$
- (a) Anion carrying a higher charge and smaller size is associated with greater lattice and hydration energy but it is expected on the basis of electronic configuration Cu^+ should be more stable because it has completely filled orbitals. But the lattice and hydration energy factors dominate and as a result Cu^{2+} is more stable.
- (d) Along the period, decrease in metallic radius is coupled with increase in atomic mass therefore results in increase in density of metal. Hence, Cu will exhibit highest density.
- (b) CuF_2 is coloured in solid state because $Cu(II)$ has d^9 configuration thus, due to the presence of unpaired electron, it exists as a coloured salts.
- (a) The compound formed can be explained by the following reaction :
 $2KMnO_4 + 2H_2SO_4 (conc.) \rightarrow Mn_2O_7 + 2KHSO_4 + H_2O$
(green oily)
- (b) Greater the number of unpaired electrons, higher will be the value of magnetic moment.

Configuration	No. of Unpaired e^- s
$3d^7$	3
$3d^5$	5
$3d^8$	2
$3d^2$	2

- (b) Lanthanoids show common oxidation state of +3.
- (a) The reaction in which oxidation as well as reduction of same metal occur is known as disproportionation reaction.

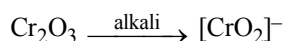
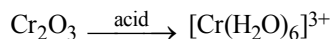
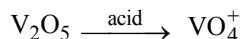
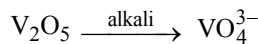


- (d) Mn^{2+} acts as autocatalyst.
 $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
- (c) Tm ; Thulium $Z = 69$ do not belong to actinoid series.
- (a) Reaction $KMnO_4$ with sulphide ions in acidic medium is as follows :
 $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$
 $H_2S + [O] \rightarrow H_2O + S \times 5$
 $2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

5 moles of S^{2-} ions react with 2 moles of $KMnO_4$ thus,

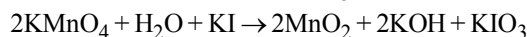
1 mole of S^{2-} ion will react with $\frac{2}{5}$ moles of $KMnO_4$.

12. (a) Amphoteric oxide react with alkalis as well as acids.

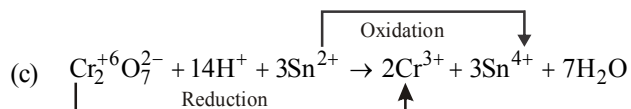


- (a) The E.C. of gadolinium is :
 $Gd = [Xe]4f^7 5d^1 6s^2$
- (d) Interstitial compounds are chemically inter.
- (b) Spin only magnetic moment (μ) = $\sqrt{n(n+2)}$ BM
 $= \sqrt{3(3+2)} = \sqrt{15}$
 $= 3.87 \text{ BM}$

16. (c) When alkaline $KMnO_4$ oxidising agent is treated with KI, iodide ion is oxidised to IO_3^- .



- (a) Copper lies below hydrogen in the electrochemical series and hence does not liberate H_2 from acids.
- As mentioned in the reaction below Sn^{2+} changes to Sn^{4+} :

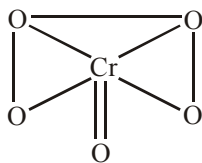


- (d) In covalent compounds fluorine can form only single bond while oxygen forms double bond.
- (c) Zr and Hf possess almost same atomic and ionic radii because of lanthanoid contraction. Hence they exhibit similar properties.
- (b) HCl is not used in oxidation reactions of $KMnO_4$ in acidic medium because $KMnO_4 + HCl$ produce nascent oxygen which will partly oxidise HCl to Cl_2 . So the end point will not be correct in the titration.

NEET/AIPMT (2013-2017) Questions

- (c) $Sm^{2+} (Z = 62)$ $[Xe]4f^6 6s^2 - 6 \text{ unpaired } e^-$
 $Eu^{2+} (Z = 63)$ $[Xe]4f^7 6s^2 - 7 \text{ unpaired } e^-$
 $Yb^{2+} (Z = 70)$ $[Xe]4f^{14} 6s^2 - 0 \text{ unpaired } e^-$
 $Ce^{2+} (Z = 58)$ $[Xe]4f^1 5d^1 6s^2 - 2 \text{ unpaired } e^-$
Only Yb^{2+} is diamagnetic.
- (b) HCl and SO_2 are reducing agents and can reduce MnO_4^- . CO_2 which is neither oxidising and nor reducing will provide only acidic medium. It can shift reaction in forward direction and reaction can go to completion.
- (c) $Gd [64] = [Xe] 4f^7 5d^1 6s^2$
- (c) A transition element must have incomplete d -subshell. Zinc have completely filled d subshell having $3d^{10}$ configuration. Hence do not show properties of transition elements to any appreciable extent except for their ability to form complexes.

26. (c) Both are reducing agents.
 27. (c) The structure of CrO_5 is



Hence CrO_5 has two peroxy linkage.

Now suppose the oxi. no. of Cr is x then

$$x + (-1 \times 4) + (-2) = 0$$

$$\therefore x = +6$$

28. (b) $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}_2 \longrightarrow$
 $\text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$
 i.e., Mn^{++} ion and O_2 .

29. (b) Magnetic moment

$$\mu = \sqrt{n(n+2)}$$

$$2.83 = \sqrt{n(n+2)}$$

On solving $n = 2$

Ni^{2+} have two unpaired electron.

30. (a) The shape of f-orbitals is very much diffused and they have poor shielding effect. The effective nuclear charge increases which causes the contraction in the size of electron charge cloud. This contraction in size is quite regular and known as lanthanoid contraction.

31. (d) Magnetic moment = 2.84 B.M. This indicates that 2 unpaired electrons are present.



Number of unpaired electrons (n) = 2

Hence Ni^{2+} gives magnetic moment 2.84 B.M.

32. (a) $\text{Fe}^{+2} = 3d^6$ (number of 'd' electrons = 6)
 In $\text{Cl} = 1s^2 2s^2 2p^6 3s^2 3p^5$
 total p electrons = 11, which are not equal to number of 'd' electrons in Fe^{+2}
 p-electrons in $\text{Ne} = 1s^2 2s^2 2p^6 = 6$
 s-electrons in $\text{Mg} = 1s^2 2s^2 2p^6 3s^2 = 6$
 33. (b) Formation of $\text{Fe}(\text{CO})_5$ from Fe involves no change in oxidation state of iron.
 34. (b) Due to lanthanoid contraction atomic radii of Zr and Hf is almost similar.

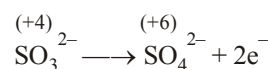
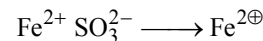
35. (d) Orbital angular momentum = $\sqrt{\ell(\ell+1)}\hbar$

For d-orbital $\ell = 2$

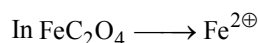
$$\text{angular momentum} = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$$

36. (a) Considering the same moles of compounds $\text{Fe}^{2+} \text{SO}_4^{2-}$

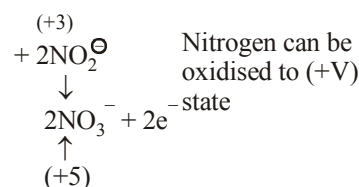
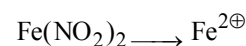
only Fe^{2+} is oxidised by KMnO_4 . SO_4^{2-} in which sulphur is in highest oxidation state cannot be oxidised.



Sulphur can be oxidised to (+6) i.e. to SO_4^{2-}

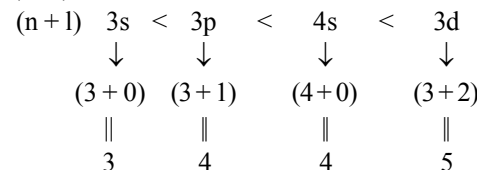


Carbon can be oxidised to (+IV) i.e. to CO_2



37. (c) $\text{Gd} (64) = [\text{Xe}] 4f^7 5d^1 6s^2$

38. (d) $(n+1)$ rule can be used. Titanium is a multi electron system



If $(n+1)$ values are same, than value of "n" has to be considered.

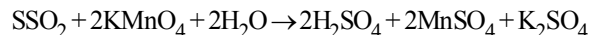
39. (d) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{SO}_2 + \text{H}_2\text{SO}_4$
 $\longrightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$

green colour

40. (d) $\text{Eu} (63) = [\text{Xe}] 4f^7 6s^2$
 $\text{Gd} (64) = [\text{Xe}] 4f^7 5d^1 6s^2$
 $\text{Tb} (65) = [\text{Xe}] 4f^9 6s^2$

41. (a) Less active metals like Cu, Ag etc react with conc acid and form nitrate and nitrogen dioxide.

42. (a) Potassium permanganate has a purple colour. When sulphur dioxide reacts with potassium permanganate the solution decolourizes.



43. (b) Minimum or comparable energy gap between 5f, 6d and 7s subshell makes electron excitation easier, hence there is a greater range of oxidation states in actinoids.

Chapter 23

Coordination Compounds

Coordination compounds in which the central metal atom is linked to a number of ions or neutral molecules by coordinate bonds, i.e. by donation of ions pairs of e^{-1} s by these ions or neutral molecules to the central metal atom.

DOUBLE SALT AND COMPLEX COMPOUND

The main difference between a double salt (like alums, Mohr's salt, etc.) and a complex (like ferrocyanide) ion is that former dissociates completely into ions in aqueous solution and does not contain any coordinate bond while later does not dissociates completely into ions and always contains coordinate bonds.

WERNER'S THEORY OF COMPLEXES

The main postulates are:

- Every metal forming a complex exhibits two types of valencies Primary valency and Secondary valency.
- Primary valency is ionisable in nature whereas secondary valency is non-ionisable.
- Primary valency is also called oxidation state. Secondary valency is also called Coordination number of metal

ex: $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, primary valency is 4 (from 4Cl^-) whereas secondary valency is 6 (from 6NH_3)

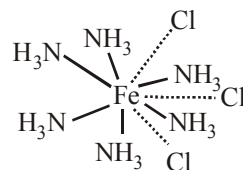
- Primary valencies are satisfied by negative ions whereas secondary valencies are satisfied by negative ion or neutral molecules.
- Secondary valencies are directional and determine geometry of the complex. On the other hand, primary valencies are non directional.

Experimental evidence to Werner's theory of complexes can be provided based on :

- Precipitation of primary valencies on the addition of a suitable reagent.
- Electrical conductance of complexes

Representation of Complexes

Werner's representation for $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$



Dotted lines indicate primary valency and solid lines indicate secondary valency of metal ion.

SOME IMPORTANT TERMS USED IN COORDINATION COMPOUNDS

Coordination Entity/ Coordination Sphere

The central metal atom/ ion and the ligands which are directly attached to it are enclosed in square brackets and are collectively called coordination entity. The ionizable groups are written outside the brackets and are called counter ions.

Central Atom / ion:

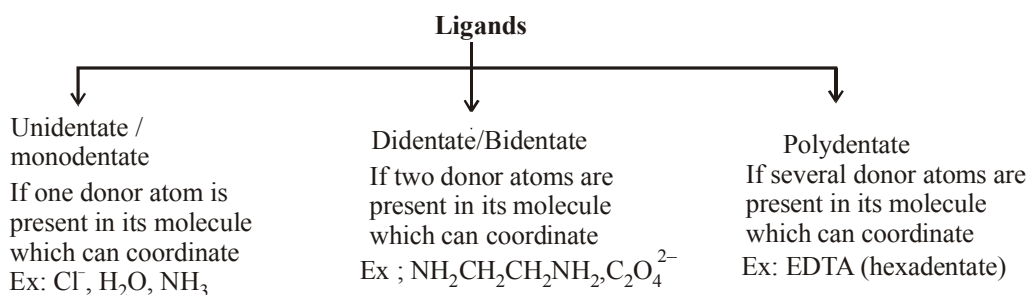
In a Coordination entity, the atom / ion to which a fixed number of ions / groups are bound in a definite geometrical arrangement around it, is called central atom / ion.

They are also referred to as **Lewis acids**

Ligands

These are ions / molecules which bound to central atom / ion in Coordination entity. Ligands may be ions (ex: Cl^-), small molecules like H_2O or NH_3 , larger molecules like $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or even macromolecules.

The number of co-ordinating or ligating groups present in a ligand is called its denticity. Based on this, ligands are classified as:



Chelating Ligands

If the ligands with two or more electron donor groups (or co-ordinating groups) positioned in such a way that they form five or six membered ring with central metal ion, then the ligands are known as **chelating ligands** and the ring formed is called **chelate ring**. The complex which is thus formed is termed as **metal chelate** or simply **chelate** while this property is called **chelation**.

Chelating ligands form more stable complexes. Complexes formed by ligands with smaller groups are more stable as compared to complexes formed by ligand with larger group.

Chelates are used in softening of hard water, in separation of lanthanoids and actinoids, in qualitative analysis of metals etc.

Ambidentate Ligands

Ligands which can bind through two different sites are called ambidentate ligands. For ex: NO_2^- , SCN^- , etc.

Coordination Number

The number of coordinate bonds formed with the central metal atom/ion by the ligands. For determining Coordination number only sigma bonds are considered not pi-bonds even if formed.

For ex: $[\text{PtCl}_6]^{2-}$, Coordination number of Pt = 6

$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, Coordination number of Fe = 6

Coordination Polyhedron

It is the spatial arrangement of ligand atoms which are directly attached to the central atom / ion.

The polyhedron can be octahedral, square planar, square pyramidal, trigonal bipyramidal or tetrahedral.

Oxidation Number of Central Atom

It is the charge which the central atom would carry if all the ligands are removed along with the e^- pairs that are shared with the central

atom. For example : Oxidation number of Cu in $[\text{Cu}(\text{CN})_4]^{3-}$ is +1 and is written as Cu (I).

Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor

groups are called homoleptic. For ex: $[\text{Cu}(\text{NH}_3)_6]^{3+}$

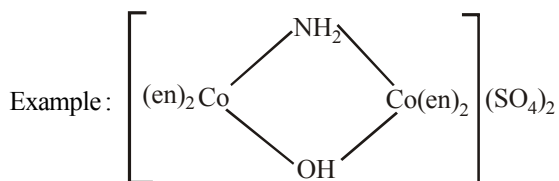
Complexes in which a metal is bound to more than one kind of donor groups are heteroleptic : For ex: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$

Homonuclear and Polynuclear Complexes :

Complexes in which only one metal atom is present are homonuclear.

Example : $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$

Complexes in which more than one metal atoms are present are known as polynuclear.

**NOMENCLATURE OF COORDINATION COMPOUNDS****Formulas of Mononuclear Coordination Compounds**

Following rules are applied:

- The central atom is listed first.
- The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- Polydentate ligands are also listed alphabetically.
- In case of abbreviated ligands (e.g., en for ethane-1, 2-diamine), the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- The formula of the entire coordination entity, whether charged or not, is enclosed in square brackets.
- There should be no space between the ligands and the metal within a co-ordination sphere.
- If the formula is written without the counter ion, the charge is indicated outside the square bracket as a superscript.
- The charge of the cation (s) is balanced by the charge of the anion (s).

Naming of Mononuclear Coordination Compounds

Following rules are used:

- The cation is named first in both positively and negatively charged Coordination entities.
- The ligands are named in alphabetical order before the name of the central atom / ion.
- The ligands can be neutral, anionic or cationic.

(a) **Neutral ligands are named as the molecule e.g. $\text{C}_5\text{H}_5\text{N}$ is named as pyridine,**

$(\text{C}_6\text{H}_5)_3\text{P}$ as Triphenyl phosphine,

$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ as ethylene diamine.

The neutral ligands which are not named as the molecule are

CO carbonyl

NO nitrosyl

H_2O aqua

NH_3 amine

(b) **Negative ligands end in 'O', i.e.,**

Cl^- chloro, SO_4^{2-} sulphato, NO_2^- Nitro

ONO^- nitrito, OH^- hydroxo, NH_2^- amido

NH_2^- imido, NO_3^- nitrato, CO_3^{2-} carbonato

CH_3COO^- acetato, CN^- cyano

(c) **Positive ligands end in 'ium' ex :** $\text{NH}_2^+ - \text{NH}_3$

Hydrazinium, NO_2^+ (nitronium), NO^+ (nitrosonium)

- Prefixes mono, di, tri, etc are used to indicate the number of individual ligands in Coordination entity.
- Oxidation state of the metal in cation, anion or neutral Coordination entity is indicated by Roman numeral in parenthesis.
- If the complex ion is a cation, the metal is named same as the element.

For example : $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

(Cationic complex is present so metal is without any suffix) Hexaminecobalt (III) chloride.

If the complex ion is an anion, the name of the metal ends with the suffix - ate.

For example : $K_4[Fe(CN)_6]$

(anionic complex is present so suffix ate is added with metal's name) Potassium hexacyanoferrate (II)

(vii) The neutral complex molecule is named similar to that of the complex cation.

(viii) When bidentate ligands are coordinated to the metal ion, their repetition is indicated by prefixes like bis, tris, tetrakis etc. For example :

(a) $[Fe(en)_3]Cl_3$

Trisethylenediamineiron (III) chloride

(b) $[Ni(gly)_2]$

Bisglycinatonickel (II)

ISOMERISM IN COORDINATION COMPOUNDS

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Coordination compounds show two main types of isomerism:

Structural Isomerism

(i) **Linkage isomerism:** It arises in complexes containing ambidentate ligand. For ex: SCN. It can bind through N or S to give $M-NCS$ or $M-SCN$. For example $[Cr(H_2O)_5(SCN)]^{2+}$ and $[Cr(H_2O)_5(NCS)]^{2+}$ are linkage isomers.

(ii) **Coordination isomers:** This type of isomerism occurs when both cation and anion of a salt are complex. The isomerism arises by the interchange of ligands between the two complex ions.

For example : $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(iii) **Ionisation Isomerism:** It arises when the counter ion in a complex salt is itself a potential ligand and can displace ligand which can then become the counter ion. This type of isomers yields different types of ions in solution.

For ex: $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

(iv) **Solvate/ Hydrate Isomerism:**

The complexes which differ with respect to the number of water molecules attached to the metal ion as ligands are called hydrate isomers.

For e.g. - $Cr(H_2O)_6Cl_3$ has three possible structures

(a) $[Cr(H_2O)_6]Cl_3$ violet

(b) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ green

(c) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ dark green.

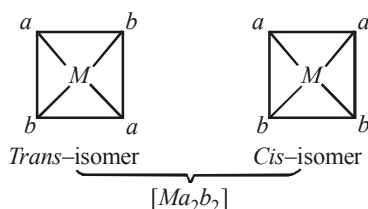
Stereo Isomerism

(I) **Geometrical Isomerism**

Geometrical isomerism is most important in compounds with coordination numbers 4 and 6. 4-coordinated complexes with tetrahedral geometry do not exhibit *cis-trans* isomerism.

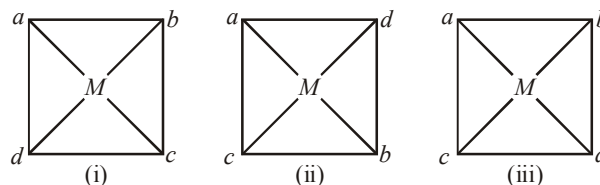
Square planar complexes showing this behaviour are of type:

(i) Ma_2b_2



ex: $Pt(NH_3)_2Cl_2$

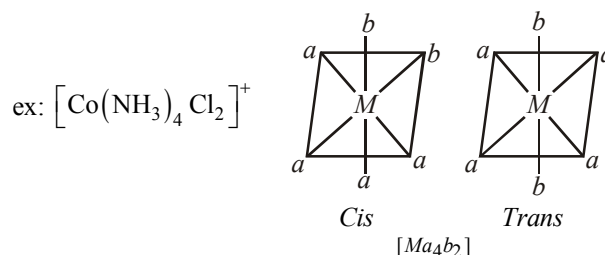
(ii) $Mabcd$ Three isomers are possible



Example : $[Pt(NH_3)(NH_2OH)(NO_2)(py)NO_2]$.

Octahedral complexes showing this behaviour are of type:

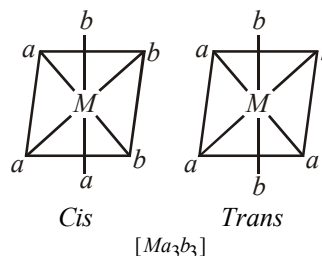
(i) Ma_4b_2



(ii) $Ma_2(b-b)_2$ i.e. with bidentate ligands $b-b$ (cis and trans forms)

ex: $CoCl_2(en)_2$.

(iii) Ma_3b_3 (facial and meridional isomers).



Octahedral complexes of general formula, $Mabcdef$, can have fifteen geometrical isomers.

(II) **Optical Isomerism**

It is shown by compounds which cannot be superimposed. An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.

It has two forms, dextro (*d*) and laevo (*l*), arise depending upon the direction in which they rotate the plane of polarised light.

This isomerism is common in octahedral complex involving bidentate ligands.

ex: $[Co(en)_3]^{3+}$, cis is isomer of $[PtCl_2(en)_2]^{2+}$

For complexes with coordination number 4, square planar complexes do not show optical isomerism but tetrahedral complexes having bidentate ligands, ex : $[Ni(gly)_2]$ shows optical isomerism.

Other examples are $[Co(en)_3]^{3+}$, $[CoCl_2(en)_2]^+$ etc.

BONDING IN COORDINATION COMPOUNDS

Valence Bond Theory (VBT)

(i) According to this theory, metal - ligand bonds are formed by the overlap of metal orbitals with those of ligands i.e., by donation of e^- -pairs by the ligands to empty hybridized orbitals of metal.

For e.g. -In the formation of $[\text{Fe}(\text{NH}_3)_6]^{3+}$, Fe^{3+} ion provides six vacant orbitals.

In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, Cu^{2+} ion provides four vacant orbitals.

- (ii) The metal orbitals undergo hybridisation, to give a set of hybrid orbitals of equal energy.
- (iii) The number of vacant orbitals provided is equal to the coordination number of metal ion.
- (iv) Octahedral, square planar and tetrahedral complexes are formed as a result of d^2sp^3 (or sp^3d^2), dsp^2 and sp^3 hybridisation respectively of the central metal atom or the ion.

A few examples are:

Complex	Hybridisation	Magnetic behaviour	Nature
(CN = 6) $[\text{Cr}(\text{NH}_3)_6]^{3+}$	d^2sp^3	paramagnetic	inner orbital
$[\text{Fe}(\text{CN})_6]^{3-}$	d^2sp^3	slightly paramagnetic	inner orbital
$[\text{Fe}(\text{CN})_6]^{4-}$	d^2sp^3	diamagnetic	inner orbital
$[\text{CoF}_6]^{3-}$	sp^3d^2	paramagnetic	outer orbital
(CN = 4) $[\text{Ni}(\text{CO})_4]^0$	sp^3	diamagnetic	—
$[\text{Zn}(\text{NH}_3)_4]^{2+}$	sp^3	diamagnetic	—
$[\text{Ni}(\text{CN})_4]^{2-}$	dsp^2	diamagnetic	—
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	dsp^2	paramagnetic	—
(CN = 5) $\text{Fe}(\text{CO})_5$	dsp^3	diamagnetic	—

Note : Number of unpaired electrons present ($\mu = \sqrt{n(n+2)}$ BM) can be calculated by determining magnetic moment value experimentally. Thus type of hybridisation involved in complex can be predicted.

Crystal Field Theory

This theory considers M - L bond to be ionic arising from electrostatic interaction.

This is shown diagrammatically as:

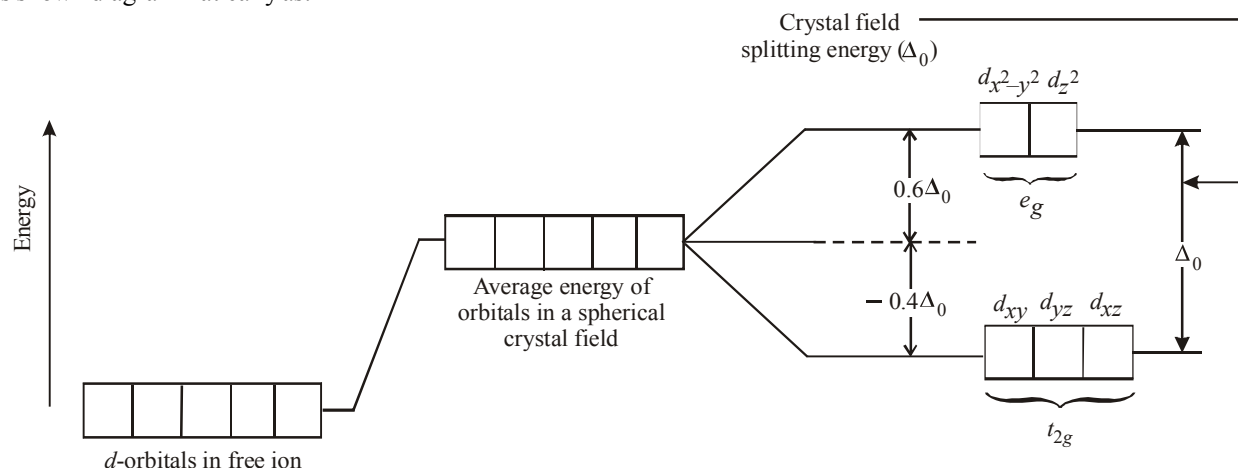


Figure : Splitting of d -orbitals in octahedral field

Inner and Outer Orbital Complexes

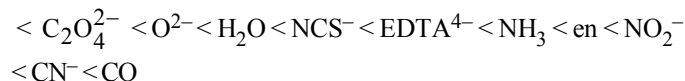
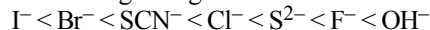
The empty ' d ' orbitals involved in hybridisation may be inner $(n-1)d$ or outer nd orbitals. The complexes thus formed are called as Inner orbital complexes and Outer orbital complexes respectively.

In case of inner orbital complex the electrons of the metal are made to pair up, so the complex will be either diamagnetic or less paramagnetic. This type of complex is also known as low spin complex. For outer orbital complex number of unpaired electrons will be large as the configuration of the metal remains unchanged. This type of complex is also known as high spin complex.

The difference of energy between the two sets of d-orbitals is called crystal field splitting energy or crystal field stabilization energy (CFSE). It is usually represented by the symbol Δ_o . For any given metal cation, the magnitude of Δ_o depends upon the nature of the ligands

Spectrochemical series

In general, ligands can be arranged in a series in order of increasing field strength as given below:



This series is called **spectrochemical series**.

Pairing of the two sets of d-orbital depends on the magnitude of Δ_o and P ($\Delta_o \rightarrow$, CFSE and P $\rightarrow$ pairing energy)

If $\Delta_o > P$, EC is $t_{2g}^4 e_g^0$. Upto d^6 pairing will occur in the t_{2g} and e_g will remain vacant. Ligands which produce this effect are called **strong field ligands** and form **low spin complex**.

If $\Delta_o < P$, EC is $t_{2g}^3 e_g^1$. For d^5 configuration $t_{2g}^3 e_g^2$ ligands which produce this effect are called **weak field ligands** and form **high spin complexes**.

For **tetrahedral complex**, $\Delta_t = \frac{4}{9} \Delta_o$

Splitting pattern for tetrahedral complexes is just the reverse of the splitting patterns of the octahedral complexes Δ_t is so small that it is unable to force the electrons to pair up.

Here, energy of $e_g <$ energy of t_{2g} .

Colour of the complexes

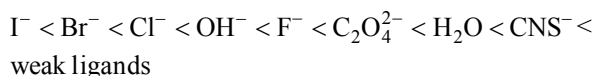
The coloured nature of solutions of coordination compounds can also be explained on the basis of crystal field theory, because in coordination compounds the energy difference between two sets of d-orbitals is usually small (as explained by crystal field splitting) thus, excitation of an electron from lower energy to higher energy is very easy and can be achieved even by the absorption of low energy radiations of visible region. As the result of the absorption of such selected wavelengths of visible light, the complexes appeared coloured.

Different complexes exhibit different colours when either metal is different or ligands are different.

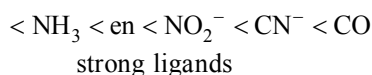
In absence of ligand, crystal field splitting does not occur and hence, the substance is colourless. For ex: $CuSO_4 \cdot 5H_2O$ is blue but anhydrous $CuSO_4$ is white.

The size of Δ depends on -

- (i) **Nature of the ligand** : In Spectrochemical series Δ decreases as shown below



weak ligands



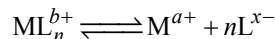
strong ligands

- (ii) **Oxidation state of the metal** : Δ is greater for M^{3+} than for M^{2+}
- (iii) **Position of the metal in the periodic table**: For a given ligand and oxidation state of the metal, Δ increases going down in a group eg. Δ is greater in $[Ru(NH_3)_6]^{3+}$ than in $[Fe(NH_3)_6]^{3+}$

STABILITY OF COORDINATION COMPOUNDS

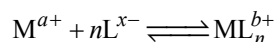
The stability of a complex in solution can be expressed in terms of equilibrium constant of the dissociation equilibrium

For a general complex dissociating reaction



$$K_i = \frac{[M^{a+}][L^{x-}]^n}{[ML_n^{b+}]}$$

K_i = instability constant



$$\beta_n = \frac{[ML_n^{b+}]}{[M^{a+}][L^{x-}]^n}$$

$\beta_n \rightarrow$ stability constant ($\therefore \beta = 1/K_i$)

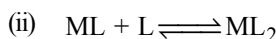
Thus more will be stability constant more will be stability of complex.

For the reaction, $M + 4L \rightleftharpoons ML_4$, overall stability constant is

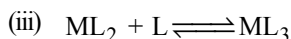
given by $\beta_4 = [ML_4]/[M][L]^4$ whereas the stepwise stability constants are:



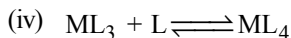
$$K_1 = [ML]/[M][L]$$



$$K_2 = [ML_2]/[ML][L]$$



$$K_3 = [ML_3]/[ML_2][L]$$



$$K_4 = [ML_4]/[ML_3][L]$$

$$\text{and, } \boxed{\beta_4 = K_1 \times K_2 \times K_3 \times K_4}$$

$$\text{or, } \boxed{\beta_n = K_1 \times K_2 \times K_3 \cdots K_n}$$

Note (i) Greater is the charge on central metal ion, greater will be the stability of the complex

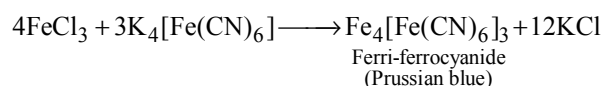
(ii) Greater will be the basic strength of ligand stable will be the complex

(iii) Formation of chelate rings increases the stability of the complex.

IMPORTANCE OF COORDINATION COMPOUNDS

- (i) **In qualitative analysis** : In salt analysis, the presence of a number of basic radicals is confirmed by converting them into suitable complexes which have definite colours.

For ex : Fe^{3+} forms a prussian blue complex with potassium ferrocyanide solution :



Ferri-ferrocyanide
(Prussian blue)

- (ii) **In extraction of metals :** The noble metals like silver and gold are extracted from their ores through the formation of cyanide complexes, $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$.
- (iii) **In biological systems :** A number of biologically important compounds are Coordination compounds, i.e., metal complexes. For ex : chlorophyll is a coordination compound of magnesium; haemoglobin is a complex compound of iron; vitamin B_{12} is a Coordination compound of cobalt, etc.

ORGANOMETALLIC COMPOUNDS

These are compounds containing one or more metal-carbon bonds. The compounds of metalloids (Ge, Sb) and non metals (B, Si, P, As etc.) which are less electronegative than carbon are also categorised under this.

e.g., $\text{R}-\text{Zn}-\text{R}$ Dialkyl zinc (Frankland reagent)
 $\text{R}-\text{Mg}-\text{X}$ Alkyl Mg halide (Grignards reagent)

Compounds like

Sodium acetate $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa}$

Sodium ethoxide $\text{C}_2\text{H}_5-\text{O}-\text{Na}$

Sodium Mercaptide $\text{H}_3\text{C}-\text{SNa}$

are not organometallic compounds as in these compounds metal is not directly attached with carbon atom.

$\text{B}(\text{OCH}_3)_3$ is not OMC $\rightarrow$ $\begin{array}{c} \text{H}_3\text{CO} \\ \diagup \\ \text{B}-\text{OCH}_3 \\ \diagdown \\ \text{H}_3\text{CO} \end{array}$

while $\text{CH}_3\text{B}(\text{OCH}_3)_2$ is OMC $\rightarrow \text{H}_3\text{C}-\text{B} \begin{array}{l} \diagup \text{OCH}_3 \\ \diagdown \text{OCH}_3 \end{array}$

Cyanides, carbides and carbonates are not considered OMC because their properties are very different from those belonging to class of OMC's.

Classification of Organometallic Compounds

OMC can be classified into three main categories

(i) σ -bonded OMC :

These compounds are formed mostly by non transition and metalloid elements.

eg. $\text{R}-\text{Mg}-\text{X}$, (Grignard reagent)

$(\text{CH}_3)_2\text{Zn}$ (Dimethyl zinc or Frankland's reagent)

$(\text{R})_2\text{Cd}$, (Dialkyl Cadmium)

(ii) π -bonded OMC :

These are usually formed by transition metals.

eg. Ferrocene $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$

where η = No. of carbon atoms combined with metal atom.

Zeise's salt $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$

(iii) σ and π -bonded OMC :

Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC.

The carbonyl compounds of these metals have both σ , and π bonds. e.g.

$[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$, $[\text{Mn}_2(\text{CO})_{10}]$

Metal carbonyls are used as industrial catalysts. They are also used as precursors in synthesis of organic compounds.

Bonding in Metal Carbonyls

Bond is formed between transition metal and C of CO group.

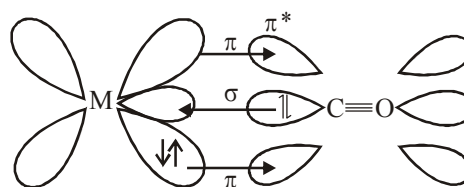
These carbonyls can have tetrahedral, trigonal bipyramidal or octahedral structure.

The M - C bond possesses both s - and p - character.

The M - C σ - bond is formed by donation of lone pair of electrons from a filled bonding π_{2p} orbital on the carbonyl carbon of CO into a vacant d-orbital of metal.

The M - C π - bond is formed by donation of a pair of electrons from a filled d - orbital of metal into vacant antibonding π_{2p}^* orbital of CO. Here, donation of electrons from a filled metal d-orbital into a vacant antibonding π^* orbital of CO occurs, thus this bonding is called back bonding.

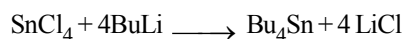
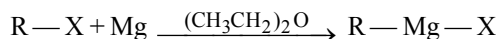
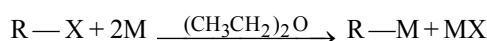
The effect of σ -bond formation strengthens the π bond and vice - versa. This is called **synergic effect** which strengthens the bond between CO and metal.



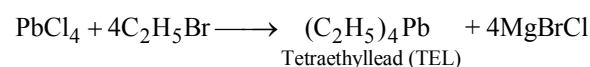
Synergic bonding

Synthesis of Organometallic Compounds

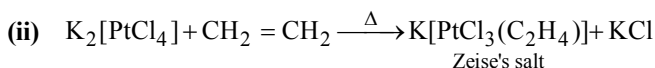
(i) σ - bonded organometallic compounds



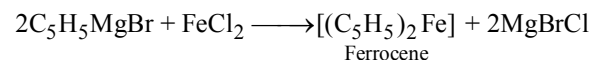
Tetrabutyltin



Tetraethyllead (TEL)



Zeise's salt



Ferrocene

Applications of Organometallic Compounds

(i) Wilkinson's Catalyst

$[\text{RhCl}(\text{Ph}_3\text{P})_3]$ is used for selective hydrogenation of alkenes.

(ii) As heterogenous catalyst

Zeigler - Natta Catalyst is used for low temperature polymerisation of alkenes.

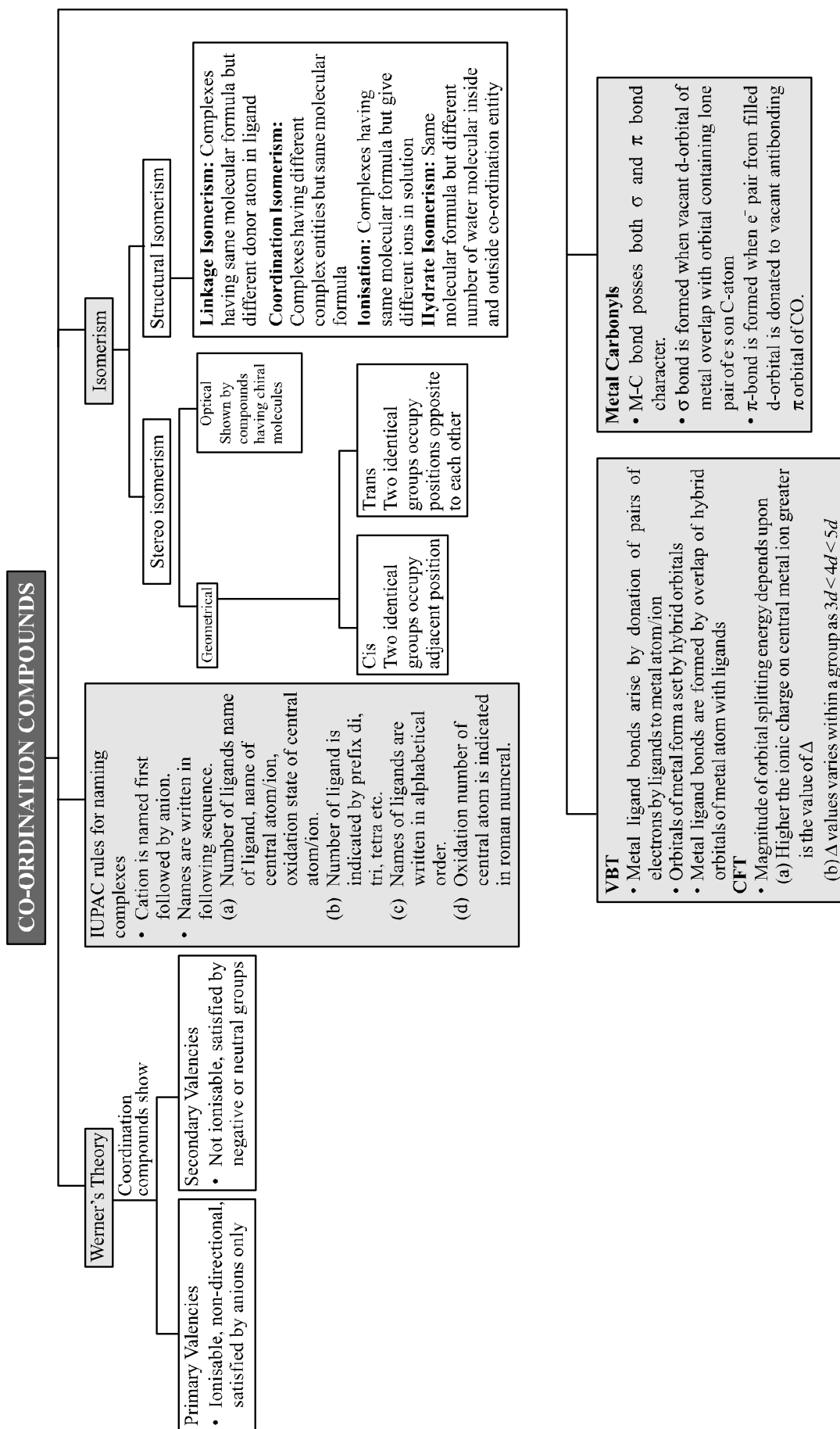
(iii) Organic synthesis - OMC like $\text{R}-\text{Mg}-\text{X}$, R_2-Cd , CH_3-Li etc. are used for preparation of almost all type of organic compounds. .

(iv) As petrol additive - TEL (Tetraethyl lead) is used as an antiknock agent in petrol.

(v) In medicine - Organo arsenic compounds are used as medicine for syphilis disease.

(vi) In agriculture - Seeds are treated with ethyl mercury chloride to protect the plants against infection.

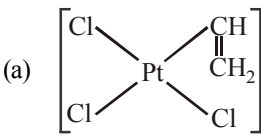
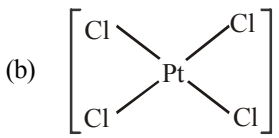
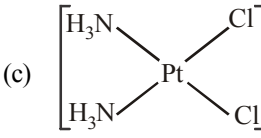
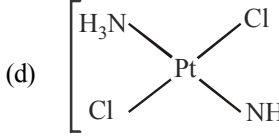
CONCEPT MAP



EXERCISE - 1

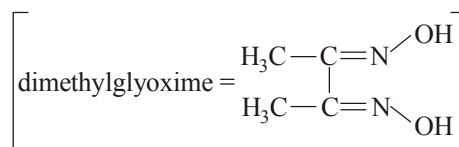
Conceptual Questions

- Which one of the following shows maximum value of paramagnetic behaviour :
 (a) $[\text{Sc}(\text{CN})_6]^{3-}$ (b) $[\text{Co}(\text{CN})_6]^{3-}$
 (c) $[\text{Fe}(\text{CN})_6]^{3-}$ (d) $[\text{Cr}(\text{CN})_6]^{3-}$
- $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ is called
 (a) Potassium aluminooxalate
 (b) Potassium trioxalatoaluminate (III)
 (c) Potassium aluminium (III) oxalate
 (d) Potassium trioxalatoaluminate (VI)
- The formula for the complex, dichlorobis (urea) copper (II) is
 (a) $[\text{Cu}\{\text{O}=\text{C}(\text{NH}_2)_2\}_2]\text{Cl}_2$
 (b) $[\text{Cu}\{\text{O}=\text{C}(\text{NH}_2)_2\}\text{Cl}]\text{Cl}$
 (c) $[\text{CuCl}_2\{\text{O}=\text{C}(\text{NH}_2)_2\}_2]$
 (d) $[\text{CuCl}_2][\{\text{O}=\text{C}(\text{NH}_2)_2\}_2]$
- Which of the following is not an organometallic compound?
 (a) sodium ethoxide
 (b) trimethyl aluminium
 (c) tetraethyl lead
 (d) ethyl magnesium bromide
- The geometry of $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ are :
 (a) both square planar
 (b) tetrahedral and square planar respectively
 (c) both tetrahedral
 (d) square planar and tetrahedral respectively
- The hypothetical complex chlorodiaquatrimminecobalt (III) chloride can be represented as
 (a) $[\text{CoCl}(\text{NH}_3)_3(\text{H}_2\text{O})_2]\text{Cl}_2$
 (b) $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Cl}_3]$
 (c) $[\text{Co}(\text{NH}_2)_3(\text{H}_2\text{O})_2]\text{Cl}$
 (d) $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$
- According to IUPAC nomenclature sodium nitroprusside is named as
 (a) Sodium pentacyanonitrosylferrate (III)
 (b) Sodium nitroferrocyanide
 (c) Sodium nitroferrocyanide
 (d) Sodium pentacyanonitrosylferrate (II)
- In the coordination compound, $\text{K}_4[\text{Ni}(\text{CN})_4]$, the oxidation state of nickel is
 (a) 0 (b) +1 (c) +2 (d) -1
- Which does not give a precipitate with AgNO_3 solution ?
 (a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (c) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (d) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
- The oxidation state of Cr in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ is
 (a) 0 (b) +1 (c) +2 (d) +3
- The IUPAC name of the coordination compound $\text{K}_3[\text{Fe}(\text{CN})_6]$ is
 (a) Tripotassium hexacyanoiron (II)
 (b) Potassium hexacyanoiron (II)
 (c) Potassium hexacyanoferrate (III)
 (d) Potassium hexacyanoferrate (II)
- The number of ions formed when triamminetrichloro chromium (III) is dissolved in water :
 (a) 2 (b) 3
 (c) 1 (d) None of these
- The IUPAC name for the complex $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$ is
 (a) pentaamminenitrito-N-cobalt(II) chloride
 (b) pentaamminenitrito-N-cobalt(III) chloride
 (c) nitrito-N-pentaamminecobalt(III) chloride
 (d) nitrito-N-pentaamminecobalt(II) chloride
- $\text{K}_4[\text{Fe}(\text{CN})_6]$ is a :
 (a) double salt (b) complex compound
 (c) acid (d) base
- $[\text{EDTA}]^{4-}$ is a :
 (a) monodentate ligand (b) bidentate ligand
 (c) quadridentate ligand (d) hexadentate ligand
- What is incorrect about homoleptic metal carbonyls ?
 (a) M – C σ - bond is formed by donation of lone pair of electrons from CO
 (b) M – C π - bond is formed by back donation of electron from filled d -orbital of metal to vacant p -orbital of carbon
 (c) M – CO bonding product synergic effect
 (d) Metal carbonyl contain only σ - bonds
- The compound having the lowest oxidation state of iron is:
 (a) $\text{K}_4\text{Fe}(\text{CN})_6$ (b) K_2FeO_4
 (c) Fe_2O_3 (d) $\text{Fe}(\text{CO})_5$
- The IUPAC name of $\text{K}_2[\text{PtCl}_6]$ is
 (a) hexachloroplatinate potassium
 (b) potassium hexachloroplatinate (IV)
 (c) potassium hexachloroplatinate
 (d) potassium hexachloroplatinum (IV)
- In $\text{K}_4[\text{Fe}(\text{CN})_6]$, the E.A.N. of Fe is
 (a) 33 (b) 35 (c) 36 (d) 26
- The organometallic compound is :
 (a) $\text{Ti}(\text{OCOCH}_3)_4$ (b) $\text{Ti}(\text{C}_2\text{H}_5)_4$
 (c) $\text{Ti}(\text{OC}_6\text{H}_5)_4$ (d) $\text{Ti}(\text{OC}_2\text{H}_5)_4$
- In $[\text{Ni}(\text{NH}_3)_4]\text{SO}_4$, the E.A.N. of Ni is
 (a) 34 (b) 35
 (c) 36 (d) 37
- The effective atomic number of cobalt in the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ is
 (a) 36 (b) 33 (c) 24 (d) 30
- The ligand called π acid is :
 (a) CO (b) NH_3
 (c) $\text{C}_2\text{O}_4^{2-}$ (d) Ethylenediamine
- Pick out the complex compound in which the central metal atom obeys EAN rule strictly
 (a) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (b) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 (c) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (d) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

25. The number of geometrical isomers for $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is
(a) 2 (b) 1 (c) 3 (d) 4
26. Which one of the following forms, with an excess of CN^- (cyanide), a complex having co-ordination number two?
(a) Cu^+ (b) Ag^+ (c) Ni^{2+} (d) $\text{Al}(\text{OH})_3$
27. Which of the following will give maximum number of isomers?
(a) $[\text{Ni}(\text{C}_2\text{O}_4)(\text{en})_2]^{2-}$ (b) $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$
(c) $[\text{Cr}(\text{SCN})_2(\text{NH}_3)_4]^+$ (d) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$
28. Which one of the following octahedral complexes will not show geometric isomerism? (A and B are monodentate ligands)
(a) $[\text{MA}_5\text{B}]$ (b) $[\text{MA}_2\text{B}_4]$
(c) $[\text{MA}_3\text{B}_3]$ (d) $[\text{MA}_4\text{B}_2]$
29. Which of the following coordination compounds would exhibit optical isomerism?
(a) pentamminenitrocobalt(III) iodide
(b) diamminedichloroplatinum(II)
(c) trans-dicyanobis(ethylenediamine) chromium(III) chloride
(d) tris(ethylenediamine) cobalt(III) bromide
30. The type of isomerism present in Pentamminenitrochromium(III) chloride is
(a) optical (b) linkage
(c) ionisation (d) polymerisation.
31. The correct order for the wavelength of absorption in the visible region is :
(a) $[\text{Ni}(\text{NO}_2)_6]^{4-} < [\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
(b) $[\text{Ni}(\text{NO}_2)_6]^{4-} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{NH}_3)_6]^{2+}$
(c) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{NO}_2)_6]^{4-}$
(d) $[\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{NO}_2)_6]^{4-}$
32. Which of the following compounds shows optical isomerism?
(a) $[\text{Co}(\text{CN})_6]^{3-}$ (b) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$
(c) $[\text{ZnCl}_4]^{2-}$ (d) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
33. Which of the following ions can exhibit optical isomerism—
(a) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (b) $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^-$
(c) $\text{Cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (d) $\text{trans-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$
34. Which would exhibit co-ordination isomerism
(a) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (b) $[\text{Co}(\text{en})_2\text{Cl}_2]$
(c) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (d) $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$
35. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ are related to each other as
(a) geometrical isomers (b) optical isomers
(c) linkage isomers (d) coordination isomers
36. Coordination isomerism is caused by the interchange of ligands between the
(a) cis and trans structure
(b) complex cation and complex anion
(c) inner sphere and outer sphere
(d) low oxidation and higher oxidation states
37. The pair in which both species have same magnetic moment (spin only value) is :
(a) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CoCl}_4]^{2-}$
(b) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
(c) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
(d) $[\text{CoCl}_4]^{2-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
38. The ligands in anti cancer drug *cis*-platin are:
(a) NH_3 , Cl (b) NH_3 , H_2O
(c) Cl , H_2O (d) NO , Cl
39. The number of precipitable halide ions in the sample $[\text{Pt}(\text{NH}_3)\text{Cl}_2\text{Br}]\text{Cl}$ will be
(a) 2 (b) 3 (c) 4 (d) 1
40. Wavelength of red light is absorbed by the complex
(a) $[\text{Cu}(\text{CN})_4]^{2-}$ (b) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
(c) CuSO_4 (d) $\text{Cu}(\text{CN})_2$
41. Which of the following is considered to be an anticancer species ?
(a)  (b) 
(c)  (d) 
42. Which one of the following will show paramagnetism corresponding to 2 unpaired electrons?
(Atomic numbers : $\text{Ni} = 28$, $\text{Fe} = 26$)
(a) $[\text{FeF}_6]^{3-}$ (b) $[\text{NiCl}_4]^{2-}$
(c) $[\text{Fe}(\text{CN})_6]^{3-}$ (d) $[\text{Ni}(\text{CN})_4]^{2-}$
43. $[\text{Fe}(\text{NO}_2)_3\text{Cl}_3]$ and $[\text{Fe}(\text{ONO})_3\text{Cl}_3]$ shows
(a) linkage isomerism (b) geometrical isomerism
(c) optical isomerism (d) none of the above
44. The number of unpaired electrons in the complex $[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$ is (Atomic number $\text{Cr} = 24$)
(a) 4 (b) 1 (c) 2 (d) 3
45. Atomic number of Cr and Fe are respectively 25 and 26, which of the following is paramagnetic?
(a) $[\text{Cr}(\text{CO})_6]$ (b) $[\text{Fe}(\text{CO})_5]$
(c) $[\text{Fe}(\text{CN})_6]^{4-}$ (d) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
46. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (at. no. of $\text{Cr} = 24$) has a magnetic moment of 3.83 B. M. The correct distribution of $3d$ electrons in the Chromium of the complex is
(a) $3d_{xy}^1, (3d_{x^2-y^2})^1, 3d_{yz}^1$
(b) $3d_{xy}^1, 3d_{yz}^1, 3d_{xz}^1$
(c) $3d_{xy}^1, 3d_{yz}^1, 3d_{z^2}^1$
(d) $(3d_{x^2-y^2})^1, 3d_{z^2}^1, 3d_{xz}^1$

47. Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour ?
 (a) $[\text{Co}(\text{CN})_6]^{3-}$ (b) $[\text{Fe}(\text{CN})_6]^{3-}$
 (c) $[\text{Mn}(\text{CN})_6]^{3-}$ (d) $[\text{Cr}(\text{CN})_6]^{3-}$
 (At. Nos : Cr = 24, Mn = 25, Fe = 26, Co = 27)
48. A chemist wants to determine the molecular geometry of the $[\text{CoCl}_4]^{2-}$ ion. Which of the following gives the best suggestion for a measurement and for the interpretation of that measurement?
 (a) Using absorption spectroscopy, measure λ_{max} then calculate Δ_o for octahedral geometry
 (b) Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be square planar; otherwise, it is likely to be tetrahedral
 (c) Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be tetrahedral; otherwise, it is likely to be square planar
 (d) Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be tetrahedral; otherwise, it is likely to be octahedral
49. The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is
 (a) d^5 (in strong ligand field)
 (b) d^3 (in weak as well as in strong fields)
 (c) d^4 (in weak ligand fields)
 (d) d^4 (in strong ligand fields)
50. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni = 28)
 (a) 6 (b) 1.73 (c) 2.84 (d) 4.90
51. How many pairs of enantiomers are possible for following complex compound, $[\text{M}(\text{AB})(\text{CD})\text{ef}]^{n\pm}$ (where AB, CD— Unsymmetrical bidentate ligand, e, f— Monodentate ligands)
 (a) 20 (b) 5 (c) 10 (d) 8
52. Which has maximum paramagnetic nature ?
 (a) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (b) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (c) $[\text{Fe}(\text{CN})_6]^{4-}$ (d) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$
53. The compound which is not coloured is
 (a) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (b) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 (c) $\text{Na}_2[\text{CdCl}_4]$ (d) $\text{Na}_2[\text{CuCl}_4]$
54. Which complex of Co^{2+} will have the weakest crystal field splitting –
 (a) $[\text{CoCl}_6]^{4-}$ (b) $[\text{Co}(\text{CN})_6]^{4-}$
 (c) $[\text{Co}(\text{NH}_3)_6]^{2+}$ (d) $[\text{Co}(\text{en})_3]^{2+}$
55. A complex $[\text{CoL}_6]^{n+}$ where L is neutral ligand has a magnetic moment $\mu = 4.5$ B. M. Hence,
 (a) Co must be in +2 oxidation state
 (b) L must be a strong ligand
 (c) Co must be in +3 oxidation state
 (d) None of these
56. Which one of the following complexes is an outer orbital complex ?
 (a) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (b) $[\text{Mn}(\text{CN})_6]^{4-}$
 (c) $[\text{Fe}(\text{CN})_6]^{4-}$ (d) $[\text{Ni}(\text{NH}_3)_6]^{2+}$
 (Atomic nos. : Mn = 25; Fe = 26; Co = 27, Ni = 28)
57. A square planar complex is formed by hybridisation of which atomic orbitals?
 (a) s, p_x, p_y, d_{yz} (b) $s, p_x, p_y, d_{x^2-y^2}$
 (c) s, p_x, p_y, d_{z^2} (d) s, p_y, p_z, d_{xy}
58. Which of the following may be considered to be an organometallic compound?
 (a) Nickel tetracarbonyl (b) Chlorophyll
 (c) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ (d) $[\text{Co}(\text{en})_3]\text{Cl}_3$
59. Which of the following organometallic compound is σ and π bonded?
 (a) $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$ (b) $\text{Fe}(\text{CH}_3)_3$
 (c) $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$ (d) $[\text{Co}(\text{CO})_5\text{NH}_3]^{2+}$
60. In $\text{Fe}_2(\text{CO})_9$, the two iron atoms are
 (a) linked only directly
 (b) linked directly along with 3 CO molecules as bridging ligands
 (c) linked only through 3 CO molecules as bridging ligands
 (d) joined through one CO group as bridging ligands.
61. Among the following, which is **not** the π -bonded organometallic compound?
 (a) $(\text{CH}_3)_4\text{Sn}$ (b) $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$
 (c) $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$ (d) $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$
62. Which one of the following is the correct order of field strength of ligands in spectrochemical series?
 (a) $\text{I}^- < \text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{CN}^-$
 (b) $\text{F}^- < \text{H}_2\text{O} < \text{I}^- < \text{CN}^- < \text{Cl}^-$
 (c) $\text{CN}^- < \text{I}^- < \text{F}^- < \text{Cl}^- < \text{H}_2\text{O}$
 (d) $\text{H}_2\text{O} < \text{F}^- < \text{CN}^- < \text{Cl}^- < \text{I}^-$
63. Which of the following does **not** have a metal-carbon bond?
 (a) $\text{Al}(\text{OC}_2\text{H}_5)_3$ (b) $\text{C}_2\text{H}_5\text{MgBr}$
 (c) $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ (d) $\text{Ni}(\text{CO})_4$
64. Coordination compounds have great importance in biological systems. In this context which of the following statements is **incorrect** ?
 (a) Cyanocobalamin is B_{12} and contains cobalt
 (b) Haemoglobin is the red pigment of blood and contains iron
 (c) Chlorophylls are green pigments in plants and contain calcium
 (d) Carboxypeptidase - A is an enzyme and contains zinc.
65. Ammonia will not form complex with
 (a) Ag^{2+} (b) Pb^{2+} (c) Cu^{2+} (d) Cd^{2+}
66. In $\text{Fe}(\text{CO})_5$, the Fe – C bond possesses
 (a) ionic character (b) σ -character only
 (c) π -character (d) both σ and π characters

67. Which method can be used to distinguish $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$
- by measurement of their conductivity
 - by titration method
 - by precipitation method with AgNO_3
 - by electrolysis of their aqueous solutions
68. The organometallic compound is :
- $\text{Ti}(\text{OCOCH}_3)_4$
 - $\text{Ti}(\text{C}_2\text{H}_4)_4$
 - $\text{Ti}(\text{OC}_6\text{H}_5)_4$
 - $\text{Ti}(\text{OC}_2\text{H}_5)_4$
69. Which of the following is an organometallic compound?
- Lithium methoxide
 - Lithium acetate
 - Lithium dimethylamide
 - Methyl lithium
70. The formula of ferrocene is
- $[\text{Fe}(\text{CN})_6]^{4-}$
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Fe}(\text{CO})_5]$
 - $[(\text{C}_5\text{H}_5)_2\text{Fe}]$
71. The π -bonded organometallic compound which has ethene as one of its component is
- Zeise's salt
 - Ferrocene
 - Dibenzene chromium
 - Tetraethyl tin
72. Which of the following will give a pair of enantiomorphs?
- $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
 - $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$
 - $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$. ($\text{en} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)
73. The d electron configurations of Cr^{2+} , Mn^{2+} , Fe^{2+} and Ni^{2+} are $3d^4$, $3d^5$, $3d^6$ and $3d^8$ respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour?
- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- (At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28)
74. Which of the following complexes exhibits the highest paramagnetic behaviour?
- $[\text{V}(\text{gly})_2(\text{OH})_2(\text{NH}_3)_2]^+$
 - $[\text{Fe}(\text{en})(\text{bpy})(\text{NH}_3)_2]^{2+}$
 - $[\text{Co}(\text{ox})_2(\text{OH})_2]^{2-}$
 - $[\text{Ti}(\text{NH}_3)_6]^{3+}$
- where gly = glycine, en = ethylenediamine and bpy = bipyridyl moieties
- (At. nos. Ti = 22, V = 23, Fe = 26, Co = 27)
75. In which of the following coordination entities the magnitude Δ_0 (CFSE in octahedral field) will be maximum?
- $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Co}(\text{CN})_6]^{3-}$
 - $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
- (At. No. Co = 27)
76. Which of the following **does not** show optical isomerism?
- $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^0$
 - $[\text{Co}(\text{en})\text{Cl}_2(\text{NH}_3)_2]^+$
 - $[\text{Co}(\text{en})_3]^{3+}$
 - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
- (en = ethylenediamine)
77. Which of the following complex ions is expected to absorb visible light?
- $[\text{Ti}(\text{en})_2(\text{NH}_3)_2]^{4+}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Zn}(\text{NH}_3)_6]^{2+}$
 - $[\text{Sc}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$
- (At. no. Zn = 30, Sc = 21, Ti = 22, Cr = 24)
78. Which of the following complex ion is not expected to absorb visible light?
- $[\text{Ni}(\text{CN})_4]^{2-}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
79. Which one of the following complexes is not expected to exhibit isomerism?
- $[\text{Ni}(\text{en})_3]^{2+}$
 - $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$
 - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 - $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$
80. Of the following complex ions, which is diamagnetic in nature?
- $[\text{NiCl}_4]^{2-}$
 - $[\text{Ni}(\text{CN})_4]^{2-}$
 - $[\text{CuCl}_4]^{2-}$
 - $[\text{CoF}_6]^{3-}$
81. The complexes $[\text{Co}(\text{NH}_3)_6]$, $[\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ are the examples of which type of isomerism?
- Linkage isomerism
 - Ionization isomerism
 - Coordination isomerism
 - Geometrical isomerism
82. The complex, $[\text{Pt}(\text{py})(\text{NH}_3)\text{BrCl}]$ will have how many geometrical isomers?
- 3
 - 4
 - 0
 - 2
83. Which of the following complex compounds will exhibit highest paramagnetic behaviour?
- (At. No. : Ti = 22, Cr = 24, Co = 27, Zn = 30)
- $[\text{Ti}(\text{NH}_3)_6]^{3+}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Zn}(\text{NH}_3)_6]^{2+}$
84. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is not true?
- Red complex has a square planar geometry.
 - Complex has symmetrical H-bonding
 - Red complex has a tetrahedral geometry.
 - Dimethylglyoxime functions as bidentate ligand.



85. Low spin complex of d^6 -cation in an octahedral field will have the following energy :
- (a) $\frac{-12}{5}\Delta_0 + P$ (b) $\frac{-12}{5}\Delta_0 + 3P$
 (c) $\frac{-2}{5}\Delta_0 + 2P$ (d) $\frac{-2}{5}\Delta_0 + P$
- (Δ_0 = Crystal Field Splitting Energy in an octahedral field, P = Electron pairing energy)
86. Which of the following has a square planar geometry?
- (a) $[\text{PtCl}_4]^{2-}$ (b) $[\text{CoCl}_4]^{2-}$
 (c) $[\text{FeCl}_4]^{2-}$ (d) $[\text{NiCl}_4]^{2-}$
- (At. nos.: Fe = 26, Co = 27, Ni = 28, Pt = 78)
87. The coordination number and the oxidation state of the element 'E' in the complex $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4)]\text{NO}_2$ (where en) is ethylene diamine) are, respectively,
- (a) 6 and 2 (b) 4 and 2
 (c) 4 and 3 (d) 6 and 3
88. Which of the following pairs represent linkage isomers?
- (a) $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$ and $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$
 (b) $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
 (c) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
 (d) $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
89. A solution containing 2.675 g of $\text{CoCl}_3 \cdot 6\text{NH}_3$ (molar mass = 267.5 g mol⁻¹) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of AgNO_3 to give 4.78 g of AgCl (molar mass = 143.5 g mol⁻¹). The formula of the complex is
- (At. mass of Ag = 108 u)
- (a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (b) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$
 (c) $[\text{CoCl}_3(\text{NH}_3)_3]$ (d) $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$
90. Which one of the following has an optical isomer?
- (a) $[\text{Zn}(\text{en})(\text{NH}_3)_2]^{2+}$ (b) $[\text{Co}(\text{en})_3]^{3+}$
 (c) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ (d) $[\text{Zn}(\text{en})_2]^{2+}$
- (en = ethylenediamine)
91. Which one of the following complex ions has geometrical isomers?
- (a) $[\text{Ni}(\text{NH}_3)_5\text{Br}]^+$ (b) $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
 (c) $[\text{Cr}(\text{NH}_3)_4(\text{en})_2]^{3+}$ (d) $[\text{Co}(\text{en})_3]^{3+}$
- (en = ethylenediamine)
92. Which of the following facts about the complex $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is wrong?
- (a) The complex involves d^2sp^3 hybridisation and is octahedral in shape.
 (b) The complex is paramagnetic.
 (c) The complex is an outer orbital complex
 (d) The complex gives white precipitate with silver nitrate solution.
93. Among the ligands NH_3 , en, CN^- and CO the correct order of their increasing field strength, is :
- (a) $\text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$
 (b) $\text{CN}^- < \text{NH}_3 < \text{CO} < \text{en}$
 (c) $\text{en} < \text{CN}^- < \text{NH}_3 < \text{CO}$
 (d) $\text{CO} < \text{NH}_3 < \text{en} < \text{CN}^-$
94. Which among the following will be named as dibromidobis(ethylene diamine) chromium (III) bromide?
- (a) $[\text{Cr}(\text{en})_3]\text{Br}_3$ (b) $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$
 (c) $[\text{Cr}(\text{en})\text{Br}_4]^-$ (d) $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$
95. As per IUPAC nomenclature, the name of the complex $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$ is :
- (a) Tetraaquadiaminecobalt (III) chloride
 (b) Tetraaquadiamminecobalt (III) chloride
 (c) Diaminetetraaquacobalt (II) chloride
 (d) Diamminetetraaquacobalt (III) chloride
96. The charge on the central metal ion in the complex $[\text{Ni}(\text{CO})_4]$ is
- (a) +2 (b) +4
 (c) 0 (d) +3
97. The ligand $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ is
- (a) tridentate (b) pentadentate
 (c) tetradentate (d) bidentate
98. The IUPAC name of the complex $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ is
- (a) aquatetramminechloridocobalt (III) chloride
 (b) chloridoaquatetramminechloridocobalt (III) chloride
 (c) chloridoaquatetramminechloridocobalt (III) chloride
 (d) tetrammineaquachloridocobalt (III) chloride
99. The magnetic moment of $[\text{NiCl}_4]^{2-}$ is expected to be
- (a) 2.88 BM (b) 1.44 BM
 (c) 5.25 BM (d) 4.91 BM
100. Ammonia will not form complex with
- (a) Ag^{2+} (b) Pb^{2+}
 (c) Cu^{2+} (d) Cd^{2+}

EXERCISE - 2

Applied Questions

- The crystal field splitting energy for octahedral (Δ_0) and tetrahedral (Δ_t) complexes is related as
 - $\Delta_t = -\frac{1}{2}\Delta_0$
 - $\Delta_t = -\frac{4}{9}\Delta_0$
 - $\Delta_t = -\frac{3}{5}\Delta_0$
 - $\Delta_t = -\frac{2}{5}\Delta_0$
- Among the following complexes, optical activity is possible in
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Cl}_2]^+$
 - $[\text{Cr}(\text{H}_2\text{O})_2\text{Cl}_2]^+$
 - $[\text{Co}(\text{CN})_5\text{NC}]$
- Facial and meridional isomerism will be exhibited by
 - $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 - $[\text{Co}(\text{en})_3]\text{Cl}_3$
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- A co-ordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of AgNO_3 solution, we get two moles of AgCl precipitate. The ionic formula for this complex would be
 - $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}][(\text{NH}_3)\text{Cl}]$
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}][\text{Cl}(\text{NO}_2)]$
 - $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$
 - $[\text{Co}(\text{NH}_3)_5][(\text{NO}_2)_2\text{Cl}_2]$
- Which of the following complexes exists as pair of enantiomers?
 - trans- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 - $[\text{Co}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2\text{ClBr}]$
 - $[\text{Cr}(\text{en})_3]^{+3}$
- Which one of the following is an inner orbital complex as well as diamagnetic in behaviour? (Atomic number: $\text{Zn} = 30$, $\text{Cr} = 24$, $\text{Co} = 27$, $\text{Ni} = 28$)
 - $[\text{Zn}(\text{NH}_3)_6]^{2+}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ exhibits
 - linkage isomerism, ionization isomerism and geometrical isomerism
 - ionization isomerism, geometrical isomerism and optical isomerism
 - linkage isomerism, geometrical isomerism and optical isomerism
 - linkage isomerism, ionization isomerism and optical isomerism
- Which one of the following has the highest molar conductivity?
 - Diamminedichloroplatinum (II)
 - Tetraamminedichlorocobalt (III) chloride
 - Potassium hexacyanoferrate (II)
 - Hexaquo chromium (III) chloride
- One mole of the complex compound $\text{Co}(\text{NH}_3)_5\text{Cl}_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of AgNO_3 solution to yield two moles of AgCl (s). The structure of the complex is
 - $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- The ligand $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ is
 - tridentate
 - pentadentate
 - tetradentate
 - bidentate
- Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is
 - c, a
 - b, c
 - a, b
 - a, b, c
- Which one of the following has largest number of isomers?
 - $[\text{Ir}(\text{PR}_3)_2\text{H}(\text{CO})]^{2+}$
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
 - $[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^+$
 - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ ($\text{R} = \text{alkyl group}$, $\text{en} = \text{ethylenediamine}$)
- Which among the following statements are true for the complex $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$?
 - It is a non-electrolyte
 - The magnitude of the charge on each complex ion is 3
 - The complex will not conduct current
 - The complex will exhibit coordination isomerism
 - The magnitude of the charge on each complex ion is 1
 - 1 and 4
 - 1 and 2
 - 1 and 3
 - 2 and 4
- The correct order of magnetic moments (spin only values in B.M.) among is
 - $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$
 - $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$
 - $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$
 - $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$
 (Atomic nos. : $\text{Mn} = 25$, $\text{Fe} = 26$, $\text{Co} = 27$)
- Among the following coordination compounds/ions
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
 Which species exhibit geometrical isomerism?
 - (ii) only
 - (i) and (ii)
 - (ii) and (iv)
 - (i) and (iii)

16. Nickel ($Z = 28$) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[\text{NiX}_4]^{2-}$. The number of unpaired electron(s) in the nickel and geometry of this complex ion are, respectively
 (a) one, square planar (b) two, square planar
 (c) one, tetrahedral (d) two, tetrahedral
17. A complex cation is formed by Pt (in some oxidation state) with ligands (in proper number so that coordination number of Pt becomes six). Which of the following can be its correct IUPAC name?
 (a) Diammineethylenediaminedithiocyanato-S-platinum (II)
 (b) Diammineethylenediaminedithiocyanato-S-platinate (IV) ion
 (c) Diammineethylenediaminedithiocyanato-S-platinum (IV) ion
 (d) Diamminebis (ethylenediamine) dithiocyanato-S-platinum (IV) ion
18. $[\text{Fe}(\text{en})_2(\text{H}_2\text{O})_2]^{2+} + \text{en} \rightarrow \text{complex (X)}$. The correct statement about the complex (X) is –
 (a) it is a low spin complex
 (b) it is diamagnetic
 (c) it shows geometrical isomerism
 (d) (a) and (b) both
19. Among the following, the species that is both paramagnetic and coloured is –
 (a) $[\text{MnO}_4]^{2-}$ (b) $[\text{TiCl}_6]^{2-}$
 (c) $[\text{VO}_4]^{3-}$ (d) CrO_2Cl_2
20. 0.02 mole of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$ and 0.02 mole of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ are present in 200 cc of a solution X. The number of moles of the precipitates Y and Z that are formed when the solution X is treated with excess silver nitrate and excess barium chloride are respectively
 (a) 0.02, 0.02 (b) 0.01, 0.02
 (c) 0.02, 0.04 (d) 0.04, 0.02
21. Crystal field stabilization energy for high spin d^4 octahedral complex is:
 (a) $-1.8 \Delta_0$ (b) $-1.6 \Delta_0 + P$
 (c) $-1.2 \Delta_0$ (d) $-0.6 \Delta_0$
22. The existence of two different coloured complexes with the composition of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is due to:
 (a) linkage isomerism (b) geometrical isomerism
 (c) coordination isomerism (d) ionization isomerism
23. The d -electron configurations of Cr^{2+} , Mn^{2+} , Fe^{2+} and Co^{2+} are d^4 , d^5 , d^6 and d^7 , respectively. Which one of the following will exhibit minimum paramagnetic behaviour?
 (a) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (c) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (d) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 (At, nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)
24. Which of the following carbonyls will have the strongest C – O bond?
 (a) $[\text{Mn}(\text{CO})_6]^+$ (b) $[\text{Cr}(\text{CO})_6]$
 (c) $[\text{V}(\text{CO})_6]^-$ (d) $[\text{Fe}(\text{CO})_5]$
25. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?
 (a) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (b) $[\text{Zn}(\text{NH}_3)_6]^{2+}$
 (c) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$
26. In which of the following complexes of the Co (at. no. 27), will the magnitude of Δ_0 be the highest?
 (a) $[\text{Co}(\text{CN})_6]^{3-}$ (b) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
 (c) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$
27. Which of the following has an optical isomer
 (a) $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$ (b) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$
 (c) $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$ (d) $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$
28. Among the following metal carbonyls, the C–O bond order is lowest in
 (a) $[\text{Mn}(\text{CO})_6]^+$ (b) $[\text{Fe}(\text{CO})_5]$
 (c) $[\text{Cr}(\text{CO})_6]$ (d) $[\text{V}(\text{CO})_6]^-$
29. The IUPAC name of $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$ is
 (a) Tetrachloronickel (II) - tetraamminenickel (II)
 (b) Tetraamminenickel (II) - tetrachloronickel (II)
 (c) Tetraamminenickel (II) - tetrachloronickelate (II)
 (d) Tetrachloronickel (II) - tetrachloronickelate (0)
30. Both $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are
 (a) sp^3 , sp^3 (b) sp^3 , dsp^2 (c) dsp^2 , sp^3 (d) dsp^2 , sp^2
31. The spin only magnetic moment value (in Bohr magneton units) of $\text{Cr}(\text{CO})_6$ is
 (a) 0 (b) 2.84 (c) 4.90 (d) 5.92
32. The ionisation isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is
 (a) $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$
 (b) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$
 (c) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$
 (d) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)]\cdot\text{H}_2\text{O}$
33. The correct structure of ethylenediaminetetraacetic acid (EDTA) is
 (a) $\text{HOOC}-\text{H}_2\text{C}-\text{N}-\text{CH}=\text{CH}-\text{N}-\text{CH}_2-\text{COOH}$
 (b) $\text{HOOC}-\text{H}_2\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{COOH}$
 (c) $\text{HOOC}-\text{H}_2\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{COOH}$
 (d) $\text{HOOC}-\text{H}_2\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{COOH}$

34. The complex showing a spin-only magnetic moment of 2.82 B.M. is :
 (a) $\text{Ni}(\text{CO})_4$ (b) $[\text{NiCl}_4]^{2-}$
 (c) $\text{Ni}(\text{PPh}_3)_4$ (d) $[\text{Ni}(\text{CN})_4]^{2-}$
35. Among the following complexes (K–P)
 $\text{K}_3[\text{Fe}(\text{CN})_6]$ (K), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (L), $\text{Na}_3[\text{Co}(\text{oxalate})_3]$ (M),
 $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (N), $\text{K}_2[\text{Pt}(\text{CN})_4]$ (O) and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (P)
 the diamagnetic complexes are
 (a) K, L, M, N (b) K, M, O, P
 (c) L, M, O, P (d) L, M, N, O
36. $[\text{NiCl}_2 \{ \text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5) \}_2]$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively
 (a) tetrahedral and tetrahedral
 (b) square planar and square planar
 (c) tetrahedral and square planar
 (d) square planar and tetrahedral
37. Which of the following complex species is not expected to exhibit optical isomerism ?
 (a) $[\text{Co}(\text{en})_3]^{3+}$ (b) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
 (c) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (d) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
38. Which one of the following is the correct order of field strength of ligands in spectrochemical series?
 (a) $\text{I}^- < \text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{CN}^-$
 (b) $\text{F}^- < \text{H}_2\text{O} < \text{I}^- < \text{CN}^- < \text{Cl}^-$
 (c) $\text{CN}^- < \text{I}^- < \text{F}^- < \text{Cl}^- < \text{H}_2\text{O}$
 (d) $\text{H}_2\text{O} < \text{F}^- < \text{CN}^- < \text{Cl}^- < \text{I}^-$
39. Which of the following organometallic compound is σ and π bonded?
 (a) $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$ (b) $\text{Fe}(\text{CH}_3)_3$
 (c) $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$ (d) $[\text{Co}(\text{CO})_5\text{NH}_3]^{2+}$
40. Which one of the following coordination compounds is used to inhibit the growth of tumours?
 (a) Trans-platin (b) EDTA complex of calcium
 (c) $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ (d) Cis-platin
41. Which of the following complexes exists as pair of enantiomers?
 (a) $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (b) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 (c) $[\text{Co}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2\text{ClBr}]$ (d) $[\text{Cr}(\text{en})_3]^{3+}$
42. Which of the following complex ions is diamagnetic?
 (a) $[\text{FeF}_6]^{3-}$ (b) $[\text{CoF}_6]^{3-}$
 (c) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ (d) $[\text{Fe}(\text{CN})_6]^{3-}$
43. Which one of the following has the highest molar conductivity?
 (a) Diamminedichloroplatinum(II)
 (b) Tetraamminedichlorocobalt(III) chloride
 (c) Potassium hexacyanoferrate(II)
 (d) Hexaquo chromium(III) chloride
44. Among the following coordination compounds/ions
 (i) $[\text{Fe}(\text{CN})_6]^{3-}$ (ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 (iii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (iv) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
 Which species exhibit geometrical isomerism?
 (a) (ii) only (b) (i) and (ii)
 (c) (ii) and (iv) (d) (i) and (iii)
45. The crystal field splitting energy for octahedral (Δ_0) and tetrahedral (Δ_t) complexes is related as
 (a) $\Delta_t = -\frac{1}{2}\Delta_0$ (b) $\Delta_t = -\frac{4}{9}\Delta_0$
 (c) $\Delta_t = -\frac{3}{5}\Delta_0$ (d) $\Delta_t = -\frac{2}{5}\Delta_0$
46. Facial and meridional isomerism will be exhibited by
 (a) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (b) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 (c) $[\text{Co}(\text{en})_3]\text{Cl}_3$ (d) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- DIRECTIONS for Qs. 47 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.**
- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True
47. **Statement-1** : $[\text{FeF}_6]^{3-}$ is a low spin complex.
Statement-2 : Low spin complexes have lesser number of unpaired electrons.
48. **Statement-1** : NF_3 is a weaker ligand than $\text{N}(\text{CH}_3)_3$.
Statement-2 : NF_3 ionizes to give F^- ions in aqueous solution.
49. **Statement-1** : $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic.
Statement-2 : $[\text{Fe}(\text{CN})_6]^{3-}$ has +3 oxidation state while $[\text{Fe}(\text{CN})_6]^{4-}$ has +2 oxidation state.
50. **Statement-1** : $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
Statement-2 : $d-d$ transition is not possible in $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Which of the following complexes formed by Cu^{2+} ions is most stable?
 - $\text{Cu}^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$, $\log K = 11.6$
 - $\text{Cu}^{2+} + 4\text{CN}^- \rightarrow [\text{Cu}(\text{CN})_4]^{2-}$, $\log K = 27.3$
 - $\text{Cu}^{2+} + 2\text{en} \rightarrow [\text{Cu}(\text{en})_2]^{2+}$, $\log K = 15.4$
 - $\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightarrow [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, $\log K = 8.9$
- The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$.
 - $[\text{Co}(\text{CN})_6]^{3-} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{CN})_6]^{3-}$
 - $[\text{Co}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{CN})_6]^{3-}$
 - $[\text{Co}(\text{CN})_6]^{3-} > [\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- When 0.1 mol $\text{CoCl}_3 \cdot (\text{NH}_3)_5$ is treated with excess of AgNO_3 , 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to
 - 1 : 3 electrolyte
 - 1 : 2 electrolyte
 - 1 : 1 electrolyte
 - 3 : 1 electrolyte
- When 1 mole of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is treated with excess of AgNO_3 , 3 moles of AgCl are obtained. The formula of the complex is
 - $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$
 - $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
 - $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 - $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
- The correct IUPAC name of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is
 - Diamminedichloridoplatinum (II)
 - Diamminedichloridoplatinum (IV)
 - Diamminedichloridoplatinum (0)
 - Dichloridodiammineplatinum (IV)
- The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?
 - $[\text{Fe}(\text{CO})_5]$
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- Indicate the complex ion which shows geometrical isomerism.
 - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
 - $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^{3-}$
 - $[\text{Co}(\text{NH}_3)_6]^{3-}$
 - $[\text{Co}(\text{CN})_5(\text{NC})]^{3-}$
- The CFSE for octahedral $[\text{CoCl}_6]^{4-}$ is $18,000 \text{ cm}^{-1}$. The CFSE for tetrahedral $[\text{CoCl}_4]^{2-}$ will be
 - $18,000 \text{ cm}^{-1}$
 - $16,000 \text{ cm}^{-1}$
 - $8,000 \text{ cm}^{-1}$
 - $20,000 \text{ cm}^{-1}$
- Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$ and $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$ are
 - linkage isomers
 - coordination isomers
 - ionisation isomers
 - geometrical isomers
- The compounds $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ and $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$ represent
 - linkage isomerism
 - ionisation isomerism
 - coordination isomerism
 - no isomerism
- A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?
 - Thiosulphato
 - Oxalato
 - Glycinato
 - Ethane-1, 2-diamine
- Which of the following species is not expected to be a ligand?
 - NO
 - NH_4^+
 - $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
 - CO
- What kind of isomerism exists between $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet) and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (greyish-green)?
 - Linkage isomerism
 - Solvate isomerism
 - Ionisation isomerism
 - Coordination isomerism
- IUPAC name of $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$ is
 - Platinum diamminechloronitrite
 - Chloronitrito-N-ammineplatinum (II)
 - Diamminechloridonitrito-N-platinum (II)
 - Diamminechloronitrito-N-platinatate (II)

NEET/AIPMT (2013-2017) Questions

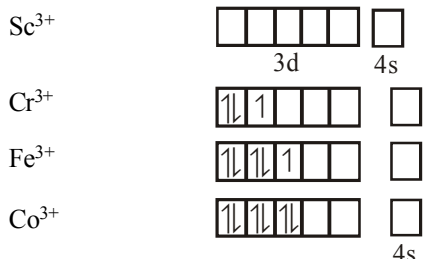
- A magnetic moment of 1.73 BM will be shown by one among the following : [2013]
 - $[\text{Ni}(\text{CN})_4]^{2-}$
 - TiCl_4
 - $[\text{CoCl}_6]^{4-}$
 - $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- An excess of AgNO_3 is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium (III) chloride. The number of moles of AgCl precipitated would be : [2013]
 - 0.002
 - 0.003
 - 0.01
 - 0.001
- The correct IUPAC name for $[\text{CrF}_2(\text{en})_2]\text{Cl}$ is: [NEET Kar. 2013]
 - Chlorodifluoridobis (ethylene diamine) chromium (III)
 - Chlorodifluoridoethylenediaminechromium (III) chloride
 - Difluoridobis (ethylene diamine) chromium (III) chloride
 - Difluorobis (ethylene diamine) chromium (III) chloride
- Crystal field splitting energy for high spin d^4 octahedral complex is: [NEET Kar. 2013]
 - $-1.6 \Delta_0$
 - $-1.2 \Delta_0$
 - $-0.6 \Delta_0$
 - $-0.8 \Delta_0$
- Which is diamagnetic? [NEET Kar. 2013]
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Co}(\text{F}_6)]^{3-}$
 - $[\text{Ni}(\text{CN})_4]^{2-}$
 - $[\text{NiCl}_4]^{2-}$
- In a particular isomer of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^0$, the Cl-Co-Cl angle is 90° , the isomer is known as [NEET Kar. 2013]
 - Linkage isomer
 - Optical isomer
 - cis-isomer
 - Position isomer

21. The anion of acetylacetone (acac) forms Co(acac)_3 chelate with Co^{3+} . The rings of the chelate are [NEET Kar. 2013]
 (a) three membered (b) five membered
 (c) four membered (d) six membered
22. Which among the following is a paramagnetic complex? [NEET Kar. 2013]
 (a) Mo(CO)_6 (b) $[\text{Co(NH}_3)_6]^{3+}$
 (c) $[\text{Pt(en)Cl}_2]$ (d) $[\text{CoBr}_4]^{2-}$
 (At. No. of Mo = 42, Pt = 78)
23. Among the following complexes the one which shows zero crystal field stabilization energy (CFSE): [2014]
 (a) $[\text{Mn(H}_2\text{O)}_6]^{3+}$ (b) $[\text{Fe(H}_2\text{O)}_6]^{3+}$
 (c) $[\text{Co(H}_2\text{O)}_6]^{2+}$ (d) $[\text{Co(H}_2\text{O)}_6]^{3+}$
24. Which of the following complexes is used as an anti-cancer agent: [2014]
 (a) *mer*- $[\text{Co(NH}_3)_3\text{Cl}_3]$ (b) *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$
 (c) *cis*- $\text{K}_2[\text{PtCl}_2\text{Br}_2]$ (d) Na_2CoCl_4
25. Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test of chloride ions with silver nitrate at 25°C ? [2015]
 (a) $\text{CoCl}_3 \cdot 4\text{NH}_3$ (b) $\text{CoCl}_3 \cdot 5\text{NH}_3$
 (c) $\text{CoCl}_3 \cdot 6\text{NH}_3$ (d) $\text{CoCl}_3 \cdot 3\text{NH}_3$
26. Which of these statements about $[\text{Co(CN)}_6]^{3-}$ is true? [2015]
 (a) $[\text{Co(CN)}_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration.
 (b) $[\text{Co(CN)}_6]^{3-}$ has four unpaired electrons and will be in a high spin configuration.
 (c) $[\text{Co(CN)}_6]^{3-}$ has no unpaired electrons and will be in a high-spin configuration.
 (d) $[\text{Co(CN)}_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration.
27. The sum of coordination number and oxidation number of the metal M in the complex $[\text{M(en)}_2(\text{C}_2\text{O}_4)]\text{Cl}$ (where en is ethylenediamine) is: [2015 RS]
 (a) 9 (b) 6
 (c) 7 (d) 8
28. The name of complex ion, $[\text{Fe(CN)}_6]^{3-}$ is: [2015 RS]
 (a) Hexacyanoiron (III) ion
 (b) Hexacyanoferrate (III) ion
 (c) Tricyanoferrate (III) ion
 (d) Hexacyanidoferrate (III) ion
29. Number of possible isomers for the complex $[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$ will be (en = ethylenediamine) [2015 RS]
 (a) 2 (b) 1
 (c) 3 (d) 4
30. Which of the following has longest C–O bond length? (Free C–O bond length in CO is $1.128\text{\AA}$) [2016]
 (a) Ni(CO)_4 (b) $[\text{Co(CO)}_4]^-$
 (c) $[\text{Fe(CO)}_4]^{2-}$ (d) $[\text{Mn(CO)}_6]^+$
31. An example of a sigma bonded organometallic compound is : [2017]
 (a) Grignard's reagent (b) Ferrocene
 (c) Cobaltocene (d) Ruthenocene
32. HgCl_2 and I_2 both when dissolved in water containing I^- ions the pair of species formed is : [2017]
 (a) HgI_2, I^- (b) $\text{HgI}_4^{2-}, \text{I}_3^-$
 (c) $\text{Hg}_2\text{I}_2, \text{I}^-$ (d) $\text{HgI}_2, \text{I}_3^-$
33. The correct order of the stoichiometries of AgCl formed when AgNO_3 in excess is treated with the complexes : $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$, $\text{CoCl}_3 \cdot 4\text{NH}_3$ respectively is :- [2017]
 (a) 3 AgCl , 1 AgCl , 2 AgCl
 (b) 3 AgCl , 2 AgCl , 1 AgCl
 (c) 2 AgCl , 3 AgCl , 1 AgCl
 (d) 1 AgCl , 3 AgCl , 2 AgCl
34. Correct increasing order for the wavelengths of absorption in the visible region the complexes of Co^{3+} is :- [2017]
 (a) $[\text{Co(H}_2\text{O)}_6]^{3+}$, $[\text{Co(en)}_3]^{3+}$, $[\text{Co(NH}_3)_6]^{3+}$
 (b) $[\text{Co(H}_2\text{O)}_6]^{3+}$, $[\text{Co(NH}_3)_6]^{3+}$, $[\text{Co(en)}_3]^{3+}$
 (c) $[\text{Co(NH}_3)_6]^{3+}$, $[\text{Co(en)}_3]^{3+}$, $[\text{Co(H}_2\text{O)}_6]^{3+}$
 (d) $[\text{Co(en)}_3]^{3+}$, $[\text{Co(NH}_3)_6]^{3+}$, $[\text{Co(H}_2\text{O)}_6]^{3+}$
35. Pick out the correct statement with respect to $[\text{Mn(CN)}_6]^{3-}$ [2017]
 (a) It is sp^3d^2 hybridised and tetrahedral
 (b) It is d^2sp^3 hybridised and octahedral
 (c) It is dsp^2 hybridised and square planar
 (d) It is sp^3d^2 hybridised and octahedral

Hints & Solutions

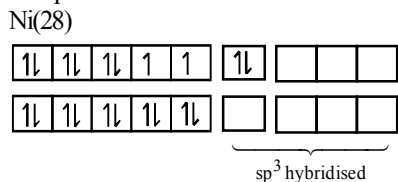
EXERCISE - 1

1. (c) CN^- is a strong ligand so it forces the electrons to pair up.

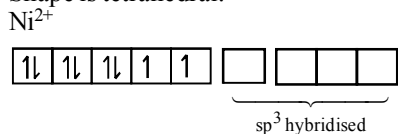


In Sc^{3+} , no electron is there in d orbital, in Cr^{3+} one electron is unpaired. In Fe^{3+} also one electron is unpaired, Co^{3+} has no unpaired electrons. As both Cr^{3+} and Fe^{3+} contain one electron in unpaired state so both may be paramagnetic. But as we know Fe has more magnetic properly. Fe^{3+} will be more paramagnetic. So option (c) is correct.

2. (b) IUPAC name is Potassium trioxalatoaluminate (III).
3. (c) $[\text{CuCl}_2\{(\text{O}=\text{C}(\text{NH}_2)_2\}_2]$
4. (a) Sodium ethoxide is not an organometallic compound as in this compound carbon is not directly attached with metal.
5. (b) Both are tetrahedral. CO is a strong ligand and $\text{P}(\text{Ph}_3)$ is a weak ligand. So, CO pair up electrons while $\text{P}(\text{Ph}_3)$ do not pair up. Oxidation state of Ni is zero in carboxyl compound which in other Ni has + 2 oxidation state.



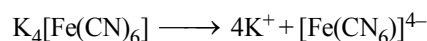
Shape is tetrahedral.



Shape is tetrahedral.

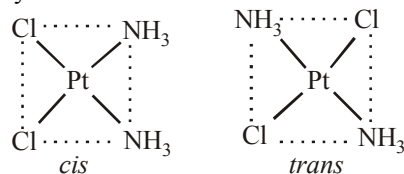
6. (a) Chlorodiaquatrimmincobalt (III) chloride is $[\text{CoCl}(\text{NH}_3)_3(\text{H}_2\text{O})_2]\text{Cl}_2$.
7. (a) IUPAC name of sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ is sodium pentacyanonitrosylferrate (III) because in it NO is neutral ligand. Hence
 $2 \times \text{O.N. of Na} + \text{O.N. of Fe} + 5 \times \text{O.N. of CN}$
 $1 \times \text{O.N. of NO} = 0$
 $2 \times (+1) + \text{O.N. of Fe} + 5 \times (-1) + 1 \times 0 = 0$
 $\text{O.N. of Fe} = 5 - 2 = +3$, Hence ferrate (III)
8. (a) Let the O. No. of Ni in $\text{K}_4[\text{Ni}(\text{CN})_4]$ be = x then
 $4(+1) + x + (-1) \times 4 = 0 \Rightarrow 4 + x - 4 = 0$
 $x = 0$

9. (d) In $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, all chlorine atoms are inside the coordination sphere so they will not ionise and this compound will not give precipitate with AgNO_3 .
10. (d) Oxidation state of Cr in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$.
 Let it be x , $1 \times x + 4 \times 0 + 2 \times (-1) = 1$ Therefore $x = 3$.
11. (c) $\text{K}_3[\text{Fe}(\text{CN})_6]$ is Potassium hexacyanoferrate (III).
12. (d) The given complex is $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]^{3+}$. When it is dissolved in water it forms none other ion.
13. (b) $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$
 pentaamminenitrito-N-cobalt (III) chloride
14. (b) Complex compounds do not dissociate into constituent ions.

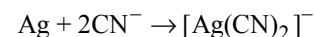


$\therefore$ It is a complex because no CN^- is formed on dissociation.

15. (d) $[\text{EDTA}]^{4-}$ is a hexadentate ligand, because it has six donor atoms and donate 6 pairs of electrons to central metal atom in the complex.
16. (c) It is incorrect statement.
 All other statements i.e. (a), (b) and (d) are correct.
17. (d) In $\text{Fe}(\text{CO})_5$, Fe is in minimum oxidation state (zero).
18. (b) $\text{K}_2[\text{PtCl}_6]$
 Potassium hexachloroplatinate (IV)
 Oxidation state of Pt is + 4 in the complex and anion is present in form of complex.
19. (c) $\text{EAN} = \text{Atomic number} - \text{Oxidation state} + 2 \times \text{number of Ligands} = 26 - 2 + 2(6) = 36$.
20. (b) Organo-metallic compound is (b) as it contains metal-carbon bonds. In others, direct link of carbon with metal is not present.
21. (a) $\text{EAN} = (\text{atomic no}) - (\text{oxidation state}) + (2 \times \text{number of Ligands}) = 28 - 2 + 2 \times 4 = 34$
22. (a) $\text{EAN} = \text{at. no. of central atom} - \text{oxidation state} + 2 \times (\text{no. of ligands}) = 27 - 3 + 2 \times 6 = 36$.
23. (a) Due to back bonding present between metal and carbonyl ligand in metal carbonyl, CO is termed as π -acid ligand.
24. (a) In complex $\text{K}_4[\text{Fe}(\text{CN})_6]$ the Fe obey EAN rule strictly. As in this complex EAN of Fe is 36, which corresponds to the atomic number of krypton
 Hence, according to sidwick the complex will be stable
25. (a) $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ is a disubstituted complex and shows only *cis*-& *trans*-isomers

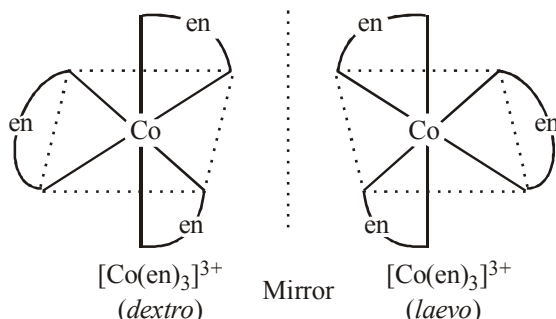


26. (b) Among the given metal ions only Ag^+ forms complex with CN^- having co-ordination number 2.



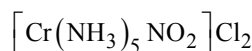
Coordination number of metals is defined as the number of σ bonds by which ligands are attached to the metal atom.

27. (c) $[\text{Cr}(\text{SCN})_2(\text{NH}_3)_4]^+$ shows linkage, geometrical and optical isomerism. Hence produces maximum no. of isomers.
28. (a) MA_3B_3 – 2 geometrical isomers
 MA_2B_4 – 2 geometrical isomers
 MA_4B_2 – 2 geometrical isomers
 The complexes of general formula MA_6 and MA_5B having octahedral geometry do not show geometrical isomerism.
29. (d) The optical isomers are pair of molecules which are non superimposable mirror images of each other.

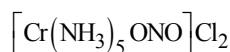
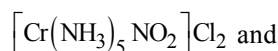


The two optically active isomers are collectively called enantiomers.

30. (b) The chemical formula of Pentamminenitrochromium (III) chloride is



It can exist in following two structures



Therefore the type of isomerism found in this compound is linkage isomerism as nitro group is linked through N as $-\text{NO}_2$ or through O as $-\text{ONO}$.

31. (a) For any metal cation, the magnitude of Δ_0 depends upon the nature of ligand. Higher the value of Δ_0 , lower will be the wave length absorbed. Δ_0 is crystal field stabilisation energy.

The value of Δ_0 for ligands varies as follows

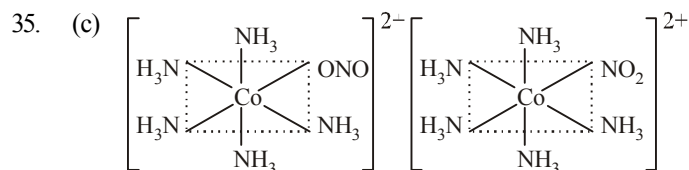


So, the wavelength absorbed will vary in reverse order



32. (b)
33. (c) $\text{cis}[\text{Co}(\text{en})_2\text{Cl}_2]^+$: $\text{cis}[\text{M}(\text{aa})_2\text{b}_2]$ can show optical isomerism.

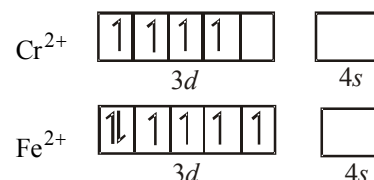
34. (a)



Here more than one atom function as donor, as oxygen

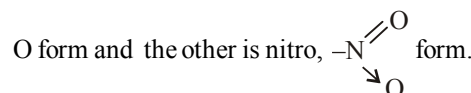
in first one and nitrogen in second, so they show linkage isomerism.

36. (b) Co-ordination isomerism is caused by the interchange of ligands between cation and anion complexes.
37. (b) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$. Here Cr is in Cr^{2+} form

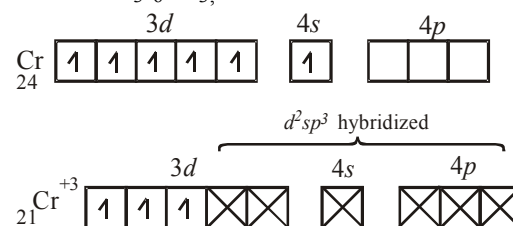


In $[\text{Fe}(\text{H}_2\text{O})]^{2+}$, Fe is in Fe^{2+} form. Both will have 4 unpaired electrons.

38. (a) The ligands in *cis*-platin $[\text{PtCl}_2(\text{NH}_3)_2]$ are Cl and NH_3 .
39. (d) $[\text{Pt}(\text{NH}_3)\text{Cl}_2\text{Br}]\text{Cl} \rightleftharpoons [\text{Pt}(\text{NH}_3)\text{Cl}_2\text{Br}]^+ + \text{Cl}^-$
 Cl^- ion is precipitable.
40. (b) The compound which appears blue green, absorb red light as blue-green is complementary to red colour. Here $[\text{Cu}(\text{NH}_3)_4]^{2+}$ appears blue-green, so it absorbs red colour.
41. (c) Diaminodichloroplatinum (II) commonly known as *cis*-platin is found to have anticancer property.
42. (b) As in $[\text{NiCl}_4]^{-2}$ Chloride ion being a weak ligand is not able to pair the electrons in d orbital.
43. (a) The given compound contains $-\text{NO}_2$ group which can donate electrons either from O- or from N-. Thus, it shows linkage isomerism. Thus the two given compounds are linkage isomers, one is nitrite $-\text{O}-\text{N}=\text{O}$



44. (d) In $[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$, Cr is in +3 oxidation state



Its ion is octahedral in nature. Due to the presence of three unpaired electrons it is paramagnetic.

45. (d) Cr^{3+} has $4s^0 3d^3$ electronic configuration with 3 unpaired electrons, hence paramagnetic. In other cases pairing of d-electrons take place in presence of strong field ligands such as CO or CN^- .

In $\text{Cr}(\text{CO})_6$ molecule 12 electrons are contributed by CO group and it contain no odd electron

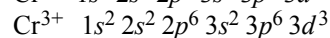
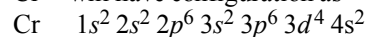
46. (b) $\mu = \sqrt{n(n+2)}$

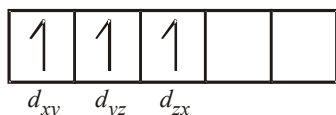
$$3.83 = \sqrt{n(n+2)}$$

on solving $n = 3$

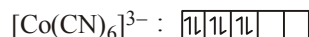
as per magnetic moment, it has three unpaired electron.

Cr^{3+} will have configuration as





So, $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$



CN^- is a strong field ligand and it causes pairing of electrons as a result number of unpaired electrons in Co^{3+} becomes zero and hence it has lowest value of paramagnetic behaviour.

48. (b) In the complexes of C.N. 4, square planar geometry gives rise to low spin (spin paired) configurations whereas tetrahedral complexes display high spin configurations.

49. (d) d^5 — strong ligand field



$$\mu = \sqrt{n(n+2)} = \sqrt{3} = 1.73 \text{ BM}$$

d^3 — in weak as well as in strong field



$$\mu = \sqrt{3(5)} = \sqrt{15} = 3.87 \text{ B.M.}$$

d^4 — in weak ligand field



$$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89$$

d^4 — in strong ligand field



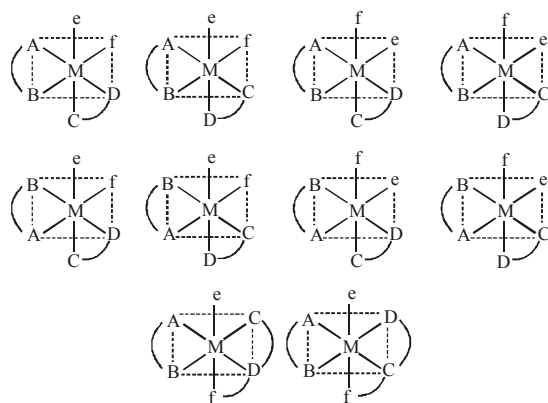
$$\mu = \sqrt{2(4)} = \sqrt{8} = 2.82$$

50. (c) The number of unpaired electrons in $\text{Ni}^{2+}(aq) = 2$
Water is weak ligand hence no pairing will take place

$$\text{spin magnetic moment} = \sqrt{n(n+2)} = \sqrt{2(2+2)}$$

$$= \sqrt{8} = 2.83$$

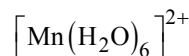
51. (c)



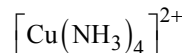
52. (a) Paramagnetic species has unpaired electron. More the no. of unpaired electrons, more will be paramagnetic character.

Complex

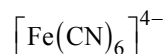
O. S. of metal



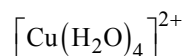
Mn^{2+}



Cu^{2+}

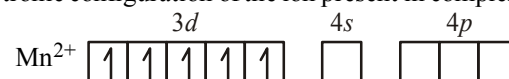


Fe^{2+}

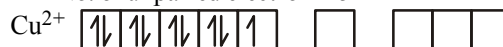


Cu^{2+}

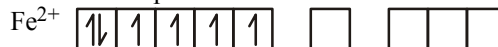
Electronic configuration of the ion present in complex



No. of unpaired electron = 5



No. of unpaired electron = 1



However, CN^- is a strong ligand, so pairing of electrons will occur in the complex having CN^- ions.

$\therefore \text{Fe}^{2+}$ in presence of CN^-



$\therefore$ No. of unpaired electron = 0

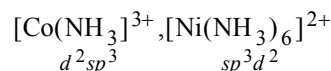
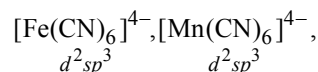
Thus $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ having maximum no. of unpaired electrons has maximum paramagnetic nature.

53. (c) In $\text{Na}_2[\text{CdCl}_4]$, Cd has oxidation state +2.
So, its electronic configuration is $4d^{10}5s^0$
or all the $4d$ orbitals are fully filled.
Hence, there will be no $d-d$ transition. So, it is colourless.
54. (a) Cl^- is a weak field ligand.
55. (c) Co must be in +3 oxidation state and the ligand L should be a weak ligand.



$$n = 4, \mu = 4.5 \text{ BM.}$$

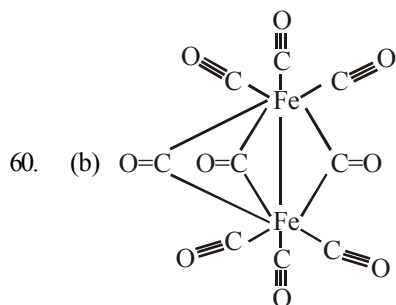
56. (d) Hybridisation



Hence $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is outer orbital complex.

57. (b) A square planar complex is formed by hybridisation of s, p_x, p_y and $d_{x^2-y^2}$ atomic orbitals.
58. (b) Organometallic compounds are those compounds in which a metal is bonded directly to a carbon atom of a molecule. In chlorophyll there is bond involving metal Mg

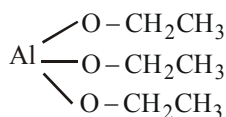
59. (d) $[\text{Co}(\text{CO})_5\text{NH}_3]^{2+}$. In this complex Co-atom attached with NH_3 through σ bonding and with CO with dative π -bond.



61. (a) The number of carbon atom found in π bonded organometallic compounds is indicated by the greek letter ' η ' with a number. The prefixes η^2 , η^5 and η^6 indicate that 2, 5 and 6 carbon atom are bound to the metal in the compound. $(\text{CH}_3)_4\text{Sn}$ does not involve any π (π) bond formation. This is a σ bonded organometallic compound.

62. (a)

63. (a) Triethoxyaluminium has no Al – C linkage



64. (c) The chlorophyll molecule plays an important role in photosynthesis, contain porphyrin ring and the metal Mg not Ca.

65. (b) The complex formation is a characteristic of d-block elements. Lead is a p-block element hence does not forms complex compounds.

66. (d) Due to some backbonding by sidewise overlapping between d-orbitals of metal and p-orbital of carbon, the Fe–C bond in $\text{Fe}(\text{CO})_5$ has both σ and π character.

67. (d) In one case, on electrolysis of aqueous solution, the complex ion of cobalt [i.e., $\{\text{Co}(\text{NH}_3)_6\}^{3+}$] of the complex $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ moves towards cathode (i.e., negative electrode) and on this electrode finally cobalt would be deposited.

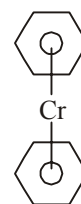
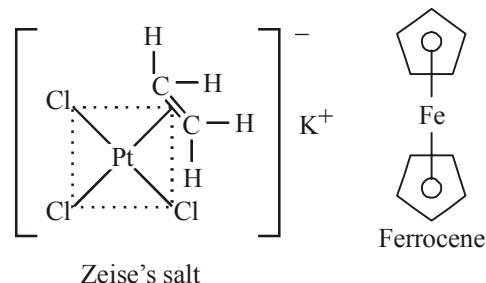
In another case, on electrolysis of aqueous solution, the complex ion of chromium [i.e., $\{\text{Cr}(\text{NH}_3)_6\}^{3+}$] of the complex $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ moves towards cathode (i.e., negative electrode) and on this electrode chromium would finally be deposited.

68. (b) Organometallic compound is (b) as it contains metal-carbon bonds. In others, direct link of carbon with metal is not present.

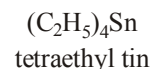
69. (d) Compounds that contain atleast one carbon metal bond are called organometallic compound. Hence, based on above definition methyl lithium is an organometallic compound. In other chemical compounds carbon is not linked with metal.

70. (d)

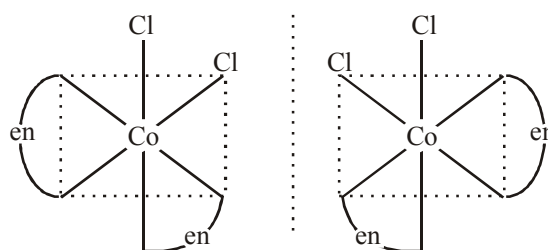
71. (a)



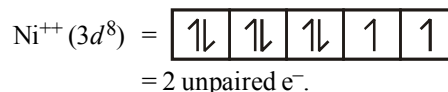
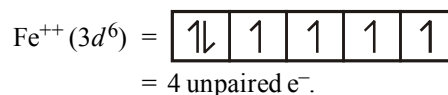
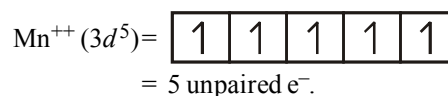
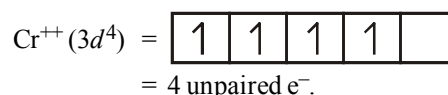
dibenzene chromium



72. (b) Non superimposable mirror images are called optical isomers and may be described as "chiral". They are also called enantiomers and rotate plane polarised light in opposite directions.



73. (b) Lesser is the number of unpaired electrons smaller will be the paramagnetic behaviour. As Cr^{++} , Mn^{++} , Fe^{++} and Ni^{++} contains.



As Ni^{++} has minimum no. of unpaired e^- thus this is least paramagnetic.

74. (c)

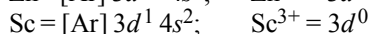
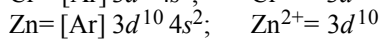
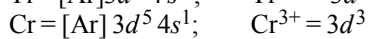
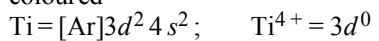
75. (c) In octahedral field the crystal field splitting of d-orbitals of a metal ion depends upon the field produced by the ligands. In general ligands can be arranged in a series in the order of increasing fields and splittings which they produce around a central metal ion. A portion of the series is given below.

cyanide > ethylene - diamine > ammonia > pyridine > thiocyanate > water > oxalate > hydroxide > fluoride > chloride > bromide > iodide.

Out of the given ligands water, ammonia, cyanide and oxalate, we can find from the above series of ligands that the maximum splitting will occur in case of cyanide (CN^-) i.e. the magnitude of Δ_0 will be maximum in case of $[\text{Co}(\text{CN})_6]^{3+}$.

76. (a) The octahedral coordination compounds of the type MA_3B_3 exhibit fac-mer isomerism.

77. (b) Since Cr^{3+} in the complex has unpaired electrons in the d orbital, hence it will absorb visible light and will be coloured



78. (a) $[\text{Ni}(\text{CN})_4]^{2-}$: Number of unpaired electrons = 0

$[\text{Cr}(\text{NH}_3)_6]^{3+}$: Number of unpaired electrons = 3

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: Number of unpaired electrons = 4

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$: Number of unpaired electrons = 2

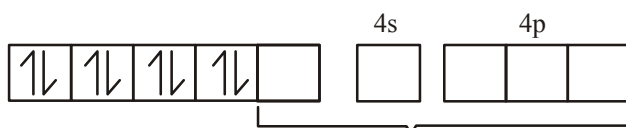
79. (d) In $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$, Ni^{2+} is in sp^3 hybridisation, thus tetrahedral in shape. Hence the four ligands are not different to exhibit optical isomerism. In tetrahedral geometry all the positions are adjacent to one another $\therefore$ geometrical isomerism is not possible.

80. (b) $\text{Ni}^{++} = 3d^8 4s^0$

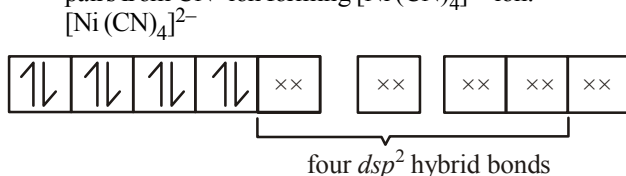


Since, the coordination number of Ni in this complex is 4, the configuration of Ni^{++} at first sight shows that the complex is paramagnetic with two unpaired electrons. However, experiments show that the complex is diamagnetic. This is possible when the 3d electrons rearrange against the Hund's rule as shown below. This is in accordance with the fact that the ligand involved here is strong i.e., CN^- ion.

Ni^{++} (after rearrangement)

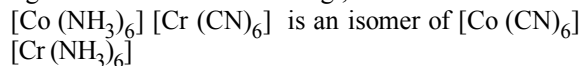


Hence, now dsp^2 hybridization involving one 3d, one 4s and two 4p orbitals, takes place leading to four dsp^2 hybrid orbitals, each of which accepts four electron pairs from CN^- ion forming $[\text{Ni}(\text{CN})_4]^{2-}$ ion.

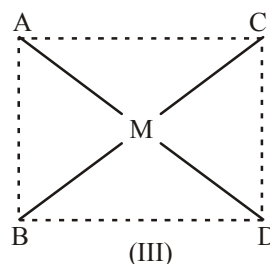
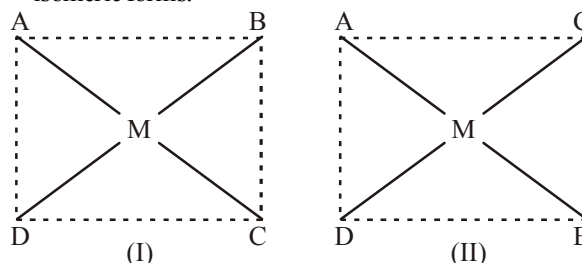


Thus, the complex is diamagnetic as it has no unpaired electron.

81. (c) Coordination isomerism occurs when cationic and anionic complexes of different metal ions are present in a salt. The two isomers differ in the distribution of ligands in cation and anion e.g.,



82. (a) Complexes of the type M_{ABCD} may exist in three isomeric forms.



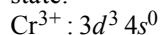
Similarly, $[\text{Pt}(\text{py})(\text{NH}_3)\text{BrCl}]$ may exist in three isomeric form in which

$\text{M} = \text{Pt}$, $\text{A} = \text{Py}$, $\text{B} = \text{NH}_3$, $\text{C} = \text{Br}$, $\text{D} = \text{Cl}$.

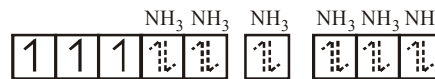
83. (b)

(a) $[\text{Ti}(\text{NH}_3)_6]^{3+}$: $3d^1$ configuration and thus has one unpaired electron.

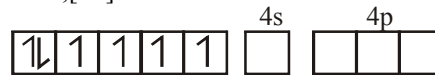
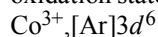
(b) $[\text{Cr}(\text{NH}_3)_6]^{3+}$: In this complex Cr is in +3 oxidation state.



It has 3 unpaired electrons thus complex is paramagnetic



(c) $[\text{Co}(\text{NH}_3)_6]^{3+}$: In this complex cobalt ion is in +3 oxidation state with $3d^6$ configuration.

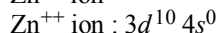


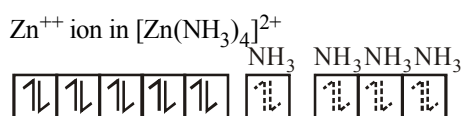
(inner orbital or d^2sp^3 hybrid orbital, low spin complex)

$\therefore$ diamagnetic

(d) In this complex Zn exists as

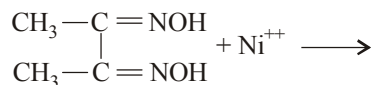
Zn^{++} ion



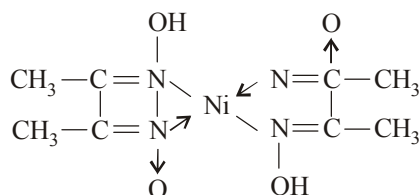


Due to presence of paired electrons complex is diamagnetic in nature.

84. (c) Nickel ions are frequently detected by the formation of red precipitate of the complex of nickel dimethylglyoxime, when heated with dimethylglyoxime.



Dimethylglyoxime



Nickel dimethylglyoxime

85. (b) $d^6 - t_{2g}^{2,2,2} e_g^{0,0}$ (in low spin)

$$\text{C.F.S.E} = -0.4 \times 6\Delta_0 + 3P = -\frac{12}{5}\Delta_0 + 3P$$

86. (a) Complexes with dsp^2 hybridisation are square planar. So, $[\text{PtCl}_4]^{2-}$ is square planar in shape.

87. (d) In the given complex we have two bidentate ligands (i.e en and C_2O_4), so coordination number of E is 6 ($2 \times 2 + 1 \times 2 = 6$)

Let the oxidation state of E in complex be x, then

$$[x + (-2) = 1] \text{ or } x - 2 = 1$$

or $x = +3$, so its oxidation state is +3

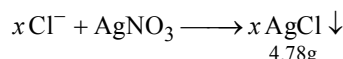
Thus option (d) is correct.

88. (a) The SCN^- ion can coordinate through S or N atom giving rise to linkage isomerism

$\text{M} \leftarrow \text{SCN}$ thiocyanato

$\text{M} \leftarrow \text{NCS}$ isothiocyanato.

89. (a) $\text{CoCl}_3 \cdot 6\text{NH}_3 \longrightarrow x\text{Cl}^-$
2.675g



Number of moles of the complex

$$= \frac{2.675}{267.5} = 0.01 \text{ moles}$$

Number of moles of AgCl obtained

$$= \frac{4.78}{143.5} = 0.03 \text{ moles}$$

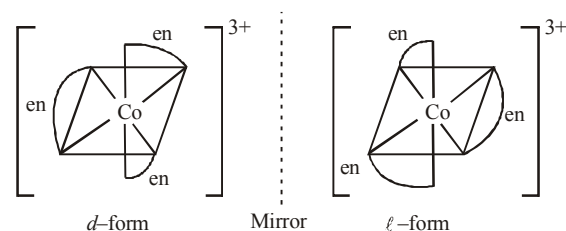
$\therefore$ No. of moles of AgCl obtained
= $3 \times$ No. of moles of complex

$$\therefore n = \frac{0.03}{0.01} = 3$$

$\therefore 3\text{Cl}^-$ ions are precipitable

Hence the formula of the complex is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

90. (b) Option (b) shows optical isomerism $[\text{Co}(\text{en})_3]^{3+}$

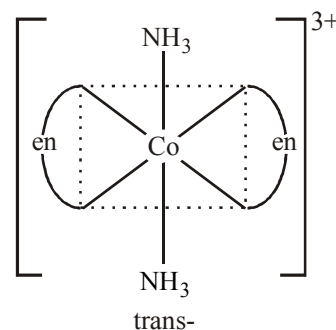


Complexes of Zn^{++} cannot show optical isomerism as they are tetrahedral complexes with plane of symmetry.

$[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$ have two planes of symmetry hence it is also optically inactive.

$[\text{Zn}(\text{en})_2]^{2+}$ cannot show optical isomerism

91. (b)



92. (c) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is an inner orbital complex, because in this complex inner d-orbital is used for hybridisation (d^2sp^3)

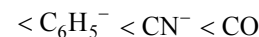
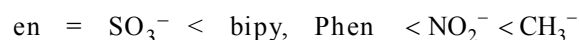
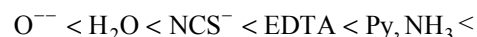
93. (a) Ligands can be arranged in a series in the orders of increasing field strength as given below :

Weak field ligands :



< Urea, OH^- < oxalate

Strong field ligands



Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

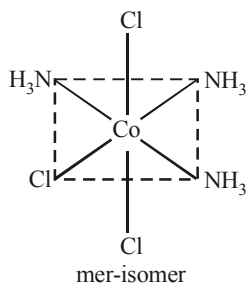
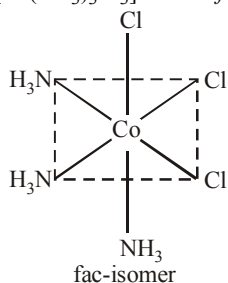
94. (b) $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$
dibromidobis(ethylenediamine) chromium (III) bromide.

95. (d) $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$
= Diamminetetraaquacobalt (III) chloride.

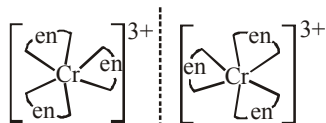
96. (c) In case of $[\text{Ni}(\text{CO})_4]$, the ligand CO, is neutral thus the charge on Ni is zero.
97. (c) Number of donor atoms (N) in $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ are four. So, $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ is a tetradentate ligand.
98. (d)
99. (a) In $[\text{NiCl}_4]^{2-}$, Ni is in +2 oxidation state
 $\text{Ni}^{2+} = 3d^8$ i.e. 2 unpaired e^-
 Magnetic moment (μ) = $\sqrt{n(n+2)} = \sqrt{8} = 2.82 \text{ B.M.}$
100. (b) The complex formation is a characteristic of d-block elements.
 Lead is a p-block element hence does not form complex compounds.

EXERCISE - 2

1. (b) The crystal field splitting in tetrahedral complexes is lower than that in octahedral complexes, and $\Delta_t = -\frac{4}{9}\Delta_0$.
2. (b) It is optically active.
3. (a) Octahedral complexes of the type $[\text{MA}_3\text{B}_3]$ like $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ exhibit *fac-mer* isomerism.



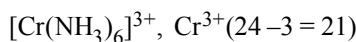
4. (c) As it forms two moles of silver chloride thus it has two moles of ionisable Cl.
 $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2 \rightarrow [\text{Co}(\text{NH}_3)_5\text{NO}_2]^{++} + 2\text{Cl}^-$
 $2\text{Cl}^- + 2\text{AgNO}_3 \rightarrow 2\text{AgCl} + 2\text{NO}_3^-$
5. (d) Optical isomerism is generally shown by octahedral complexes of the formula, $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$, $[\text{Mabcdef}]^{\text{th}}$, $[\text{M}(\text{AA})_3]^{n\pm}$, $[\text{M}(\text{AA})_2\text{a}_2]^{n\pm}$, $[\text{M}(\text{AA})_2\text{ab}]^{n\pm}$ and $[\text{M}(\text{AB})_3]^{\text{th}}$. Thus, among the given compounds, only $[\text{Cr}(\text{en})_3]^{3+}$ exhibits optical isomerism and exists as a pair of enantiomers.



6. (c) $[\text{Co}(\text{NH}_3)_6]^{3+}$, $\text{Co}^{3+}(27-3=24)$



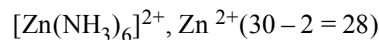
$d^2 sp^3 \rightarrow$ (inner octahedral complex & diamagnetic)



$d^2 sp^3 \rightarrow$ (inner octahedral complex & paramagnetic)



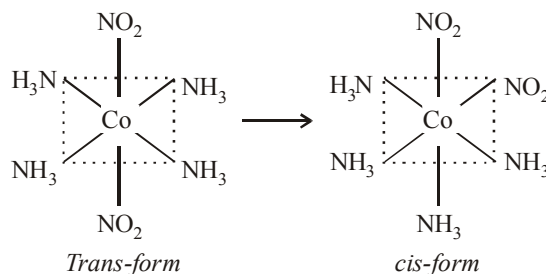
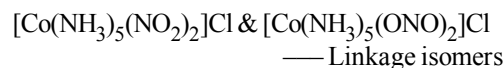
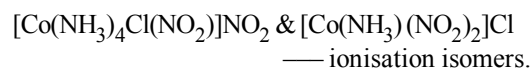
$sp^3 d^2 \rightarrow$ (outer octahedral complex & paramagnetic)



$sp^3 d^2 \rightarrow$ (outer octahedral complex & diamagnetic)

7. (a) The given compound may have linkage isomerism due to presence of NO_2 group which may be in the form $-\text{NO}_2$ or $-\text{ONO}$.

It may have ionisation isomerism due to presence of two ionisable group $-\text{NO}_2$ & $-\text{Cl}$. It may have geometrical isomerism in the form of *cis-trans* form as follows:

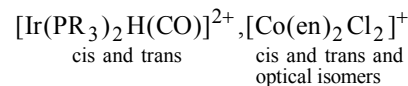
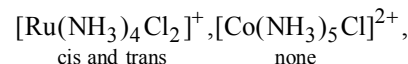


Geometrical isomers

8. (c) $\text{K}_4[\text{Fe}(\text{CN})_6]$ produces maximum number of ions (5) in the solution.
 $\text{K}_4[\text{Fe}(\text{CN})_6] \rightleftharpoons 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$
9. (d) $\text{Co}(\text{NH}_3)_5\text{Cl}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2} + 2\text{Cl}^-$
 $\therefore$ Structure is $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.
 Now $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + 2\text{AgNO}_3$

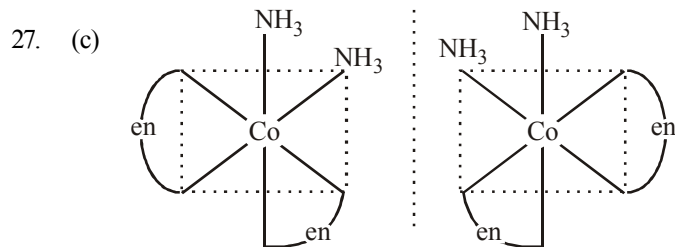


10. (c) Number of donor atoms (N) in $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ are four. So, $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ is a tetradentate ligand.
11. (a) CN^- ion acts good complexing as well as reducing agent.
12. (d) Isomers



13. (d) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ is an ionic compound. Both cation and anion carry 3 unit charges. It exhibits co-ordination isomerism.
14. (c) $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow$
 — no. of unpaired electrons = 0

the given ligands CN^- is strongest. So, Δ_o will be highest for $[\text{Co}(\text{CN})_6]^{3-}$. Thus option (a) is correct.



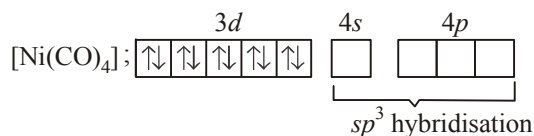
Enantiomers of $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$

28. (d) An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.

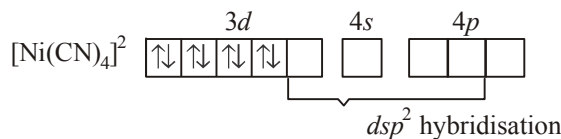
29. (c) The correct IUPAC name of the given compound is tetramminenickel (II) - tetrachloronickelate (II) thus (c) is the correct answer.

30. (b) In carbonyls O.S. of metal is zero

In $[\text{Ni}(\text{CO})_4]$, the oxidation state of nickel is zero. Its configuration in $\text{Ni}(\text{CO})_4$ is



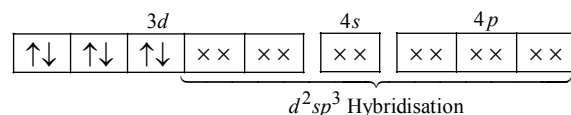
In $[\text{Ni}(\text{CN})_4]^{2-}$ the oxidation state of Ni is $2+$ and its configuration is



Thus the hybridisations of nickel in these compounds are sp^3 and dsp^2 respectively.

Hence (b) is the correct answer.

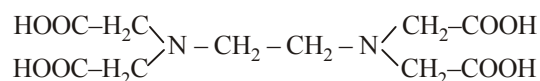
31. (a) Chromium in $\text{Cr}(\text{CO})_6$ is in zero oxidation state and has $[\text{Ar}]^{18} 3d^5 4s^1$ as the electronic configuration. However, CO is a strong ligand, hence pairing up of electrons takes place leading to following configuration in $\text{Cr}(\text{CO})_6$.



Since the complex has no unpaired electron, its magnetic moment is zero.

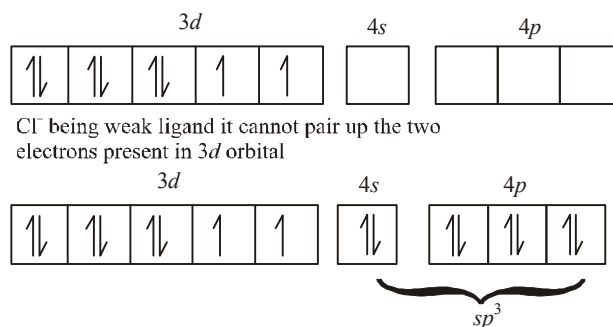
32. (b) Ionisation isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_2$.

33. (c) The correct structure of EDTA is



34. (b) $[\text{NiCl}_4]^{2-}$, O.S. of Ni = $+2$

$$\text{Ni}(28) = 3d^8 4s^2$$



No. of unpaired electrons = 2

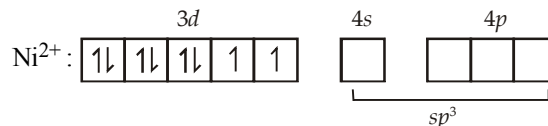
Magnetic moment, $\mu = 2.82 \text{ BM}$.

35. (c)

Complex	No. of electrons in outer d orbital	No. of unpaired electron (s)
$[\text{Fe}(\text{CN})_6]^{3-}$	$3d^5$	1 (CN^- causes pairing of electrons)
$[\text{Co}(\text{NH}_3)_6]^{3+}$	$3d^6$	0
$[\text{Co}(\text{oxal})_3]^{3-}$	$3d^6$	0
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	$3d^8$	2
$[\text{Pt}(\text{CN})_4]^{2-}$	$5d^8$	0 (CN^- causes pairing of electrons)
$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	$3d^{10}$	0

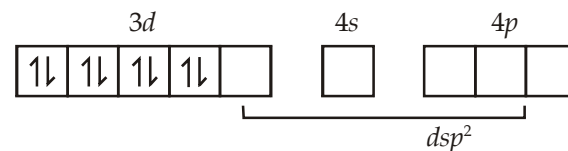
Thus L, M, O and P are diamagnetic.

36. (c) In both states (paramagnetic and diamagnetic) of the given complex, Ni exists as Ni^{2+} whose electronic configuration is $[\text{Ar}] 3d^8 4s^0$.



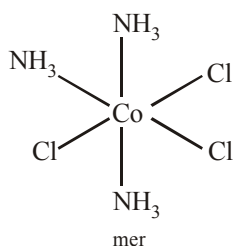
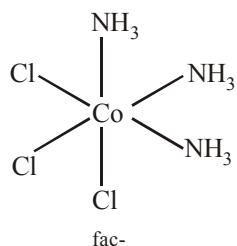
In the above paramagnetic state the geometry of the complex is sp^3 giving tetrahedral geometry.

The diamagnetic state is achieved by pairing of electrons in $3d$ orbital.

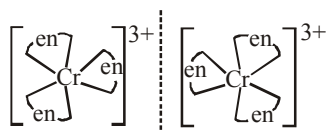


Thus the geometry of the complex will be dsp^2 giving square planar geometry.

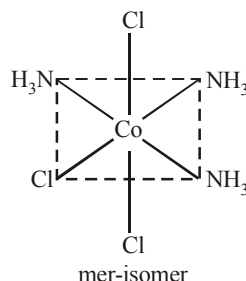
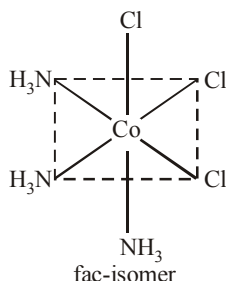
37. (c) Octahedral coordination entities of the type Ma_3b_3 exhibit geometrical isomerism. The compound exists both as facial and meridional isomers, both contain plane of symmetry



38. (a)
39. (d) $[\text{Co}(\text{CO})_5\text{NH}_3]^{2+}$. In this complex, Co-atom attached with NH_3 through σ bonding while with CO it is attached with dative π -bond.
40. (d)
41. (d) Optical isomerism is generally shown by octahedral complexes of the formula, $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$, $[\text{Mabcdef}]^{\text{th}}$, $[\text{M}(\text{AA})_3]^{n\pm}$, $[\text{M}(\text{AA})_2\text{a}_2]^{n\pm}$, $[\text{M}(\text{AA})_2\text{ab}]^{n\pm}$ and $[\text{M}(\text{AB})_3]^{\text{th}}$. Thus, among the given compounds, only $[\text{Cr}(\text{en})_3]^{3+}$ exhibits optical isomerism and exists as a pair of enantiomers.



42. (c) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ has Co^{3+} (d^6 system) due to presence of stronger $\text{C}_2\text{O}_4^{2-}$ chelating ligand pairing of electrons occurs in this case.
 Co^{3+} :
43. (c) $\text{K}_4[\text{Fe}(\text{CN})_6]$ produces maximum number of ions (5) in the solution.
 $\text{K}_4[\text{Fe}(\text{CN})_6] \rightleftharpoons 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$
44. (a) Geometrical isomerism is possible only in square planar complexes of the type MA_2B_2 and MA_2BC and for octahedral complexes of the type MA_4B_2 and MA_4BC . Hence only (ii) will show geometrical isomerism.
45. (b) The crystal field splitting in tetrahedral complexes is lower than that in octahedral complexes, and
 $\Delta_t = -\frac{4}{9}\Delta_o$.
46. (a) Octahedral complexes of the type $[\text{MA}_3\text{B}_3]$ like $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ exhibit *fac-mer* isomerism.



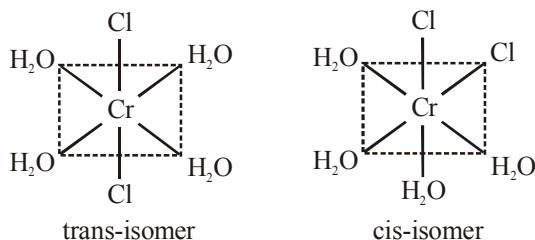
47. (d) $[\text{FeF}_6]^{3-}$ is a high spin complex since F^- is a weak ligand.

48. (c) It is correct statement that NF_3 is a weaker ligand than $\text{N}(\text{CH}_3)_3$, the reason is that fluorine is highly electronegative therefore, it will draw electrons from nitrogen atom. Hence, the lone pair of nitrogen atom cannot be ligated. While $\text{N}(\text{CH}_3)_3$ is a strong ligand because CH_3 is electron releasing group.
49. (b) Both statement-1 and statement-2 are true but statement-2 is not the correct explanation of statement-1. $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic as it has unpaired electrons while $[\text{Fe}(\text{CN})_6]^{2-}$ has no unpaired electron.
 $\therefore$ It is diamagnetic.
50. (a) Both statement-1 and statement-2 are true and statement-2 is the correct explanation of statement-1. $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ has no unpaired electron in its d subshell and thus $d-d$ transition is not possible whereas $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has one unpaired electron in its d subshell which gives rise to $d-d$ transition to impart colour.

EXERCISE - 3

Exemplar Questions

1. (b) Higher the value of $\log K$, higher will be stability of complex compound formed.
2. (c) Strength of ligand increases as crystal field splitting energy increases.
 Ligand strength order : $\text{CN}^- > \text{NH}_3 > \text{H}_2\text{O}$
 As energy separation increases, wavelength decreases.
 Thus, the correct order is :
 $[\text{Co}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{CN})_6]^{3-}$
3. (b) In above reaction, when 0.1 mol $\text{CoCl}_3 \cdot 5\text{NH}_3$ is treated with excess of AgNO_3 , 0.2 mol of AgCl are obtained thus, there must be two free chloride ions in the solution of electrolyte as one mole of AgNO_3 precipitates one mole of chloride. So, molecular formula of complex will be $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and electrolytic solution must contain $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and two Cl^- as constituent ions. Thus, it is 1 : 2 electrolyte.
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightarrow [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$
4. (d) 1 mole of AgNO_3 precipitates one free chloride ion (Cl^-). Here, 3 moles of AgCl are precipitated by excess of AgNO_3 . Hence, there must be three free Cl^- ions. So, the formula of the complex can be $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
5. (a) Ligands present in the compound are
 (i) NH_3
 (ii) Cl (chlorido; di prefixed to represent two ligands.)
 The oxidation number of platinum in the compound is 2. Hence, correct IUPAC name is Diamminedichloridoplatinum (II)
6. (c) Ligand which chelates the metal ion are known as chelating ligand. Here, only oxalate ion is a chelating ligand. Hence, it stabilises coordination compound by chelating Fe^{3+} ion.
7. (a) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ shows geometrical isomerism. The possible geometrical isomers are



8. (c) Relation between CFSE of octahedral and tetrahedral

complexes is $\Delta_t = \frac{4}{9}\Delta_o$

According to question, $\Delta_o = 18,000\text{cm}^{-1}$

$$\therefore \Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18,000\text{cm}^{-1}$$

$$= 4 \times 2,000\text{cm}^{-1} = 8,000\text{cm}^{-1}$$

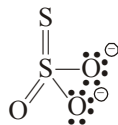
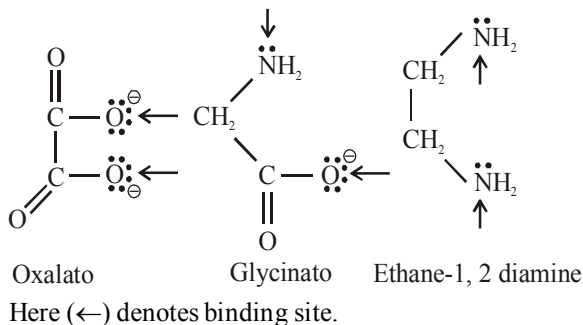
9. (a) NCS (thiocyanate) can bind to the metal ion in two ways :



Thus, coordination compounds $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$ and $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NSC})_2]$ are linkage isomers.

10. (d) Isomers are the compounds having same molecular formula but different structural formula. $[\text{Co}(\text{SO}_4)_2(\text{NH}_3)_5]\text{Br}$ and $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$ do not have same molecular formula. Hence, they are not isomers.

11. (a) Chelating ligand has two or more donor atoms to a single metal ion e.g.,



Thiosulphato ($\text{S}_2\text{O}_3^{2-}$) is not a chelating ligand because geometrically it is not favourable for $\text{S}_2\text{O}_3^{2-}$ to chelate a metal ion.

12. (b) Ligand should have a pair of electron which is loosely held and form a $M-L$ bond.



Amongst the species given NH_4^+ does not have any pair of electron.

So, it is not expected to be a ligand.

13. (b) The compounds having same molecular formula but differ in ligands inside & outside the coordination sphere are solvate (hydration) isomers.

Coordination compound $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{H}_2\text{O} \cdot \text{Cl}_2$ are solvate isomers, because water is exchanged by chloride ion. This is why both of them show different colour on exposure to sunlight.

14. (c) Ligands (based on priority) present are :

(i) NH_3

(ii) Cl^-

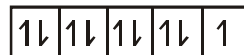
(iii) NO_2^-

So, IUPAC name will be Diamminechloridonitrito-N-platinum (II).

NEET/AIPMT (2013-2017) Questions

15. (d) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ hybridisation dsp^2

$\text{Cu}^{+2} - 3d^9$ has one unpaired e^-



So magnetic moment

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)}$$

$$= \sqrt{3} = 1.73$$

16. (d) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} + \text{AgNO}_3 \longrightarrow \text{AgCl} + [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_3$

$$\text{Molarity} = \frac{\text{wt}}{\text{mol. mass}} \times \frac{1000}{\text{vol.}}$$

$$\frac{\text{wt}}{\text{mol. mass}} = \text{molarity} \times \frac{\text{vol.}}{1000} = \frac{0.01 \times 100}{1000}$$

$$= 0.001$$

17. (c) IUPAC name of $[\text{CrF}_2(\text{en})_2]\text{Cl}$ is Difluoridobis(ethylenediamine) chromium (III) chloride.

18. (c) $\text{CFSE} = (-0.4x + 0.6y)\Delta_o$

where

$x \rightarrow e^-$ s in t_{2g} orbital

$y \rightarrow e^-$ s in e_g orbital

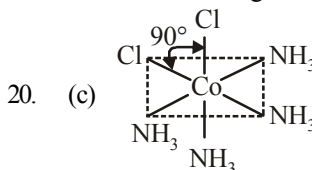
For high spin $4d$ complex, $x = 3$ & $y = 1$

$$\therefore -0.4 \times 3 + 0.6 \times 1 = -0.6\Delta_o$$

19. (c) $\text{Ni}^{+2} \rightarrow 3d^8 = \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$

CN^- is a strong ligand and causes pairing of $3d$ electrons of Ni^{2+} .

$\therefore$ It is diamagnetic.



cis-isomer

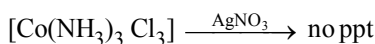
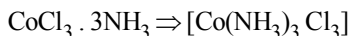
21. (d) Acetylacetone forms six membered stable ring complexes.

22. (d) $\text{Co}^{2+} \Rightarrow [\text{Ar}]3d^74s^0$, here, Br^- is a weak field ligand so will not cause pairing of d -electrons in Co^{2+} .

$\therefore [\text{CoBr}_4]^{2-}$ will exhibit paramagnetic behaviour due to unpaired electrons.

23. (b) Due to d^5 configuration CFSE is zero.

24. (b)
25. (d) $\text{CoCl}_3 \cdot 3\text{NH}_3$ will not give test for chloride ions with silver nitrate due to absence of ionisable chloride atoms.

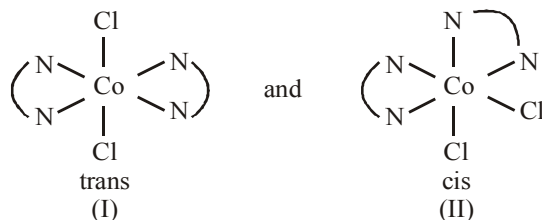


26. (d) In $[\text{Co}(\text{CN})_6]^{-3}$, O.N. of Co is +3
 $\therefore \text{Co}^{+3} = 3d^6 4s^0$
 CN^- is a strong field ligand
 $\therefore$ Pairing of electrons occurs so in this complex no unpaired electron is present and it is low spin complex.

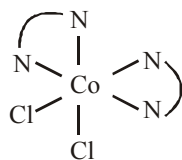
27. (a) $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)] \text{Cl}$
 $\text{C}_2\text{O}_4 =$ bidentate ligand, carry -2 charge
 $\text{en} =$ bidentate ligand, carry 0 charge
 $\therefore \text{M}$ carry +3 charge; coordination number = 6
 $\therefore \text{Sum} = +3 + 6 = 9$

28. (d) Hexacyanidoterrate (III) ion.

29. (c) $[\text{Co}(\text{en})_2 \text{Cl}_2] \text{Cl}$



Mirror image of (II)

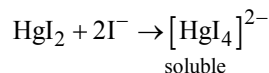
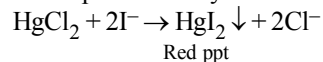


30. (c) $[\text{Fe}(\text{CO})_4]^{2-}$
 Since metal atom is carrying maximum -ve charge therefore it would show maximum synergic bonding as a resultant C—O bond length would be maximum.
31. (a) Grignard's reagent (RMgX) is a σ -bonded organometallic compound.
32. (b) In a solution containing HgCl_2 , I_2 and I^- , both HgCl_2 and I_2 compete for I^- .

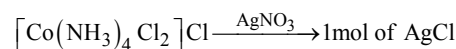
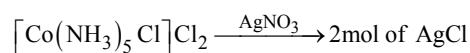
Since formation constant of $[\text{HgI}_4]^{2-}$ is very large (1.9×10^{30}) as compared with I_3

($K_f = 700$)

$\therefore \text{I}^-$ will preferentially combine with HgCl_2 .



33. (b) $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3 \xrightarrow{\text{AgNO}_3} 3\text{mol of AgCl}$



Complexes are respectively $[\text{Co}(\text{NH}_3)_6 \text{Cl}_3]$, $[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}$

34. (d) The order of the ligand in the spectrochemical series is :
 $\text{H}_2\text{O} < \text{NH}_3 < \text{en}$

Hence, the wavelength of the light observed will be in the order

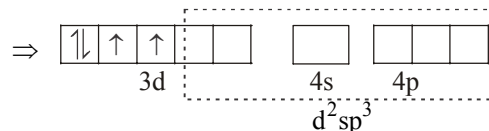


Thus, wavelength absorbed will be in the opposite order i.e., $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

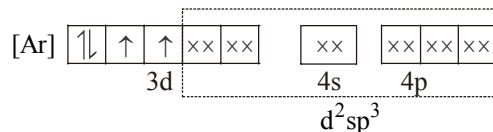
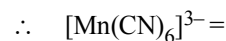
35. (b) In the complex $[\text{Mn}(\text{CN})_6]^{3-}$, O.S. of Mn is +3



The presence of a strong field ligand CN^- causes pairing of electrons.



As, coordination number of Mn = 6, so it will form an octahedral complex.



Chapter 24

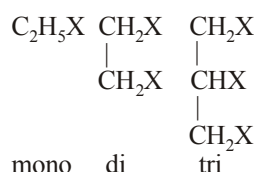
Haloalkanes and Haloarenes

The replacement of H-atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene).

CLASSIFICATION

On the Basis of No. of Halogen Atoms :

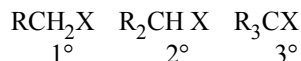
Mono, di, tri, tetra, etc. depending on whether they contain one, two, three, four halogen atoms in structures.



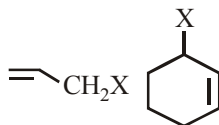
Classification Based on Nature of C – X Bond

(i) Compounds containing sp^3 hybridised C–X bond

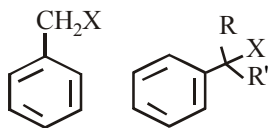
(a) Alkyl halides or halo alkanes :



(b) **Allylic halides** : In these compounds the halogen atom is linked to an sp^3 hybridised carbon atom which has a C = C bond attached to it.

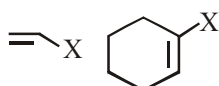


(c) **Benzylic halides** : The tetrahedral carbon involved in C – X bond is linked to an aromatic ring.

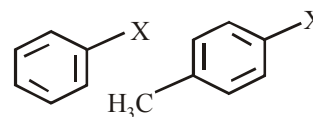


(ii) Compounds containing sp^2 hybridised C–X bond

(a) **Vinyl halides** : The halogen atom is attached to sp^2 hybridised carbon atom of C = C bond.



(b) **Aryl halides** : The halogen atom is attached directly to the carbon atom of the benzene ring.

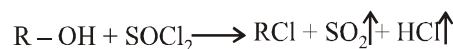
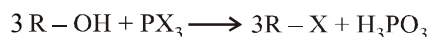
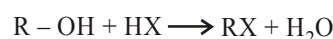


Note :

- Down the group, size of X increases, $\therefore$ C – X bond length increases down the group from F to I.
- Although F is more electronegative than Cl, yet dipole moment of CH_3Cl is more than CH_3F . This is because of small size of F due to which C – F bond distance (d) becomes small in comparison to C – Cl bond distance dipole moment is given as $\mu = q \times d$. Thus dipole moment of C – Cl bond is greater in comparison to dipole moment of C – F bond.

METHODS OF PREPARATION OF ALKYL HALIDES

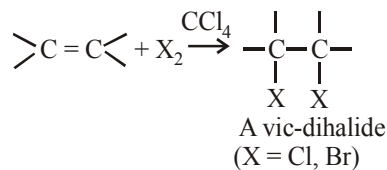
(i) From Alcohols



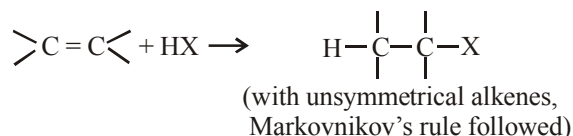
Thionyl chloride method is preferred over hydrogen chloride or phosphorus pentachloride method for the preparation of chloroalkanes since both the by-products (SO_2 and HCl) in this reaction being gases escape out leaving behind the chloroalkanes in almost pure state.

Note :

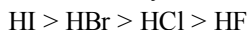
- Order of reactivity among HX : $\text{HI} > \text{HBr} > \text{HCl} >> \text{HF}$
- Order of reactivity among ROH : $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{OH}$
- Mixture of conc. HCl and anhydrous ZnCl_2 is used for differentiating three types of alcohols ($3^\circ > 2^\circ > 1^\circ$) under the name of **Lucas reagent**.
- SOBr_2 is less stable and SOI_2 does not exist, PBr_5 and PI_5 are highly unstable hence not used.

(ii) From Alkenes

When above reaction is carried out by using Br_2/CCl_4 the reddish brown colour of Br_2 is discharged. Therefore this reaction is used as a test for detection of unsaturation in organic molecules.

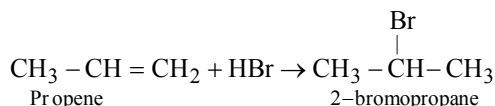


Alkenes react with halogen acids to form haloalkanes. The order of reactivity is

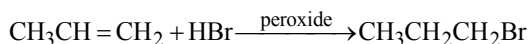
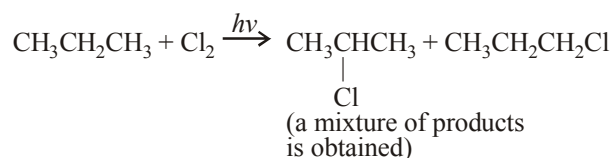
**Markownikoff's rule :**

When an unsymmetrical alkene or alkyne reacts with unsymmetrical reagent, then negative part of reagent attach with that carbon atom which contains lesser number of hydrogen atom during the addition.

For example:

**Anti-Markownikoff's rule :**

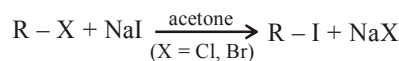
Addition of HBr (not HCl , HI and HF) on alkenes in presence of peroxides takes place in *anti-Markownikoff's way* (*Peroxide effect*). Here addition takes place via *free-radical mechanism*.

**(iii) From Alkanes****By free radical halogenation**

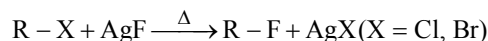
However, compounds containing only one type of hydrogen atom can be converted into monohalogenated products in good yield by taking excess of the concerned hydrocarbon; examples of such compounds are CH_4 , CH_3CH_3 , $(CH_3)_4C$, $C_6H_5CH_3$ etc. The reactivity of the alkanes follows the following order: Tertiary alkane > Secondary alkane > Primary alkane.

Note:

- Chlorination and bromination can be achieved by above method while iodination is done in presence of oxidising agent (i.e., HNO_3 or HIO_3). Direct fluorination is highly exothermic. Thus it is done by heating alkyl chlorides with inorganic fluorides (Hg_2F_2 , AgF , SbF_3 etc.).
- Benzylic hydrogens (hydrogen present on C attached directly to benzene) are more reactive, hence easily replaced than 1° , 2° or 3° hydrogens.

(iv) By Halogen Exchange**(a) Finkelstein reaction****(b) Swarts reaction**

Alkyl chlorides/ bromides is heated in presence of a metallic fluoride such as AgF , Hg_2F_2 , CoF_2 or SbF_3 to form alkyl fluorides.

**PHYSICAL PROPERTIES OF ALKYL HALIDES**

- Lower halides are gaseous in nature whereas higher halides are either liquid or solids (having 18 or more C-atoms)
- Alkyl halides are colourless when pure. The bromides and iodides develop colour when exposed to light.
- Melting and Boiling points**

The m.pts and b.pts of chlorides, bromides and iodides are higher than those of analogous hydrocarbons due to presence of dipole-dipole interactions in them besides van der waal's forces.

The m.pts. and b.pt. follows the order: $RI > RBr > RCl > RF$. This is because with increase in size and mass of halogen, magnitude of van der Waal's forces also increases. The b.pts of isomeric haloalkanes decrease with increase in branching. For isomeric alkyl halides, order of boiling point is

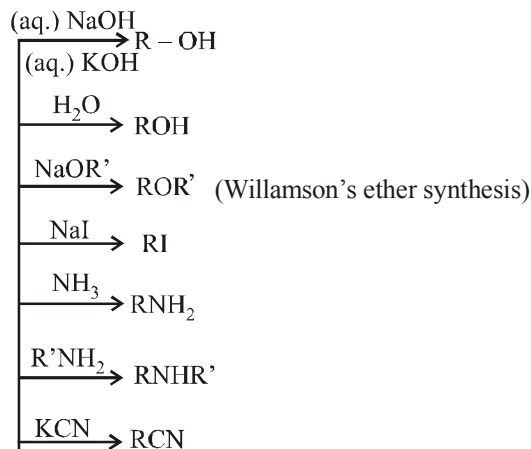
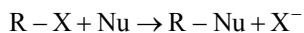
Primary > Secondary > Tertiary

(iv) Solubility

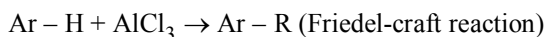
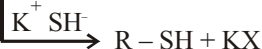
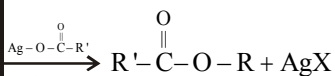
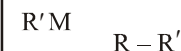
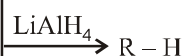
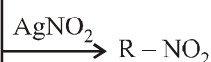
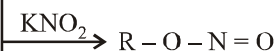
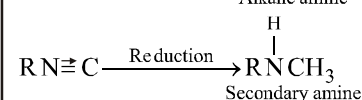
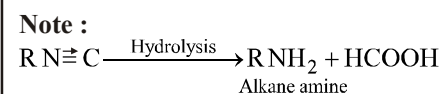
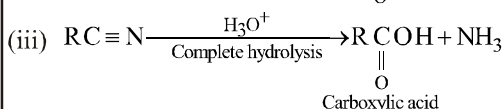
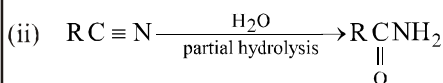
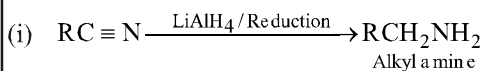
The haloalkanes are only very slightly soluble in water. This is because less energy is released when new interactions are set up between haloalkane and water molecules and these are not as strong as original H-bonds in water. Haloalkanes are completely soluble in organic solvents.

CHEMICAL PROPERTIES OF ALKYL HALIDES

1. Nucleophilic Substitution Reactions

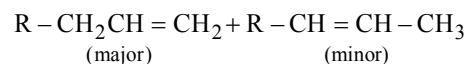


Note: Alkane nitrile is an important compound which gives following products.



(ii) Elimination Reactions

Alkyl halide loses a molecule of hydrogen halide when heated with alc KOH and alkene is formed.



This is also called β -elimination or Dehydrohalogenation reaction.

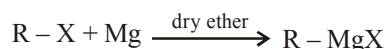
The product formed is determined by Saytzeff's rule i.e. the preferred alkene is that which has greater no. of alkyl groups attached to doubly bonded C-atoms. Ease of dehydrohalogenation among halides is : $3^\circ > 2^\circ > 1^\circ$

Note :

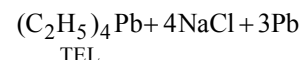
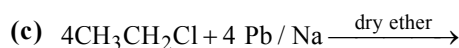
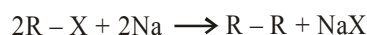
Elimination reactions dominate over substitution when strong base i.e., Bronsted base [e.g. NH_2^- , Me_3CO^- , $\overline{OC_2H_5}$ etc.] is used and alkyl halide is 3° or 2° .

(iii) Reaction with Metals

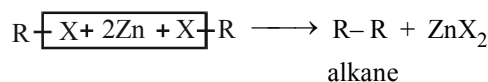
(a) Grignard reaction:



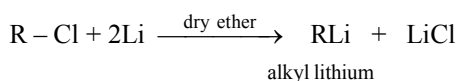
(b) Wurtz reaction:



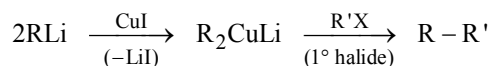
(d) With Zn dust : (Frankland reaction)



(e) With Li :

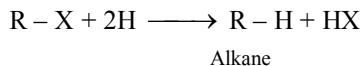


Alkyl lithiums react with copper halides to form higher alkanes (**Corey-House synthesis**)



(iv) Reduction

Haloalkanes on reduction produces alkanes frequently.

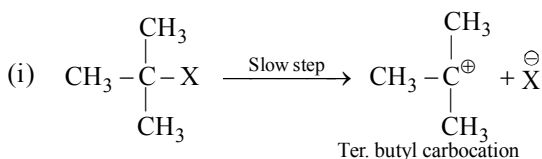


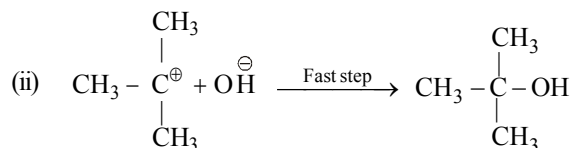
MECHANISM OF NUCLEOPHILIC SUBSTITUTION

Nucleophilic substitution rxns can proceed via two mechanism S_N^1 or S_N^2 .

 S_N^1 (Unimolecular Nucleophilic Substitution)

This reaction occurs in two steps. In first step, a carbocation is formed from alkyl halide molecule. First step is slow step so it is also rate determining step. In second step, an attacking nucleophile attacks on this carbocation and forms the final product.





Rate of reaction $\propto [(\text{CH}_3)_3\text{C} - \text{X}]$ It is a unimolecular substitution reaction.

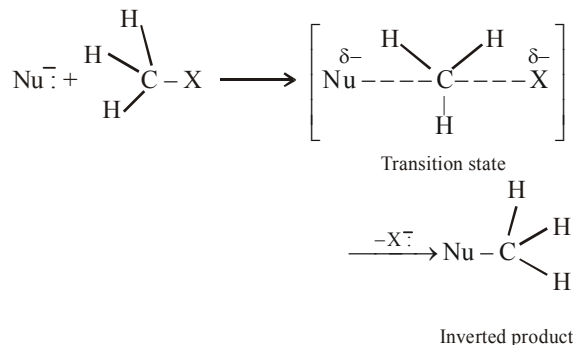
In $\text{S}_{\text{N}}1$ mechanism, carbocations are formed as intermediate, hence more the stability of the intermediate carbocation, greater are chances for their formation and hence more reactive will be the parent alkyl halide for $\text{S}_{\text{N}}1$ reaction. Hence the order of reactivity of alkyl halides toward $\text{S}_{\text{N}}1$ reaction follows the order : $3^\circ > 2^\circ > 1^\circ$

When the intermediate carbocation is capable of undergoing rearrangement, lesser stable carbocation ($1^\circ < 2^\circ < 3^\circ$) rearranges to the more stable carbocation and hence under such conditions unexpected product is formed.

Note: Allylic and benzylic halides show high reactivity towards the $\text{S}_{\text{N}}1$ reaction because carbocation formed gets stabilised via resonance.

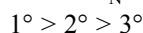
$\text{S}_{\text{N}}2$ (Bimolecular Nucleophilic Substitution) :

The rate of $\text{S}_{\text{N}}2$ reactions depends on the concentration of alkyl halide as well as nucleophile, i.e. $r = k[\text{RX}][\text{Nu}]$. This implies that both the reactants are involved in the rate-determining step, i.e. the reaction occurs in one step only or it is a *concerted reaction*. Concerted reactions occur through a transition state (an imaginary state in which both the reactant molecules are partially linked to each other).

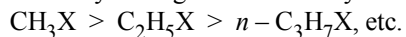


The nucleophile attacks from the back side of the halide ion, bulkier the alkyl group present on the carbon bearing halogen lesser will be its tendency to undergo $\text{S}_{\text{N}}2$ reaction. Thus the reactivity of alkyl halides towards $\text{S}_{\text{N}}2$ mechanism is

The reactivity of alkyl halides in $\text{S}_{\text{N}}2$ reactions is:



The order of reactivity among various 1° alkyl halides is



Bulkier the alkyl group, more is the steric hindrance in the formation of transition state and less is the reactivity of alkyl halide.

Note :

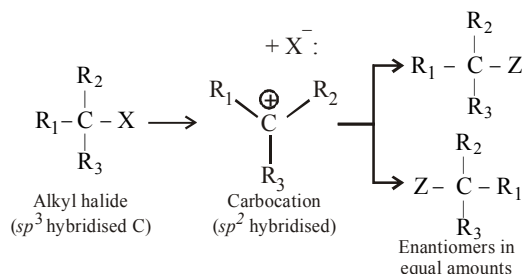
- (a) 3° alkyl halides react by $\text{S}_{\text{N}}1$, 1° by $\text{S}_{\text{N}}2$ and 2° by either or both of these mechanism depending upon the nature of the alkyl halide and the reagent.

- (b) For a given alkyl group, the reactivity of halide, $\text{R}-\text{X}$ follows the same order in both the mechanisms:
 $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$

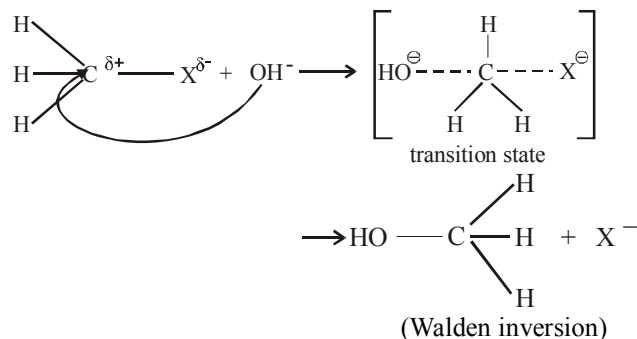
- (c) Polar solvents favour $\text{S}_{\text{N}}1$ reactions while non-polar solvents favour $\text{S}_{\text{N}}2$ reactions.

Stereochemical aspects of nucleophilic substitution.

If the alkyl halide is optically active, the product formed in $\text{S}_{\text{N}}1$ reaction is always a racemic mixture. This is due to the formation of carbocations as intermediates which, being planar (sp^2 hybridised) can be equally attacked by the nucleophile on either side of the face forming two enantiomers.

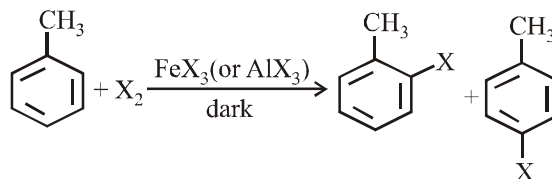


Since the nucleophile attacks from the back side and the halide ion leaves from the front side, the product obtained will have an *inverted configuration [Walden inversion]*. This implies that if the alkyl halide is optically active, the product will also be optically active, although the sign of rotation may be same or different.

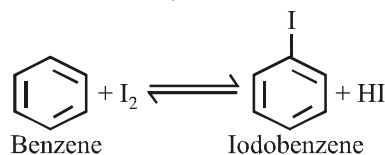


METHODS OF PREPARATION OF ARYL AND ARALKYL HALIDES

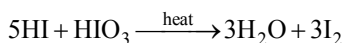
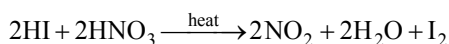
(i) By Electrophilic Substitution



Chlorobenzene and bromobenzene can be prepared by above methods whereas iodobenzene cannot be done in the same way because HI formed in the reaction is a powerful reducing agent due to low bond dissociation enthalpy (299 kJ mol^{-1}). It will therefore, make the reaction reversible in nature.

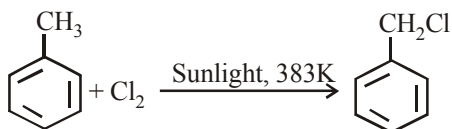


On account of this, HI formed in the reaction is oxidised by carrying the reaction in the presence of iodic acid (HIO_3) or conc. HNO_3 .



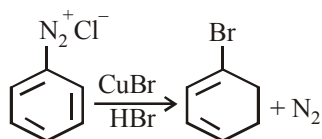
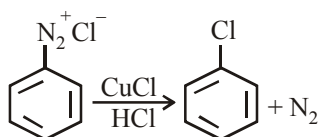
Fluorination being extremely violent is difficult to control.

Substitution in alkyl group

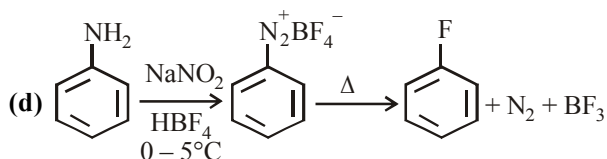
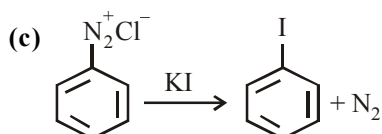
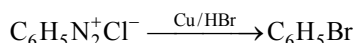
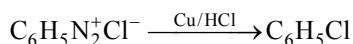


(ii) By the Decomposition of Diazonium Salts.

(a) Sandmeyer's reaction

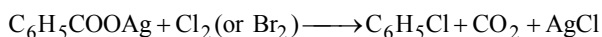


(b) Gattermann reaction:



Thermal decomposition of benzenediazonium tetrafluoroborate to give fluorobenzene is called *Balz-Schiemann reaction*.

(iii) Hunsdiecker Method :



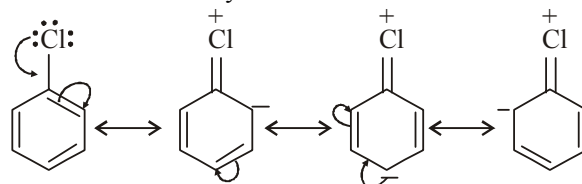
PHYSICAL PROPERTIES OF ARYL AND ARALKYL HALIDES

- Like alkyl halides, aryl halides are insoluble in water due to their incapability of forming H-bonds.
- Aryl halides are less polar than alkyl halides because in aryl halides, halogen is present on sp^2 hybridised carbon which is more electronegative than the sp^3 hybridised carbon of alkyl halides.

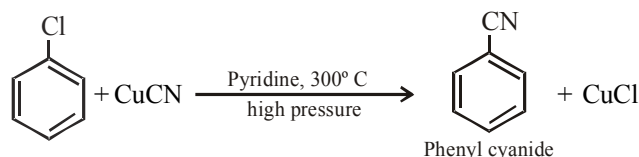
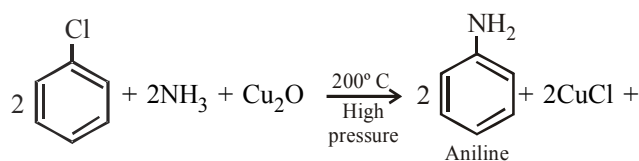
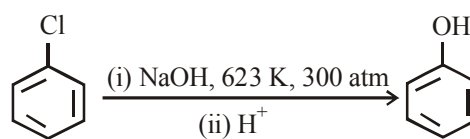
CHEMICAL PROPERTIES OF ARYL AND ARALKYL HALIDES

(i) Nucleophilic Substitution :

The halogen atom is firmly attached with the benzene nucleus and acquires extra stability due to resonance (+M) effect. Hence, the halogen atom cannot be easily replaced by other atoms or group of atoms. So, aryl halides are less reactive than alkyl halides.



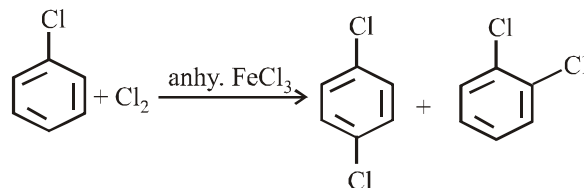
The halogen atom is replaced by other nucleophiles under drastic conditions.



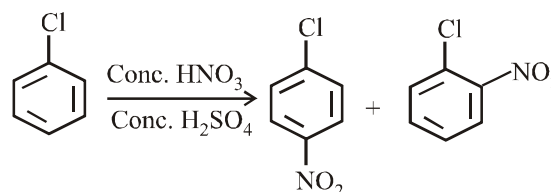
Note : Haloarenes do not undergo nucleophilic substitution as cleavage of C – X bond is difficult. When electron withdrawing groups like $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$, $-\text{COOH}$ etc. are present at ortho or para positions the bond cleavage becomes easier.

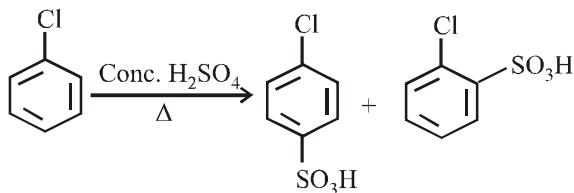
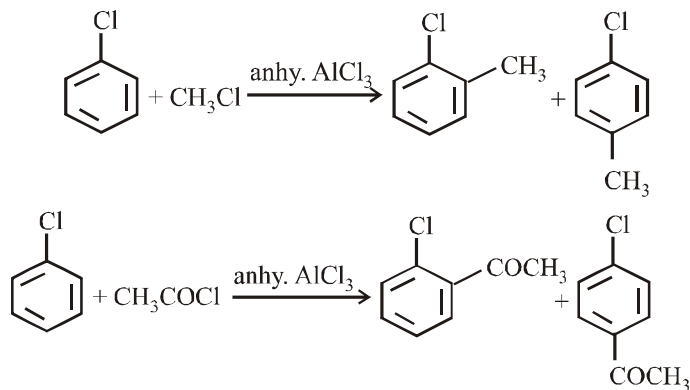
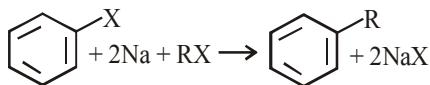
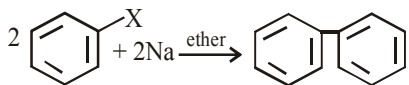
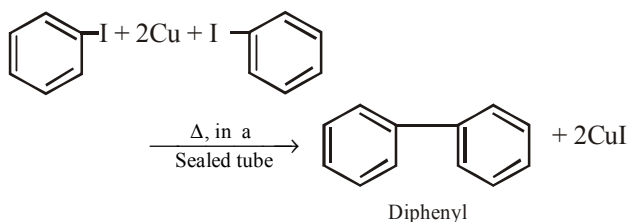
(ii) Electrophilic Substitution Reactions

(a) Halogenation :

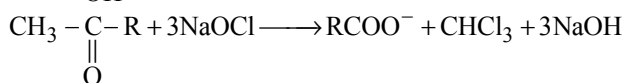
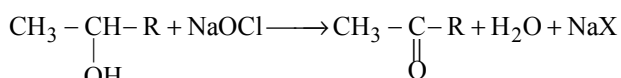


(b) Nitration :

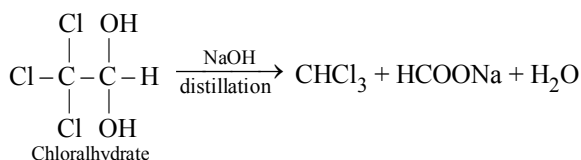
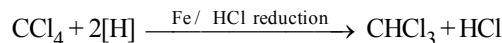


(c) **Sulfonation :**(d) **Friedel-Crafts reaction :**(iii) **Reaction with Metals:**(a) **Wurtz-Fittig reaction**(b) **Fittig reaction**(iv) **Ullmann Reaction:****POLYHALOGEN COMPOUNDS****Chloroform****Preparation of CHCl₃**

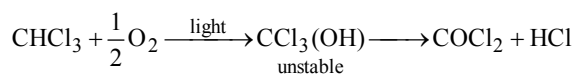
- (i) **Haloform reaction :** Aldehydes and ketones with CH₃CO group, and alcohols with CH₃CH(OH) group give this reaction.



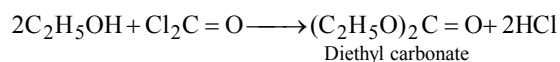
- (ii) **Preparation of pure chloroform :**

(iii) **From carbon tetrachloride (Pyrene) :****Properties**

- Chloroform is colourless with sweet smelling, liquid.
- Insoluble in water and soluble in organic solvent.
- Boiling point of CHCl₃ is 61°C.
- It is best solvent for fats, oil and wax.
- On exposure to air and sunlight, chloroform, a colourless heavy liquid, oxidises to **carbonyl chloride (phosgene)**, a highly poisonous gas used in warfare.



To avoid this oxidation chloroform is always stored in dark coloured bottles filled to the brim to exclude any air. Further nearly 1% alcohol is also added to destroy traces of phosgene, if formed, to harmless diethyl carbonate.

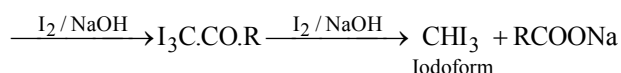
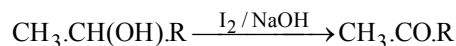
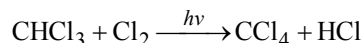
**Uses :**

- As an anaesthetic agent. However, it has been replaced by less toxic and safer anaesthetic agents.
- CHCl₃ acts as a solvent for fat, waxes, rubber etc.

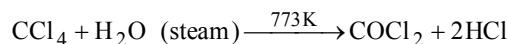
Iodoform (Triiodomethane) CHI₃ :

CHI₃ was earlier used as an antiseptic for dressing wounds. Its antiseptic properties are due to the liberation of iodine when iodoform comes in contact with skin.

Any compound containing CH₃CO– or CH₃CH(OH)– group, when heated with iodine and aqueous NaOH or NaOI (sodium hypoiodite) gives yellow precipitate of iodoform, this reaction is called **iodoform reaction**.

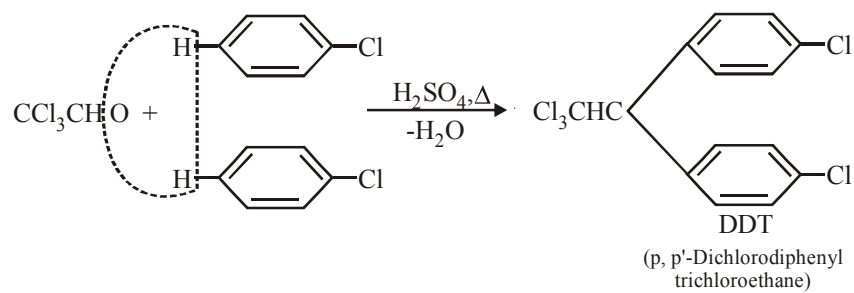
**Carbon Tetrachloride (Tetrachloro Methane or Perchloromethane) :****Preparation :****Properties :**

- It is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.
- On heating with steam at about 773K, it undergoes **oxidation** forming carbonyl chloride.

**Uses :**

Carbon tetrachloride is used

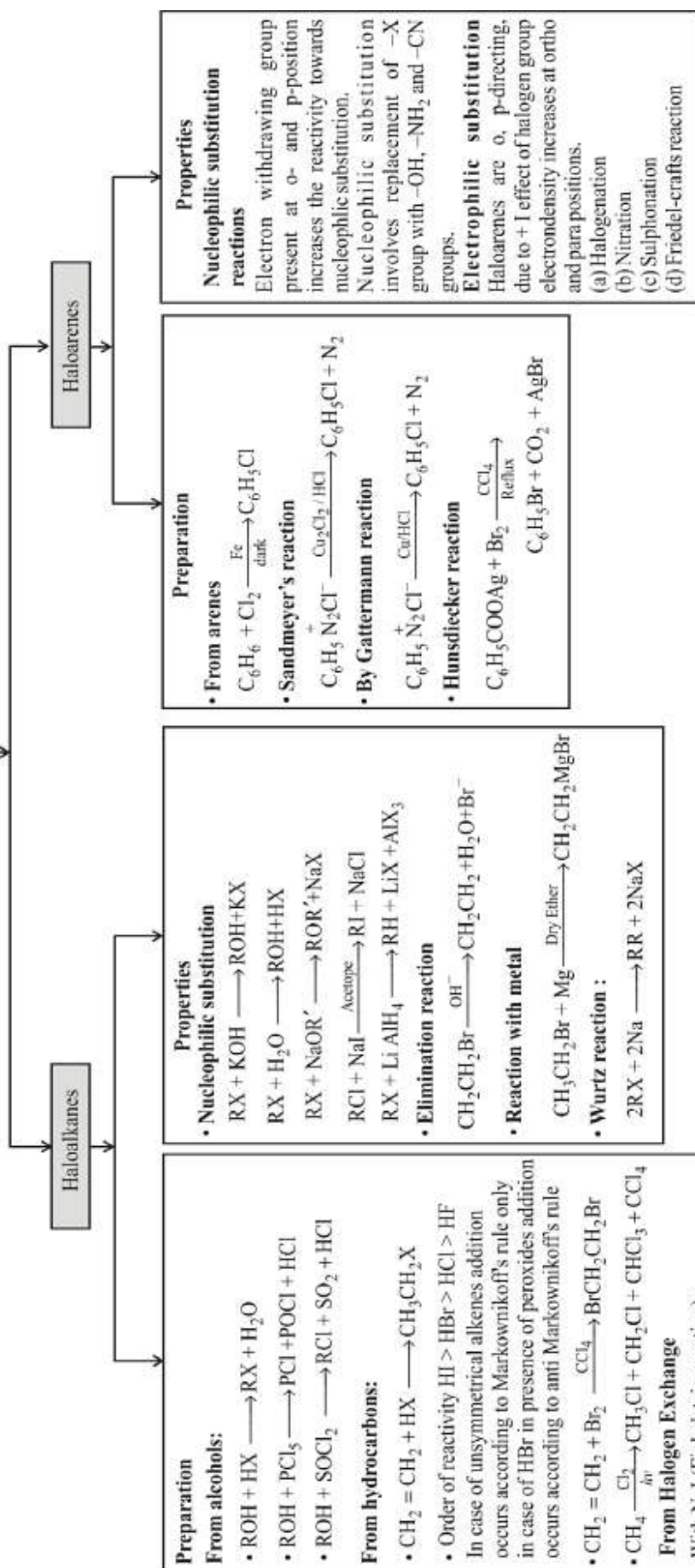
- as a solvent for oils, fats, resins
- in dry cleaning
- as a laboratory reagent
- as anthelmintic (removal of worms) for hook worms and
- as a fire extinguisher under the name of **pyrene**.

DDT**Preparation:****Uses**

It is priorly widely used as a insecticide but later researches have shown that DDT is very harmful for aquatic life as it is non-biodegradable.

CONCEPT MAP

HALOALKANES AND HALOARENES



EXERCISE - 1

Conceptual Questions

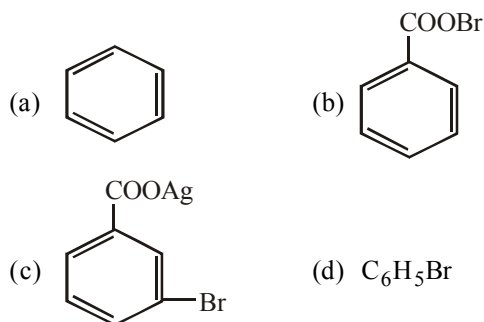
- Under basic conditions which one suffers elimination the most
 - $(\text{CH}_3)_3\text{CCl}$
 - $$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}-\text{CH}_2\text{Cl} \\ \diagup \\ \text{CH}_3 \end{array}$$
 - $$\text{CH}_3\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$$
 - $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2-\text{Cl}$
- The total number of acyclic isomers including the stereoisomers with the molecular formula $\text{C}_4\text{H}_7\text{Cl}$
 - 11
 - 12
 - 9
 - 10
- Gem dihalides on treatment with alcoholic KOH give :
 - alkyne
 - alkene
 - alkane
 - all of these
- When two halogen atoms are attached to same carbon atom then it is :
 - vic*-dihalide
 - gem*-dihalide
 - α, ω -halide
 - α, β -halide
- Full name of DDT is
 - 1, 1, 1-trichloro-2, 2-bis(*p*-chlorophenyl) ethane
 - 1, 1-dichloro-2, 2-diphenyl trimethylethane
 - 1, 1-dichloro-2, 2-diphenyl trichloroethane
 - None of these
- How many structural isomers are possible for a compound with molecular formula $\text{C}_3\text{H}_7\text{Cl}$
 - 2
 - 5
 - 7
 - 9
- Which one of the following is least reactive in a nucleophilic substitution reaction?
 - $\text{CH}_3\text{CH}_2\text{Cl}$
 - $\text{CH}_2=\text{CHCH}_2\text{Cl}$
 - $(\text{CH}_3)_3\text{C}-\text{Cl}$
 - $\text{CH}_2=\text{CHCl}$
- The compound which contains all the four $1^\circ, 2^\circ, 3^\circ$ and 4° carbon atoms is
 - 2, 3-dimethyl pentane
 - 3-chloro-2, 3 dimethylpentane
 - 2, 3, 4-trimethylpentane
 - 3,3-dimethylpentane
- Benzene hexachloride is
 - 1, 2, 3, 4, 5, 6-hexachlorocyclohexane
 - 1, 1, 1, 6, 6, 6-hexachlorocyclohexane
 - 1, 6-phenyl-1, 6-chlorohexane
 - 1, 1-phenyl-6, 6-chlorohexane
- A compound on treatment with NaOH followed by addition of AgNO_3 produces white precipitate at room temperature. The precipitate is soluble in NH_4OH . The compound is identified as
 - vinyl chloride
 - benzyl chloride
 - chlorobenzene
 - ethyl bromide
- When hydrochloric acid gas is treated with propene in presence of benzoyl peroxide, it gives
 - 2-chloropropane
 - allyl chloride
 - n*-propyl chloride
 - No reaction occurs
- $\text{C}_6\text{H}_6\text{Cl}_6$ on treatment with KOH produces
 - C_6H_6
 - $\text{C}_6\text{H}_6\text{Cl}_4$
 - $\text{C}_6\text{H}_3\text{Cl}_3$
 - $\text{C}_6\text{H}_6\text{OH}$
- 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is
 - 2-ethoxypentane
 - pentene-1
 - trans-2-pentene
 - cis-pentene-2
- When $\text{CH}_3\text{CH}_2\text{CHCl}_2$ is treated with NaNH_2 , the product formed is
 - $\text{CH}_3-\text{CH}=\text{CH}_2$
 - $\text{CH}_3-\text{C}\equiv\text{CH}$
 - $$\text{CH}_3\text{CH}_2\text{CH} \begin{array}{l} \swarrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array}$$
 - $$\text{CH}_3\text{CH}_2\text{CH} \begin{array}{l} \swarrow \text{Cl} \\ \searrow \text{NH}_2 \end{array}$$
- When 2-bromobutane reacts with alcoholic KOH, the reaction is called
 - halogenation
 - chlorination
 - hydrogenation
 - dehydro-halogenation
- Elimination of bromine from 2-bromobutane results in the formation of –
 - predominantly 2-butyne
 - predominantly 1-butene
 - predominantly 2-butene
 - equimolar mixture of 1 and 2-butene
- $\text{C}_3\text{H}_8 + \text{Cl}_2 \xrightarrow{\text{Light}} \text{C}_3\text{H}_7\text{Cl} + \text{HCl}$ is an example of
 - substitution
 - elimination
 - addition
 - rearrangement reaction
- The reaction of tert-butyl bromide with sodium methoxide produces mainly –
 - iso-butane
 - iso-butylene
 - tert-butyl methyl ether
 - sodium tert butoxide
- $$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl} \xrightarrow[\text{KOH}]{\text{alc.}} \text{B} \xrightarrow{\text{HBr}} \text{C} \xrightarrow[\text{ether}]{\text{Na}} \text{D}$$

In the above sequence of reactions, the product D is –

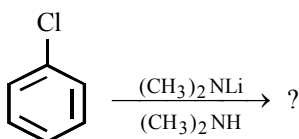
 - propane
 - 2, 3-dimethylbutane
 - hexane
 - allyl bromide
- The compounds CHCl_3 and HF lead to the formation of a compound of fluorine of molecular weight 70. The compound is
 - fluoroform
 - fluoric monoxide
 - fluoride dioxide
 - fluoro methanol

21. When two halogens are attached to same carbon atom, it is known as :
 (a) *vic*-dihalide (b) *gem*-dihalide
 (c) α, ω -dihalide (d) α, β -dihalide
22. Reaction of alkyl halides with aromatic compounds in presence of anhydrous AlCl_3 is known as :
 (a) Friedel Craft reaction (b) Corey house synthesis
 (c) Kolbe's synthesis (d) Beckmann rearrangement
23. Chlorobenzene gives aniline with :
 (a) $\text{NH}_3 + \text{Cu}_2\text{O}$ (b) $\text{NH}_3 + \text{H}_2\text{SO}_4$
 (c) NaNH_2 (d) None of these
24. In the following sequence of reactions
 $\text{C}_2\text{H}_5\text{Br} \xrightarrow{\text{AgCN}} \text{X} \xrightarrow{\text{Reduction}} \text{Y}$; Y is
 (a) *n*-propyl amine (b) isopropylamine
 (c) ethylamine (d) ethylmethyl amine
25. Ethanol can be prepared more easily by which reaction ?
 (i) $\text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$
 (ii) $\text{CH}_3\text{CH}_2\text{Br} + \text{Ag}_2\text{O}$ (in boiling water)
 $\longrightarrow \text{CH}_3\text{CH}_2\text{OH}$
 (a) by (i) reaction
 (b) by (ii) reaction
 (c) Both reactions proceed at same rate
 (d) by none
26. The reaction conditions leading to the best yields of $\text{C}_2\text{H}_5\text{Cl}$ are :
 (a) C_2H_6 (excess) + $\text{Cl}_2 \xrightarrow{\text{UV light}}$
 (b) $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow[\text{room temperature}]{\text{dark}}$
 (c) $\text{C}_2\text{H}_6 + \text{Cl}_2$ (excess) $\xrightarrow{\text{UV light}}$
 (d) $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}$
27. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with
 (a) PCl_5
 (b) dry HCl in the presence of anhydrous ZnCl_2
 (c) SOCl_2 in presence of pyridine
 (d) None of these
28. $(\text{CH}_3)_3\text{CMgCl}$ on reaction with D_2O produces :
 (a) $(\text{CH}_3)_3\text{CD}$ (b) $(\text{CH}_3)_3\text{OD}$
 (c) $(\text{CD}_3)_3\text{CD}$ (d) $(\text{CD}_3)_3\text{OD}$
29. Identify the set of reagents 'X' and 'Y' in the following set of transformations
 $\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Br} \xrightarrow{\text{X}} \text{Product} \xrightarrow{\text{Y}} \text{CH}_3 - \underset{\text{Br}}{\text{CH}} - \text{CH}_3$
- (a) X = dilute aqueous NaOH , 20°C ; Y = HBr /acetic acid, 20°C
 (b) X = concentrated alcoholic NaOH , 80°C ; Y = HBr /acetic acid, 20°C
 (c) X = dilute aqueous NaOH , 20°C ; Y = $\text{Br}_2/\text{CHCl}_3$, 0°C
 (d) X = concentrated alcoholic NaOH , 80°C ; Y = $\text{Br}_2/\text{CHCl}_3$, 0°C
30. *n*-Propyl bromide on treatment with ethanolic potassium hydroxide produces
 (a) propane (b) propene
 (c) propyne (d) propanol
31. The compound which forms acetaldehyde when heated with dilute NaOH , is
 (a) 1, 1-dichloroethane (b) 1, 1, 1-trichloroethane
 (c) 1-chloroethane (d) 1, 2-dichloroethane
32. The number of structural and configurational isomers of a bromo compound, $\text{C}_5\text{H}_9\text{Br}$, formed by the addition of HBr to 2-pentyne respectively are
 (a) 1 and 2 (b) 2 and 4
 (c) 4 and 2 (d) 2 and 1
33. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous KOH gives
 (a) *o*-cresol (b) *m*-cresol
 (c) *p*-cresol (d) benzyl alcohol
34. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives :
 (a) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{OH}$ & $\text{CH}_3\text{CH}_2\text{MgBr}$
 (b) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_3$ & $\text{MgBr}(\text{OC}_2\text{H}_5)$
 (c) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH} = \text{CH}_2$ & $\text{Mg}(\text{OH})\text{Br}$
 (d) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_3$ & $\text{CH}_3\text{CH}_2\text{OMgBr}$
35. During debromination of *meso*-2,3-dibromobutane, the major compound formed is
 (a) *n*-butane (b) 1-butene
 (c) *cis*-2-butene (d) *trans*-2-butene
36. Which of the following isomeric heptanes can yield seven different monochlorinated products upon free radical chlorination?
 (a) 3-methylhexane (b) 2,2-dimethylpentane
 (c) 2-methylhexane (d) 2,3-dimethylpentane
37. Benzene reacts with *n*-propyl chloride in the presence of anhydrous AlCl_3 to give
 (a) 3-Propyl-1-chlorobenzene
 (b) *n*-Propylbenzene
 (c) Isopropylbenzene.
 (d) No reaction occurs

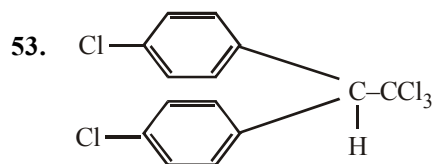
38. Methyl bromide reacts with AgF to give methyl fluoride and AgBr. This reaction is called
 (a) Finkelstein reaction (b) Swarts reaction
 (c) Fittig reaction (d) Wurtz reaction
39. Bromobenzene reacts with Mg in dry ether to give a compound (A) which further reacts with ethanol to yield
 (a) phenol (b) benzene
 (c) ethylbenzene (d) phenyl ether.
40. Phenyl magnesium bromide reacts with methanol to give
 (a) a mixture of toluene and Mg(OH)Br
 (b) a mixture of phenol and Mg(Me)Br
 (c) a mixture of anisole and Mg(OH)Br
 (d) a mixture of benzene and Mg(OMe)Br
41. In alkaline hydrolysis of a tertiary alkyl halide by aqueous alkali, if concentration of alkali is doubled, then the reaction rate of constant temperature
 (a) will be doubled
 (b) will be halved
 (c) will become four times greater
 (d) will remain constant
42. Bromination of toluene gives
 (a) only *m*-substituted product
 (b) only *p*-substituted product
 (c) mixture of *o*- and *p*-substituted products
 (d) mixture of *o*- and *m*-substituted products
43. On sulphonation of C_6H_5Cl
 (a) *m*-chlorobenzenesulphonic acid is formed
 (b) benzenesulphonic acid is formed
 (c) *o*-chlorobenzenesulphonic acid is formed
 (d) mixture of *o*- and *p*-Chlorobenzenesulphonic acid is formed
44. An alkyl halide with molecular formula $C_6H_{13}Br$ on dehydrohalogenation gave two isomeric alkenes X and Y with molecular formula C_6H_{12} . On reductive ozonolysis, X and Y gave four compounds CH_3COCH_3 , CH_3CHO , CH_3CH_2CHO and $(CH_3)_2CHCHO$. The alkyl halide is
 (a) 2-bromohexane
 (b) 2, 2-dimethyl-1-bromobutane
 (c) 4-bromo-2-methylpentane
 (d) 3-bromo-2-methylpentane
45. Silver benzoate reacts with bromine to form



46. What is the product of the following reaction ?



- (a) N, N-dimethyl aniline
 (b) phenyl lithium (C_6H_5Li)
 (c) para chloro-N, N-dimethyl aniline
 (d) meta chloro-N, N-dimethyl aniline
47. To prepare 3-ethylpentan-3-ol the reagents needed are –
 (a) $CH_3CH_2MgBr + CH_3COCH_2CH_3$
 (b) $CH_3MgBr + CH_3CH_2CH_2COCH_2CH_3$
 (c) $CH_3CH_2MgBr + CH_3CH_2COCH_2CH_3$
 (d) $CH_3CH_2CH_2MgBr + CH_3COCH_2CH_3$
48. Which one of the following alkyl halides has the lowest boiling point?
 (a) *n*-Butyl chloride (b) *iso*-Butyl chloride
 (c) *sec*-Butyl chloride (d) *tert*-Butyl chloride
49. When phenyl magnesium bromide reacts with *tert*-butanol, the product would be
 (a) benzene (b) phenol
 (c) *ter*-butylbenzene (d) *ter*-butyl phenyl ether
50. Which Chloride is least reactive with the hydrolysis point of view
 (a) CH_3Cl (b) CH_3CH_2Cl
 (c) $(CH_3)_3CCl$ (d) $CH_2=CH-Cl$
51. 2-Bromopentane is treated with alcoholic KOH solution. The major product formed in this reaction and the type of reaction respectively are
 (a) pent-2-ene, β -elimination
 (b) pent-1-ene, β -elimination
 (c) 2-pentanol, nucleophilic substitution
 (d) pent-1-ene, nucleophilic substitution
52. Chloropicrin is obtained by the reaction of
 (a) steam on carbon tetrachloride
 (b) nitric acid on chlorobenzene
 (c) chlorine on picric acid
 (d) nitric acid on chloroform



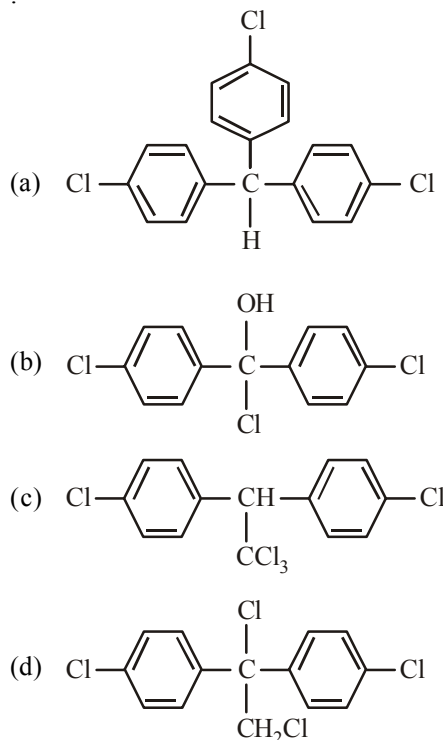
The above structural formula refers to

- (a) BHC (b) DNA
 (c) DDT (d) RNA
54. The pesticide DDT slowly changes to
 (a) CCl_3-CHO and chlorobenzene
 (b) *p*, *p'*-Dichlorodiphenylethene
 (c) *p*, *p'*-Dichlorodiphenyldichloroethane
 (d) *p*, *p'*-Dichlorodiphenyldichloroethene
55. Which one of the following on hydrolysis produces a ketone?
 (a) Isobutylidene chloride
 (b) Secondarybutylidene chloride
 (c) Benzylidene chloride
 (d) Ethylidene chloride

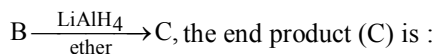
56. Pure chloroform is prepared by
 (a) distilling chloral hydrate with aqueous sodium hydroxide
 (b) heating ethanol with bleaching powder
 (c) heating acetone with bleaching powder
 (d) reducing carbon tetrachloride
57. The organic compound used as feedstock in the synthesis of chlorofluorocarbons is
 (a) CH_2Cl_2 (b) CHCl_3
 (c) CH_3Cl (d) CCl_4
58. If chloroform is left open in air in the presence of sunlight, it gives
 (a) carbon tetrachloride (b) carbonyl chloride
 (c) mustard gas (d) lewisite
59. On warming with silver powder, chloroform is converted into
 (a) acetylene
 (b) hexachloroethane
 (c) 1,1,2,2-tetrachloroethane
 (d) ethylene
60. Cl_2 reacts with CS_2 in presence of I_2 to form
 (a) CHCl_3 (b) CCl_4
 (c) $\text{C}_2\text{H}_5\text{Cl}$ (d) $\text{Cl}_3\text{C}-\text{NO}_2$
61. Reaction of chloroform with KOH in presence of a primary aromatic amine is called :
 (a) carbylamine reaction (b) reduction
 (c) hydrolysis (d) Wurtz reaction
62. The product formed by heating iodoform with KOH is :
 (a) HCHO (d) HCOOK
 (c) CH_3COOK (d) CH_3CHO
63. Ethyl alcohol is used as a preservative for chloroform because it :
 (a) prevents aerial oxidation of chloroform
 (b) prevents decomposition of chloroform
 (c) decomposes phosgene to CO and Cl_2
 (d) removes phosgene by converting it to ethyl carbonate
64. When chlorobenzene is reacted with acetyl chloride in the presence of anhydrous AlCl_3 , the major product formed is
 (a) 2-chloroacetophenone
 (b) 3-chloroacetophenone
 (c) 4-chloroacetophenone
 (d) 1, 4-dichlorobenzene
65. In a $\text{S}_\text{N}2$ substitution reaction of the type

$$\text{R}-\text{Br} + \text{Cl}^- \xrightarrow{\text{DMF}} \text{R}-\text{Cl} + \text{Br}^-$$
 which one of the following has the highest relative rate ?
 (a) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$ (b) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{Br}$
 (c) $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2\text{Br}$ (d) $\text{CH}_3\text{CH}_2\text{Br}$
66. Which of the following reactions is an example of nucleophilic substitution reaction?
 (a) $2\text{RX} + 2\text{Na} \rightarrow \text{R}-\text{R} + 2\text{NaX}$
 (b) $\text{RX} + \text{H}_2 \rightarrow \text{RH} + \text{HX}$

- (c) $\text{RX} + \text{Mg} \rightarrow \text{RMgX}$
 (d) $\text{RX} + \text{KOH} \rightarrow \text{ROH} + \text{KX}$
67. Benzene reacts with CH_3Cl in the presence of anhydrous AlCl_3 to form:
 (a) chlorobenzene (b) benzylchloride
 (c) xylene (d) toluene
68. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces :



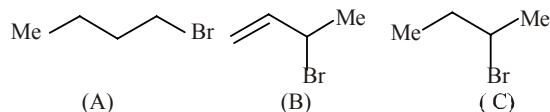
69. Which one is most reactive towards $\text{S}_\text{N}1$ reaction ?
 (a) $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$
 (b) $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$
 (c) $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$
 (d) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$
70. In the following sequence of reactions



- (a) acetone (b) methane
 (c) acetaldehyde (d) ethyl alcohol
71. Which of the following is the correct order of decreasing $\text{S}_\text{N}2$ reactivity?
 (a) $\text{R}_2\text{CHX} > \text{R}_3\text{CX} > \text{RCH}_2\text{X}$
 (b) $\text{RCHX} > \text{R}_3\text{CX} > \text{R}_2\text{CHX}$
 (c) $\text{RCH}_2\text{X} > \text{R}_2\text{CHX} > \text{R}_3\text{CX}$
 (d) $\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{X}$.
 (X is a halogen)
72. Iodoform can be prepared from all except :
 (a) Ethyl methyl ketone
 (b) Isopropyl alcohol
 (c) 3-Methyl 2-butanone
 (d) Isobutyl alcohol

73. Which one of the following is not an allylic halide?
- 4-Bromopent-2-ene
 - 3-Bromo-2-methylbut-1-ene
 - 1-Bromobut-2-ene
 - 4-Bromobut-1-ene
74. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is
- $(C_2H_5)_2CHCl$
 - $(CH_3)_3CCl$
 - $(CH_3)_2CHCl$
 - CH_3Cl

75. Consider the following bromides :



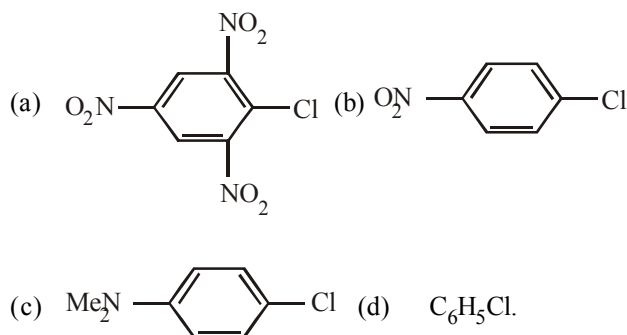
The correct order of S_N1 reactivity is

- $B > C > A$
- $B > A > C$
- $C > B > A$
- $A > B > C$

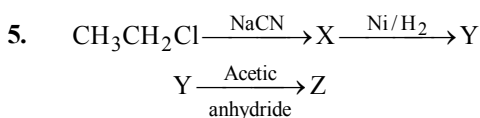
EXERCISE - 2

Applied Questions

1. Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

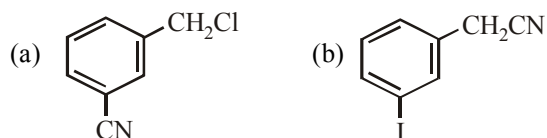
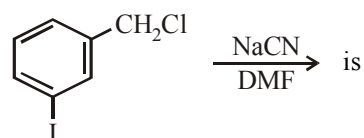


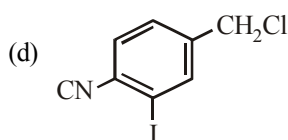
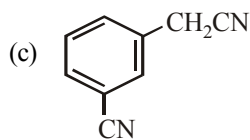
2. The alkyl halide that undergoes S_N1 reaction more readily is
- ethyl bromide
 - isopropyl bromide
 - vinyl bromide
 - n-propyl bromide
3. $CH_3-CH_2-\underset{\substack{| \\ Cl}}{CH}-CH_3$ obtained by chlorination of n-butane, will be
- l-form
 - d-form
 - meso form
 - racemic mixture
4. Aryl halides do not undergo nucleophilic substitution reactions under ordinary conditions because
- approach of nucleophile is retarded
 - carbon carrying halogen atom is sp^3 hybridised
 - the substrate molecule is destabilised due to resonance
 - partial double bond character between carbon and halogen
- 2 and 4 only
 - 1 and 4 only
 - 2 and 3 only
 - 2, 3 and 4 only



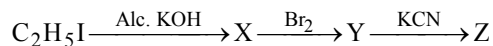
Z in the above reaction sequence is

- $CH_3CH_2CH_2NHCOCH_3$
 - $CH_3CH_2CH_2NH_2$
 - $CH_3CH_2CH_2CONHCH_3$
 - $CH_3CH_2CH_2CONHCOCH_3$
6. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment?
- A was $C_6H_5CH_2I$
 - B was C_6H_5I
 - Addition of HNO_3 was unnecessary
 - A was C_6H_5I
7. Which of the following is the correct method of preparation of methyl fluoride?
- $CH_4 + HF \rightarrow$
 - $CH_3OH + HF \rightarrow$
 - $CH_4 + F_2 \rightarrow$
 - $CH_3Br + AgF \rightarrow$
8. The structure of the major product formed in the following reaction





9. Identify Z in the following series

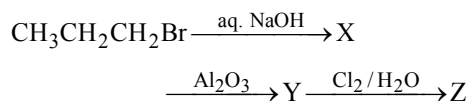


- (a) CH_3CH_2CN (b) $NCCH_2-CH_2CN$
 (c) $BrCH_2-CH_2CN$ (d) $BrCH=CHCN$

10. Which of the following pairs is/are correctly matched?

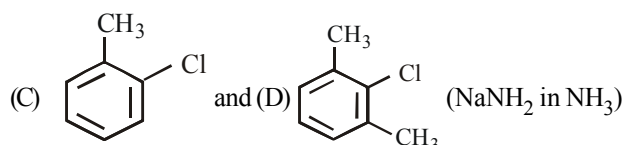
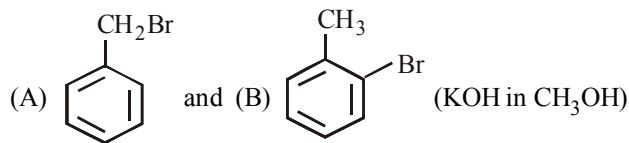
Reaction	Product
I. $RX + AgCN$	RNC
II. $RX + KCN$	RCN
III. $RX + KNO_2$	$R-N \begin{array}{c} \nearrow O \\ \searrow O \end{array}$
IV. $RX + AgNO_2$	$R-O-N=O$
(a) Only I	(b) I and II
(c) III and IV	(d) I, II, III and IV

11. Identify Z in



- (a) Mixture of $CH_3CHClCH_2Cl$ and $CH_3CHOHCH_2Cl$
 (b) $CH_3CHOHCH_2Cl$
 (c) $CH_3CHClCH_2OH$
 (d) $CH_3CHClCH_2Cl$

12. Which compound in each of the following pairs is most reactive to the conditions indicated?



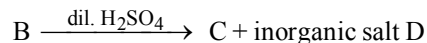
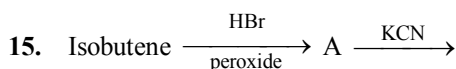
- (a) A and C (b) B and C
 (c) A and D (d) B and D

13. The correct kinetic rate equation for the addition-elimination mechanism of nucleophilic aromatic substitution

- (a) $\text{rate} = K [\text{aryl halide}] [\text{nucleophile}]$
 (b) $\text{rate} = K [\text{aryl halide}]$
 (c) $\text{rate} = K [\text{aryl halide}] [\text{nucleophile}]^2$
 (d) $\text{rate} = K [\text{nucleophile}]$

14. Which of the following reagents react readily with bromobenzene?

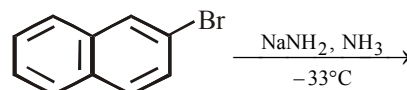
- (a) $NaNH_2 / NH_3$ at $-33^\circ C$
 (b) $(CH_3)_2NH$ at $25^\circ C$
 (c) CH_3CH_2ONa at $25^\circ C$
 (d) $NaCN / DMSO$ at $25^\circ C$



C and D are

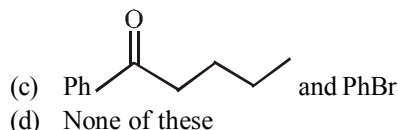
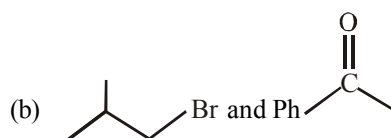
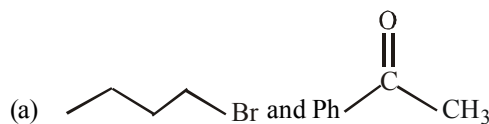
- (a) $Me_2CH.CH_2COOH, (NH_4)_2SO_4$
 (b) $Me_2CH.COOH, (NH_4)_2SO_4$
 (c) $Me_2CH.CH_2COOK, NH_4OH$
 (d) $Me_2CH.CH_2COOK, K_2SO_4$

16. How many isomeric naphthylamines are expected in the following reaction?



- (a) two (b) only single product
 (c) four (d) three

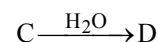
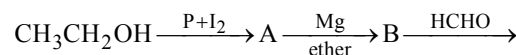
17. 2-phenyl-2-hexanol can be prepared by Grignard synthesis. The pair of compounds giving the desired product is



18. Which will undergo S_N2 reaction fastest among the following halogen compounds?

- (a) CH_3CH_2F (b) CH_3CH_2Cl
 (c) CH_3CH_2Br (d) CH_3CH_2I

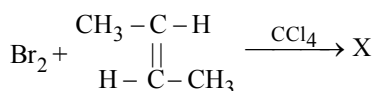
19. In the following sequence of reactions



the compound D is

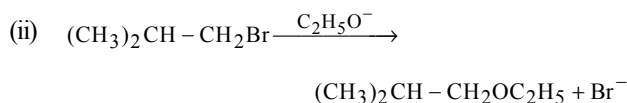
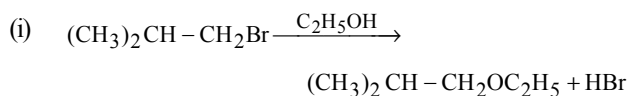
- (a) propanal (b) butanal
 (c) *n*-butyl alcohol (d) *n*-propyl alcohol.

20. X in the following reaction is –



- (a) (+) 2, 3-Dibromobutane
 (b) (–) 2, 3-Dibromobutane
 (c) Rac. 2, 3-Dibromobutane
 (d) Meso-2, 3-Dibromobutane

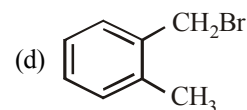
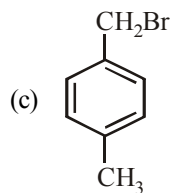
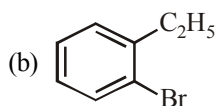
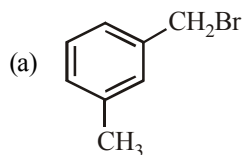
21. Consider the reactions :



The mechanisms of reactions (i) and (ii) are respectively :

- (a) S_N1 and S_N2 (b) S_N1 and S_N1
 (c) S_N2 and S_N2 (d) S_N2 and S_N1

22. Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).



DIRECTIONS for Qs. 23 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True

23. **Statement-1** : $CHCl_3$ is stored in dark bottles.

Statement-2 : $CHCl_3$ is oxidised in dark.

24. **Statement-1** : Addition of bromine to trans-2-butene yields meso-2, 3-dibromobutane

Statement-2 : Bromine addition to an alkene is an electrophilic addition.

25. **Statement-1** : CCl_4 is not a fire extinguisher.

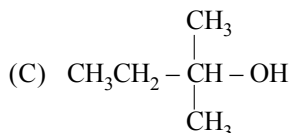
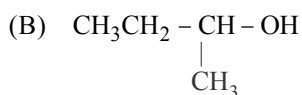
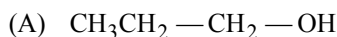
Statement-2 : CCl_4 is insoluble in water.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

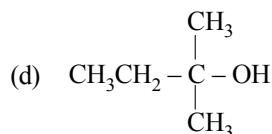
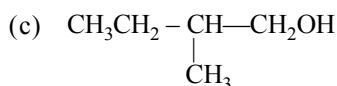
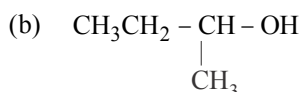
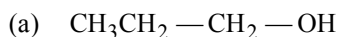
Exemplar Questions

1. The order of reactivity of following alcohols with halogen acids is

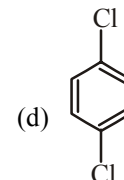
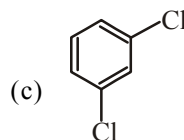
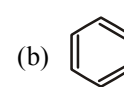
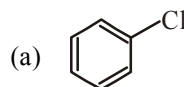
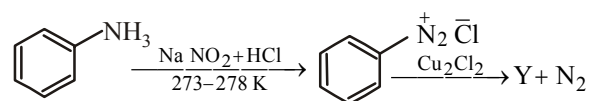


- (a) (A) > (B) > (C) (b) (C) > (B) > (A)
 (c) (B) > (A) > (C) (d) (A) > (C) > (B)

2. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?



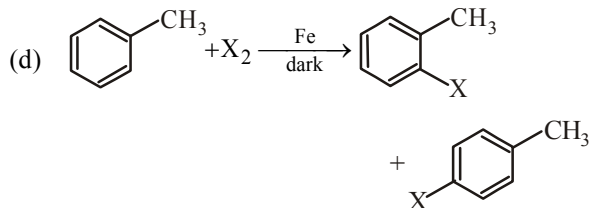
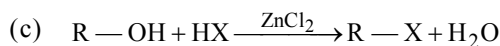
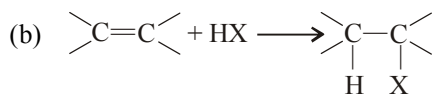
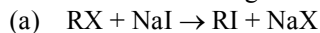
3. Identify the compound Y in the following reaction.



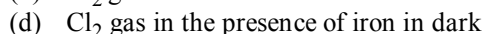
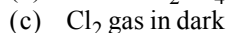
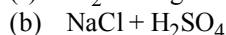
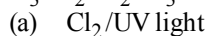
4. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

- (a) electrophilic elimination reaction
 (b) electrophilic substitution reaction
 (c) free radical addition reaction
 (d) nucleophilic substitution reaction

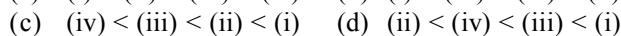
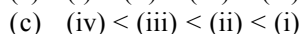
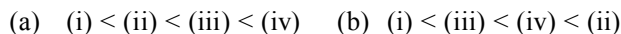
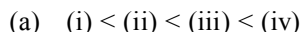
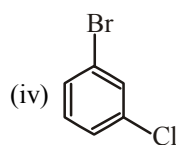
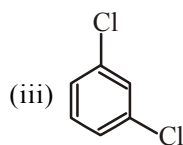
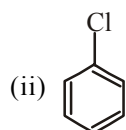
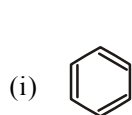
5. Which of the following is halogen exchange reactions?



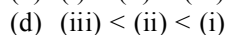
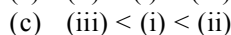
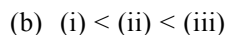
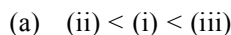
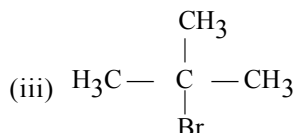
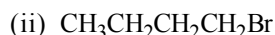
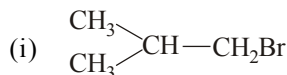
6. Which reagent will you use for the following reaction?



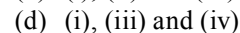
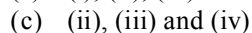
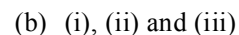
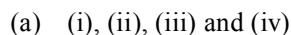
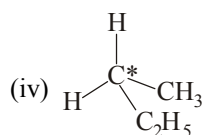
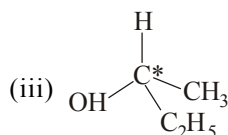
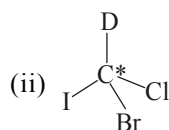
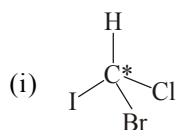
7. Arrange the following compounds in the increasing order of their densities.



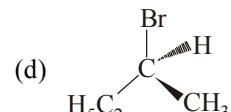
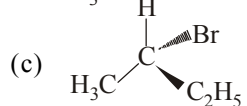
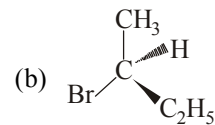
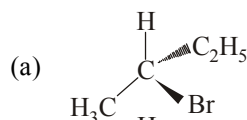
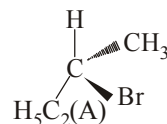
8. Arrange the following compounds in increasing order of their boiling points.



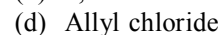
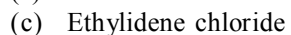
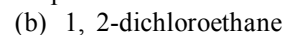
9. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric?



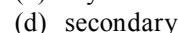
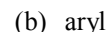
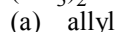
10. Which of the following structures is enantiomeric with the molecule (A) given below?



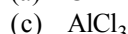
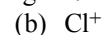
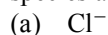
11. Which of the following is an example of *vic*-dihalide?



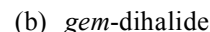
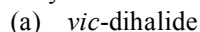
12. The position of Br in the compound $CH_3CH = CHC(Br)(CH_3)_2$ can be classified as



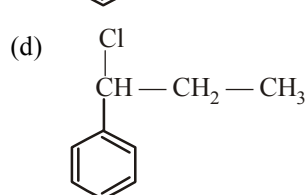
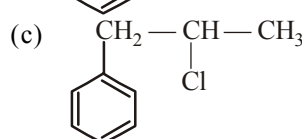
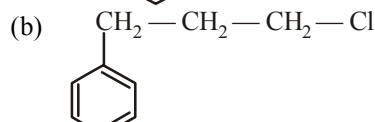
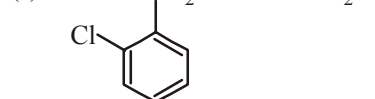
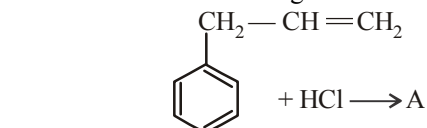
13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?



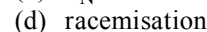
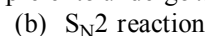
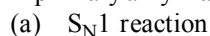
14. Ethylidene chloride is a/an



15. What is 'A' in the following reaction?



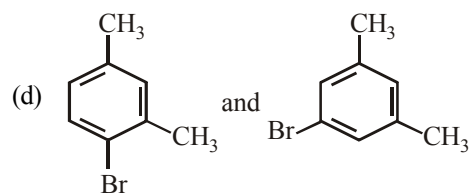
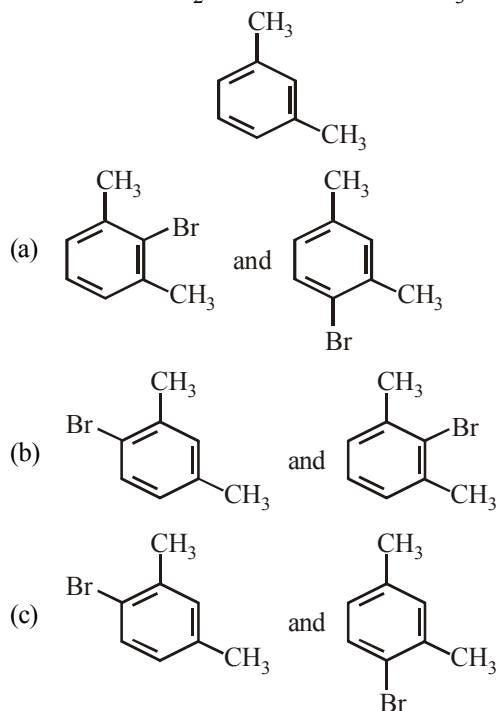
16. A primary alkyl halide would prefer to undergo



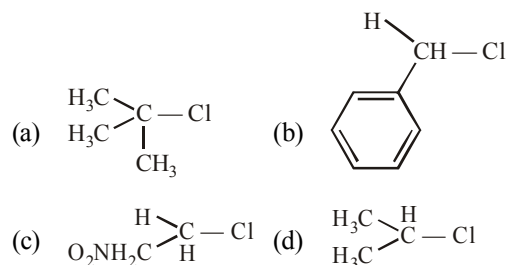
- (c) Butane < 1 - iodobutane < 1 - bromobutane < 1 - chlorobutane
 (d) Butane < 1 - chlorobutane < 1 - iodobutane < 1 - bromobutane
31. Which is the correct increasing order of boiling points of the following compounds?
 1 - bromoethane, 1 - bromopropane, 1 - bromobutane, Bromobenzene
- (a) Bromobenzene < 1 - bromobutane < 1 - bromopropane < 1 - bromoethane
 (b) Bromobenzene < 1 - bromobutane < 1 - bromopropane < 1 - bromoethane
 (c) 1 - bromopropane < 1 - bromopropane < 1 - bromoethane < Bromobenzene
 (d) 1 - bromoethane < 1 - bromopropane < 1 - bromobutane < Bromobenzene

NEET/AIPMT (2013-2017) Questions

32. What products are formed when the following compounds is treated with Br_2 in the presence of FeBr_3 ? [2014]



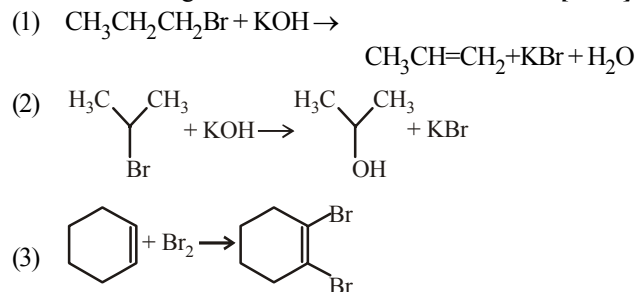
33. In which of the following compounds, the C - Cl bond ionisation shall give most stable carbonium ion? [2015]



34. In an $\text{S}_{\text{N}}1$ reaction on chiral centres there is: [2015 RS]

- (a) 100 % racemization
 (b) inversion more than retention leading to partial racemization
 (c) 100 % retention
 (d) 100 % inversion

35. For the following reactions: [2016]



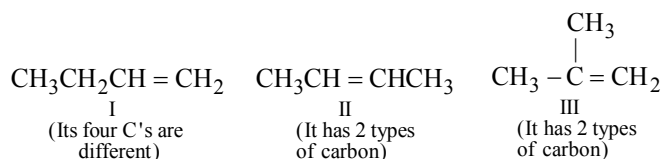
Which of the following statements is correct ?

- (a) (1) and (2) are elimination reaction and (3) is addition reaction
 (b) (1) is elimination, (2) is substitution and (3) is addition reaction
 (c) (1) is elimination, (2) and (3) are substitution reactions
 (d) (1) is substitution, (2) and (3) are addition reaction

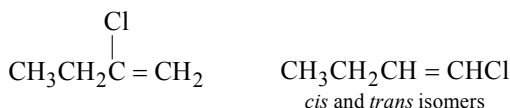
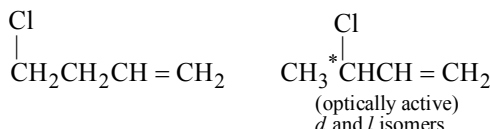
Hints & Solutions

EXERCISE - 1

1. (b) In basic conditions, the reactivity by elimination increases from 1° carbocation to 3° carbocation. So, $(\text{CH}_3)_3\text{CCl}$ suffers elimination the most among the given choices.
Note: Elimination reactions are of two types E_1 and E_2 . Reactivity by E_1 and E_2 mechanism increases in the same order but due to different reasons. The rate of E_2 depends upon the concentration of base and rate of E_1 depends upon the nature of base.
 Here we can not decide whether the reaction is proceed via E_1 mechanism or E_2 mechanism because nothing is given about the basic conditions.
2. (b) $\text{C}_4\text{H}_7\text{Cl}$ is a monochloro derivative of C_4H_8 which itself exists in three acyclic isomeric forms.

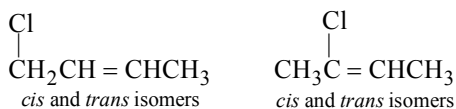


Four monochloro derivatives of I



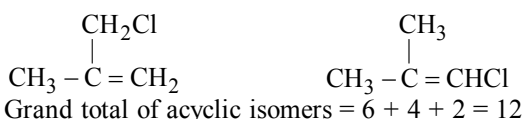
Hence total isomers from I = 6

Two monochloro derivatives of II

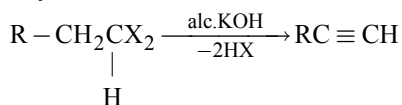


Hence total isomers from II = 4

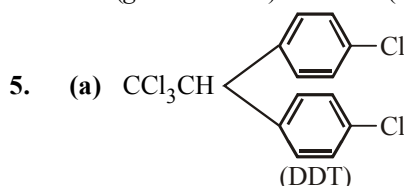
Two monochloro derivatives from III



3. (a) Gem dihalides on treatment with alcoholic KOH gives alkyne as follows :

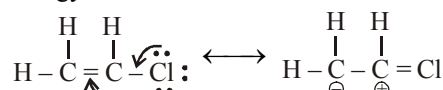


4. (b) CHCl_2 CH_2Cl
 CH_3 CH_2Cl
 (gem-dihalide) (vic-dihalide)



6. (a)
 7. (d) Among the given structures, $\text{CH}_2=\text{CHCl}$ is least reactive.

As reaction of substitution involves breakage of carbon-halogen bond. Here the carbon is vinylic carbon hence is sp^2 hybridised. The bond length is shorter than single bond and has a very high bond energy. This is because of resonance:



Also vinylic carbocation is very less stable.

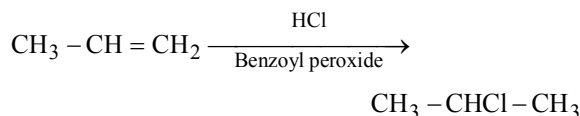
Thus option (d) is correct choice.

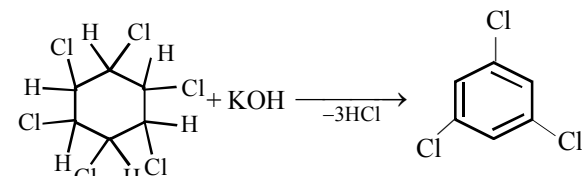
In structure $\text{CH}_2=\text{CHCH}_2\text{Cl}$, allylic carbon is present. Allylic carbocation is infact stabilized by resonance.

8. (b) $\overset{1^\circ}{\text{CH}_3}-\overset{3^\circ}{\underset{\text{Cl}}{\text{CH}}}-\overset{1^\circ}{\underset{\text{Cl}}{\text{C}}}-\overset{2^\circ}{\text{CH}_2}-\overset{1^\circ}{\text{CH}_3}$
 3-Chloro-2,3-dimethylpentane

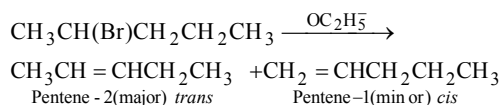
9. (a)

10. (b) Halides Cl^- , Br^- , I^- React with AgNO_3 to give
 $\text{AgCl} \longrightarrow$ soluble in NH_4OH
 $\text{AgBr} \longrightarrow$ sparingly soluble in NH_4OH
 $\text{AgI} \longrightarrow$ Insoluble
 and the C-Cl bond is weakest in benzyl chloride [sp^3 hybridised carbon is attached to Cl]
11. (a) Peroxide effect is observed only in case of HBr. Therefore, addition of HCl to propene even in the presence of benzoyl peroxide occurs according to Markonikov's rule :



12. (c) 

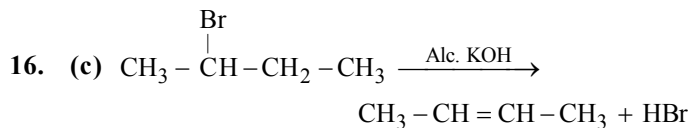
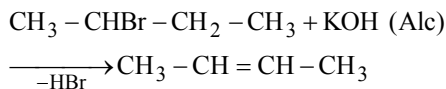
13. (c) Potassium ethoxide is a strong base, and 2-bromopentane is a 2° bromide, so elimination reaction predominates



Since *trans*-alkene is more stable than *cis*, thus *trans*-pentene-2 is the main product.

14. (b) $\text{CH}_3-\text{CH}_2-\text{CHCl}_2 \xrightarrow[\Delta]{\text{NaNH}_2} \text{CH}_3-\text{CH}=\text{CHCl} \xrightarrow[\Delta]{\text{NaNH}_2} \text{CH}_3-\text{C}\equiv\text{CH}$
 Final Product

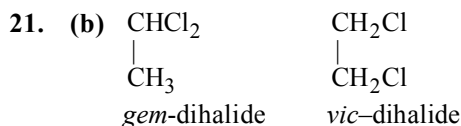
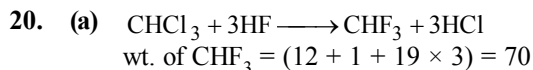
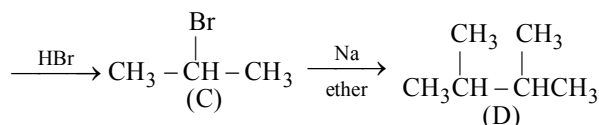
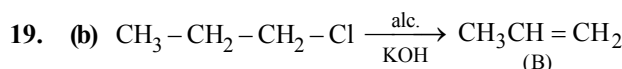
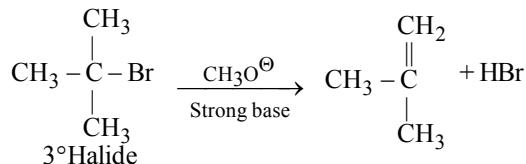
15. (d) Alcoholic KOH, reduces haloalkane into alkene by the process dehydrohalogenation



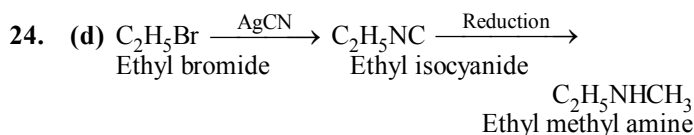
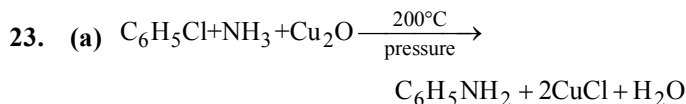
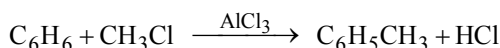
The formation of 2-butene is in accordance to **Saytzeff's rule**. The more substituted alkene is formed in major quantity.

17. (a)

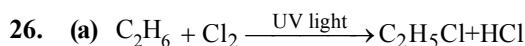
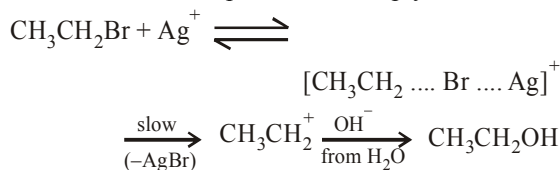
18. (b) 3° halide on reaction with strong base ($\text{CH}_3\text{O}^\ominus$) undergo elimination reaction and forms alkene as major product.



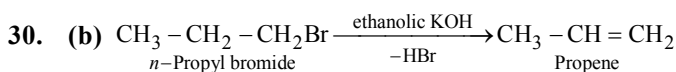
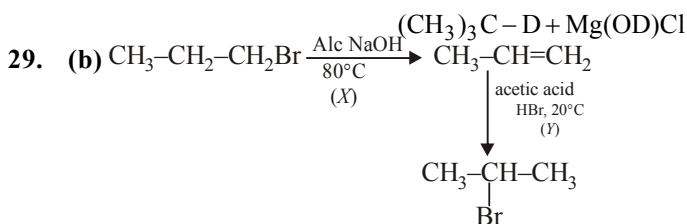
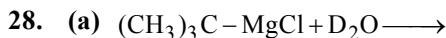
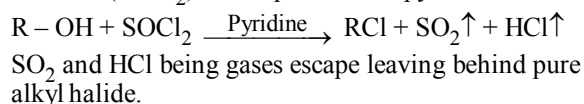
22. (a) Friedel Craft reactions are examples of aromatic electrophilic substitution. In this, a Lewis acid (like AlCl_3 , FeBr_3 etc.) is used as catalyst.



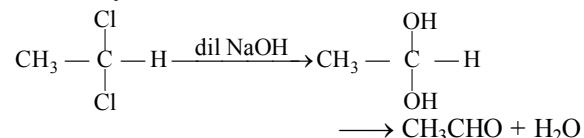
25. (b) Heavy metal ions, particularly Ag^+ , catalyse $\text{S}_{\text{N}}1$ reaction because of presence of empty orbital.



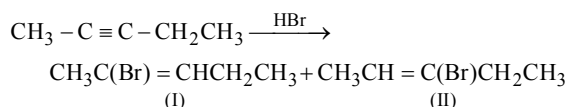
27. (c) The best method for the conversion of an alcohol into an alkyl chloride is reaction of the alcohol with thionyl chloride (SOCl_2) in the presence of pyridine.



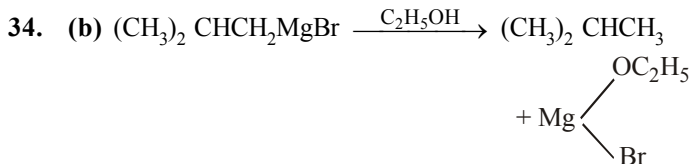
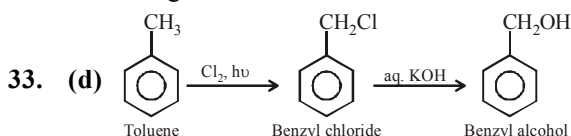
31. (a) 1, 1-dichloroethane on heating with dil. NaOH gives acetaldehyde.



32. (b) Addition of HBr to 2-pentyne gives two structural isomers (I) and (II)

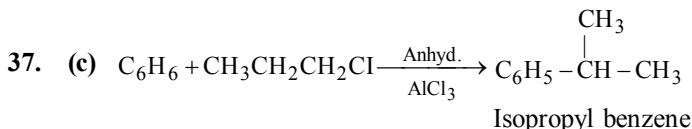
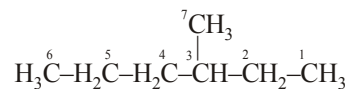


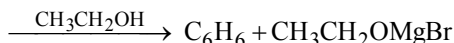
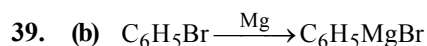
Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers.



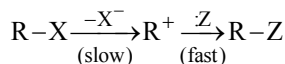
35. (d) Debromination is a *trans*-elimination reaction. *meso*- 2, 3-Dibromobutane on debromination gives *trans*-2-butene.

36. (a) 3-methylhexane can yield seven different monochlorinated products upon free radical chlorination.



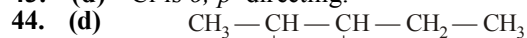


41. (d) **S_N1 (Unimolecular nucleophilic substitution)** : Although it is a two step process, the rate of reaction depends only upon the **first (slow)** step which involves ionization of the alkyl halide to form carbocation. Hence rate of reaction depends only upon the concentration of the alkyl halides, $r = k[\text{RX}]$ and is independent of the concentration of the nucleophile which adds on the carbocation in the **second (fast)** step.



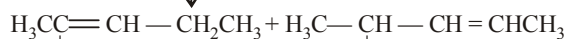
42. (c) $-\text{CH}_3$ group is *o*, *p*-directing.

43. (d) $-\text{Cl}$ is *o*, *p*-directing.



3-bromo-2-methyl Pentane

↓ dehydrohalogenation

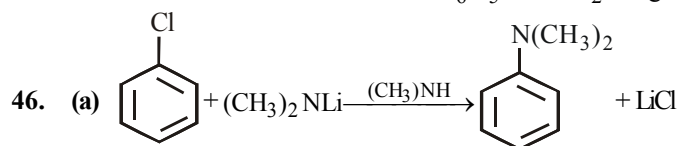
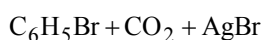
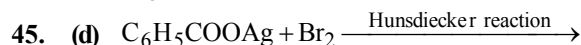
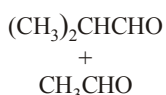
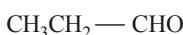
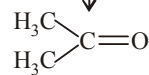


(X)

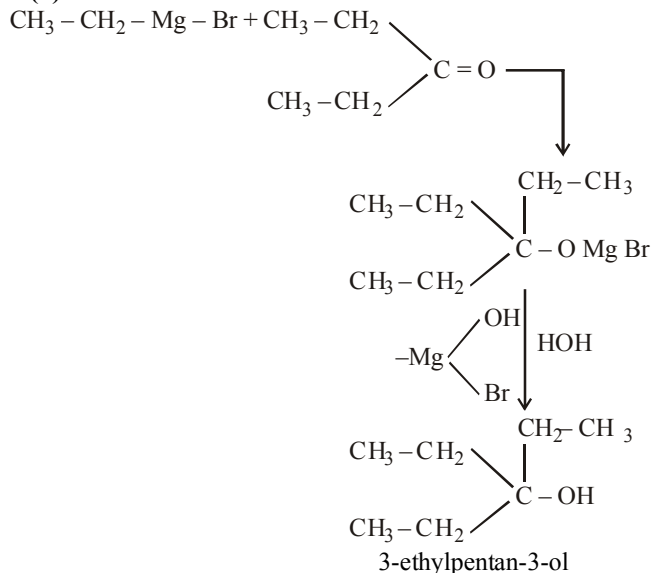
(Y)

↓ ozonolysis

↓ ozonolysis

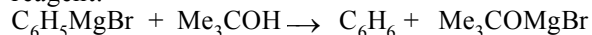


47. (c)



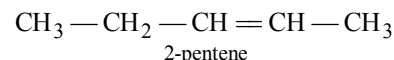
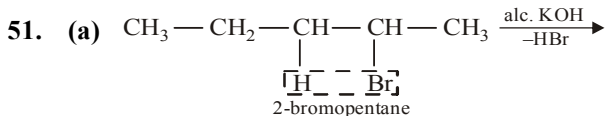
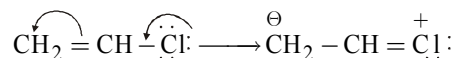
48. (d) The boiling points of alkyl chlorides increases with increase in molecular weight. In case of isomeric alkyl chloride, the order of boiling point is primary > secondary > tertiary

49. (a) Grignard reagents react with compounds containing active hydrogen to form hydrocarbons corresponding to alkyl (or aryl) part of the Grignard reagent.



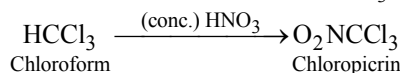
50. (d) $\text{CH}_2 = \text{CH} - \text{Cl}$
(Vinyl Chloride)

The halogen atom in vinyl chloride is not reactive as in other alkyl halides. The non-reactivity of chlorine atom is due to resonance stabilisation. The *l.p.* on Cl-atom can participate in delocalisation (Resonance) to give two canonical structure.

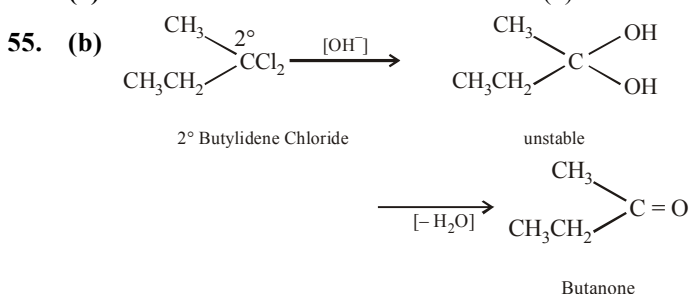


These reactions are known as β -elimination.

52. (d) Chloropicrin is nitrochloroform. It is obtained by the nitration of chloroform with HNO_3 .

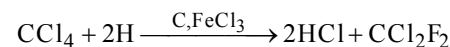


53. (c)



56. (a) $\text{CCl}_3\text{CH}(\text{OH})_2 + \text{NaOH} \xrightarrow{\text{distil}} \text{CHCl}_3 + \text{HCOONa} + \text{H}_2\text{O}$

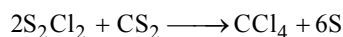
57. (d) $3\text{CCl}_4 + 2\text{SbF}_5 \xrightarrow{\text{SbCl}_5} 2\text{SbCl}_3 + 3\text{CCl}_2\text{F}_2$
freon-12



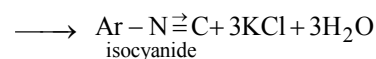
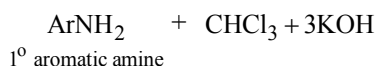
58. (b) $\text{CHCl}_3 + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Light}} \text{CCl}(\text{OH})_3 \rightarrow \text{COCl}_2 + \text{HCl}$
unstable

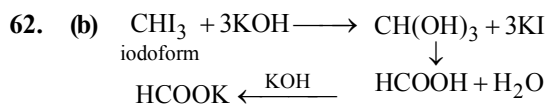
59. (a) $\text{HCCl}_3 + 6\text{Ag} + \text{HCCl}_3 \xrightarrow{\Delta} \text{HC} \equiv \text{CH} + 6\text{AgCl}$

60. (b) $\text{CS}_2 + 3\text{Cl}_2 \xrightarrow[\text{or SbCl}_5]{\text{anhy. AlCl}_3} \text{CCl}_4 + \text{S}_2\text{Cl}_2$

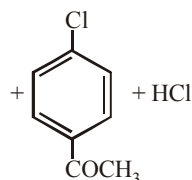
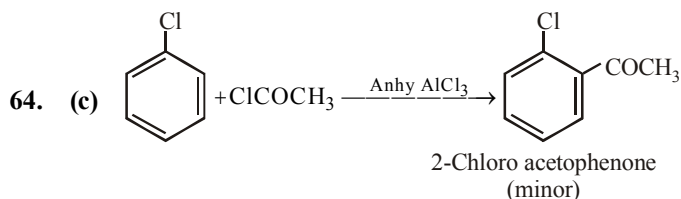
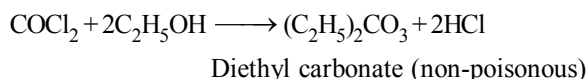
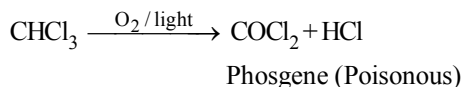


61. (a) This is carbylamine reaction



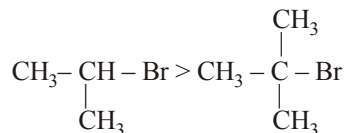


63. (d) CHCl_3 on exposure to air forms phosgene which is poisonous gas and removed by converting it into diethyl carbonate (which is non-poisonous substance).



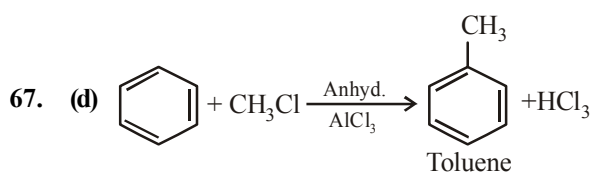
[Note : Para product predominates over the ortho product]

65. (d) For such a reaction the rate of $\text{S}_{\text{N}}2$ substitution reaction is maximum in case of $\text{CH}_3\text{CH}_2\text{Br}$ because $\text{S}_{\text{N}}2$ mechanism is followed in case of primary and secondary halides i.e., $\text{S}_{\text{N}}2$ reaction is favoured by small groups on the carbon atom attached to halogens so order of $\text{S}_{\text{N}}2$ substitution reaction will be

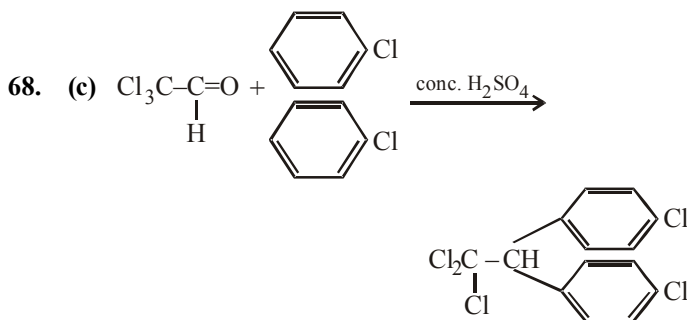


i.e. option (d) is correct.

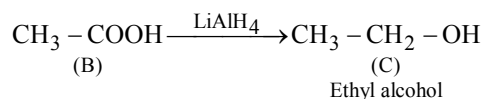
66. (d) It is a nucleophilic substitution reaction as here stronger nucleophile OH^- is replacing weaker nucleophile X^-



Friedel Craft's reaction.

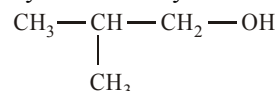


69. (c) $\text{S}_{\text{N}}1$ reactions involve the formation of carbocations, order of stability of carbocation is $3^\circ > 2^\circ > 1^\circ$ hence higher the stability of carbocation, more will be the reactivity of the parent alkyl halide. Moreover the tertiary carbocation formed from (c) is stabilized by two phenyl groups.



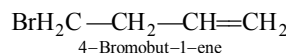
71. (c) In $\text{S}_{\text{N}}2$ mechanism transition state is pentavalent. Thus bulky alkyl group will be sterically hindered and smaller alkyl group will favour the $\text{S}_{\text{N}}2$ mechanism. So the decreasing order of reactivity of alkyl halides is $\text{RCH}_2\text{X} > \text{R}_2\text{CHX} > \text{R}_3\text{CX}$

72. (d) Iodoform test is given by methyl ketones, acetaldehyde and methyl secondary alcohols.



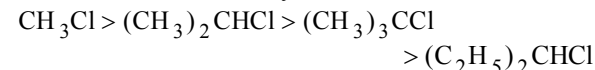
Isobutyl alcohol is a primary alcohol hence doesn't give positive iodoform test.

73. (d) 4-Bromobut-1-ene is not an allylic halide

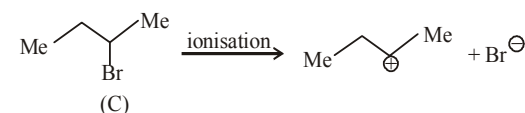
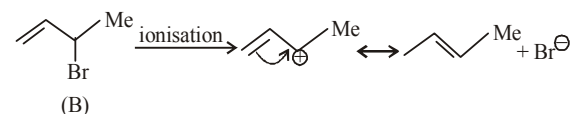
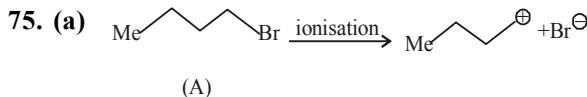


74. (d) $\text{S}_{\text{N}}2$ reaction is favoured by small groups on the carbon atom attached to halogen.

So, the order of reactivity is



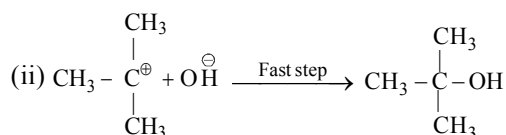
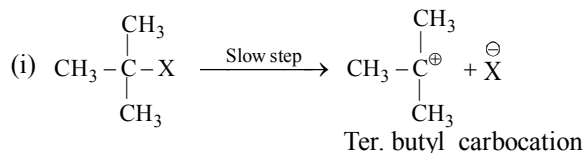
$\text{S}_{\text{N}}2$ reaction is shown to maximum extent by primary halides. The only primary halides given is CH_3Cl so the correct answer is (d).



Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards S_N1 route. Now we know that stability of carbocations follows the order : $3^\circ > 2^\circ > 1^\circ$, so S_N1 reactivity should also follow the same order. $3^\circ > 2^\circ > 1^\circ > \text{Methyl}$ (S_N1 reactivity)

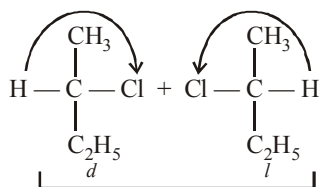
EXERCISE - 2

- (a) Cl in 2, 4, 6-trinitrochlorobenzene is activated by three NO_2 groups at *o*, and *p*-positions and hence undergoes hydrolysis most readily.
- (d) This reaction occurs in two steps. In first step, a carbocation is formed from alkyl halide molecule. First step is slow step so it is also rate determining step. In second step, an attacking nucleophile attacks on this carbocation and forms the final product. Thus the stability of the carbocation influences the rate of reaction. More stable the carbocation, higher is its rate of formation. Thus those alkyl halides which form stable, 3° carbocations undergo S_N1 reaction readily. Thus, *t*-butyl bromide is the favourable substrate.



$$\text{Rate of reaction} \propto [(\text{CH}_3)_3\text{C} - \text{X}]$$

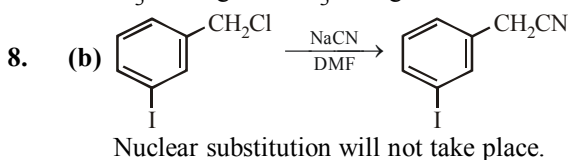
- (d) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{Cl}_2/h\nu}$



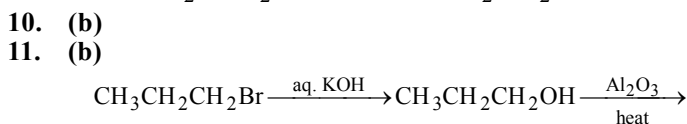
$\text{Cl}^\bullet$ may attack on either side and give a racemic mixture of 2-chloro butane which contain 50% *d* form and 50% *l*-form.

- (b) Aryl halides are less reactive towards nucleophilic substitution because of the partial double bond character of carbon-halogen bonds. It is also partly due to repulsion between the electron cloud of the benzene ring and the nucleophile.
- (a) $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{NaCN}} \text{CH}_3\text{CH}_2\text{CN} + \text{NaCl} \xrightarrow{\text{Ni}/\text{H}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{NHCOCH}_3 + \text{CH}_3\text{COOH}$
- (d)

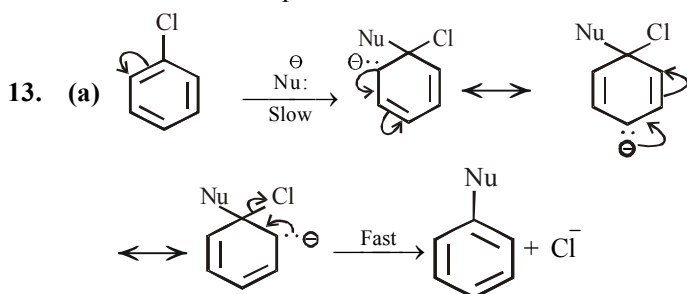
- (d) Fluoroalkanes are difficult to prepare directly because fluorination of hydrocarbons with pure F_2 gas occurs explosively. Therefore these are prepared by treating alkyl chloride or bromide with salts such as Hg_2F_2 , AgF . The reaction is called Swarts reaction.
 $\text{CH}_3\text{Br} + \text{AgF} \rightarrow \text{CH}_3\text{F} + \text{AgBr}$



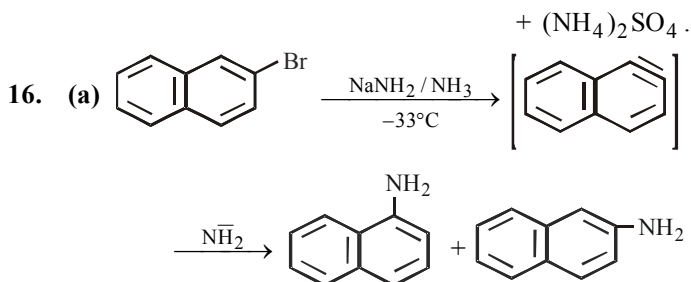
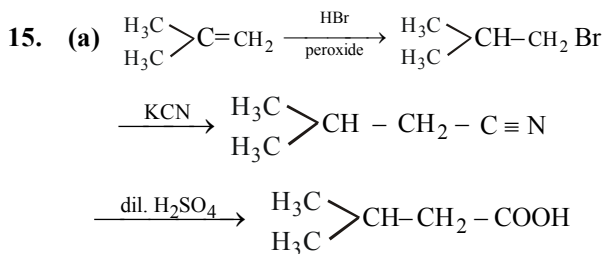
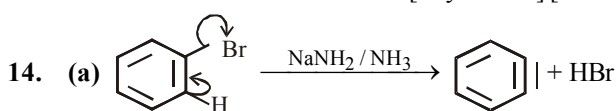
- (b) $\text{C}_2\text{H}_5\text{I} \xrightarrow{\text{alc. KOH}} \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{Br}_2} \text{BrCH}_2 - \text{CH}_2\text{Br} \xrightarrow{\text{KCN}} \text{CNCH}_2\text{CH}_2\text{CN}$

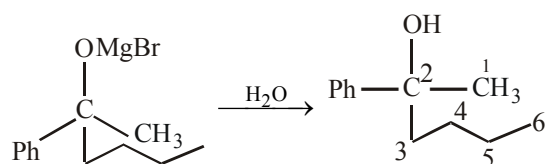
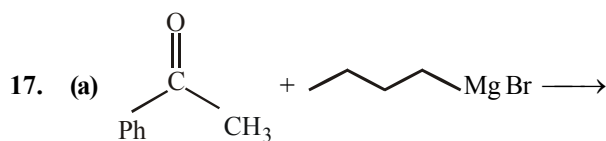


- (a) $\text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{Cl}_2/\text{H}_2\text{O}} \text{CH}_3\text{CHOHCH}_2\text{Cl}$
- (a) In the first case the reaction gives side chain substitution product which is easier in A. In the second case the reaction will proceed by benzyne mechanism for which ortho position w. r. to Cl must have H-atoms.



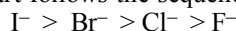
$$\text{Rate} \propto [\text{C}_6\text{H}_5\text{Cl}] [\text{Nu}^-] = K [\text{Aryl halide}] [\text{nucleophile}]$$





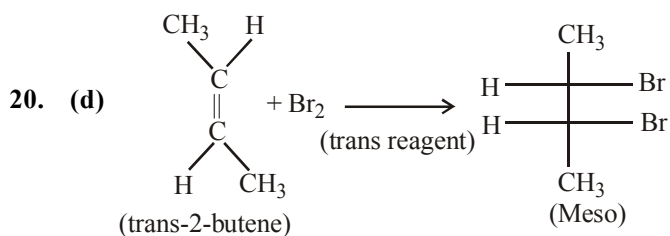
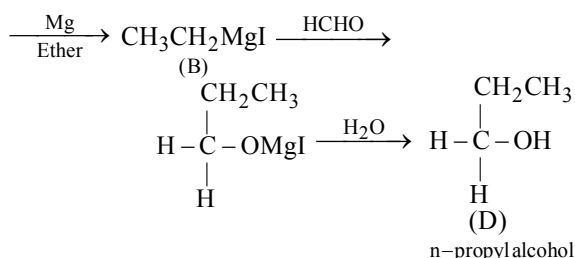
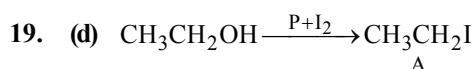
2-phenyl-2-hexanol

18. (d) Smaller the R group reactivity will be higher towards S_N2 reaction. For alkyl halides containing similar alkyl group better will be the leaving group, more facile is the nucleophilic substitution reaction. Amongst the halide ions, the order in which the leaving groups depart follows the sequence :

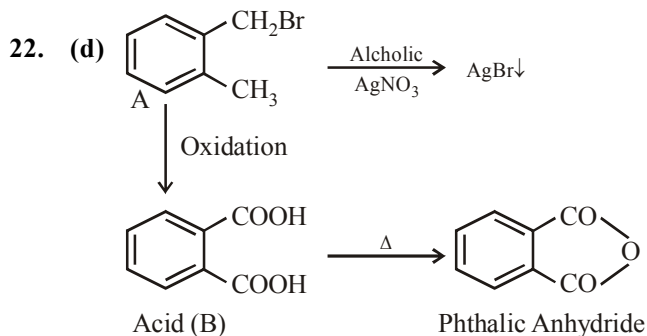


It is because of this reason that the order of reactivity of haloalkanes follows the sequence :

iodoalkanes > bromoalkanes
> chloroalkanes > fluoroalkanes



21. (a) A strong nucleophile favours the S_N2 reaction and a weak nucleophile favours the S_N1 reaction. First reaction is S_N1 reaction because C_2H_5OH is used as solvent which is a weak nucleophile. Second reaction is S_N2 reaction because $C_2H_5O^-$ is strong nucleophile.



23. (c) $CHCl_3$ is stored in dark bottles to prevent oxidation of $CHCl_3$ in presence of sunlight.

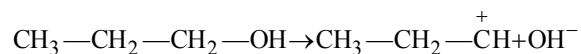
24. (b)

25. (d) CCl_4 is used as a fire extinguisher. The dense, non combustible vapours cover the burning substance and prevents the availability of oxygen around burning material.

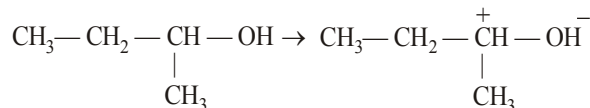
EXERCISE - 3

Exemplar Questions

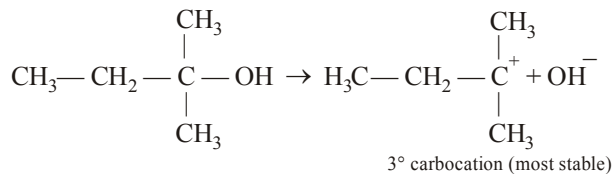
1. (b) Alcohols and halogen acid react through S_N1 mechanism.



In this case, 1° carbocation is formed. It is least stable. So, here S_N2 mechanism is followed. In this S_N2 mechanism a transition state is observed in which α -carbon is linked with two nucleophiles.



2° Carbocation (more stable than 1° carbocation)



3° carbocation (most stable)

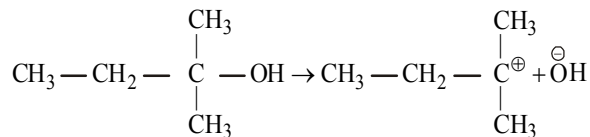
Greater the stability of carbocation, greater will be the possibilities of attack of X^- ion on the carbocation. Order of stability of carbocation is : $3^\circ > 2^\circ > 1^\circ$.

So order of reactivity will be $C > B > A$.

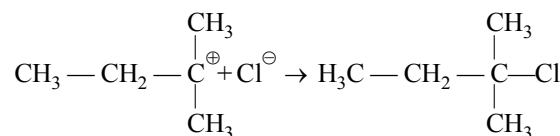
2. (d) Reaction of alcohols with conc. HCl at room temperature follows S_N1 mechanism.

The attack of nucleophile to the carbocation is possible only on stable carbocation as at room temperature only 3° carbocation is stable.

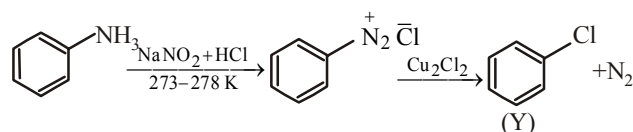
Step I



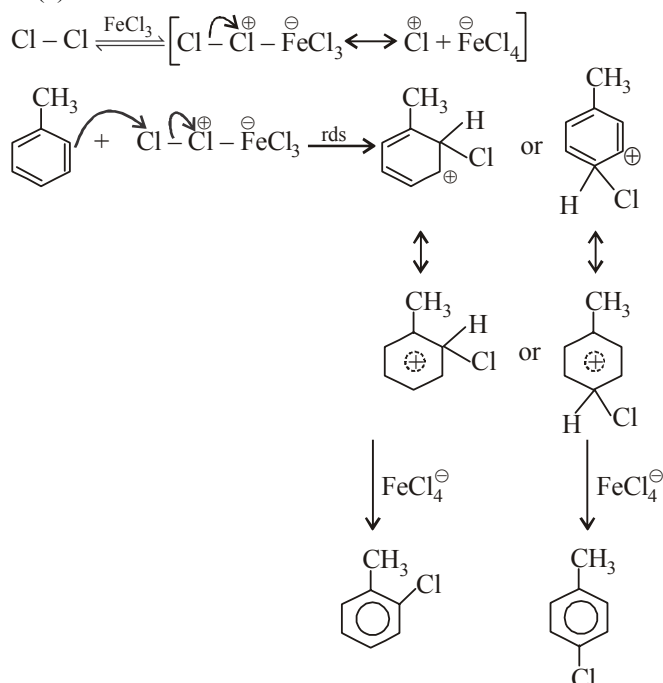
Step II



3. (a) Sandmeyer's Reaction

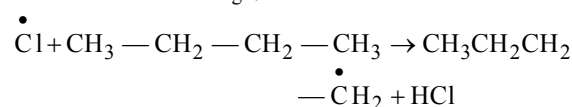
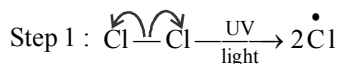


4. (b)

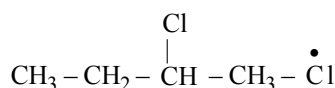
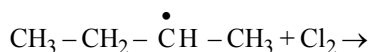
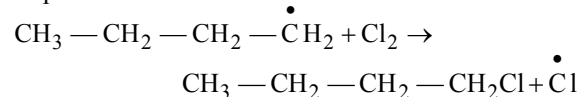


As electrophile Cl^+ attacks on electron rich benzene ring and substitutes hydrogen. So, the reaction is electrophilic substitution reaction.

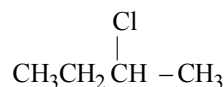
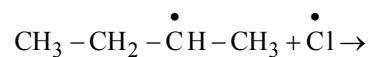
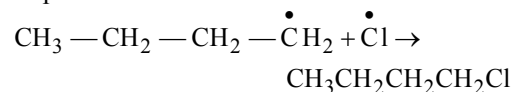
5. (a) Halogen exchange reactions are those reactions in which one halide replaces another (Finkelstein reaction).

6. (a) It is a substitution reaction which involves the replacement of 1° and 2° hydrogen of alkanes by chlorine. It occurs in presence of ultraviolet light.

Step 2 :



Step 3 :

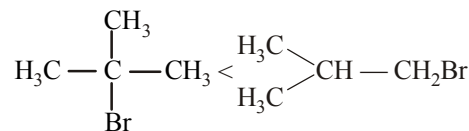


7. (a) Density is directly related to molecular mass. More the molecular mass, more will be the density of the compound. The order of molecular mass is

benzene < chlorobenzene < dichlorobenzene < bromochlorobenzene

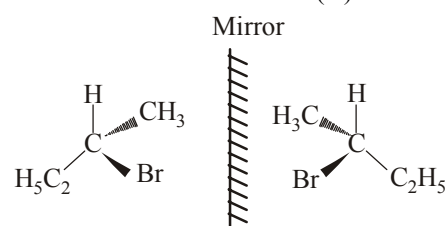
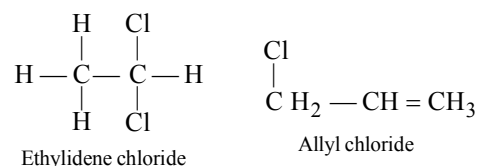
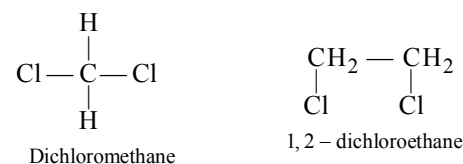
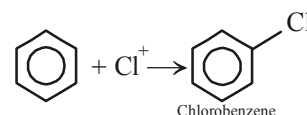
8. (c) Greater the surface area, greater will be the boiling point of a compound. Surface area decreases with increases in branching.

Increasing order of boiling point

< $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

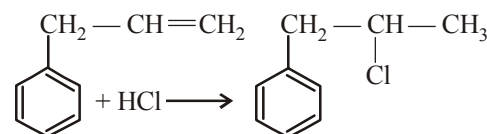
9. (b) Carbon atom in which all four valencies are different is known as Asymmetrical/chiral.

10. (a) Enantiomers are the stereoisomers which are related to each other as non-superimposable mirror images. The enantiomer of molecule (A) is

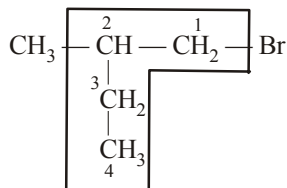
11. (b) Halides in which two halogen atoms are present on the two adjacent carbon atoms are known as *vic*-dihalides.12. (a) Compounds in which the halogen atom is bonded to sp^3 hybridised carbon atom next to carbon-carbon double bond are known as allyl halides.13. (b) $\text{AlCl}_3 + \text{Cl}_2 \longrightarrow [\text{AlCl}_4]^- + \text{Cl}^+$ 

14. (b) If halogen atoms present on the same carbon atom then they are known as gem-dihalides or alkylidene halides.

15. (c) Addition of HCl takes place in accordance with Markownikoff's rule.

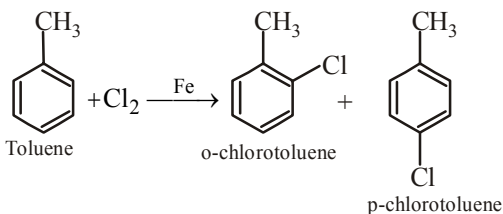


16. (b) It would prefer to undergo S_N2 reaction.
 S_N2 reactions occur if there is less steric crowding on α -carbon of alkyl halide. In case of primary alkyl halides, steric crowding is very less. So, it would prefer to undergo S_N2 reaction.
17. (d) All compounds are tertiary alkyl but bond formed between carbon and iodine (C—I) is weakest bond due to higher difference in size of carbon and iodine.
18. (c) IUPAC name

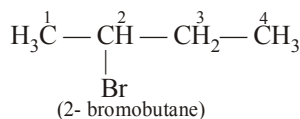


1-bromo-2 methylbutane

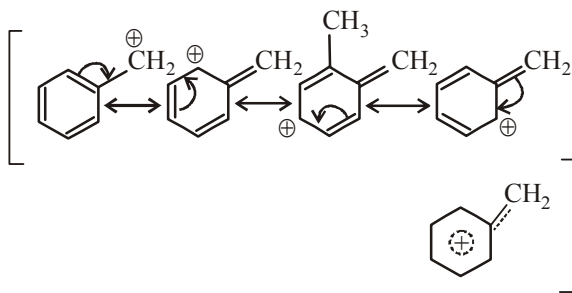
19. (b) $\text{H}_3\text{C}-\text{H}_2\text{C}-\text{H}-\text{C}(\text{Br})-\text{CH}_2-\text{CH}_3$
 IUPAC name is 3-bromopentane.
20. (d) Toluene react with chlorine in presence of iron and in absence of light, by substitution on benzene ring.



21. (c) $\text{CH}_3\text{Cl} + \text{NH}_3 \xrightarrow{\text{Excess}} \text{CH}_3\text{NH}_2 + \text{HCl}$
 Methanamine
22. (a) Carbon in which four bonds are different is known as Chiral carbon.



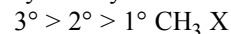
23. (a) In $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ carbocation is $\text{C}_6\text{H}_5\text{CH}_2^+$ which is stable due to resonance.



24. (b) If carbon atom has all four valencies with four different groups then it is called as asymmetric/chiral carbon.

25. (a) All those compounds which follow S_N1 mechanism during nucleophilic substitution reaction will give racemic mixture.

Order of reactivity of alkyl halides for S_N1 .



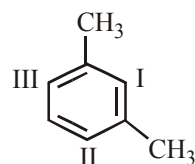
Thus, $\text{CH}_3-\text{CH}(\text{C}_2\text{H}_5)-\text{Br}$ contains a 2° carbon so

gives a racemic product.

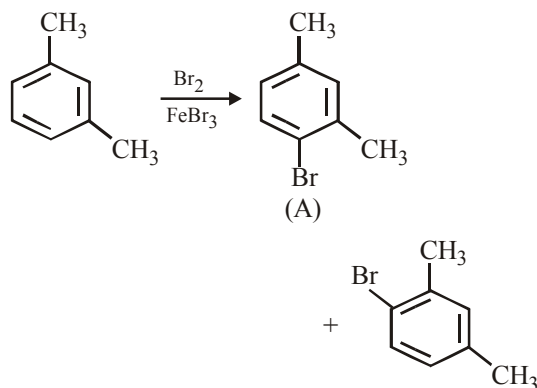
26. (c) The substitution is faster if the electron withdrawing group is at ortho and para position because electron density is high at these positions as chlorine is electron donating group which increase electron density at ortho and para position. Therefore, it has partial double bond character, and is not easy to break. In compound (ii) and (iii) both has one electron withdrawing group but in compound (ii) electron withdrawing ($-\text{NO}_2$) group is present at ortho position, so rate of reaction in compound (ii) is more than that of (iii) while (i) has no electron withdrawing group.
27. (d) If electron releasing group is present at ortho or para position it decreases the rate of nucleophilic substitution reaction. In compound (iii) electron releasing group is present at meta position w.r.t. chlorine, so the impact is nothing but in compound (ii) it is present at ortho position.
28. (d) If electron withdrawing group is present at ortho and para position then the nucleophilic substitution reaction rate increases.
29. (c) If electron releasing group is present at ortho and para position w.r.t. to chlorine it decreases the rate of nucleophilic substitution reaction.
30. (a) Greater the surface area, greater will be the intermolecular forces of attraction and intermolecular forces of attraction is directly proportional to boiling point. Surface area is larger for larger size of halogen.
31. (d) Boiling point is directly proportional to size of the molecule. All contains same halogen atom but different hydrocarbon part. Larger the different hydrocarbon part larger the boiling point.

NEET/AIPMT (2013-2017) Questions

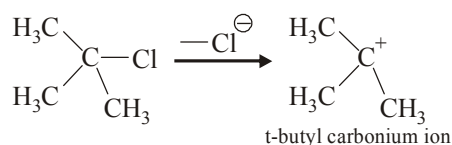
32. (c) Methyl group is ortho para directing but due to steric hindrance effect, generated by two CH_3 groups substitution will not take place on position (I). Hence only two products are possible.



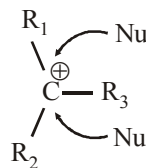
i.e.



33. (a) Tertiary butyl chloride will give the most stable tertiary carbonium ion among the other given compounds



34. (b) In $\text{S}_{\text{N}}1$ reaction, carbocation a planar species as intermediate is formed.



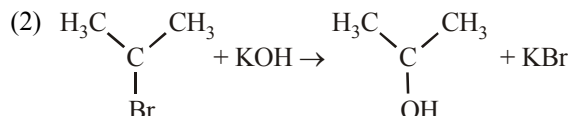
So attack from below or above the plane can take place.

If 50% attack below and above the plane of carbocation take place than 100% racemization occurs but it may not be highly probable.

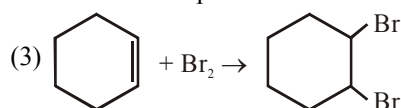
i.e. if inversion occurs more than retention leading to partial racemization.

35. (b) (1) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{Br} + \text{KOH} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$

This is dehydrohalogenation reaction which is an example of elimination reaction.



Replacement of Br^- by OH^- is substitution reaction thus it is a nucleophilic substitution reaction.



Above reaction involves addition of Br_2 across double bond. Thus it is called addition reaction.

Chapter 25

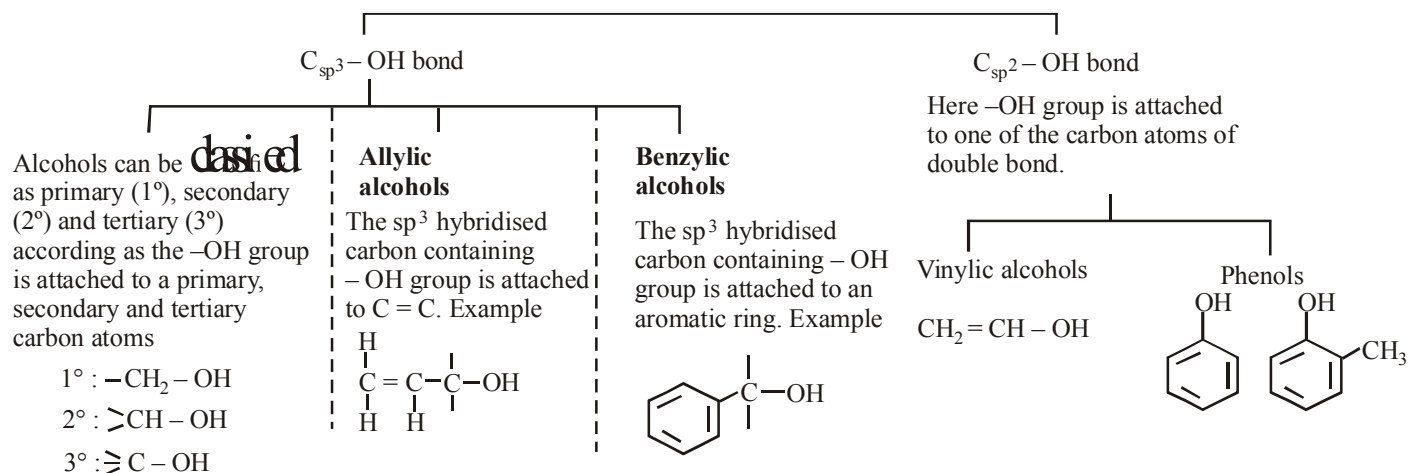
Alcohols, Phenols And Ethers

A. ALCOHOLS AND PHENOLS

CLASSIFICATION

Alcohols and phenols are classified as mono-, di-, tri- or polyhydric depending upon whether they contain one, two, three or many hydroxyl groups in their structures.

Monohydric alcohols are further classified according to hybridisation of C-atom to which -OH is attached.



Ethers are classified as

- (i) simple or symmetrical, if alkyl or aryl groups attached to O-atom are same. Example: CH₃OCH₃.
- (ii) mixed or unsymmetrical if the two groups attached to O-atom are different. Example: CH₃OC₂H₅.

Ethers can be further classified into aliphatic and aromatic ethers. Aromatic ethers can be further classified into phenolic or alkylarylethers (contain alkyl and aryl group) and aryl ethers (contain aryl group only).

STRUCTURES OF FUNCTIONAL GROUPS

In alcohols, O of -OH bond is attached to sp³ hybridised carbon.

The bond angle  is less than tetrahedral angle (109°28') due

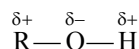
to repulsion between unshared pair of e⁻1s on O.

In phenols, -OH group is attached to sp² hybridised C of aromatic ring. The C-O bond length in phenols is less than methanol.

This is because of

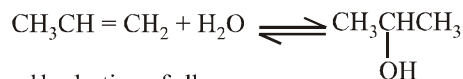
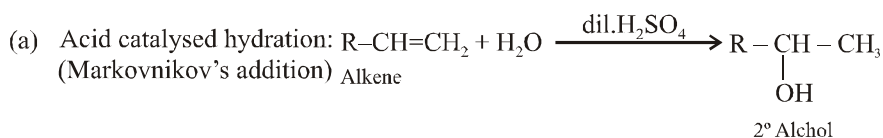
- (i) partial double bond character of C-O bond
- (ii) sp² - hybridised state of C to which O is attached.

In alcohols and phenols due to high electronegativity O-atom acquires partial negative charge and results in formation of dipole.

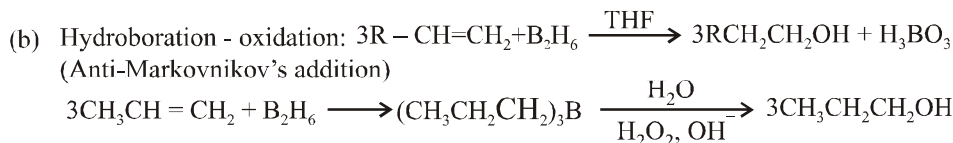
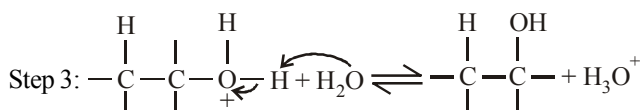
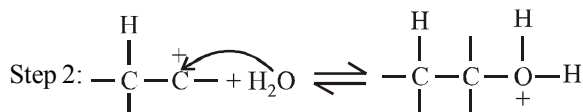
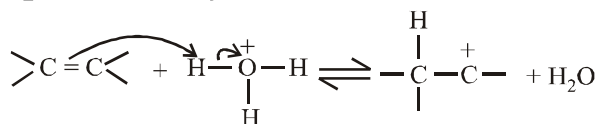
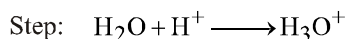
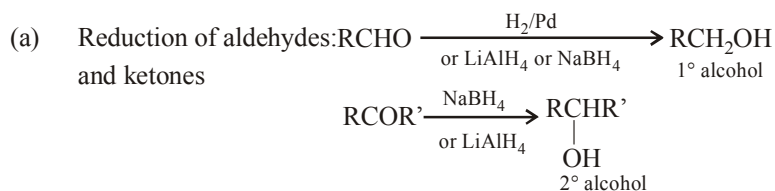


Dipole moment of alcohols are higher than phenols. It is because C-O bond in phenol is less polar due to electron-withdrawing effect of the benzene ring whereas in alcohols C-O bond is more polar due to electron donating effect of -R group.

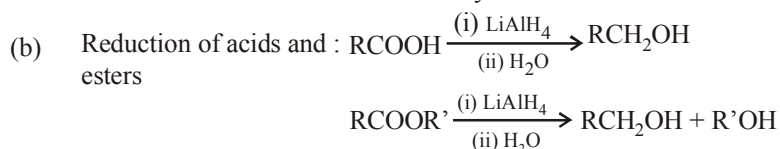
In ethers, 2 bond pairs and 2 lone pairs on O are arranged approximately tetrahedrally. The bond angle is slightly greater than tetrahedral angle due to repulsive interaction between bulky -R groups. The C-O bond length is almost same as that in alcohols.

PREPARATION OF ALCOHOLS**(i) From Alkenes:**

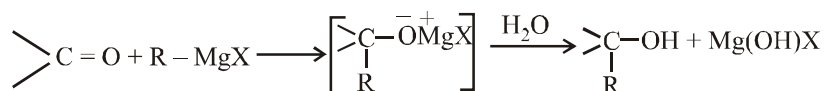
Mechanism of acid catalysed hydration of alkenes:

**(ii) Carbonyl Compounds**

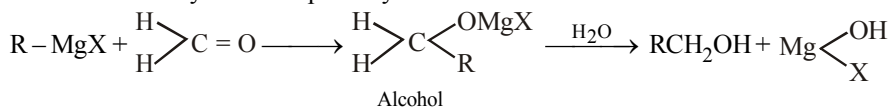
Note: 3° alcohol cannot be obtained by this method.



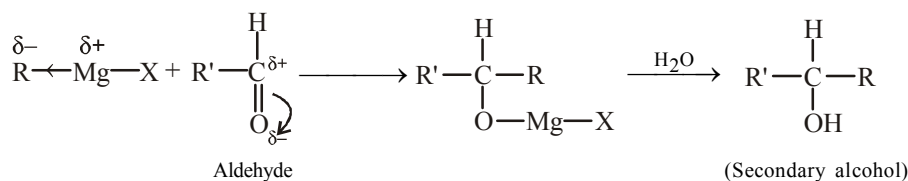
Commercially, acids are reduced to alcohols by first converting them into esters.

(iii) Grignard Reagents:

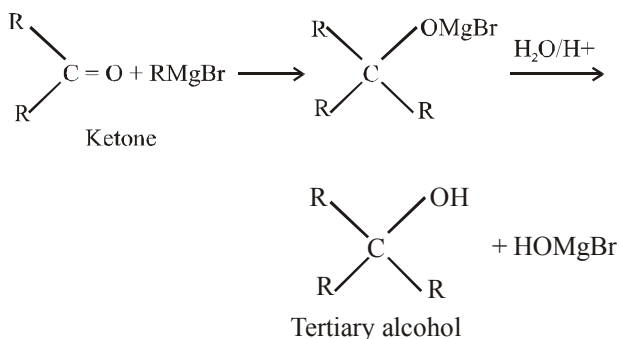
When formaldehyde is used primary alcohols are formed.



with aldehydes other than HCHO secondary alcohols are obtained. Secondary alcohol can also be prepared by addition of esters.

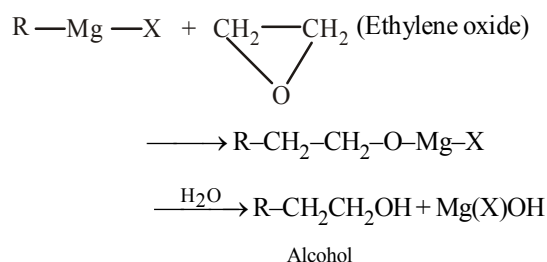


If carbonyl compound is ketone, product will be tertiary alcohol.



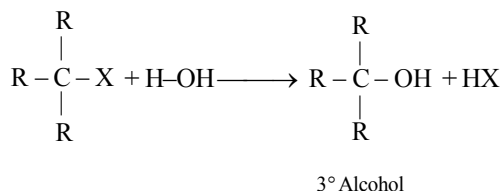
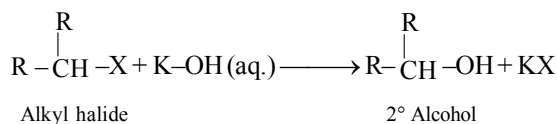
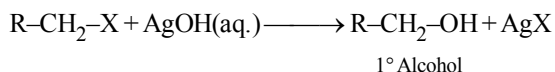
(iv) With Ethylene Oxide :

The alcohol obtained has two carbon atoms more than alkyl group of the Grignard reagent.



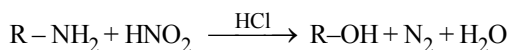
(v) From Alkyl Halides (Hydrolysis) :

The hydrolysis occurs by nucleophilic substitution reaction.



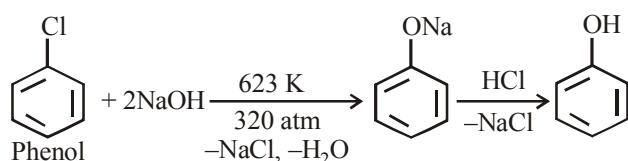
(vi) From Primary Amines :

Primary alcohols are formed when primary amines are treated with nitrous acid (HNO₂)

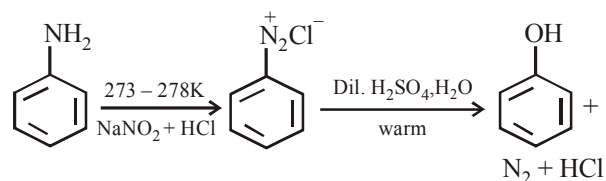


PREPARATION OF PHENOLS

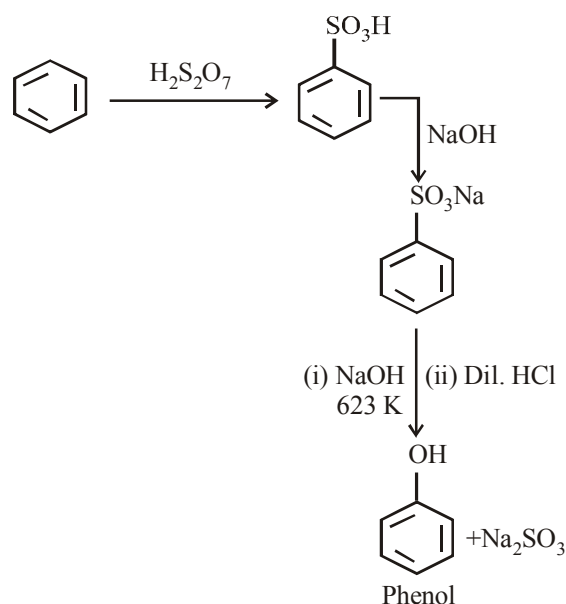
(i) From Haloarenes



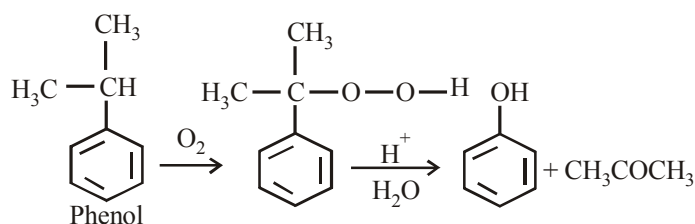
(ii) From Diazonium Salts



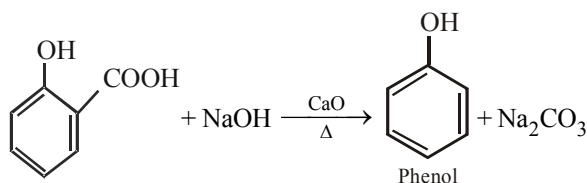
(iii) From Benzene Sulphonic Acid



(iv) From Cumene



(v) By Distilling a Phenolic Acid with Soda Lime (Decarboxylation).



PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS**(i) Boiling points:**

Boiling point increases with increase in number of C-atoms due to increase in van der Waals force.

Among isomeric alcohols, the boiling points decrease with branching as surface area decreases. Thus b. pts. decrease in the order.

Primary > Secondary > Tertiary

B.Pts. of alcohols and phenols are higher than hydrocarbons, alkyl halides and ethers. This is due to intermolecular H-bonding in them as a result of which they exist as associated molecules. This intermolecular H-bonding is missing in hydrocarbons and ethers.

(ii) Solubility:

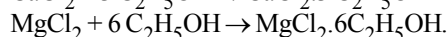
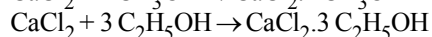
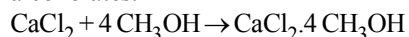
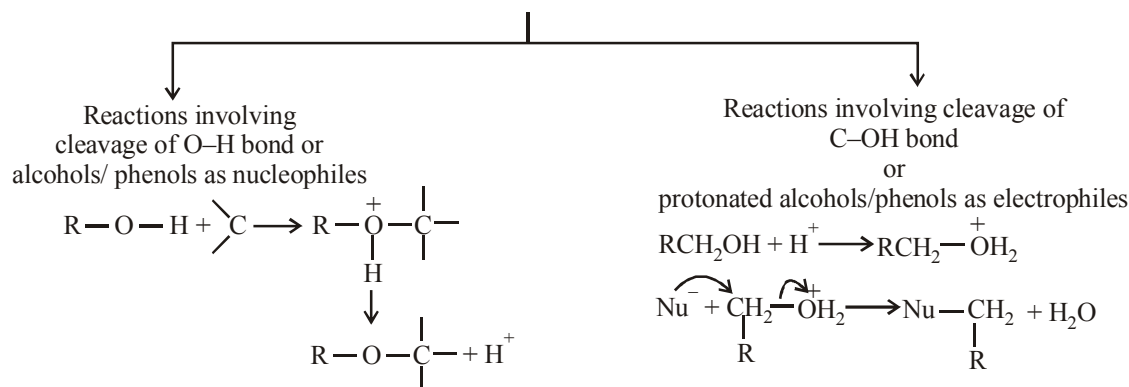
Their solubility in water is due to formation of H-bonds with water. Thus more will be the capability to form H-bonds more will be solubility of given alcohol and phenol.

Solubility decreases with increase in size of alkyl / aryl groups (i.e., hydrophobic group).

The solubility of phenols in water is much lower than that of alcohols because of the larger hydrocarbon part.

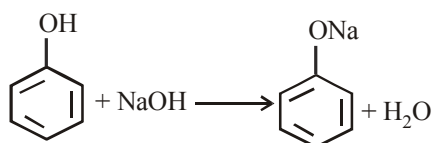
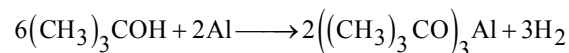
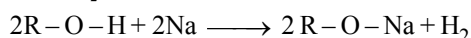
(iii) Formation of Alcoholate

Lower alcohols such as CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ react with anhydrous CaCl_2 or MgCl_2 to form solid derivatives called alcoholates.

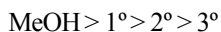
**CHEMICAL PROPERTIES OF ALCOHOLS AND PHENOLS****I. Cleavage of O–H Bond**

The general order of reactivity of alcohols in this type of reaction is :-

Primary > Secondary > Tertiary

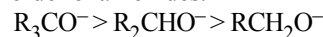
(i) Acidity of Alcohols and Phenols:

The acidic order of alcohols is



Acidity of alcohols: They are acidic due to polar O–H bond. Alkyl groups increase the e^- density on O atom of the O–H bond. As a result, the electrons of the O–H bond are not sufficiently attracted towards the oxygen atom thereby decreasing the polarity of O–H bond. Thus tending to decrease the acid strength. Acid strength order of alcohols will be $1^\circ > 2^\circ > 3^\circ$. Due to same reason, alcohols are weaker acids than water.

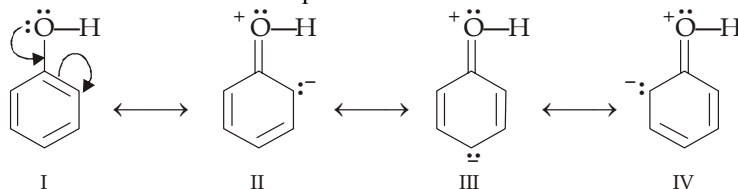
Basic strength order of alkoxides.



Acidity of phenols: Phenols are stronger acids than alcohols and water. This is explained as follows:

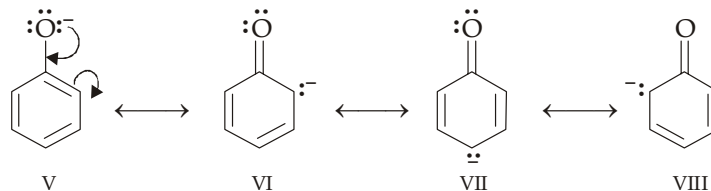
(a) In phenols, –OH is directly attached to sp^2 -hybridised carbon. As a result, e^- density on O decreases. This increases polarity of O–H bond resulting in increased ionisation of phenols than alcohols.

Further, greater acidity of a phenol than an alcohol is due to possibility of resonance in phenol which leads to electron-deficient oxygen atom. Presence of electron-deficient oxygen atom (see structures II, III and IV) in turn weakens the $-\text{O}^+-\text{H}$ bond, and thus facilitates release of proton.



Such structures are not possible in alcohols.

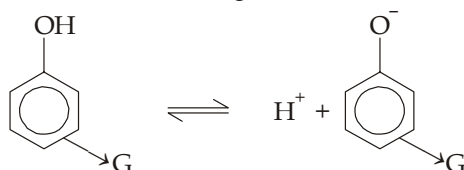
- (b) Once hydrogen atom is removed from phenol, the ion (phenoxide) is very much stabilized due to delocalization of its negative charge.



Resonance in phenoxide ion (note that structures VI to VIII are equivalent)

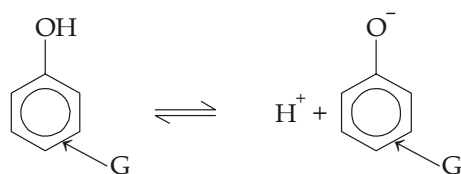
Remember that phenoxide ion is very much more stable than the parent compound phenol because phenoxide ion does not involve charge separation, while in phenol three equivalent resonating structures (II to IV) involve charge separation.

- (c) Electron-withdrawing substituents increase the acidity of phenols; while electron-releasing substituents decrease acidity.



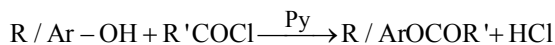
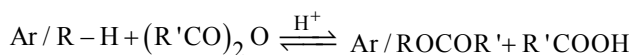
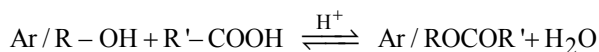
G withdraws electrons, thus disperses the -ve charge of the ion, stabilises it and hence increases ionization of the parent phenol.

(where $G = -\text{NO}_2, -\text{CN}, -\text{CHO}, -\text{COOH}, -\text{NR}_3^+, -\text{X}$)



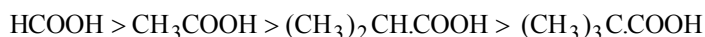
G releases electrons, thus intensifies the -ve charge of the ion, destabilises it and hence decreases ionization of the parent phenol.

(ii) Esterification:

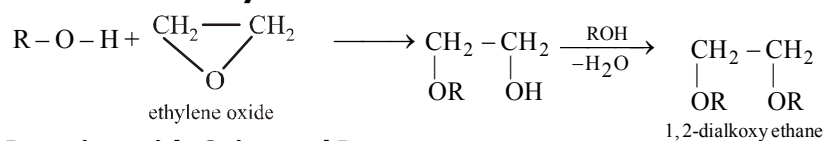


The order of ease of formation of ester

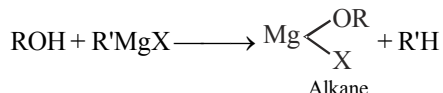
Primary alcohol > Secondary alcohol > Tertiary alcohol



(iii) Reaction with Ethylene Oxide :

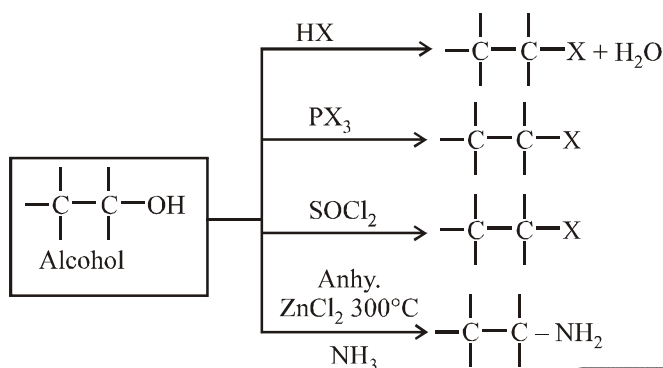


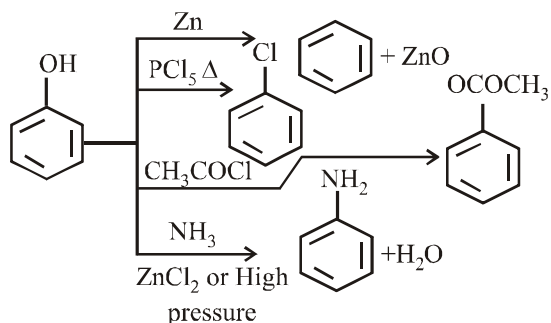
(iv) Reaction with Grignard Reagent :



II. Cleavage of C-OH Bond

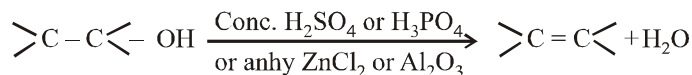
The order of reactivity in this type of reaction is –
3° alcohol > 2° alcohol > 1° alcohol



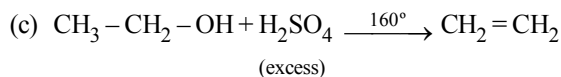
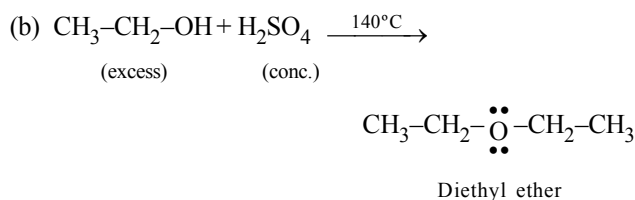
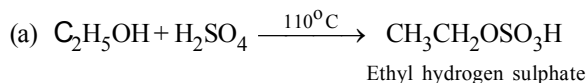


Reactions Involving the Alcohol Molecule as a Whole.

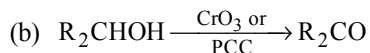
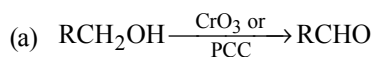
(i) Dehydration:



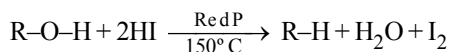
(ii) Reaction with H_2SO_4 :



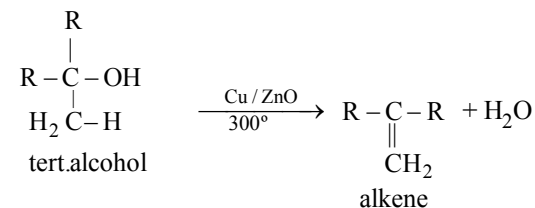
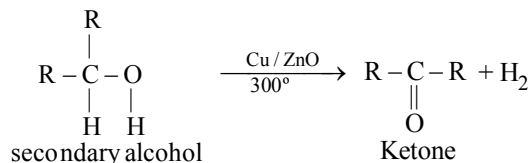
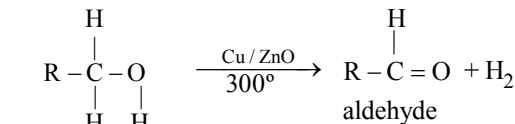
(iii) Oxidation :



(iv) Reduction :



(v) Dehydrogenation :



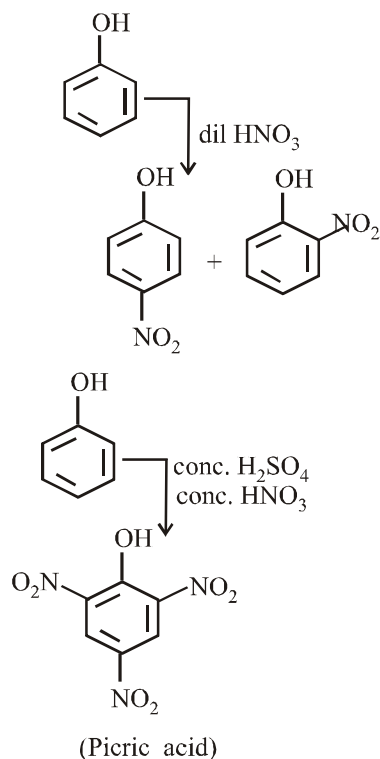
Note:

- Reaction of $\text{R}-\text{OH}$ with HX is used to distinguish between 1° , 2° , 3° alcohols (Lucas test) is discussed later. Reactivity order of halogen acid is $\text{HI} > \text{HBr} > \text{HCl}$
- 1° alcohols on oxidation give aldehydes while 2° alcohols give ketones. 3° alcohols do not undergo oxidation reactions. Under strong conditions like strong oxidising agent (KMnO_4) and elevated temperatures, cleavage of various $\text{C}-\text{C}$ bonds takes place and a mixture of acids with lesser no. of C -atoms is formed.
- With Cu , 3° alcohols undergo dehydration to form alkenes. (where $\text{G} = -\text{R}, -\text{OR}, -\text{NR}_2$)

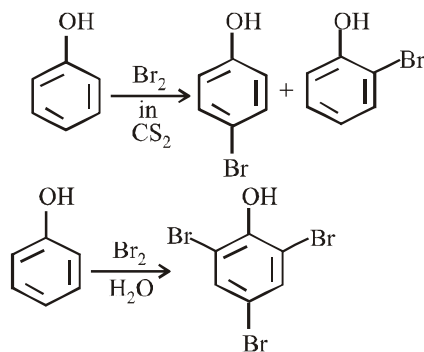
Reactions of Phenols

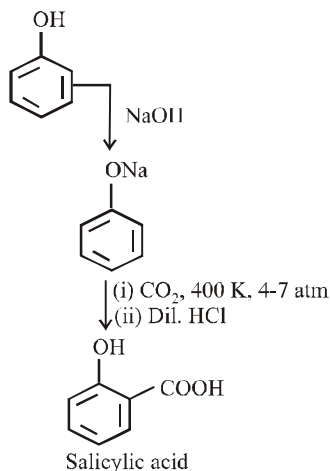
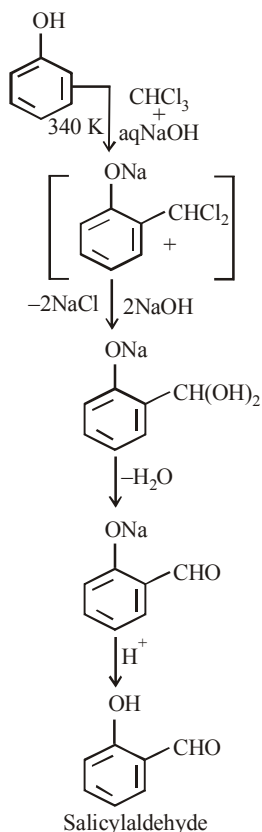
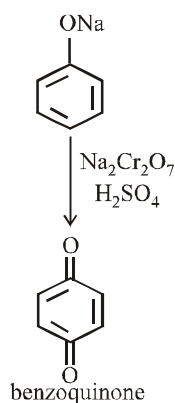
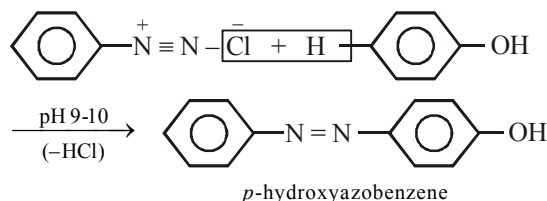
(i) Electrophilic aromatic substitution

(a) Nitration



(b) Halogenation

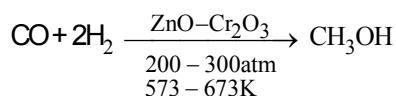


(ii) Kolbe's Reaction**(iii) Riemer-Tiemann Reaction****(iv) Oxidation****(v) Coupling Reaction**

Note: *o*- and *p*- nitrophenols can be separated by steam distillation. *o*- isomer is steam volatile due to intramolecular H-bonding while *p*-isomer is less volatile due to intermolecular H-bonding which causes association of molecules.

SOME IMPORTANT ALCOHOLS**(i) Methanol (CH₃OH)**

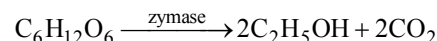
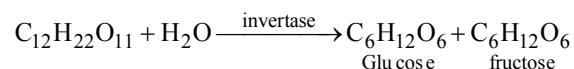
It is also known as wood spirit



It is a colourless liquid and boils at 337 K. It is highly poisonous, even small quantities can cause blindness and large amounts can cause death. It is used as a solvent in paints, varnishes and for making formaldehyde

(ii) Ethanol (C₂H₅OH)

It is obtained by fermentation



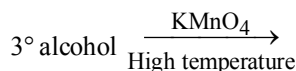
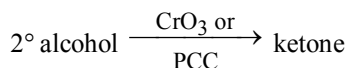
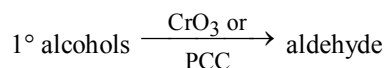
It is a colourless liquid and boils at 351 K. It is used as a solvent in paint industry and in preparation of a number of carbon compounds.

(iii) Denatured Alcohol

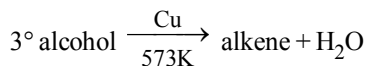
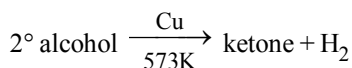
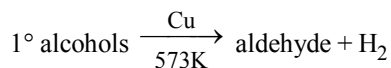
The commercial alcohol is made unfit for drinking by mixing in it some CuSO₄ (to give it a colour) and pyridine (a foul smelling liquid) It is known as **denaturation** of alcohol.

(iv) Power Alcohol

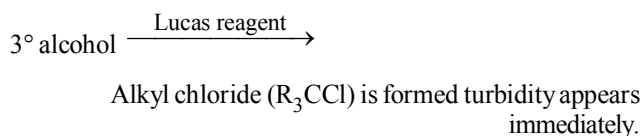
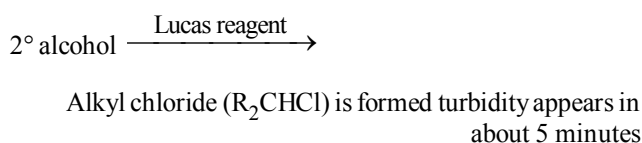
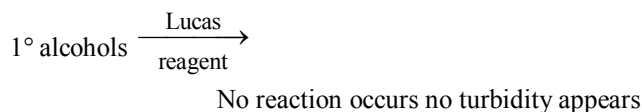
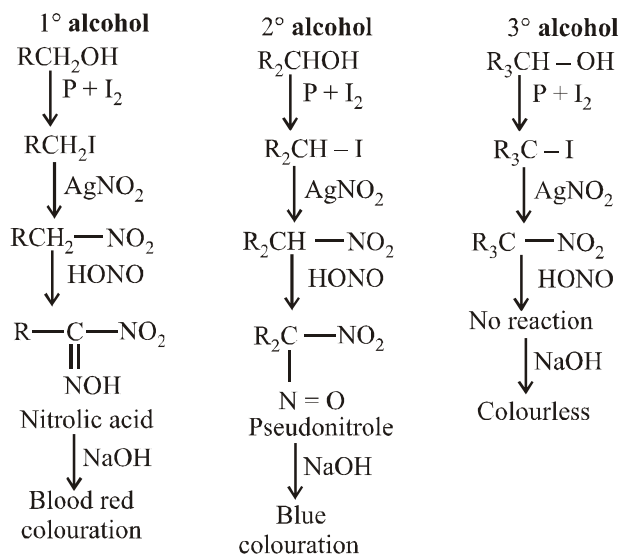
Alcohol used for generating power is called power alcohol. It consists of a mixture of absolute alcohol and petrol roughly in the ratio 20:80.

DISTINCTION BETWEEN 1°, 2° AND 3° - ALCOHOLS**(i) Oxidation**

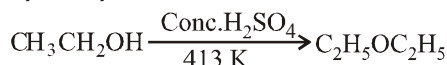
Mixture of acids with lesser no. of C-atoms.

(ii) Action of hot copper**(iii) Lucas Test**

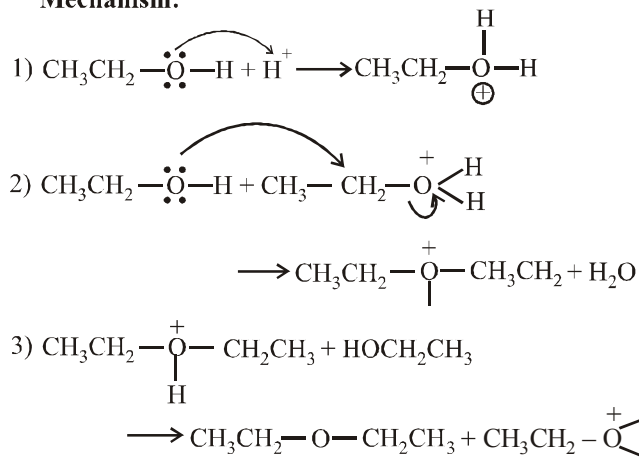
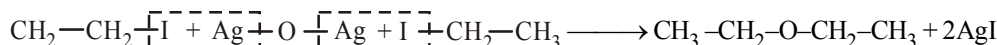
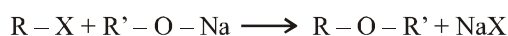
Lucas reagent is an equimolar mixture of conc. HCl and anhydrous ZnCl_2 .

**(iv) Victor Meyer's Test****DISTINGUISH BETWEEN ALCOHOLS AND PHENOLS:**

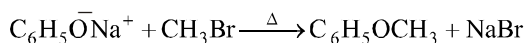
- (i) Phenols react with FeCl_3 to give violet colouration whereas alcohols do not react.
- (ii) Phenols on shaking with bromine water gives a white ppt. of 2, 4, 6-tribromophenol but alcohols do not.

(B) ETHERS**PREPARATION OF ETHERS****(i) By Dehydration of Alcohols**

Mechanism:

**(ii) By reaction of ethyl halide with dry Ag_2O :****(iii) Williamson's Synthesis**

Williamson synthesis can be applied for the synthesis of symmetrical as well as unsymmetrical ethers. It follows S_{N}^2 path, hence it is most successful when the alkyl halide, sulphonate, or sulphate is primary (or methyl). For preparation of 3° ethers, better results are obtained if alkyl halide is 1° . If 3° alkyl halide is used, alkene is formed instead of ether. For phenol ether, phenol is used as phenoxide moiety



This method cannot be used for preparing diaryl ethers since aryl halides do not undergo nucleophilic substitution reactions easily.

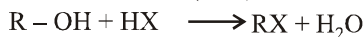
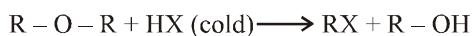
PHYSICAL PROPERTIES OF ETHERS

Ethers are polar but very weakly. Their B.Pts. are comparable to those of alkanes and are much less than alcohols due to absence of H-bonding.

Ethers are only slightly soluble in water. Solubility of lower ethers in water is due to formation of H-bonds. As the molecular mass increases, the solubility of ethers in water decreases due to increase in hydrocarbon part.

CHEMICAL PROPERTIES OF ETHERS

(i) Reaction with HX



with unsymm ethrical ethers,

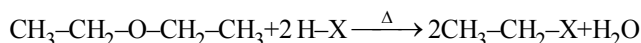


The smaller alkyl group forms the alkyl halide.

If one alkyl group is 3°, then 3° alkyl halide is formed

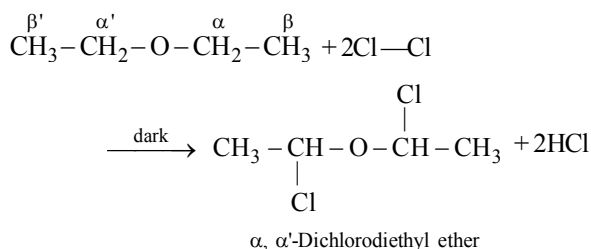
In anisole, CH₃I is the product formed

If HX is hot :

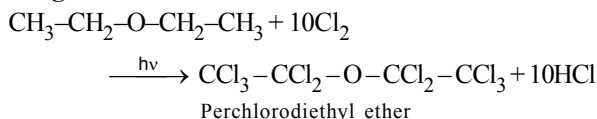


(ii) Halogenation :

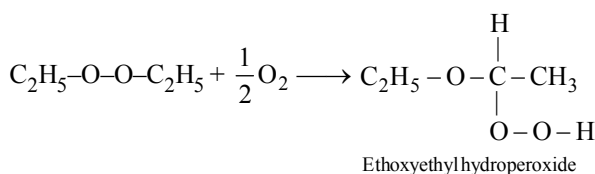
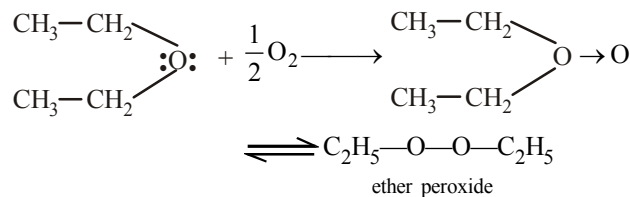
(a) In dark :



(b) In light

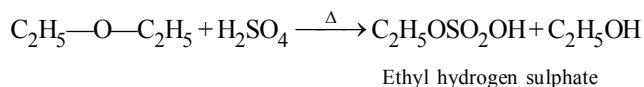


(iii) Oxidation :

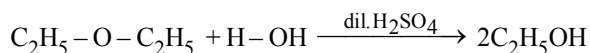


(iv) Reaction with H₂SO₄ :

(a) With conc. H₂SO₄

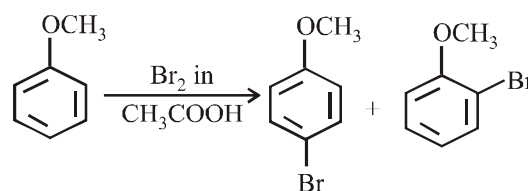


(b) With dil. H₂SO₄ :

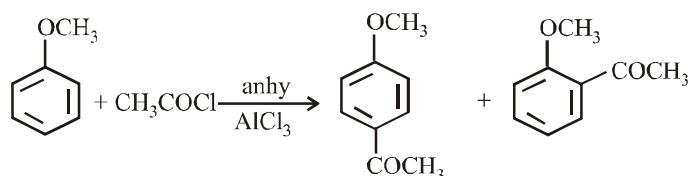
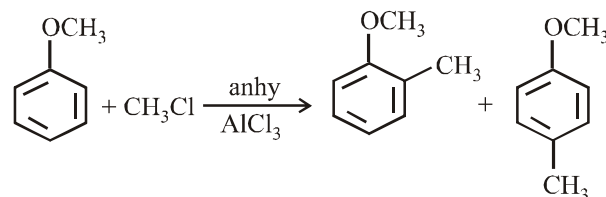


(v) Electrophilic Substitution

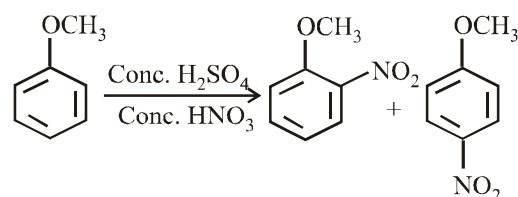
(a) Halogenation:



(b) Friedel-Crafts reaction:

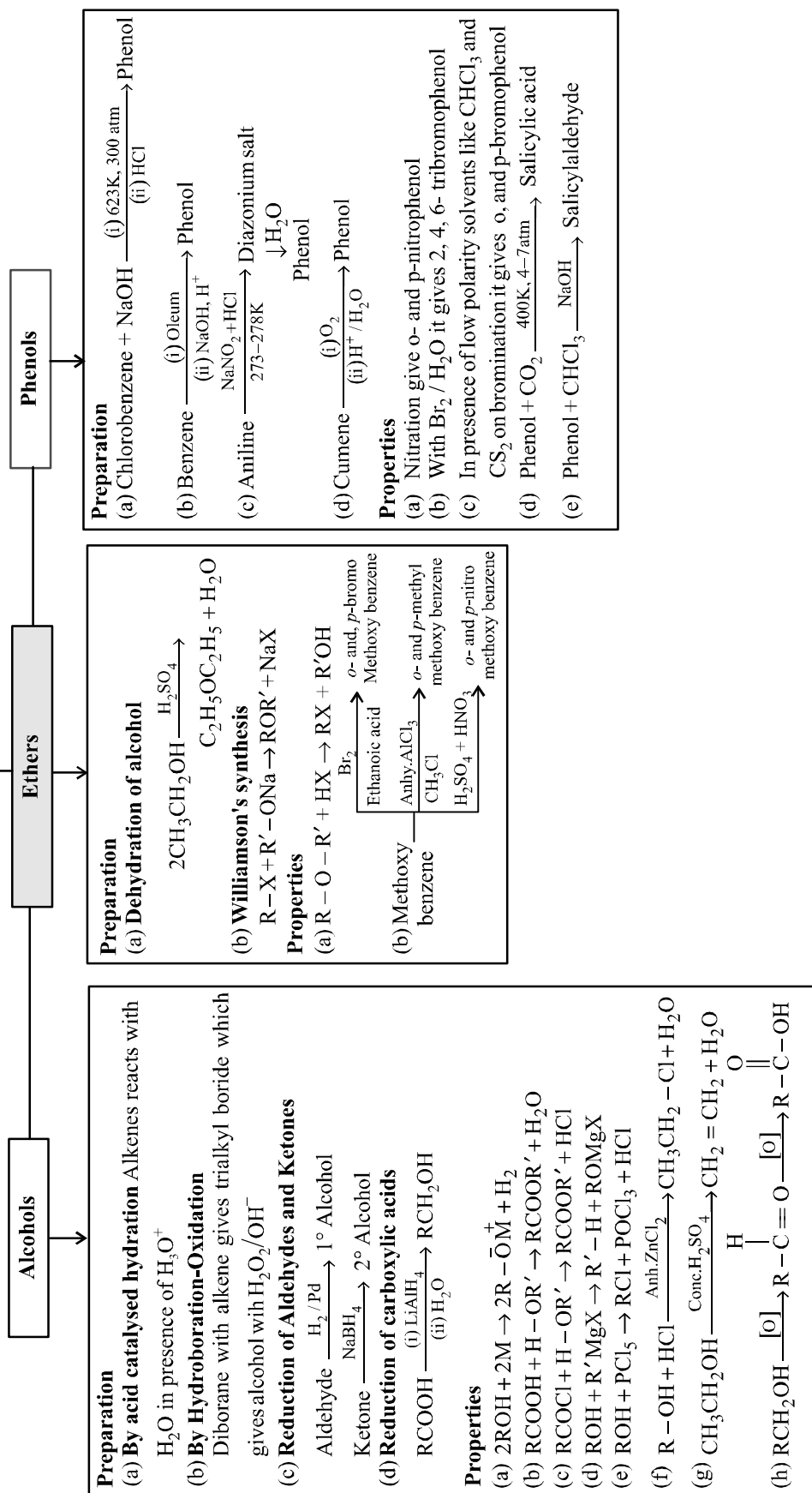


(c) Nitration:



CONCEPT MAP

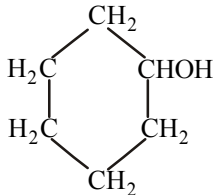
ALCOHOLS, PHENOLS AND ETHERS



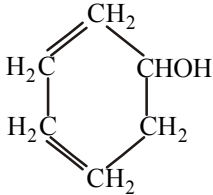
EXERCISE - 1

Conceptual Questions

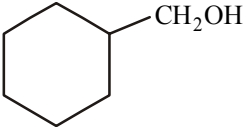
- Lucas reagent is
 - conc. HCl and anhydrous ZnCl_2
 - conc. HNO_3 and hydrous ZnCl_2
 - conc. HCl and hydrous ZnCl_2
 - conc. HNO_3 and anhydrous ZnCl_2
- Glycerol on oxidation with bismuth nitrate produces
 - oxalic acid
 - glyceric acid
 - glyoxalic acid
 - meso oxalic acid
- The alcohol manufactured from water gas is
 - ethanol
 - methanol
 - isobutanol
 - butanol
- Which of the following are isomers ?
 - Methyl alcohol and dimethyl ether
 - Ethyl alcohol and dimethyl ether
 - Acetone and acetaldehyde
 - Propionic acid and propanone
- Dehydration of alcohol is an example of
 - Redox reaction
 - Elimination reaction
 - Substitution reaction
 - Addition reaction
- Methylated spirit is
 - methanol
 - methanol + ethanol
 - methanoic acid
 - methanamide
- The structural formula of cyclohexanol is



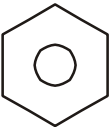
(a)



(b)



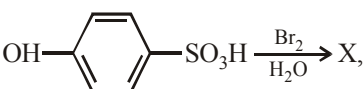
(c)



(d)
- Molecular formula of amyl alcohol is
 - $\text{C}_7\text{H}_{14}\text{O}$
 - $\text{C}_6\text{H}_{13}\text{O}$
 - $\text{C}_5\text{H}_{12}\text{O}$
 - $\text{C}_5\text{H}_{10}\text{O}$
- Phenol is more readily soluble in
 - NaOH solution
 - dil. HCl
 - both NaOH and HCl
 - NaHCO_3
- Absolute alcohol is
 - 100% pure ethanol
 - 95% alcohol + 5% H_2O
 - ethanol + water + phenol
 - 95% ethanol + 5% methanol

- Which of the following is dihydric alcohol ?
 - Glycerol
 - Ethylene glycol
 - Catechol
 - Resorcinol

- The IUPAC name of $\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}} - \text{CH}_3$ is :
 - 1, 1-dimethyl-1, 3-butanediol
 - 2-methyl-2, 4-pentanediol
 - 4-methyl-2, 4-pentanediol
 - 1, 3, 3-trimethyl-1, 3-propanediol

- 

X is identified as

- 2, 4, 6-tribromophenol
 - 2-bromo-4-hydroxybenzene sulphonic acid
 - 3, 5-dibromo-4-hydroxybenzene sulphonic acid
 - 2-bromophenol
- The C–O–H bond angle in ethanol is nearly
 - 90°
 - 104°
 - 120°
 - 180°
 - Methanol is industrially prepared by
 - oxidation of CH_4 by steam at 900°C
 - reduction of HCHO using LiAlH_4
 - reaction HCHO with a solution of NaOH
 - reduction of CO using H_2 and $\text{ZnO} - \text{Cr}_2\text{O}_3$.
 - When alcohol reacts with concentrated H_2SO_4 , intermediate compound formed is :
 - carbonium ion
 - alkoxy ion
 - alkyl hydrogen sulphate
 - none of the above
 - HBr reacts fastest with
 - 2-Methylpropan-1-ol
 - 2-Methylpropan-2-ol
 - propan-2-ol
 - propan-1-ol.
 - In the following reaction 'A' is

$$\text{C}_2\text{H}_5\text{MgBr} + \text{H}_2\text{C} - \underset{\text{O}}{\text{CH}_2} \xrightarrow{\text{H}_2\text{O}} \text{A}$$
 - $\text{C}_2\text{H}_5\text{CH}_2\text{CHO}$
 - $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$
 - $\text{C}_2\text{H}_5\text{CH}_2\text{OH}$
 - $\text{C}_2\text{H}_5\text{CHO}$
 - n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?
 - PCl_5
 - Reduction
 - Oxidation with potassium dichromate
 - Ozonolysis

20. Ethylene oxide when treated with Grignard reagent yields
 (a) tertiary alcohol (b) cyclopropyl alcohol
 (c) primary alcohol (d) secondary alcohol
21. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is
 (a) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CHCH}_2\text{OH} \end{array}$
 (b) PhCHOHCH_3
 (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$
22. The best method to prepare cyclohexene from cyclohexanol is by using
 (a) Conc. HCl + ZnCl_2 (b) Conc. H_3PO_4
 (c) HBr (d) Conc. HCl
23. $\text{C}_6\text{H}_5 - \text{CH} = \text{CHCHO} \xrightarrow{\text{X}} \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_2\text{OH}$. In the above sequence X can be
 (a) H_2 / Ni (b) NaBH_4
 (c) $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$ (d) Both (a) and (b)
24. Which of the following reactions will not result in the formation of anisole?
 (a) Phenol + dimethyl sulphate in presence of a base
 (b) Sodium phenoxide is treated with methyl iodide
 (c) Reaction of diazomethane with phenol
 (d) Reaction of methylmagnesium iodide with phenol
25. Acid catalyzed hydration of alkenes except ethene leads to the formation of
 (a) primary alcohol
 (b) secondary or tertiary alcohol
 (c) mixture of primary and secondary alcohols
 (d) mixture of secondary and tertiary alcohols
26. Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H_2SO_4 followed by boiling with H_2O ?
 (a) Ethylene (b) Propylene
 (c) 2-Methylpropene (d) Isoprene
27. Which one of the following is not formed when glycerol reacts with HI?
 (a) $\text{CH}_3 - \text{CHI} - \text{CH}_3$
 (b) $\text{CH}_3 - \text{CH} = \text{CH}_2$
 (c) $\text{CH}_2\text{OH} - \text{CHI} - \text{CH}_2\text{OH}$
 (d) $\text{CH}_2 = \text{CH} - \text{CH}_2\text{I}$
28. Dehydration of 2-butanol yields
 (a) 1-butene (b) 2-butene
 (c) 2-butyne (d) both (a) and (b)
29. Which of the following reagent is best to change glycerol to acrolein?
 (a) P_2O_5 (b) Conc. H_2SO_4
 (c) Anhydrous CaCl_2 (d) KHSO_4
30. The reaction of Lucas reagent is fastest with:
 (a) $(\text{CH}_3)_2\text{CHOH}$ (b) $\text{CH}_3(\text{CH}_2)_2\text{OH}$
 (c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{COH}$
31. Which one of the following statements is correct?
 (a) Phenol is more acidic than carbonic acid
 (b) Phenol is less acidic than ethyl alcohol
 (c) Phenol is more acidic than ethanol
 (d) Phenol is more acidic than acetic acid
32. Which one of the following alcohols is least soluble in water?
 (a) CH_3OH (b) $\text{C}_3\text{H}_7\text{OH}$
 (c) $\text{C}_4\text{H}_9\text{OH}$ (d) $\text{C}_{10}\text{H}_{21}\text{OH}$
33. In a reaction :

$$\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{hypochlorous acid}} \text{M} \xrightarrow{\text{R}} \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$

 Here M = molecule and R = reagent. The M and R are :
 (a) $\text{CH}_2 - \text{CH}_2$ and KOH
 (b) $\text{CH}_3\text{CH}_2\text{Cl}$ and NaOH
 (c) $\text{CH}_2\text{OH} - \text{CH}_2\text{Cl}$ and aq. NaHCO_3
 (d) $\text{CH}_3\text{CH}_2\text{OH}$ and KOH
34. The dehydration of 2-methylbutanol with conc. H_2SO_4 gives :
 (a) 2-Methylbutene as major product
 (b) Pentene
 (c) 2-Methylbut-2-ene as major product
 (d) 2-Methylpent-2-ene
35. The product formed by the reduction of glycolic acid with HI, is :
 (a) formic acid (b) ethane
 (c) iodoacetic acid (d) glycol
36. Ethyl alcohol can be prepared from Grignard reagent by the reaction of :
 (a) HCHO (b) R_2CO
 (c) RCN (d) RCOCl
37. Which one can differentiate between $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH ?
 (a) H_2O (b) $\text{Na}_2\text{CO}_3 + \text{I}_2$
 (c) NH_3 (d) HCl
38. In the reaction :

$$\text{A} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7} \text{acetone} \xrightarrow{\text{oxidation}} \text{acetic acid}$$

 A is
 (a) 1-propanol (b) 2-butanol
 (c) 2-propanol (d) ethanol
39. In the reaction :

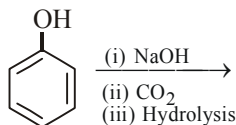
$$\text{CH}_3\text{OH} \xrightarrow{\text{oxidation}} \text{A} \xrightarrow{\text{NH}_3} \text{B} ; \text{A and B respectively are}$$

 (a) HCHO, HCOONH_4 (b) HCOOH , HCOONH_4
 (c) HCOOH , HCONH_2 (d) HCHO, HCONH_2
40. The end product of the reaction

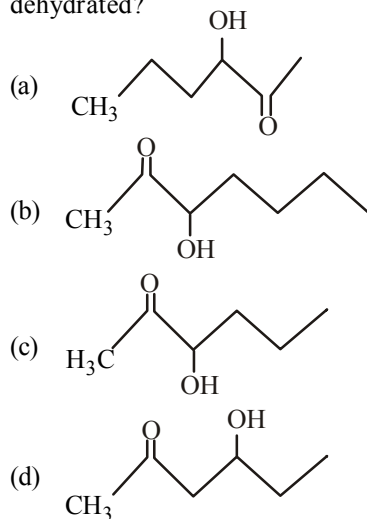
$$\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{PCl}_5} \text{A} \xrightarrow{\text{KCN}} \text{B} \xrightarrow{\text{H}_3\text{O}^+} \text{C}$$
 is
 (a) propanol (b) propanoic acid
 (c) propanamide (d) none of these

41. Glycerol is more viscous than ethanol due to
 (a) high molecular weight
 (b) high boiling point
 (c) many hydrogen bonds per molecule
 (d) Fajan's rule

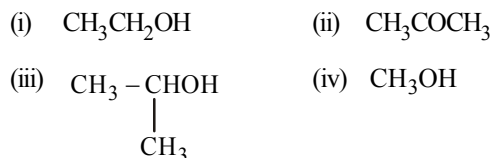
42. The product obtained from the reaction is:



- (a) Benzene (b) Toluene
 (c) Salicylic acid (d) Benzoic acid
43. Which one of the following compounds will be most readily dehydrated?



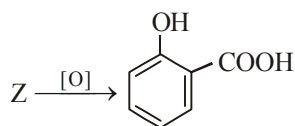
44. Following compounds are given:



Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

- (a) (i) and (ii) (b) (i), (iii) and (iv)
 (c) only (i) (d) (i), (ii) and (iii)
45. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of
 (a) H-bonding in ethanol
 (b) H-bonding in dimethyl ether
 (c) CH_3 group in ethanol
 (d) CH_3 group in dimethyl ether

46. $\text{X} \xrightarrow[\text{Heat}]{\text{NaOH}} \text{Y} \xrightarrow{\text{CHCl}_3 + \text{KOH}} \text{Z}$



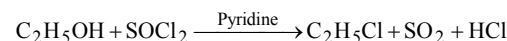
in the above reaction, Z is :

- (a) phenol (b) benzoic acid
 (c) salicylaldehyde (d) carboic acid
47. When phenol is heated with CHCl_3 and NaOH then salicylaldehyde is produced. This reaction is known as
 (a) Rosenmund's reaction (b) Reimer-Tiemann reaction
 (c) Friedel-Crafts reaction (d) Sommelet reaction
48. The intermediate formed in aldol condensation is
 (a) aldol (b) carbanion
 (c) alcohol (d) α -hydrogen ester
49. When phenol is treated with excess bromine water. It gives
 (a) *m*-Bromophenol (b) *o*- and *p*-Bromophenols
 (c) 2,4-Dibromophenol (d) 2,4,6-Tribromophenol.

50. Which is formed when benzaldehyde reacts with nitrous acid



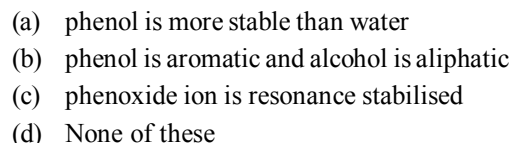
51. The reaction :



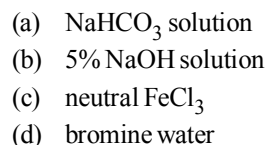
is known as

- (a) Kharasch effect (b) Williamson's synthesis
 (c) Darzen's procedure (d) Hunsdiecker reaction
52. Benzyl alcohol is obtained from benzaldehyde by:
 (a) Perkin's reaction (b) Wurtz reaction
 (c) Cannizzaro's reaction (d) Claisen's reaction
53. On distillation with Zn dust, phenol gives :
 (a) acetophenone (b) benzoic acid
 (c) benzene (d) benzophenone
54. The most suitable reagent for the conversion of $\text{RCH}_2\text{OH} \longrightarrow \text{RCHO}$ is :
 (a) KMnO_4
 (b) $\text{K}_2\text{Cr}_2\text{O}_7$
 (c) CrO_3
 (d) PCC (pyridine chlorochromate)

55. Phenol is more acidic than alcohol because.



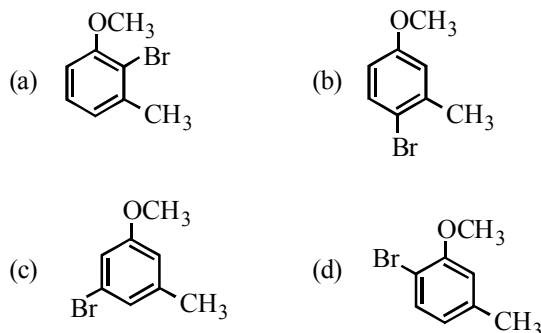
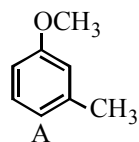
56. To distinguish between salicylic acid and phenol, one can use :



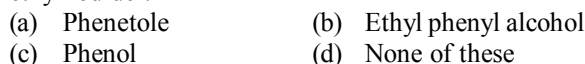
57. Which of the following has lowest boiling point ?



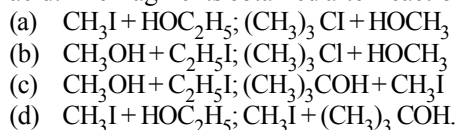
58. The major product obtained on the monobromination (with $\text{Br}_2/\text{FeBr}_3$) of the following compound A is :



59. Which one is formed when sodium phenoxide is heated with ethyl iodide ?



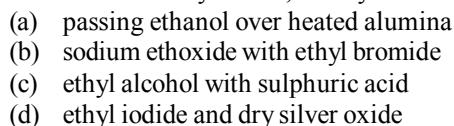
60. $\text{CH}_3\text{OC}_2\text{H}_5$ and $(\text{CH}_3)_3\text{C}-\text{OCH}_3$ are treated with hydriodic acid. The fragments obtained after reactions are



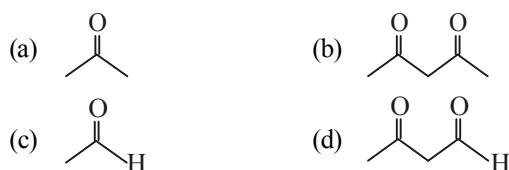
61. In the reaction $\text{Ar}-\text{OH} + \text{RX} \xrightarrow{\text{alkali}} \text{A}$, A is



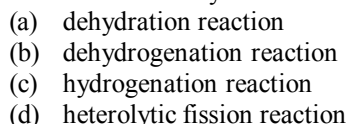
62. In Williamson's synthesis, ethoxyethane is prepared by



63. Maximum enol content is in



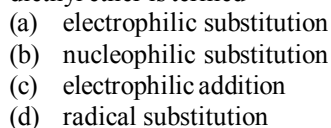
64. Formation of diethyl ether from ethanol is based on a



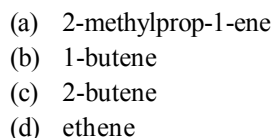
65. A fruity smell is produced by the reaction of $\text{C}_2\text{H}_5\text{OH}$ with



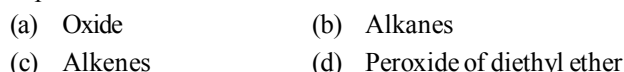
66. The reaction of sodium ethoxide with ethyl iodide to form diethyl ether is termed



67. The major product of the reaction between tert-butyl chloride and sodium ethoxide is



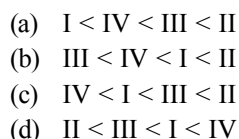
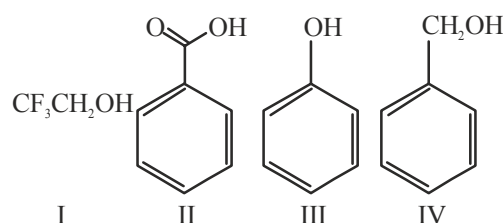
68. Which of the following product is formed, when ether is exposed to air ?



69. Ether which is liquid at room temperature is



70. What is the correct order of acidity from weakest to strongest acid for these compounds?



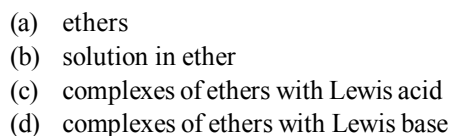
71. In the following reaction



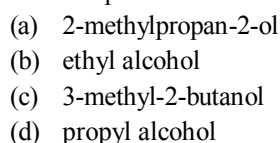
72. The ether that undergoes electrophilic substitution reactions is



73. Etherates are



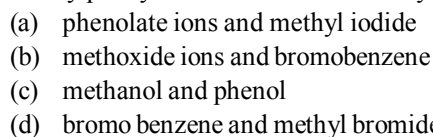
74. The compound that undergoes dehydration very easily is



75. Diethyl ether on heating with conc. HI gives two moles of



76. Methylphenyl ether can be obtained by reacting

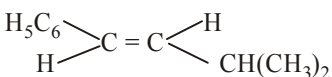
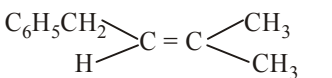
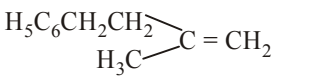
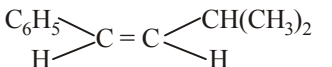


93. Isopropylbenzene is oxidized in the presence of air to compound 'A'. When compound 'A' is treated with dilute mineral acid, the aromatic product formed is

- (a) phenol (b) benzene
(c) benzaldehyde (d) acetophenone

94. The main product of the following reaction is



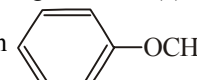
- (a) 
(b) 
(c) 
(d) 

95. Phenol is heated with a solution of mixture of KBr and KBrO_3 . The major product obtained in the above reaction is :

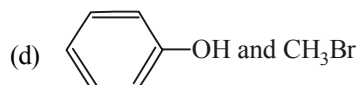
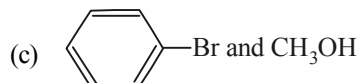
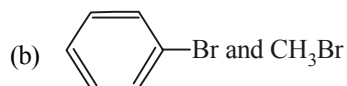
- (a) 2-Bromophenol (b) 3-Bromophenol
(c) 4-Bromophenol (d) 2, 4, 6-Tribromophenol

96. Which of the following reagents may be used to distinguish between phenol and benzoic acid?

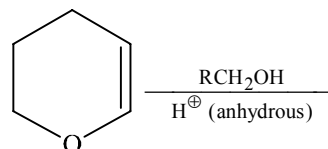
- (a) Aqueous NaOH (b) Tollen's reagent
(c) Molisch reagent (d) Neutral FeCl_3

97. In the reaction  $\xrightarrow{\text{HBr}}$ the products are

- (a)  and H_2



98. The major product of the following reaction is



- (a) a hemiacetal (b) an acetal
(c) an ether (d) an ester

99. Which one of the following compounds will be most readily attacked by an electrophile ?

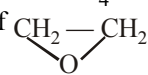
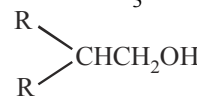
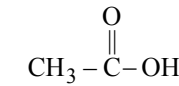
- (a) Chlorobenzene (b) Benzene
(c) Phenol (d) Toluene

100. Propene, $\text{CH}_3\text{CH}=\text{CH}_2$ can be converted into 1-propanol by oxidation. Indicate which set of reagents amongst the following is ideal to effect the above conversion ?

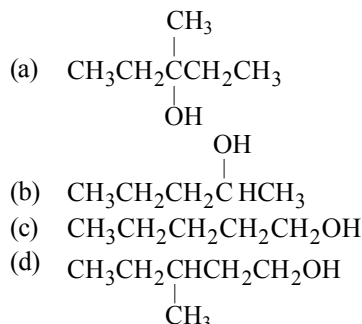
- (a) KMnO_4 (alkaline)
(b) Osmium tetroxide ($\text{OsO}_4/\text{CH}_2\text{Cl}_2$)
(c) B_2H_6 and alk. H_2O_2
(d) O_3/Zn

EXERCISE - 2

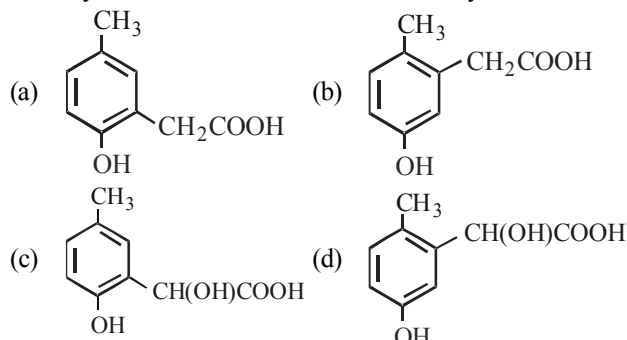
Applied Questions

- Which one of the following reagents is used to reduce an aldehyde to primary alcohol?
 - $\text{N}_2\text{H}_4/\text{KOH}$
 - Zn/Hg and conc. HCl
 - LiAlH_4
 - Alkaline CuSO_4 containing Rochelle salt
- Reaction of  with RMgX leads to formation of
 - RCHOHR
 - RCHOHCH_3
 - $\text{RCH}_2\text{CH}_2\text{OH}$
 - 
- The ionization constant of phenol is higher than that of ethanol because :
 - phenoxide ion is bulkier than ethoxide
 - phenoxide ion is stronger base than ethoxide
 - phenoxide ion is stabilized through delocalization
 - phenoxide ion is less stable than ethoxide
- Which one of the following reaction provides a primary alcohol?
 - Hydration of alkyne
 - Oxymercuration of alkene
 - Oxidation hydroboration of alkene
 - Reaction of Grignard reagent with acetaldehyde
- Propan-1-ol may be prepared by the reaction of propene with
 - H_3BO_3
 - $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$
 - $\text{B}_2\text{H}_6, \text{NaOH}-\text{H}_2\text{O}_2$
 - 
- During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is
 - formation of carbocation
 - elimination of water
 - formation of an ester
 - protonation of alcohol molecule

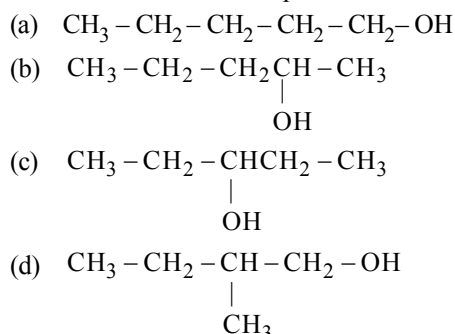
7. When 2-methoxypropane is heated with HI, in the mole ratio 1 : 1, the major products formed are
 (a) methanol and 2-iodopropane
 (b) methyl iodide and 2-propanol
 (c) methyl iodide and 2-iodopropane
 (d) methanol and 2-propanol
8. Among the following compounds which can be dehydrated very easily is



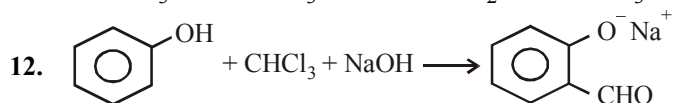
9. *p*-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is



10. A compound 'A' having the molecular formula $\text{C}_5\text{H}_{12}\text{O}$, on oxidation gives a compound 'B' with molecular formula $\text{C}_5\text{H}_{10}\text{O}$. Compound 'B' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirror test. The structure of compound 'A' is



11. HBr reacts with $\text{CH}_2 = \text{CH} - \text{OCH}_3$ under anhydrous conditions at room temperature to give
 (a) $\text{BrCH}_2 - \text{CH}_2 - \text{OCH}_3$ (b) $\text{H}_3\text{C} - \text{CHBr} - \text{OCH}_3$
 (c) CH_3CHO and CH_3Br (d) BrCH_2CHO and CH_3O^-



The electrophile involved in the above reaction is

- (a) trichloromethyl anion (CCl_3^-)
 (b) formyl cation (CHO^+)
 (c) dichloromethyl cation (CHCl_2^+)
 (d) dichlorocarbene ($:\text{CCl}_2$)

13. Phenol $\xrightarrow{\text{NaNO}_2 / \text{H}_2\text{SO}_4}$ B $\xrightarrow{\text{H}_2\text{O}}$ C $\xrightarrow{\text{NaOH}}$ D
 Name of the above reaction is

- (a) Liebermann's reaction
 (b) Phthalein fusion test
 (c) Reimer-Tiemann reaction
 (d) Schotten-Baumann reaction

14. Phenol can be converted to *o*-hydroxy-benzaldehyde by
 (a) Kolbe's reaction (b) Reimer-Tiemann reaction
 (c) Wurtz reaction (d) Cannizzaro reaction

15. $\text{Y (mix)} \xleftarrow[2]{\text{conc. HI}} (\text{CH}_3)_3\text{C} - \text{O} - \text{CH}_3$
 $\xrightarrow[1]{\text{Anhydrous HI}} \text{X (mix)}$

- (a) X and Y are identical mixture of CH_3I and $(\text{CH}_3)_3\text{C} - \text{OH}$
 (b) X and Y are identical mixture of CH_3OH & $(\text{CH}_3)_3\text{C} - \text{I}$
 (c) X is mixture of CH_3I and $(\text{CH}_3)_3\text{C} - \text{OH}$
 (d) Y is mixture of CH_3OH & $(\text{CH}_3)_3\text{C} - \text{I}$

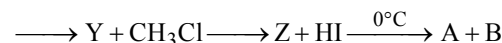
16. What are the starting materials to get 2-methylpropene as the major product ?

- (a) Sodium methoxide and *sec*-butyl bromide.
 (b) Sodium ethoxide and *sec*-butyl bromide.
 (c) Sodium *tert*-butoxide and ethyl bromide.
 (d) Sodium methoxide and *tert*-butyl bromide.

17. $\text{ClCH}_2\text{CH}_2\text{OH}$ is stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$ because of

- (a) -I effect of Cl increases negative charge on O atom of alcohol
 (b) -I effect of Cl disperses negative charge on O atom to produce more stable cation
 (c) -I effect of Cl disperses negative charge on O atom to produce more stable anion
 (d) None of these

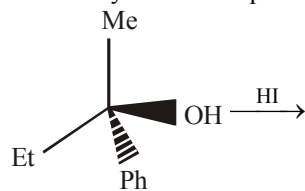
18. $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2 / \text{H}_2\text{O}} \text{X} + \text{Na}$



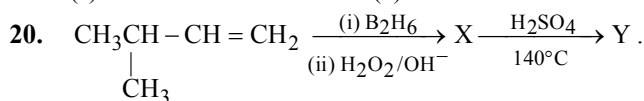
What are A and B ?

- (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$ & CH_3I
 (b) $\text{CH}_3 - \overset{\text{CH}_3}{\text{CH}} - \text{OH}$ & CH_3I
 (c) $\text{CH}_3 - \overset{\text{CH}_3}{\text{CH}} - \text{I}$ & CH_3OH
 (d) $\text{CH}_3 - \text{CH}_2\text{CH}_2\text{I}$ & CH_3OH

19. How many iodides are produced in more than 5% yield?



- (a) 5 (b) 2
(c) 3 (d) 1



What is Y?

- (a) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_3$
(b) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}=\text{CH}_2$
(c) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{CH}_3$
(d) $\text{CH}_3-\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)-\text{O}-\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)-\text{CH}_3$

21. Compound 'A' of molecular formula $\text{C}_4\text{H}_{10}\text{O}$ on treatment with Lucas reagent at room temperature gives compound 'B'. When compound 'B' is heated with alcoholic KOH, it gives isobutene. Compound 'A' and 'B' are respectively
(a) 2-methyl-2-propanol and 2-methyl-2-chloropropane
(b) 2-methyl-1-propanol and 1-chloro-2-methylpropane
(c) 2-methyl-1-propanol and 2-methyl-2-chloropropane
(d) butan-2-ol and 2-chlorobutane

22. (X) $\xrightarrow{\text{H}_3\text{O}^+} \text{Y} + \text{Z}$ (Y and Z both give the Iodoform test). The compound X is –

- (a) $\text{CH}_3-\text{CH}=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_3$
(b) $\text{CH}_3-\text{C}(\text{H})(\text{CH}_3)-\text{O}-\text{CH}_2-\text{CH}_3$
(c) $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_3$
(d) Both (a) and (c)

DIRECTIONS for Qs. 23 to 25 : These are Assertion-Reason type questions. Each of these questions contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is true, Statement-2 is true; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement-1 is true, Statement-2 is false
(d) Statement-1 is false, Statement-2 is true
23. **Statement-1** : A triester of glycerol and palmitic acid on boiling with aqueous NaOH gives a solid cake having soapy touch
Statement-2 : Free glycerol is liberated which is a greasy solid
24. **Statement-1** : Phenol undergo Kolbe reaction, ethanol does not.
Statement-2 : Phenoxide ion is more basic than ethoxide ion.
25. **Statement-1** : Lucas reagent is a mixture of anhydrous ZnCl_2 and concentrate HCl
Statement-2 : Primary alcohol produce ppt. with Lucas reagents.

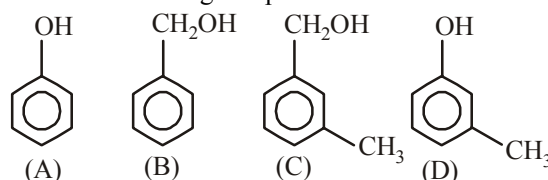
EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

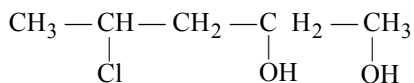
1. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields
(a) *o*-cresol (b) *m*-cresol
(c) 2,4-dihydroxytoluene (d) benzyl alcohol
2. How many alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ are chiral in nature?
(a) 1 (b) 2
(c) 3 (d) 4
3. What is the correct order of reactivity of alcohols in the following reaction?
 $\text{R}-\text{OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{R}-\text{Cl} + \text{H}_2\text{O}$
(a) $1^\circ > 2^\circ > 3^\circ$ (b) $1^\circ < 2^\circ < 3^\circ$
(c) $3^\circ > 2^\circ > 1^\circ$ (d) $3^\circ > 1^\circ > 2^\circ$
4. $\text{CH}_3\text{CH}_2\text{OH}$ can be converted into CH_3CHO by

- (a) catalytic hydrogenation
(b) treatment with LiAlH_4
(c) treatment with pyridinium chlorochromate
(d) treatment with KMnO_4
5. The process of converting alkyl halides into alcohols involves
(a) addition reaction (b) substitution reaction
(c) dehydrohalogenation (d) rearrangement reaction
6. Which of the following compounds is aromatic alcohol?



- (a) A, B, C, D (b) A, D
(c) B, C (d) A

7. Give IUPAC name of the compound given below.



- (a) 2-chloro-5-hydroxyhexane
 (b) 2-hydroxy-5-chlorohexane
 (c) 5-chlorohexan-2-ol
 (d) 2-chlorohexan-5-ol
8. IUPAC name of m-cresol is
- (a) 3-methylphenol (b) 3-chlorophenol
 (c) 3-methoxyphenol (d) benzene-1,3-diol
9. IUPAC name of the compound $\text{CH}_3 - \text{CH} - \text{OCH}_3$ is



-
- (a) 1-methoxy-1-methylethane
 (b) 2-methoxy-2-methylethane
 (c) 2-methoxypropane
 (d) isopropylmethyl ether
10. Which of the following species can act as the strongest base?

- (a) $^{\ominus}\text{OH}$ (b) $^{\ominus}\text{OR}$
 (c) $^{\ominus}\text{OC}_6\text{H}_5$ (d) $^{\ominus}\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$

11. Which of the following compounds will react with sodium hydroxide solution in water?

- (a) $\text{C}_6\text{H}_5\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (c) $(\text{CH}_3)_3\text{COH}$ (d) $\text{C}_2\text{H}_5\text{OH}$

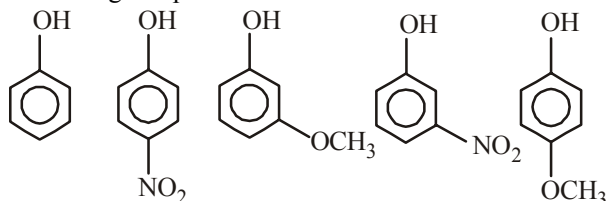
12. Phenol is less acidic than

- (a) ethanol (b) o-nitrophenol
 (c) o-methylphenol (d) o-methoxyphenol

13. Which of the following is most acidic?

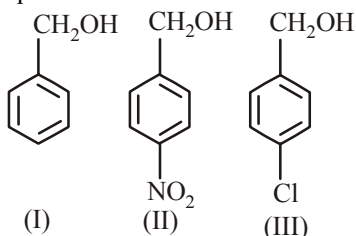
- (a) Benzyl alcohol (b) Cyclohexanol
 (c) Phenol (d) m-chlorophenol

14. Mark the correct order of decreasing acid strength of the following compounds.



- (a) $\text{V} > \text{IV} > \text{II} > \text{I} > \text{III}$ (b) $\text{II} > \text{IV} > \text{I} > \text{III} > \text{V}$
 (c) $\text{IV} > \text{V} > \text{III} > \text{II} > \text{I}$ (d) $\text{V} > \text{IV} > \text{III} > \text{II} > \text{I}$

15. Mark the correct increasing order of reactivity of the following compounds with HBr/HCl .



- (a) $\text{I} < \text{II} < \text{III}$ (b) $\text{II} < \text{I} < \text{III}$
 (c) $\text{II} < \text{III} < \text{I}$ (d) $\text{III} < \text{II} < \text{I}$

16. Arrange the following compounds in increasing order of boiling point.

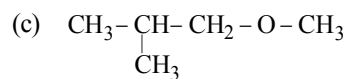
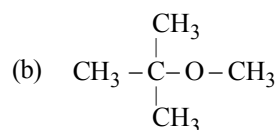
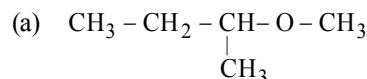
Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

- (a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
 (b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
 (c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
 (d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

NEET/AIPMT (2013-2017) Questions

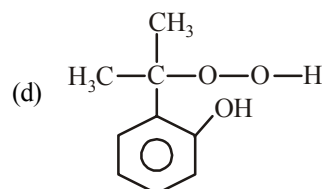
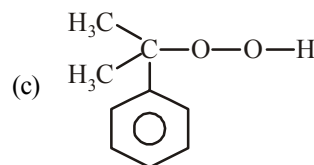
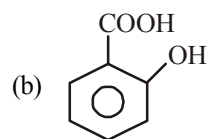
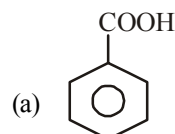
17. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI ?

[2013]



18. Phenol is distilled with Zn dust followed by Friedel Crafts alkylation with propyl chloride in the presence of AlCl_3 to give a compound (B). (B) is oxidised in the presence of air to form the compound (C). The structural formula of (C) is

[NEET Kar. 2013]



19. Number of isomeric alcohols of molecular formula $\text{C}_6\text{H}_{14}\text{O}$ which give positive iodoform test is [NEET Kar. 2013]

- (a) two (b) three
 (c) four (d) five

20. Among the following sets of reactants which one produces anisole? [2014]

(a) CH_3CHO ; RMgX
 (b) $\text{C}_6\text{H}_5\text{OH}$; NaOH ; CH_3I
 (c) $\text{C}_6\text{H}_5\text{OH}$; neutral FeCl_3
 (d) $\text{C}_6\text{H}_5\text{—CH}_3$; CH_3COCl ; AlCl_3

21. Which of the following will not be soluble in sodium hydrogen carbonate? [2014]

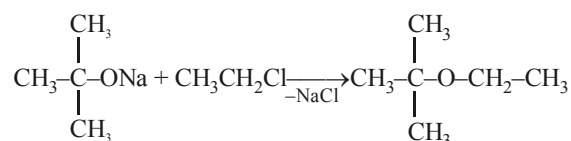
(a) 2, 4, 6-trinitrophenol
 (b) Benzoic acid
 (c) *o*-Nitrophenol
 (d) Benzenesulphonic acid

22. Identify Z in the sequence of reactions: [2014]



(a) $\text{CH}_3\text{—}(\text{CH}_2)_3\text{—O—CH}_2\text{CH}_3$
 (b) $(\text{CH}_3)_2\text{CH}_2\text{—O—CH}_2\text{CH}_3$
 (c) $\text{CH}_3(\text{CH}_2)_4\text{—O—CH}_3$
 (d) $\text{CH}_3\text{CH}_2\text{—CH}(\text{CH}_3)\text{—O—CH}_2\text{CH}_3$

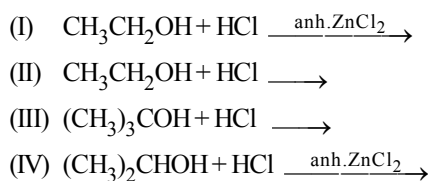
23. The reaction



is called :-

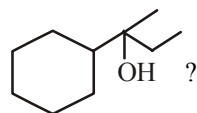
- (a) Williamson continuous etherification process [2015]
 (b) Etard reaction
 (c) Gatterman - Koch reaction
 (d) Williamson Synthesis
24. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group? [2015 RS]
- (a) $\text{—CH}_2\text{Cl}$ (b) —COOH
 (c) —CHCl_2 (d) —CHO

25. Which of the following reaction (s) can be used for the preparation of alkyl halides? [2015 RS]

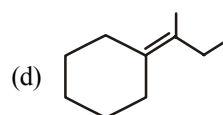
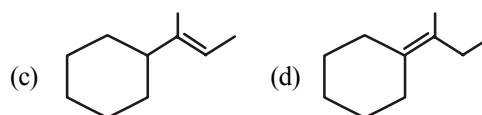
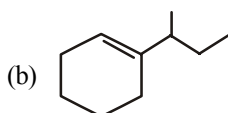
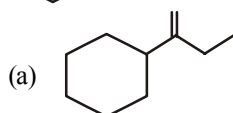


(a) (I), (III) and (IV) only
 (b) (I) and (II) only
 (c) (IV) only
 (d) (III) and (IV) only

26. Which of the following is not the product of dehydration of



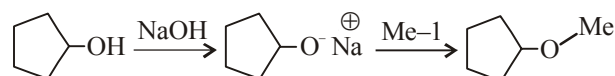
[2015 RS]



27. Which of the following reagents would distinguish cis-cyclopenta-1,2-diol from the trans-isomer? [2016]

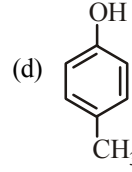
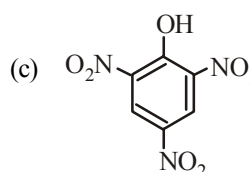
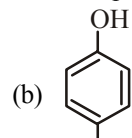
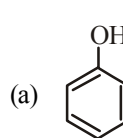
(a) Acetone
 (b) Ozone
 (c) MnO_2
 (d) Aluminium isopropoxide

28. The reaction



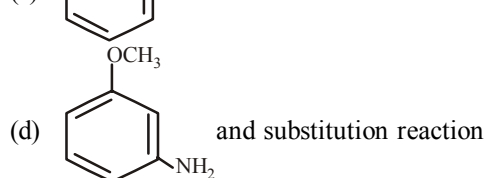
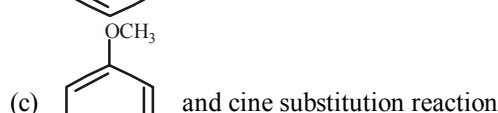
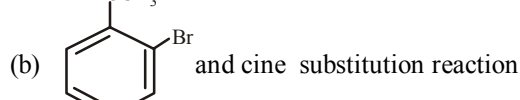
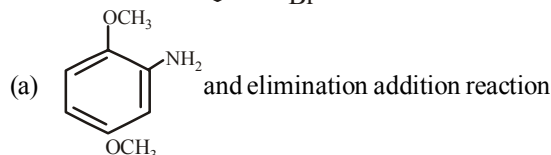
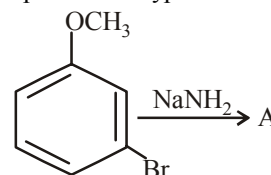
Can be classified as :-

- (a) Williamson ether synthesis reaction [2016]
 (b) Alcohol formation reaction
 (c) Dehydration reaction
 (d) Williamson alcohol synthesis reaction
29. Which one is the most acidic compound? [2017]



30. The heating of phenyl-methyl ethers with HI produces [2017]
- (a) Iodobenzene (b) Phenol
 (c) Benzene (d) Ethyl chlorides

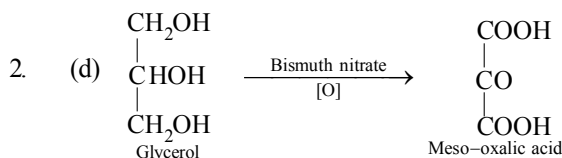
31. Identify A and predict the type of reaction [2017]



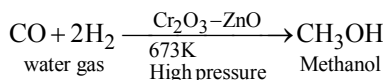
Hints & Solutions

EXERCISE - 1

1. (a) Lucas reagent is conc. HCl + anhyd. ZnCl_2 .

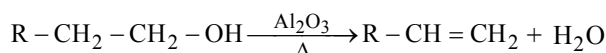


3. (b) Methanol

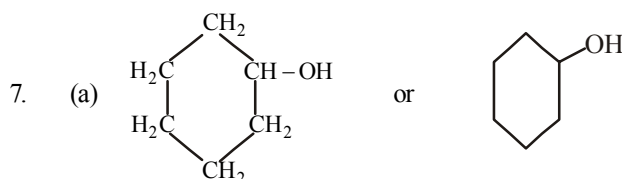


4. (b) $\text{C}_2\text{H}_5\text{OH}$ and $\text{CH}_3 - \text{O} - \text{CH}_3$ are isomers.

5. (b) Example

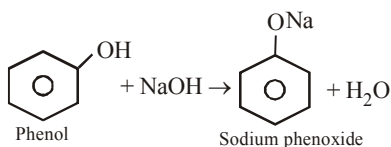


6. (b) 5-10 % methanol and remaining ethanol is called methylated spirit. It is also known as denatured alcohol because it is unfit for drinking.



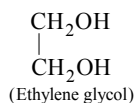
8. (c)

9. (a) Phenol is more soluble in NaOH and forms salts.

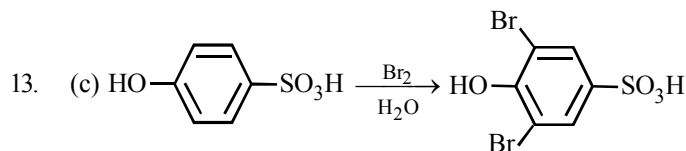


10. (a)

11. (b) Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.

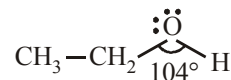


12. (b)
- $$\begin{array}{ccccccc} & & & \text{CH}_3 & & & \\ & & & | & & & \\ \text{CH}_3 - & \text{CH} - & \text{CH}_2 - & \text{C} - & \text{CH}_3 \\ & | & & | & \\ & \text{OH} & & \text{OH} & \end{array}$$
- 2-methyl- 2, 4-pentanediol.



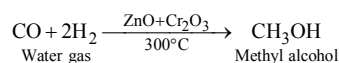
– OH group is highly activating. This is a type of electrophilic substitution reaction at ortho and para position.

14. (b) In $\text{C}_2\text{H}_5\text{OH}$,

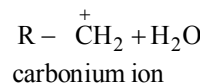


Due to presence of lone pair of electrons on oxygen, there occurs a small decrease in bond angle from the normal tetrahedral bond angle ($109^\circ 28'$)

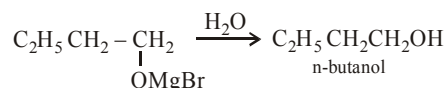
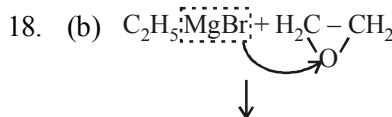
15. (d) Water gas is mixed with half its volume of hydrogen. The mixture is compressed to approximately 200 – 300 atmospheres. It is then passed over a catalyst [$\text{ZnO} + \text{Cr}_2\text{O}_3$] at 300°C . Methyl alcohol vapours are formed which are condensed



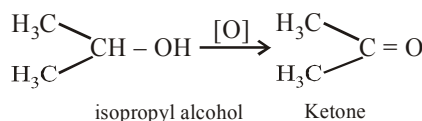
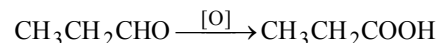
16. (a) $\text{R} - \text{CH}_2 - \text{OH} \xrightarrow[\text{Protonation}]{\text{H}^+}$



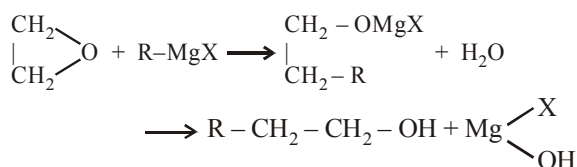
17. (b) Greater the stability of the intermediate carbocation, more reactive is the alcohol. Since 2-methylpropan-2-ol generates 3° carbocation, therefore, it reacts fastest with HBr.



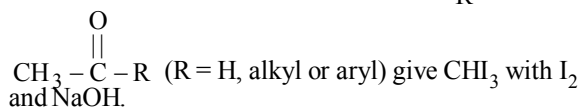
19. (c) Primary alcohol on oxidation give aldehyde which on further oxidation give carboxylic acid whereas secondary alcohols give ketone.



20. (c) Ethylene oxide when treated with Grignard Reagent gives primary alcohol.

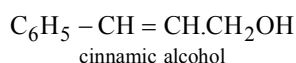


21. (b) The compounds containing $\text{CH}_3 - \underset{\text{R}}{\overset{\text{H}}{\text{C}}} - \text{OH}$ or

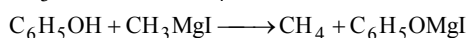


22. (b) Conc. HCl, HBr and conc. HCl + ZnCl₂ all are nucleophiles, thus convert alcohols to alkyl halides. However, conc. H₃PO₄ is a good dehydrating agent which converts an alcohol to an alkene.

23. (b) NaBH₄ and LiAlH₄ attacks only carbonyl group and reduce it into alcohol group.

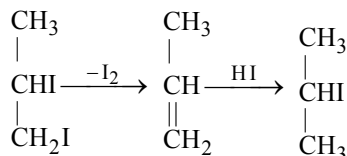
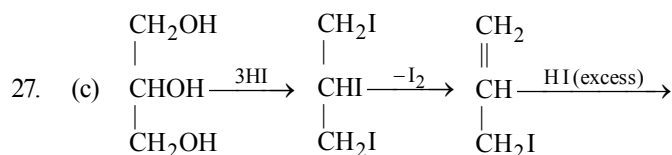
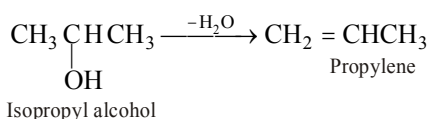


24. (d) Phenol has active (acidic) hydrogen so it reacts with CH₃MgI to give CH₄, and not anisole

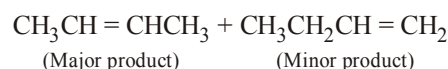
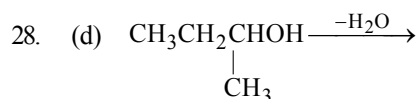


25. (b)

26. (b) Since the compound is formed by hydration of an alkene, to get the structure of alkene remove a molecule of water from the alcohol.



∴ All the compounds except (C), CH₂OH-CHI-CH₂OH are formed during reaction of glycerol with excess HI.



29. (d) Glycerol is dehydrated by using dehydrating agent like P₂O₅ or conc H₂SO₄ or KHSO₄ but KHSO₄ is best of them.

30. (d) Lucas reagent is anhydrous ZnCl₂ and conc. HCl. It is used to distinguish between 1°, 2° and 3° alcohols.

3° alcohols → immediate turbidity

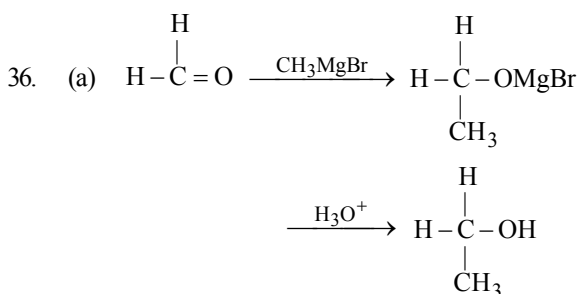
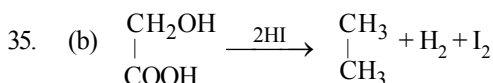
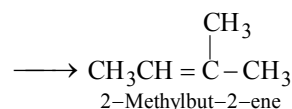
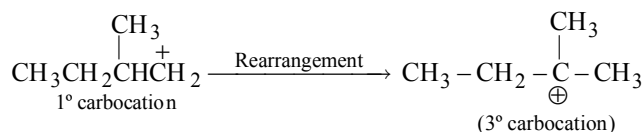
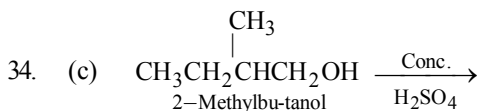
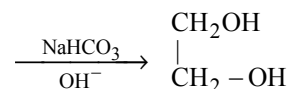
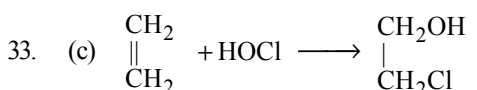
2° alcohols → turbidity after 5 minutes

1° alcohols → No turbidity at room temp.

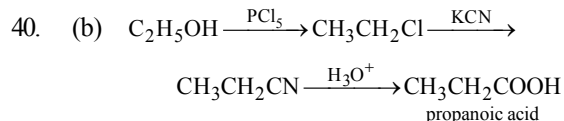
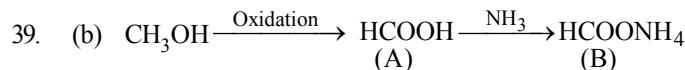
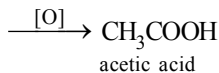
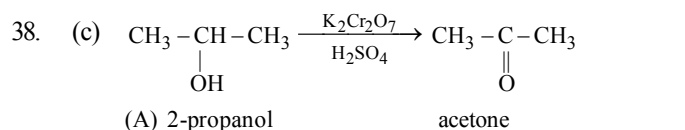
$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{OH} \\ | \\ \text{CH}_3 \end{array}$ is a tertiary alcohol hence it will give fastest reaction with Lucas reagent.

31. (b) Phenol is more acidic than ethanol. Phenols can turn blue litmus paper red but ethanol can not do so.

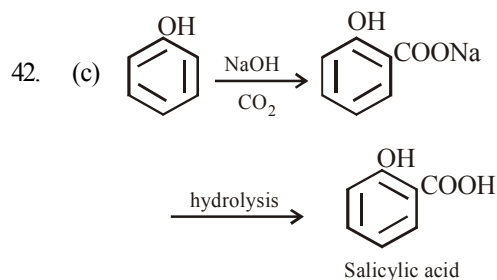
32. (d) Solubility of alcohol in water decreases with increase in molecular mass due to increase in water repelling alkyl part in alcohol.



37. (b) Iodoform test can differentiate between ethyl alcohol and methyl alcohol. Ethyl alcohol contains CH₃CO group so it gives Iodoform test whereas methyl alcohol does not give this test.



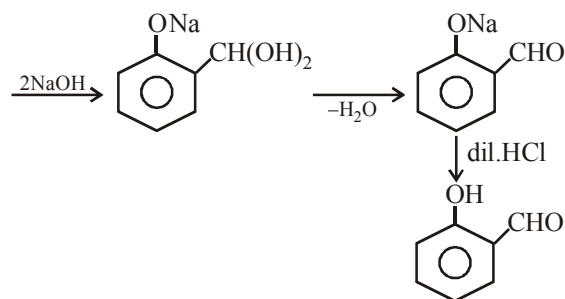
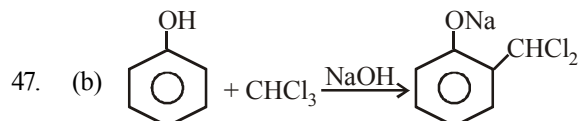
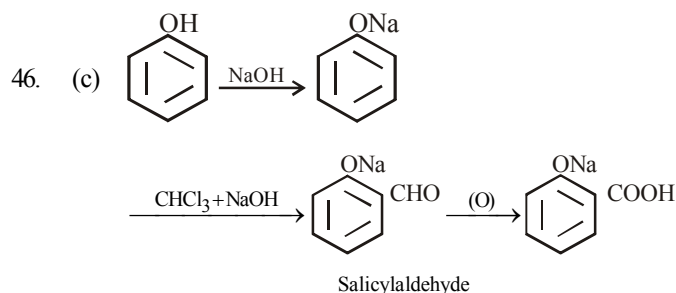
41. (c) Because of larger (three per molecule) number of intermolecular hydrogen bonding in case of glycerol ($\text{CH}_2\text{OH} - \text{CHOH} - \text{CH}_2\text{OH}$) as compared to ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), the attraction between molecules of glycerol is more than that of molecules of ethanol. Due to this glycerol is more viscous than ethanol.



43. (d) The intermediate is carbocation which is destabilised by C = O group (present on α -carbon to the -OH group) in the first three cases. In (d), α -hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the C = O group.

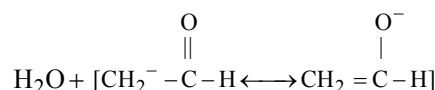
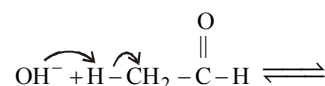
44. (d) Among the given compounds only CH_3OH does not give iodoform reaction.

45. (a) Due to H-bonding boiling point of $\text{C}_2\text{H}_5\text{OH}$ is much higher than isomeric $(\text{CH}_3)_2\text{O}$.

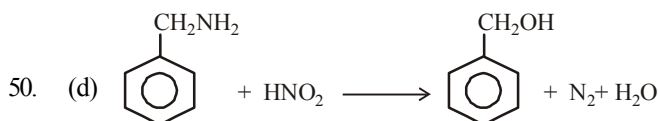
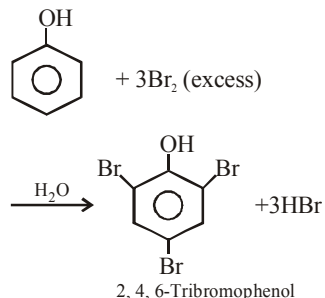


Reimer-Tiemann reaction.

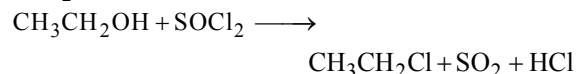
48. (b) Aldol condensation is carried out on aldehydes or ketones having α -hydrogen atom in presence of base which abstracts α -H atom from aldehyde/ketone to form corresponding carbanion which is stabilised by resonance.



49. (d) With Br_2 water, phenol gives 2, 4, 6-tribromophenol.



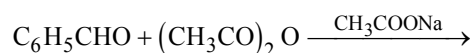
51. (c) Alkyl halides can be prepared by treating alcohol with SOCl_2 .



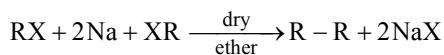
This reaction is known as Darzen's procedure.

Note : SOBr_2 and SOI_2 are not used in this reaction because SOBr_2 is less stable and SOI_2 does not exist.

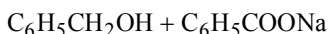
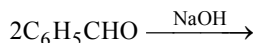
52. (c) Perkin reaction involves reaction of aromatic aldehyde with aliphatic acid anhydride in presence of sodium salt of the same acid as anhydride to form α , β -unsaturated acid.



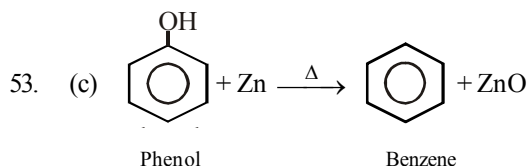
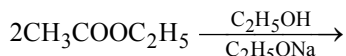
Wurtz reaction involves the reaction of an alkyl halide with metallic sodium in dry ether to form higher hydrocarbon.



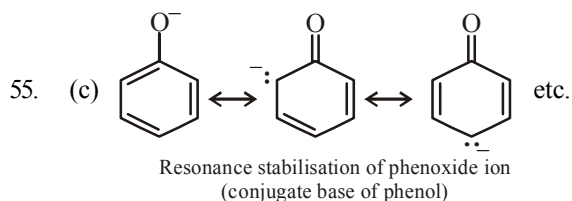
Cannizzaro reaction is given by aldehydes having no α -hydrogen atom to form a mixture of alcohol and sodium salt of the acid. It is a disproportionation reaction in which half of the aldehyde molecules are oxidised and other half reduced in presence of NaOH.



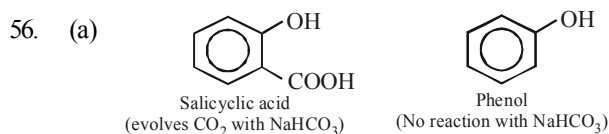
Claisen reaction is the self condensation of esters having α -hydrogen atom in presence of strong base to form β -keto ester.



54. (d) The most suitable reagent for converting alcohol to acetaldehyde is PCC. Other reagent will convert alcohol to acid.

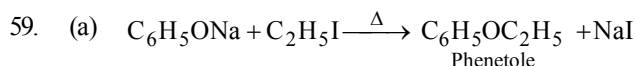


Conjugate base of ethyl alcohol, i.e., $C_2H_5O^-$ does not show resonance.

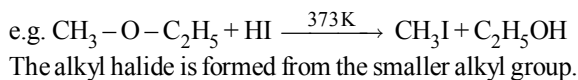


57. (c) *o*-Nitrophenol has intramolecular *H*-bonding.

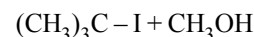
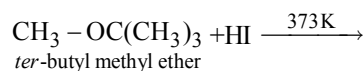
58. (b) The reaction is an example of electrophilic aromatic substitution. Although both OCH_3 and CH_3 groups are *o,p*-directing, the OCH_3 group dominates. Product (b) is favoured because the new coming group (Br) experiences least hindrance.



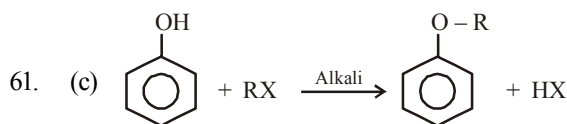
60. (a) In case of unsymmetrical ethers, the site of cleavage depends on the nature of alkyl group.



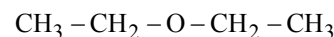
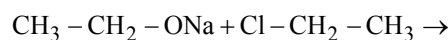
However, in case of tertiary alkyl ether following reaction occurs.



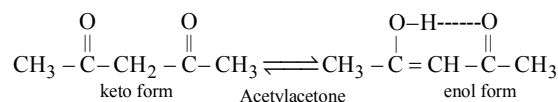
The alkyl halide is formed from the tertiary alkyl group and the cleavage of such ethers occurs by S_N1 mechanism as the product is controlled by the formation of more stable intermediate tertiary carbocation from protonated ether.



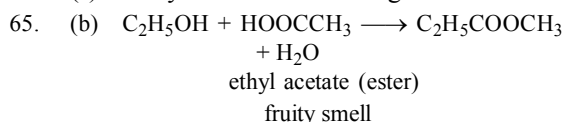
62. (b) Williamson's synthesis -



63. (b) Maximum enol content is in structure (b) because here the enol form is stabilised by H-bonding.

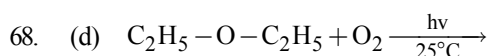
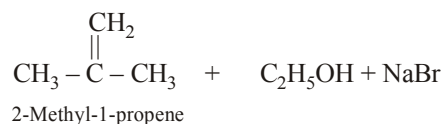
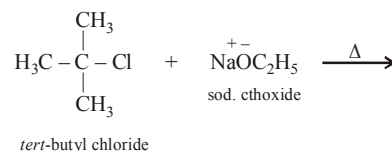


64. (a) Dehydration of alcohols gives ethers



66. (b) Reaction of sodium ethoxide with ethyl iodide to produce diethyl ether is known as Williamson synthesis. It is a nucleophilic substitution reaction and proceeds via S_N2 mechanism.

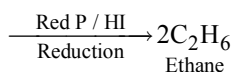
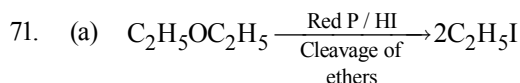
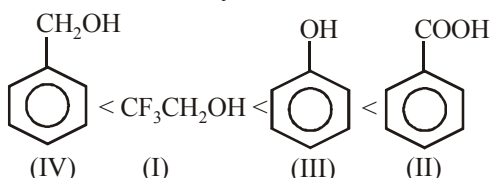
67. (a) In Williamson's synthesis the reaction of alkyl halides with sodium alkoxides give ethers. However, if the alkyl halide is 3° , it undergoes elimination to give an alkene.



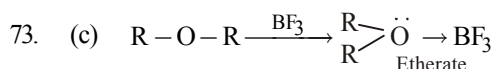
69. (c) CH_3OCH_3 and $C_2H_5OCH_3$ are gases while $C_2H_5OC_2H_5$ (b. p. 308 K) is low boiling liquid.

70. (c) Carboxylic acids are stronger acids than phenols which in turn are stronger than alcohols. Out of benzyl alcohol and trifluoroethanol, the latter is more acidic due to the

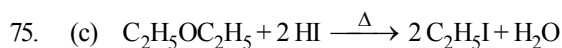
presence of highly electronegative fluorine atoms.
Thus, order of acidity is:



72. (b) Only alkyl aryl ethers e.g., $\text{C}_6\text{H}_5\text{OCH}_3$ undergoes electrophilic substitution reactions.

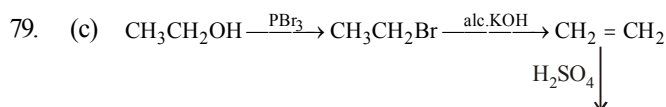
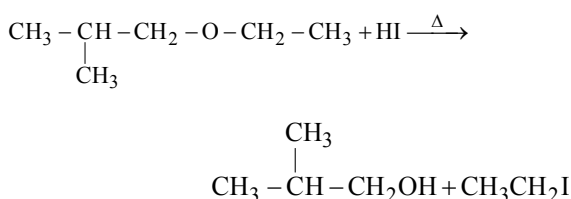


74. (a) The ease of dehydration of alcohols is $3^\circ > 2^\circ > 1^\circ$. Tertiary alcohols undergo dehydration more easily than primary and secondary alcohols.

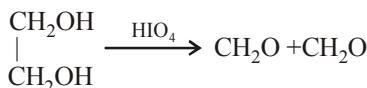


77. (d) 1-pentanol
Primary alcohols readily form ether when heated with conc. H_2SO_4 .

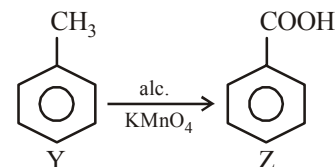
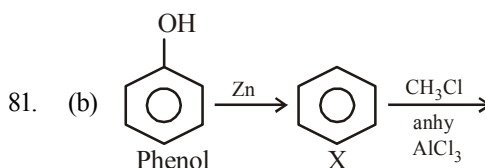
78. (c) In the cleavage of mixed ethers having two different alkyl groups, the alcohol and alkyl iodide that form depend on the nature of alkyl group. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide therefore



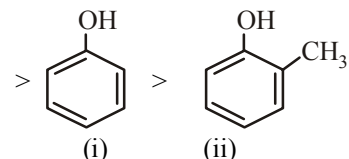
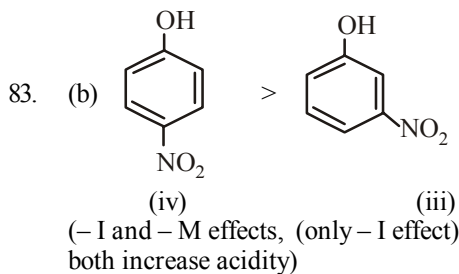
80. (c) 1, 2 - Diols, when treated with an aqueous solution of periodic acid give aldehyde



Note that a 1° alcohol gives CH_2O . Since in glycol both the OH groups, are primary hence give 2 molecules of CH_2O as by product.

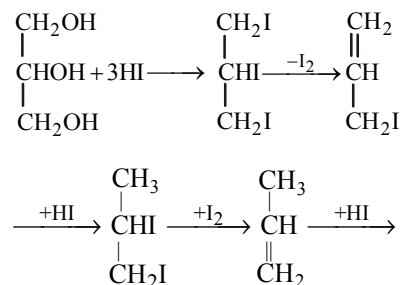


82. (b) Phenol is most acidic because its conjugate base is stabilised due to resonance, while the rest three compounds are alcohols, hence, their corresponding conjugate bases do not exhibit resonance

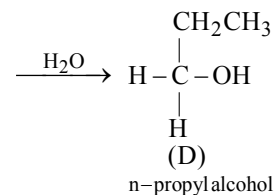
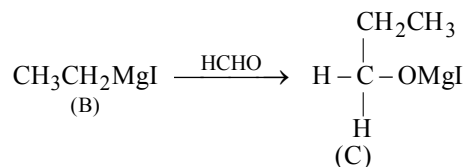
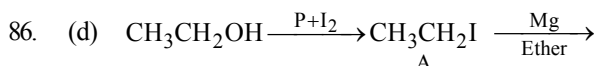


(+ I effect of CH_3 group decreases acidity)

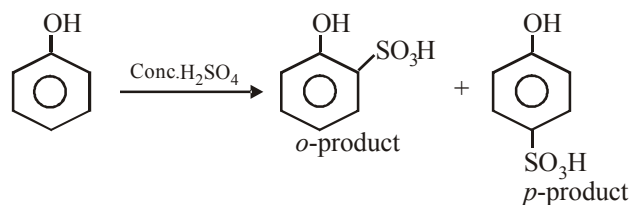
84. (b) Glycerol when treated with excess HI produces 2-iodopropane



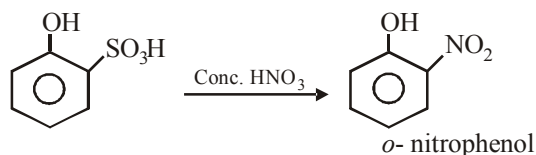
85. (b) Glycol is used as an antifreeze in automobiles.



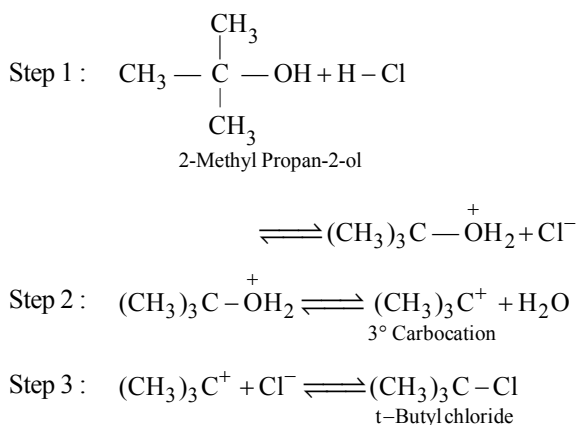
87. (b) Phenol on reaction with conc. H_2SO_4 gives a mixture of *o*- and *p*- products (i.e., $-\text{SO}_3\text{H}$ group, occupies *o*-, *p*- position). At room temperature *o*-product is more stable, which on treatment with conc. HNO_3 will yield *o*-nitrophenol.



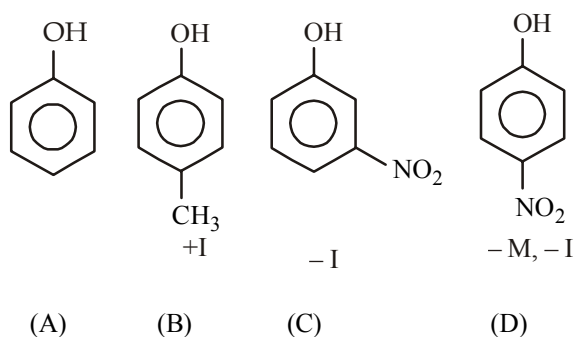
At room temperature *o*- product is more stable



88. (b)
89. (b) Tertiary alcohols react fastest with conc. HCl and anhydrous ZnCl_2 (lucas reagent) as its mechanism proceeds through the formation of stable tertiary carbocation.



90. (a)

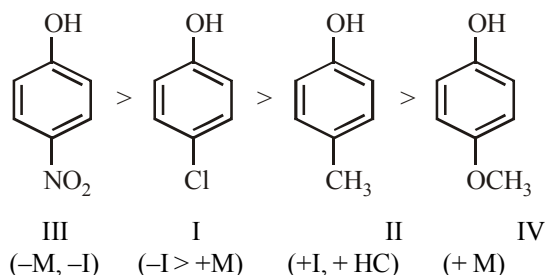


Electron withdrawing substituents increases the acidity of phenols; while electron releasing substituents decreases acidity. Further the particular effect (acidity increasing or decreasing) is more when a substituent is present in *o*- or *p*- position to phenolic group. Thus the correct order will be $\text{D} > \text{C} > \text{A} > \text{B}$

91. (b)

Acetylene is not formed under any conditions.

92. (c) Electron withdrawing substituents like $-\text{NO}_2$, Cl increase the acidity of phenol while electron releasing substituents like $-\text{CH}_3$, $-\text{OCH}_3$ decreases acidity. hence the correct order of acidity will be



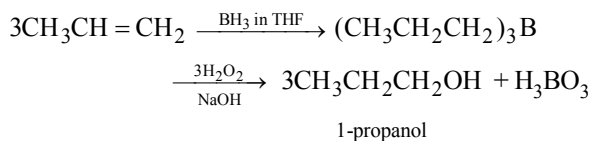
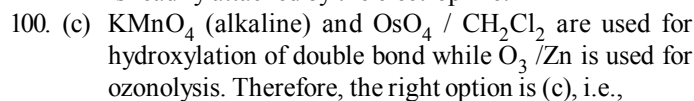
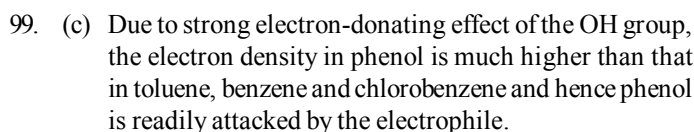
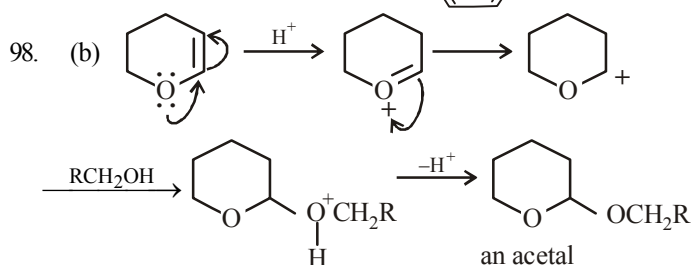
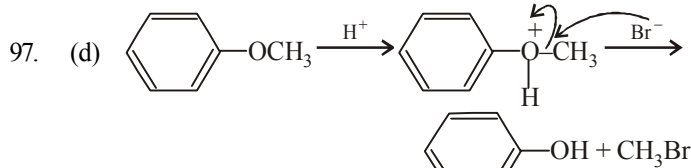
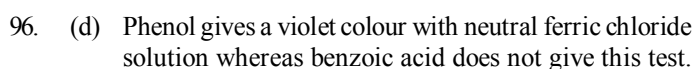
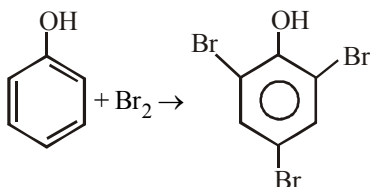
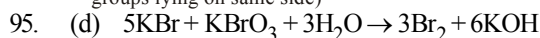
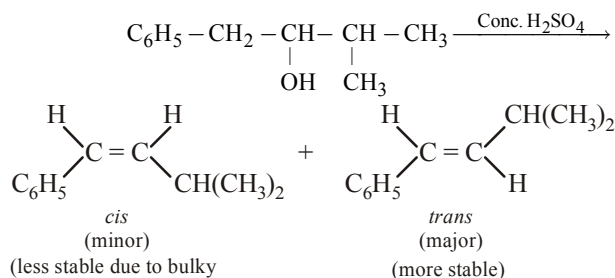
93. (a)

It is a commercial method for the manufacture of phenol.

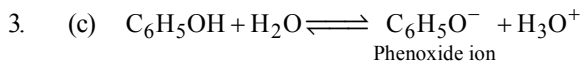
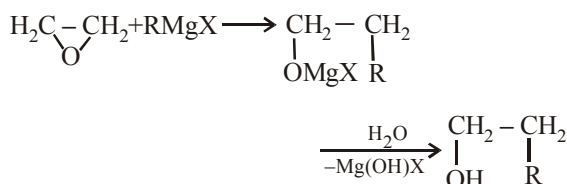
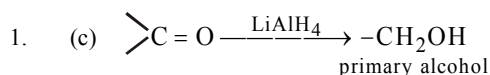
94. (a) Whenever dehydration can produce two different alkenes, major product is formed according to Saytzeff rule i.e. more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product.

Such reactions which can produce two or more structural isomers but one of them in greater amount than the other are called regioselective; in case a reaction is 100% regioselective, it is termed as regiospecific.

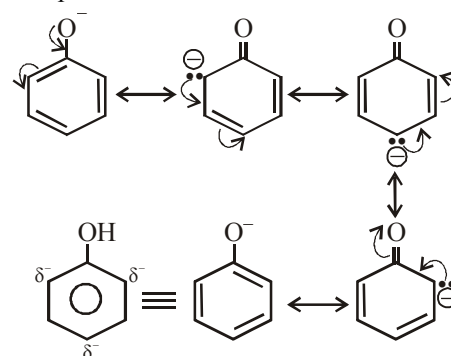
In addition to being regioselective, alcohol dehydrations are stereoselective (a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).



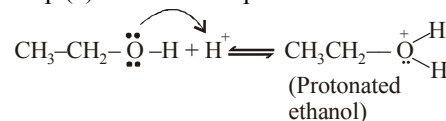
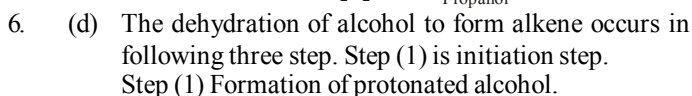
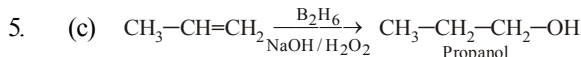
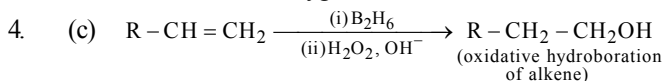
EXERCISE - 2



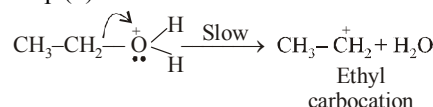
The phenoxide ion is stable due to resonance.



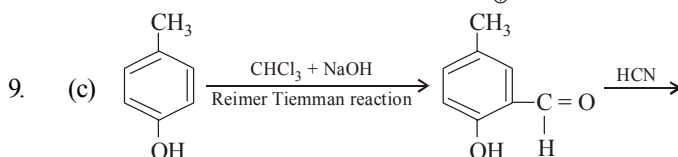
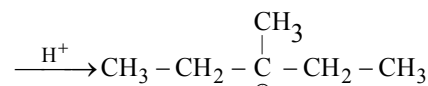
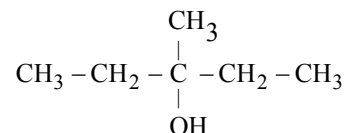
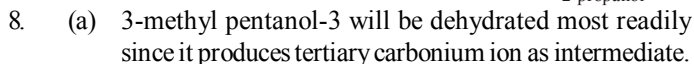
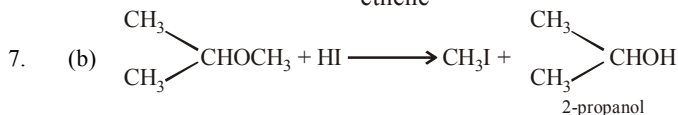
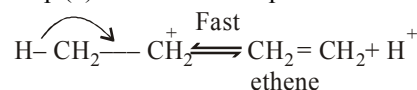
The negative charge is delocalized in the benzene ring which is a stabilizing factor in the phenoxide ion and because of this reason ionization constant of phenol is higher whereas no resonance is possible in alkoxide ions (RO^-) derived from alcohol. The negative charge is localized on oxygen atom in case of alcohols.

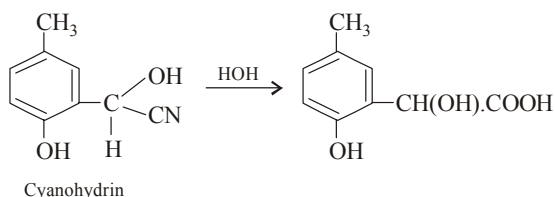


Step (2) Formation of carbocation

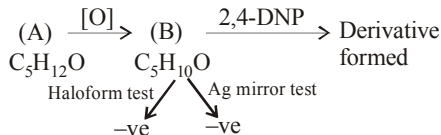


Step (3) Elimination of a proton to form ethene





10. (c) According to question



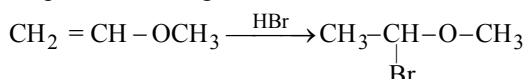
Since (B) on reaction with 2,4-DNP forms a derivative, it implies that (B) has carbonyl ($>C=O$) group (B) gives -ve Tollen's test, hence it is not an aldehyde, it is a ketone.

(B) gives -ve haloform test, thus it is not a methyl ketone. (B) is formed from the oxidation of (A), thus (A) is a 2° alcohol, and among the given options,

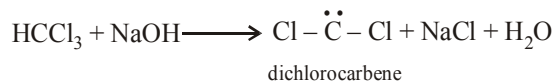
(A) is: $\text{CH}_3-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_3$

and $\therefore$ (B) is $\text{CH}_3-\text{CH}_2-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_3$

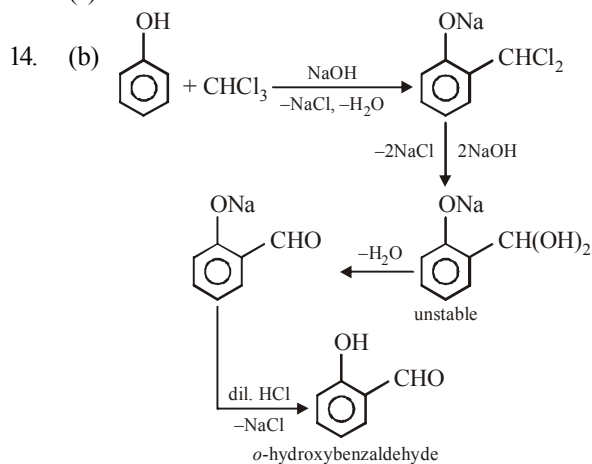
11. (b) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.



12. (d) This is Reimer-Tiemann reaction and the electrophile is dichlorocarbene.



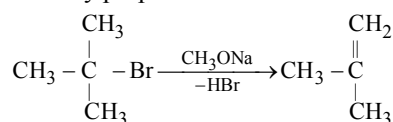
13. (a)



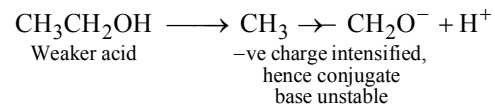
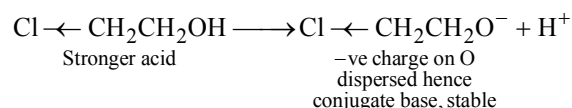
This reaction is called Reimer-Tiemann reaction.

15. (b) By path 1
- $(\text{CH}_3)_3\text{C}-\text{I}$
- and
- CH_3OH
- are formed and path 2 also form the same.

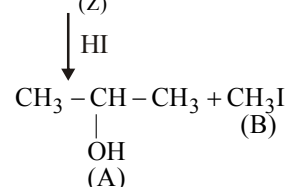
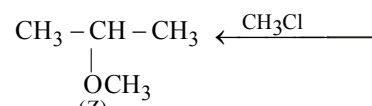
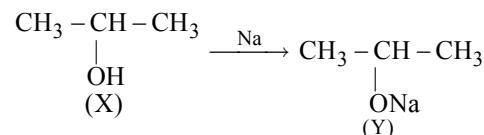
16. (d) tert-butylbromide undergoes elimination readily in presence of the base sodium methoxide to form 2-methylpropene



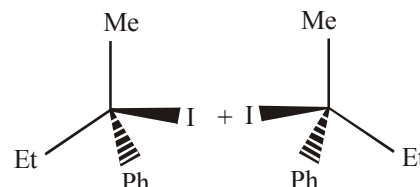
17. (c)
- $\text{ClCH}_2\text{CH}_2\text{OH}$
- is stronger acid than
- $\text{CH}_3\text{CH}_2\text{OH}$
- due to -I effect of Cl.



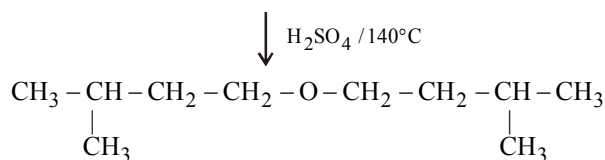
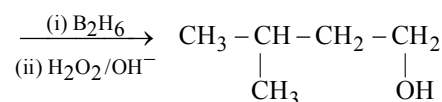
18. (b)
- $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2/\text{H}_2\text{O}}$



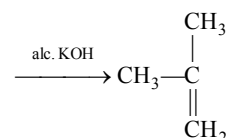
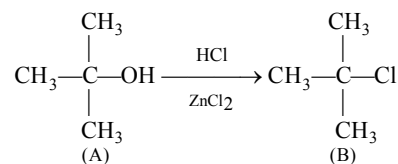
19. (b) [Two]



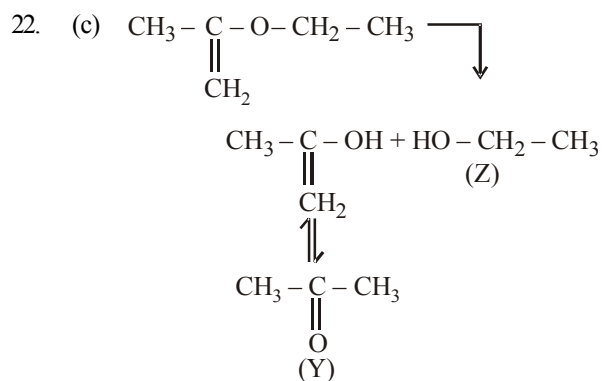
20. (a)
- $\text{CH}_3\text{CH}(\text{CH}_3)-\text{CH}=\text{CH}_2$



21. (a) Reaction involved is given as :



Hence (a) is the correct option.



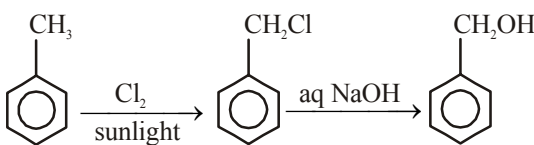
23. (c)

24. (c) It is correct that sodium phenoxide (sodium salt of phenol) and CO_2 on heating form sodium salicylate. This is known as Kolbe's reaction. Ethanol does not respond to this reaction. Therefore, statement-1 is true. But the statement-2 that phenoxide ion is more basic than ethoxide ion is not correct.

25. (c) Lucas reagent is a mixture of anhydrous ZnCl_2 and conc. HCl . It is used for the distinction of monohydric alcohol. Tertiary alcohols on addition produce a precipitate immediately while secondary alcohols produce ppt. after 5 minutes. Primary alcohols do not produce any precipitate. Therefore, statement-1 is true but statement-2 is false.

EXERCISE - 3

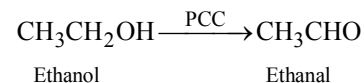
Exemplar Questions

1. (d) 
- Toluene Benzyl chloride Benzyl alcohol
2. (a) Following are the three possible isomers of butanol.
- (i) $\text{CH}_3\text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{OH}$
Butan-1-ol
no chiral carbon.
- (ii) $\text{CH}_3 - \text{CH}_2 - \overset{*}{\underset{\text{OH}}{\text{CH}}} - \text{CH}_3$
Butan-2-ol
1-Chiral Carbon
- (iii) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ | \\ \text{OH} \end{array}$
2-methylpropan-2-ol
No Chiral Carbon
3. (c) $\text{HCl} + \text{An. ZnCl}_2$ is known as Lucas reagent. It is used to determine degree of an alcohol.

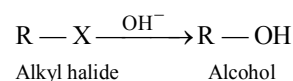
The reaction follows nucleophilic substitution reaction in which $-\text{OH}$ group is replaced by $-\text{Cl}$. In this reaction carbocation is formed as intermediate. Higher the stability of intermediate carbocation higher will be the reactivity of reactant molecule. Since 3° carbocation is more stable than 2° carbocation as well as 1° carbocation.

Hence, the order of reactivity of alcohols is $3^\circ > 2^\circ > 1^\circ$.

4. (c) Less powerful oxidizing agent, Pyridinium chlorochromate ($\text{C}_5\text{H}_5\text{N}^+\text{HCrCl}_2\text{O}_3^-$) oxidises primary alcohols to aldehydes.

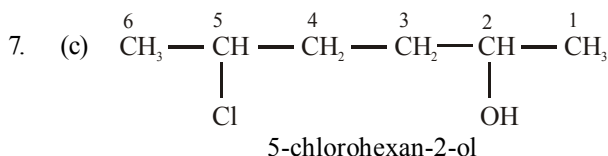


5. (b) The process of conversion of alkyl halides into alcohols involves substitution reaction.

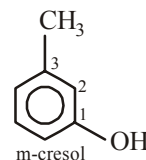


6. (c) Compound (A) i.e., phenol and compound (D) i.e., a derivative of phenol cannot be considered as aromatic alcohol.

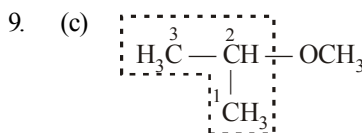
On the other hand, in compounds (B) and (C), $-\text{OH}$ group is bonded to sp^3 hybridised carbon which in turn is bonded to benzene ring. Hence, are considered as aromatic.



8. (a) The structure of *m*-cresol is

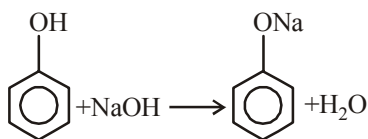


Here $-\text{OH}$ is the functional group and the methyl is substituents. Hence the IUPAC name is 3-methylphenol.



IUPAC name of the above compound is 2-methoxypropane.

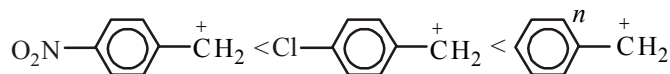
10. (b) Weakest acid has the strongest conjugate base. Among all these acids, ROH is the weakest acid. Therefore, the strongest base is RO^- .
11. (a) Phenol being more acidic in nature reacts with sodium hydroxide solution and by the loss of one proton, it gives phenoxide ion. This phenoxide ion is resonance stabilised.



12. (b) Presence of electron withdrawing group at ortho position ~~increase~~ **increases the acidic strength**. In *o*-nitrophenol, nitro group is present at ortho position. On the other hand, in *o*-methylphenol and in *o*-methoxyphenol, electron releasing group ($-\text{CH}_3$, $-\text{OCH}_3$) are present. Presence of these groups at ortho & Para positions of phenol decreases the acidic strength of phenols. So, phenol is less acidic than *o*-nitrophenol.
13. (d) Presence of electron withdrawing group increases the acidic strength. So, *m*-chlorophenol is most acidic among all the given compounds.
14. (b) Electron withdrawing substituents increase the acidic strength of phenols. so, *p*-nitrophenol (II) and *m*-nitrophenol (IV) are stronger acid than Phenol (I). If $-\text{NO}_2$ group is present at *p*-position, then it exerts both $-I$ and $-R$ effect but if it is present at meta position, then it exerts only $-I$ effect. Therefore, *p*-nitrophenol is stronger than *m*-nitrophenol. On the other hand, electron releasing substituents decreases the acidic strength of phenol. If $-\text{OCH}_3$ group is present at meta position, it will exert $-I$ effect only. But, if it is present at para position, it will exert $+R$ effect. Thus, *m*-methoxyphenol is more acidic than *p*-methoxyphenol. Hence, the correct order of decreasing acidic strength will be: $\text{II} > \text{IV} > \text{I} > \text{III} > \text{V}$.
15. (c) Nucleophilic substitution reactions depends upon the stability of carbocation. As, presence of electron withdrawing group decreases the stability of carbocation in compound (II) and (III). Therefore, will give less stable carbocation than (I). Now NO_2 group is a stronger EWG than $-\text{Cl}$.

Thus, $\text{NO}_2-\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$ will be less stable than $\text{Cl}-\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$

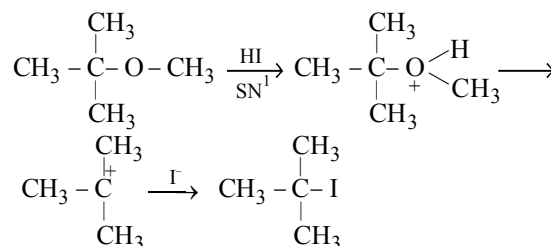
Hence, the order of reactivity of carbocations will be:



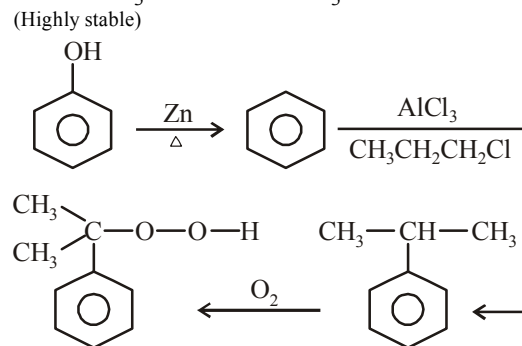
16. (a) With increase in molecular mass boiling point increases. Thus the b.p. of pentan-1-ol will be more than other given compounds. Now, among isomeric alcohols 1° alcohols will have higher boiling points than 2° alcohols due of higher surface area. Hence, increasing order of b.p.ts. will be Propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol.

NEET/AIPMT (2013-2017) Questions

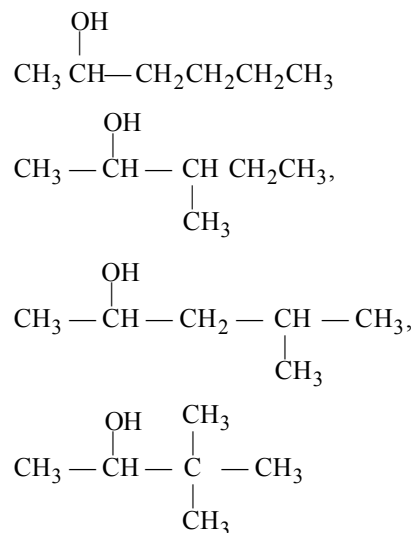
17. (b) The reaction will proceed via S_N^1 mechanism because alkyl group attached is 3° .



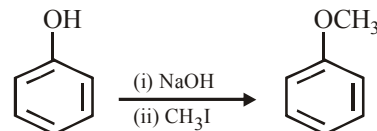
18. (c)



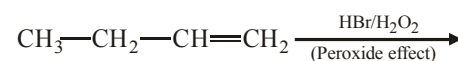
19. (c) Compound containing $\text{CH}_3\text{CH}(\text{OH})$ or CH_3CO -group give positive iodoform test.



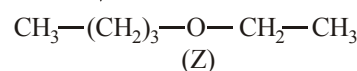
20. (b) Phenols react with alkyl halides in alkaline medium to form ethers. Therefore,



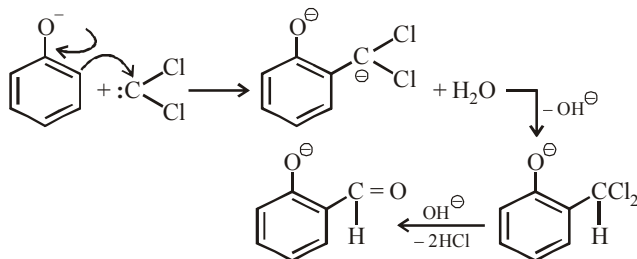
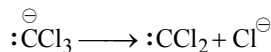
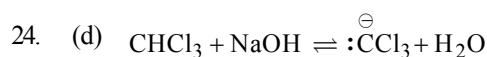
21. (c) *o*-nitrophenol will not be soluble in NaHCO_3 . Due to intramolecular hydrogen bonding hydrogen on OH is strongly bound. So it can not be have as an acid and can not react with sodium bicarbonate.



22. (a) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2$
(Y) $\downarrow$ Br

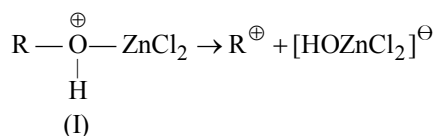
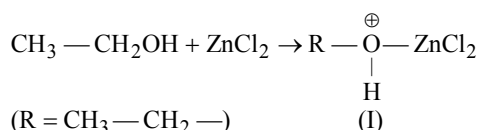


23. (d) Williamson synthesis is one of the best methods for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.



Therefore functional group $-\text{CHO}$ is introduced.

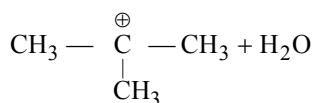
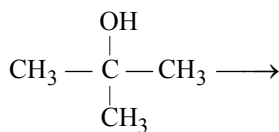
25. (a) ZnCl_2 is a Lewis acid and interacts with alcohol.



Carbocation is formed as intermediate in the $\text{S}_{\text{N}}1$ mechanism which this reaction undergoes.

In the absence of ZnCl_2 , formation of primary carbocation is difficult which is the case with (ii) while (i) undergoes reaction.

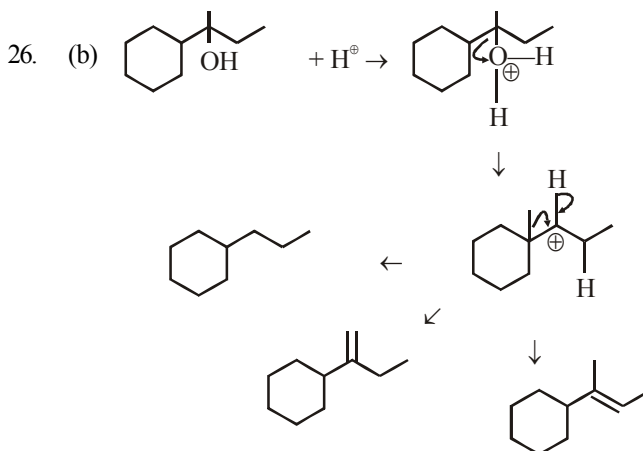
(iii) Tertiary carbocation easily formed due to the stability.



(iv) In the presence of ZnCl_2 , 2° carbocation is formed from $(\text{CH}_3)_2\text{CH}-\text{OH}$



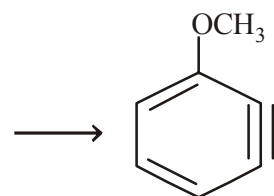
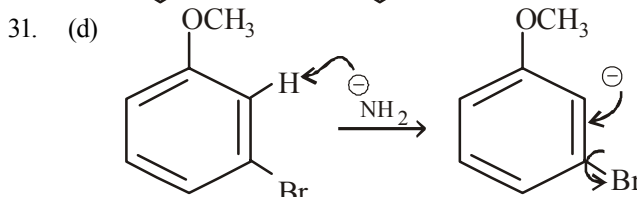
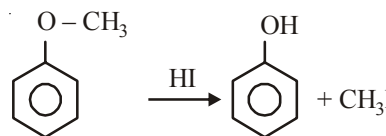
i.e., $\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{CH}_3$



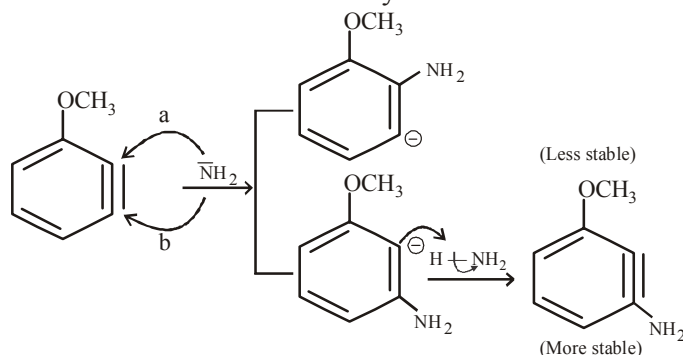
27. (a)
28. (a) This is an example of Williamson ether synthesis reaction in which sodium alkoxide reacts with alkyl halide and gives ether.

29. (c) Electron withdrawing $-\text{NO}_2$ group has very strong $-I$ and $-R$ effects so, compound 3 will be most acidic.

30. (b) When $\text{Ar}-\text{O}-\text{R}$ ethers are reacted with HI , they are cleaved at weaker $\text{O}-\text{R}$ bond to give phenol and alkyl iodide.



Benzyne



More stable as $-ve$ charge is close to electron withdrawing group.

Also, incoming nucleophile gets attached on same 'C' on which 'Br' (Leaving group) was present.

$\therefore$ not a cine substitution reaction

Chapter 26 Aldehydes, Ketones and Carboxylic acids

(A) ALDEHYDES AND KETONES

Structure of carbonyl group

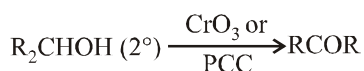
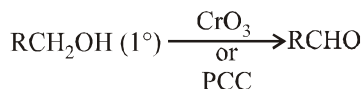
Hybridisation state of carbon in carbonyl group is sp^2 and sp^2 orbital overlaps with p -orbital of oxygen and forms C-O, sp^2-p , σ -bond.

The carbonyl group is polar in nature. The π -bond cloud is unsymmetrical because of the greater electronegativity of oxygen (3.5) than the carbon (2.5).

PREPARATION OF ALDEHYDES AND KETONES

I. For Both Aldehydes and Ketones

(i) By Oxidation of Alcohols



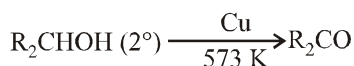
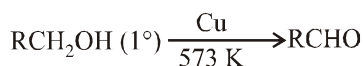
Aldehydes are quite susceptible to further oxidation to acids.



Thus oxidation of primary alcohols is made at the temperature much above the B.P. of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

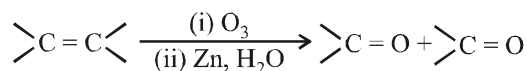
Note : Collins reagent ($CrO_3 \cdot 2C_5H_5N$) and pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$) are mild oxidising agents thereby preventing the further oxidation of aldehydes to carboxylic acids.

(ii) By Dehydrogenation of Alcohols

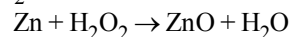


(iii) From Hydrocarbons

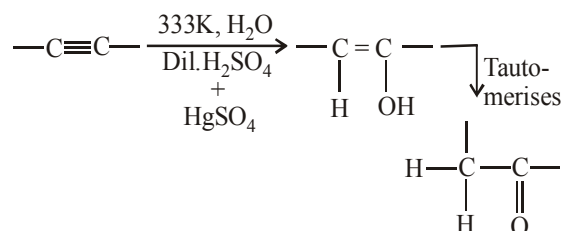
(a) By ozonolysis of alkenes



To prevent further oxidation of carbonyl compound by H_2O_2 , we add zinc in the reaction to destroy H_2O_2



(b) By hydration of alkynes



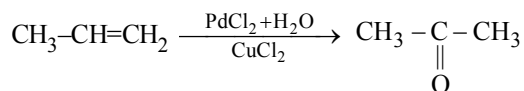
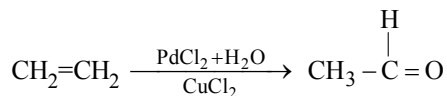
This is called Kucherov reaction.

Note:

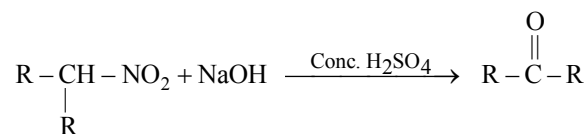
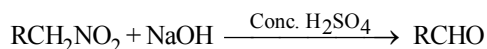
- (i) Formaldehyde can't be prepared by this method
- (ii) Only ethyne gives acetaldehyde while other alkynes give ketones.

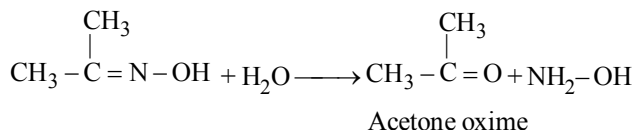
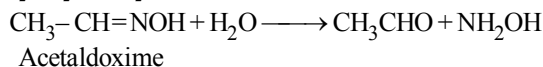
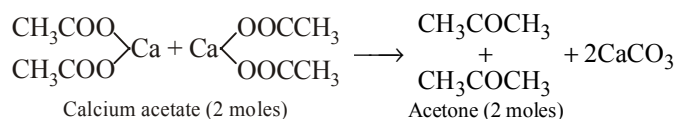
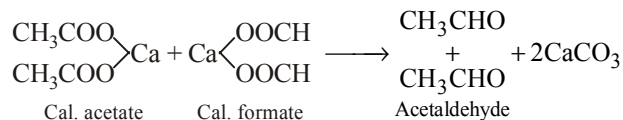
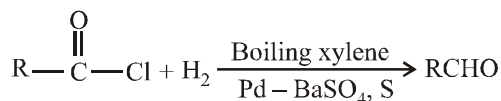
(c) By Wacker's process

Reagent : Acidified aqueous solution of $PdCl_2$ and $CuCl_2$



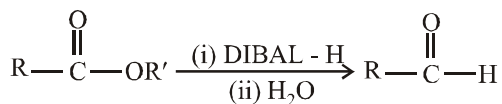
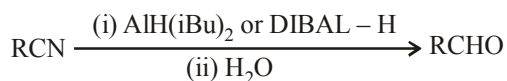
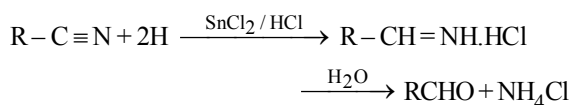
(iv) Oxidation of Nitroalkane (NEF Reaction)



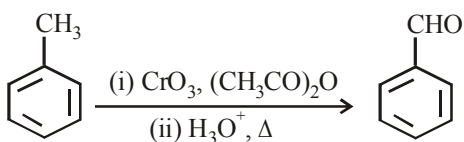
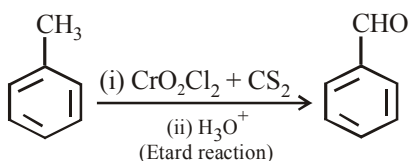
(v) By Hydrolysis of Oximes:**(vi) By Dry Distillation of Calcium Salts of Fatty Acids****II. For Aldehydes Only****(i) From Acyl/Acid Chloride**

Note: Formaldehyde can not be prepared by this method because, the corresponding acid chloride (HCOCl) is unstable.

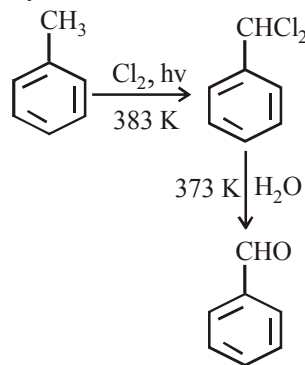
In the above reaction BaSO_4 acts as catalyst poison and decreases the catalytic efficiency of Pd, due to which further reduction of aldehyde to alcohol can't take place.

(ii) From Nitriles and Esters**(iii) From Hydrocarbons**

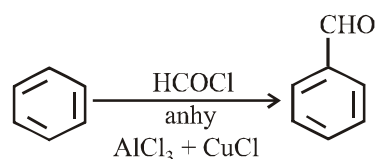
(a) By oxidation of methyl benzene



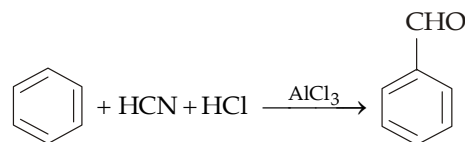
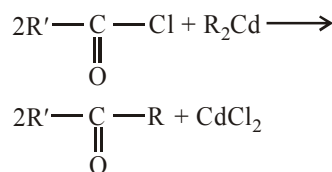
(b) By side-chain chlorination followed by hydrolysis



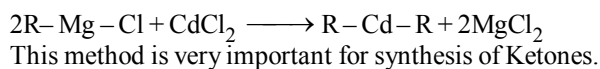
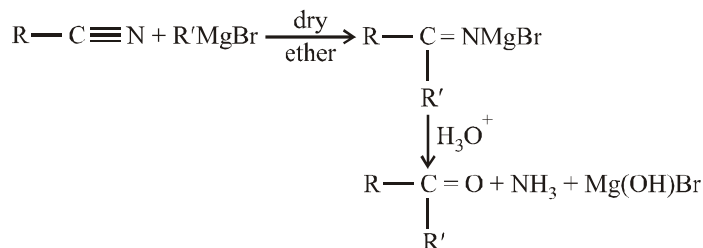
(c) By Gatterman-Koch reaction



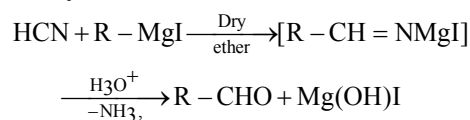
(d) By Gattermann reaction

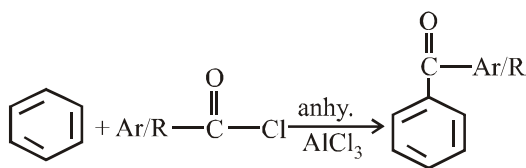
**III. For Ketones Only****(i) From Acyl Chloride**

Dialkyl cadmium can be obtained by

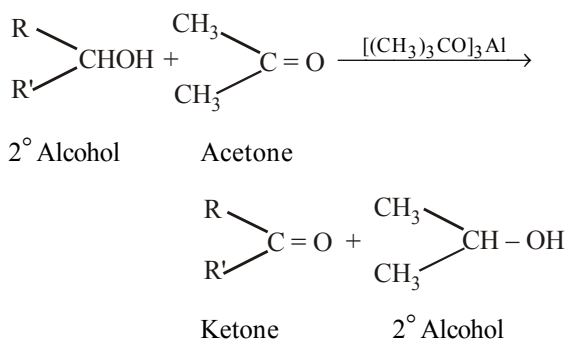
**(ii) From Nitriles**

Note: If instead of alkyl or aryl nitriles, HCN is used aldehydes are formed.



(iii) By Friedel-Crafts Acylation Reaction

Note: Oppenauer oxidation:

**PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES****(i) Physical State**

Formaldehyde is a gas. All other aldehydes and ketones upto C_{11} are colourless volatile liquids. Higher members are solids at room temperature.

(ii) Odour

Lower aldehydes have an unpleasant odour. Higher aldehydes and ketones have a pleasant odour.

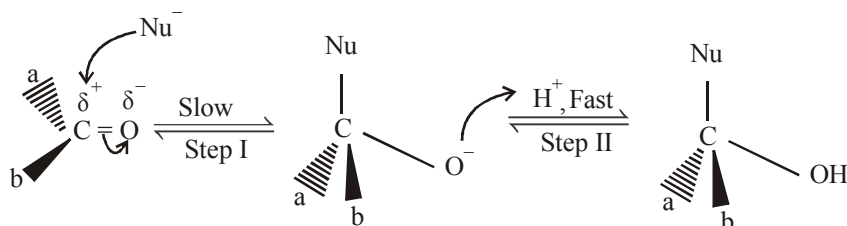
(iii) Boiling and melting points:

Boiling point and melting point $\propto$ Molecular weight $\propto$

$$\frac{1}{\text{Branching}}$$

1. Nucleophilic Addition Reactions

Mechanism of nucleophilic addition to carbonyl group.



Aldehydes are more reactive than ketones due to:

- (i) **Inductive effect:** Alkyl group has + I effect which decreases polarity of carbonyl group. Thus ketones containing two alkyl groups are more reactive in comparison to one alkyl group containing aldehydes.
- (ii) **Steric effects:** As the number and size of alkyl groups increases the attack of the nucleophile on carbonyl group C becomes more and more difficult due to steric hindrance.

Boiling point of aldehydes and ketones are higher than those of hydrocarbons and ethers. This is due to dipole-dipole interactions between the opposite ends of >C=O dipoles.

Ketones have higher Boiling point than isomeric aldehydes. This is due to presence of two electrons donating alkyl groups around >C=O group which makes them more polar.

Boiling point of alcohols and carboxylic acids are higher than aldehydes and ketones. This is due to intermolecular H-bonding in alcohols and acids which is much stronger than dipole-dipole interactions in aldehydes and ketones.

(iv) Solubility :

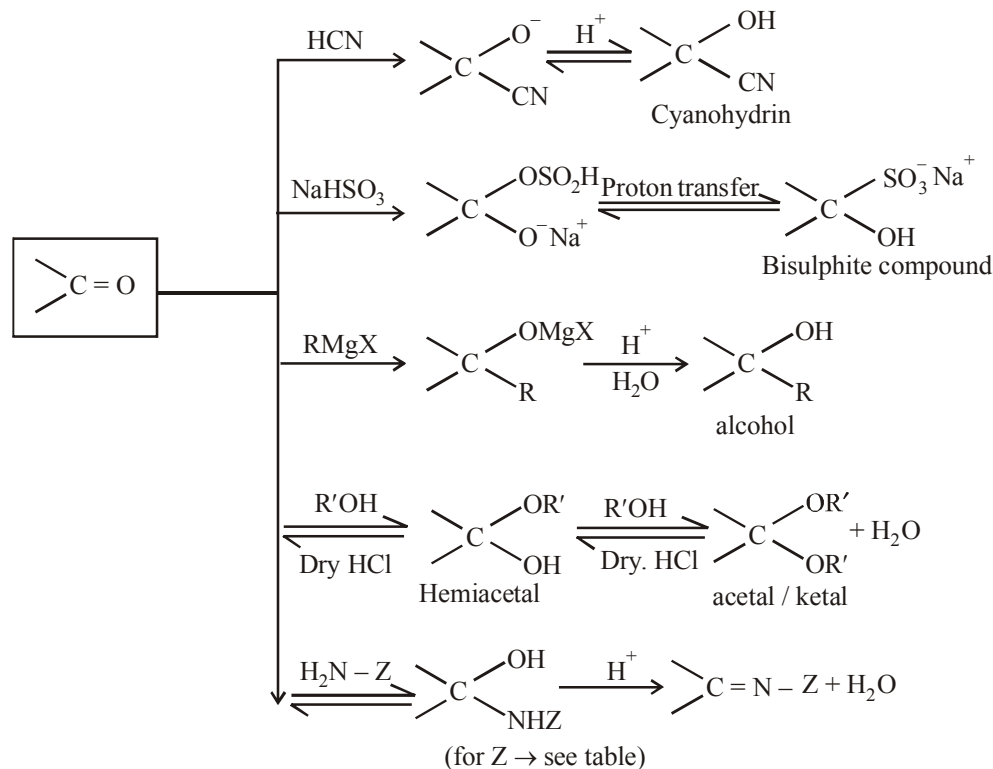
Lower aldehydes and ketones are soluble in water due to H-bonding between the polar carbonyl group and the water molecules. Solubility in H_2O decreases with increase in size of alkyl group. Due to larger hydrocarbon part, aromatic aldehydes and ketones are much less soluble than aliphatic analogues. All aldehydes and ketones are fairly soluble in organic solvents.

CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

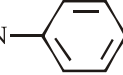
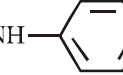
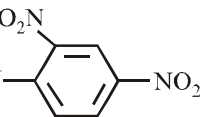
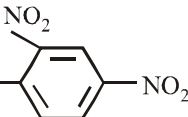
The reaction of aldehydes and ketones can be divided into the following categories :

1. Nucleophilic addition reactions.
2. Reduction reactions.
3. Oxidation reactions
4. Reactions with alkalies.
5. Miscellaneous reactions.

The various nucleophilic addition reactions are:



Some ammonia-substituted derivatives of aldehydes and ketones

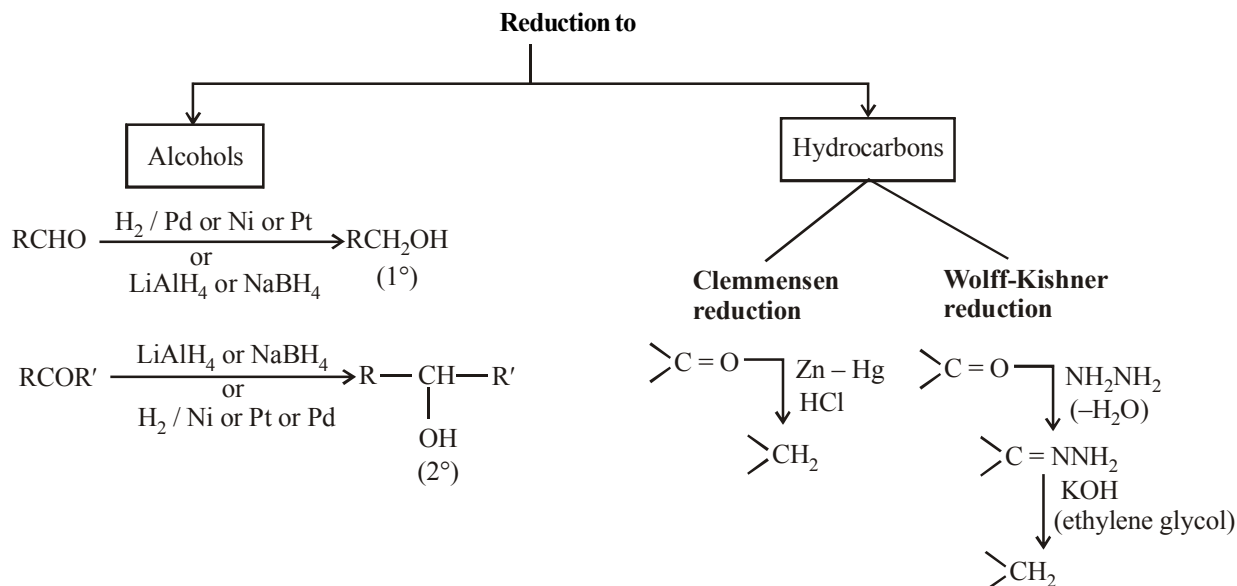
Z	Reagent Name	Carbonyl derivative	Product name
- H	Ammonia	>C=NH	Imine
- R	Amine	>C=NR	Substituted imine (Schiff's base)
- OH	Hydroxylamine	>C=N-OH	Oxime
- NH ₂	Hydrazine	>C=N-NH_2	Hydrazone
- HN- 	Phenylhydrazine	>C=N-NH- 	Phenylhydrazone
- HN- 	2, 4 - Dinitrophenylhydrazine	>C=N-NH- 	2, 4-Dinitrophenylhydrazone
- NH- 	Semicarbazide	$\text{>C=N-NH-C(=O)-NH}_2$	Semicarbazone

Note: (i) Benzaldehyde forms NaHSO₃ adduct but acetophenone does not.

(ii) In addition of alcohols if dihydric alcohol is used a cyclic acetal or ketal is formed.

(iii) In addition of NH₃ derivatives resulting compounds formed are crystalline solids with sharp melting points. Thus these derivatives are used for identification and characterization of aldehydes and ketones.

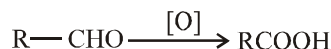
2. Reduction Reactions



Note: Aldehydes and ketones can be also reduced to corresponding hydrocarbons by heating with HI in presence of red P at 423K.

3. Oxidation Reactions

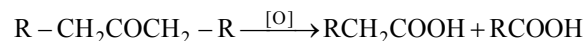
Oxidation of Aldehydes



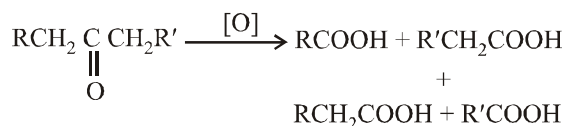
Aldehydes get easily oxidised by strong oxidising agents like HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 etc. as well as by weak oxidising agents like Fehling's and Tollen's reagents.

Oxidation of Ketones

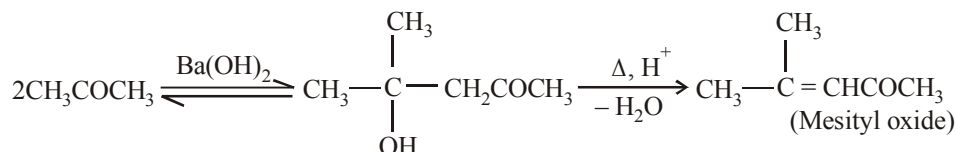
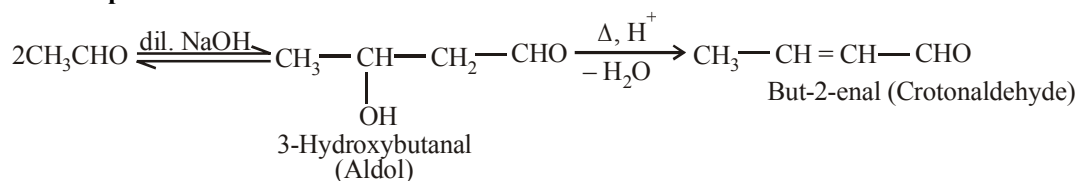
Strong oxidising agent and elevated temperatures needed. In case of symmetrical ketones mixture of two acids is always obtained.



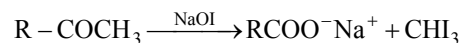
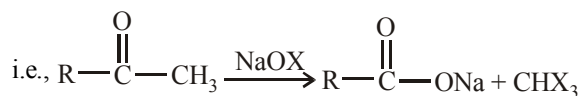
In case of unsymmetrical ketones ($\text{R} \neq \text{R}'$), keto group stays with smaller alkyl group (Popoff's rule).



For example:



Note: Aldehydes and ketones having one methyl group linked to carbonyl C-atom, i.e., methyl ketones, show haloform reaction



This is **Iodoform** test and is used for characterising compounds with CH_3CO group or $\text{CH}_3\text{CH}(\text{OH})$ group.

4. Reactions with Alkalies

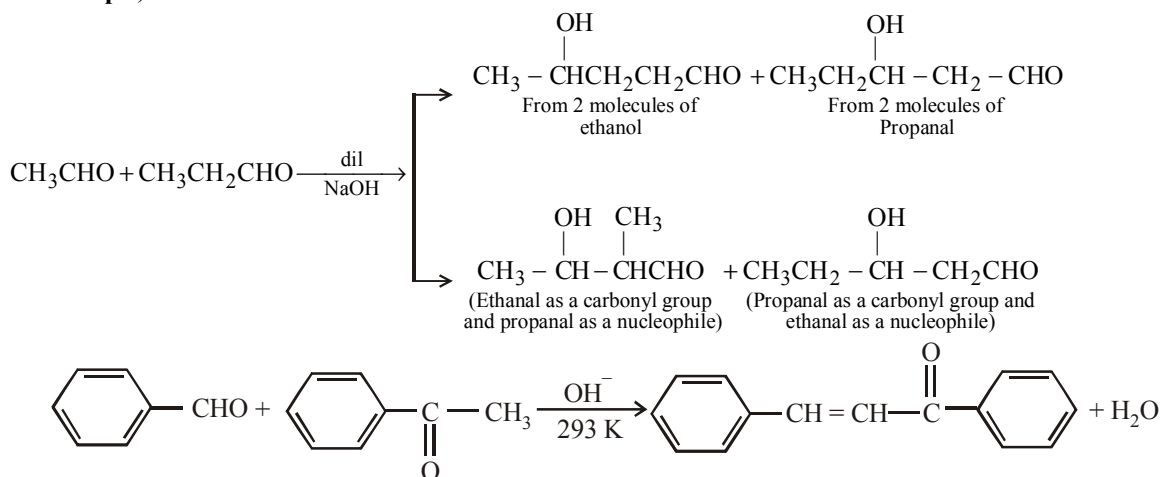
Due to strong electron withdrawing nature ($-\text{I}$ effect) of the carbonyl group and resonance stabilisation of the conjugate base, α -H-atoms of carbonyl compounds are acidic in nature. This acidic nature of α -H gives rise to a large number of reactions of carbonyl compounds.

(i) Aldol Condensation

Two molecules of aldehyde or ketone containing atleast one α -H atom condense in presence of a dilute alkali to form a β -hydroxyaldehyde or a β -hydroxyketone respectively.

- (ii) **Cross-aldol condensation:** An aldol condensation between two different aldehydes or two ketones or between one aldehyde and one ketone.

For example,



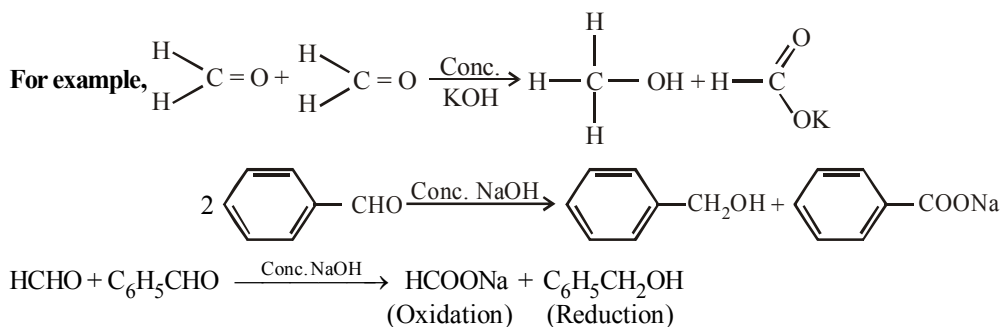
Note: Cross aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or a ketone is called Claisen-Schmidt condensation.

- (iii) **Cannizzaro reaction:** Those aldehydes, which do not contain α -hydrogen atoms give this reaction with conc. alkali like conc. NaOH or KOH. In this reaction two molecules of aldehyde react in such a way that one molecule gets oxidised and the other gets reduced. This type of reaction is called disproportionation reaction.

When two molecules in a reaction are same it is called simple Cannizzaro reaction. In case of different molecules, it is a mixed cross Cannizzaro reaction. In mixed cross Cannizzaro reaction

More reactive aldehyde $\longrightarrow$ Gets oxidised

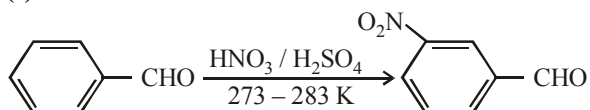
Less reactive aldehyde $\longrightarrow$ Gets reduced



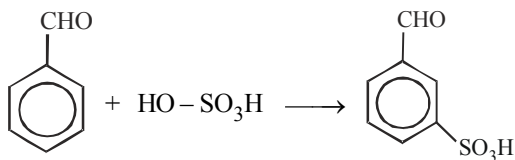
Miscellaneous Reactions

- (i) **Electrophilic substitution reactions:** Carbonyl group is a deactivating and meta-directing group.

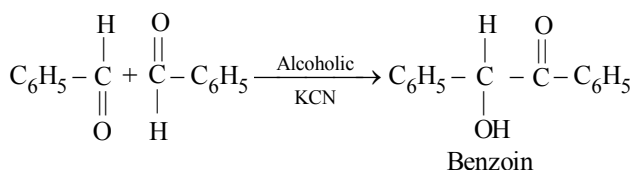
(a) **Nitration :**



(b) **Sulphonation :**

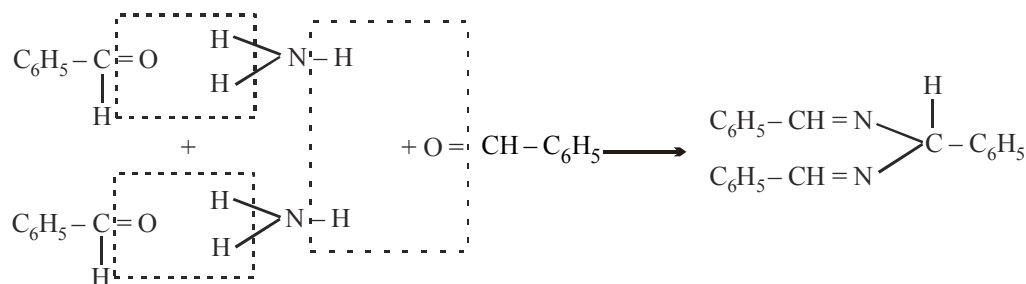
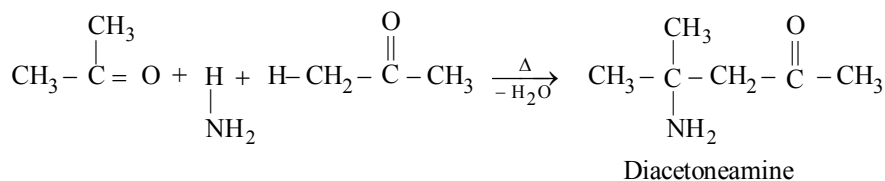


- (ii) **Benzoin condensation :**



(iii) Cold dilute Schiff's reagent (colour less) + Aldehyde $\longrightarrow$ Pink coloured solution

(iv) With ammonia :



Hydrobenzamide (amide without $-\text{CONH}_2$ group)

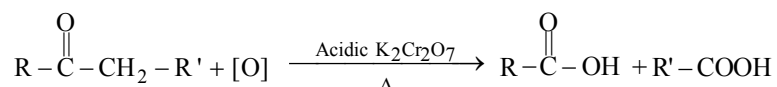
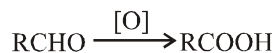
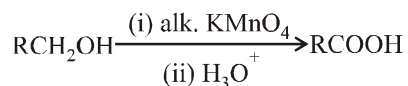
DISTINCTION BETWEEN ALDEHYDES AND KETONES

Test	Aldehydes	Ketones
1. With Tollen's reagent	give silver mirror $\text{RCHO} + 2 [\text{Ag}(\text{NH}_3)_2]^+ + 3\text{OH}^- \longrightarrow \text{RCOO}^- + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$	No action
2. With Fehling's solution	give red ppt of Cu_2O (only aliphatic aldehydes)	No action
3. Reduction with LiAlH_4	1° alcohols are formed	2° alcohols are formed
4. Action with alcohols in presence of dry HCl gas	Form acetals easily	Do not form ketals easily
5. Action with ammonia	Give aldehyde-ammonia adducts	Form complex condensation products
6. With Schiff's reagent	Restore pink colour	No action

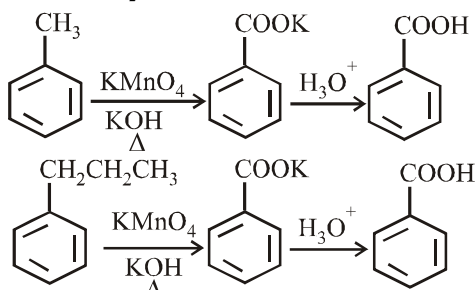
(B) CARBOXYLIC ACIDS

PREPARATION OF CARBOXYLIC ACIDS

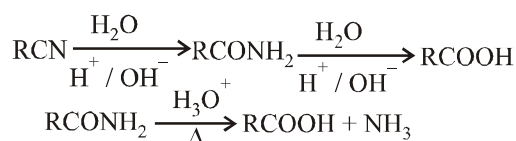
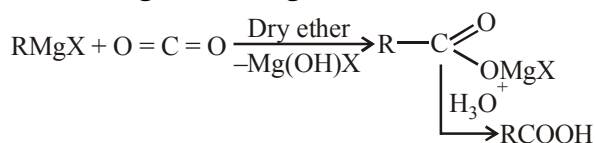
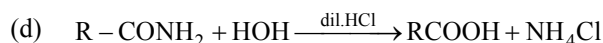
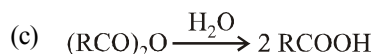
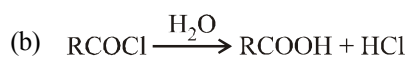
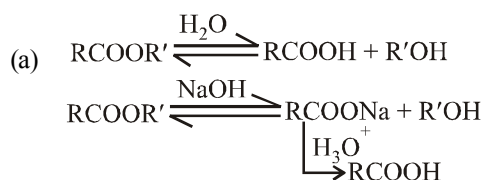
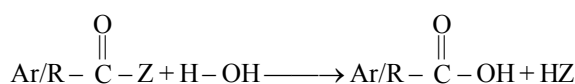
(i) From 1° Alcohols, Aldehydes and Ketones.



This gives poor yield of carboxylic acids.

(ii) From alkylbenzenes.

Note : Presence of electron withdrawing groups in benzene ring increases the reactivity of the benzylic hydrogens. Thus p-nitrotoluene is much more easily oxidised than toluene.

(iii) From Nitriles and Amides.**(iv) From Grignard Reagent.****(v) From Hydrolysis of Acid Derivatives:****PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS**

- (i) Melting point (M.P.) :** Melting point of carboxylic acid do not vary smoothly from one molecule to another

For first ten members



Reason : In acids of even number of carbon atoms, terminal $-\text{CH}_3$ and $-\text{COOH}$ groups lie on the opposite sides of the carbon chain which results in more effective packing of the molecules in the lattice. While in acids of odd number of carbon atoms they lie on the same sides on the carbon chain.

- (ii) Boiling points:** Boiling point $\propto$ Molecular weight

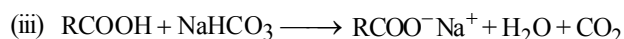
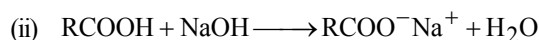
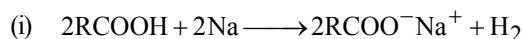
The boiling points of carboxylic acids are higher than hydrocarbons, aldehydes, ketones and even alcohols of comparable molecular masses.

This is due to extensive H-bonding resulting in association of carboxylic acid molecules. The H-bonds formed in carboxylic acids are even more stronger than alcohols. Carboxylic acids exist as cyclic dimer in vapour phase or in aprotic solvents.

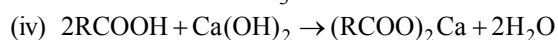
- (iii) Solubility:** Simple aliphatic acids (upto 4 C-atoms) are soluble in H_2O due to H-bonding. Higher acids are insoluble in H_2O due to increased hydrophobic interaction of hydrocarbon part. Aromatic acids are also insoluble due to their large hydrocarbon part. Carboxylic acids are soluble in organic solvents like C_6H_6 , ether, CHCl_3 , etc.

CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS**I. Reactions Due to Cleavage of O-H Bond:**

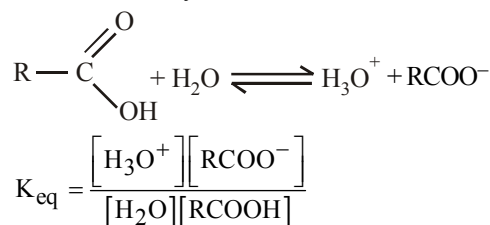
Acid strength of acids



Note: Acids liberate CO_2 (gas) with NaHCO_3 . This reaction is used to distinguish carboxylic acids from phenols which do not react with NaHCO_3 .



In water, carboxylic acids dissociate as :



$$\Rightarrow K_a = K_{\text{eq}} [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}]}$$

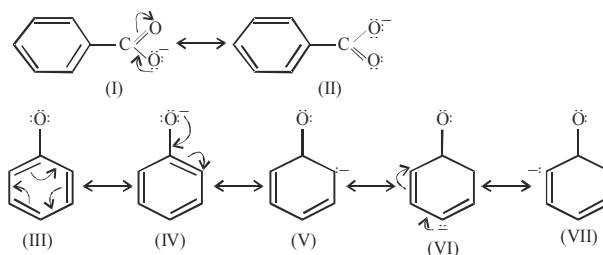
and $\text{p}K_a = -\log K_a$

$\therefore$ smaller the $\text{p}K_a$, stronger the acid.

The acidity of carboxylic acids, phenols and alcohols follows the order:

Carboxylic acid > phenol > alcohol

Consider the resonating structures of carboxylate ion and phenoxide ion.



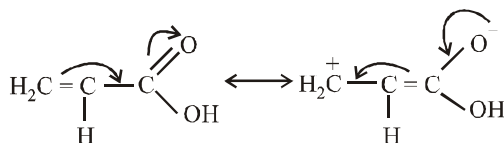
This is because the carboxylate ion is stabilised by two equivalent resonance structures with $-ve$ charge at more electronegative O-atom. On the other hand, phenoxide ion has non-equivalent structures with $-ve$ charge on less electronegative C-atom. Thus, contribution of resonating structures of phenoxide ion towards resonance is very small.

Therefore, carboxylate ion is more stable than phenoxide ion so carboxylic acids are more acidic than phenols.

EWG increase the acidity of acid by stabilising the carboxylate ion whereas EDG decrease the acidity by destabilising the ion.

Note:

- More will be the electron withdrawing nature of substituent greater will be acidic strength.
- More will be the number of electron withdrawing substituents greater will be acidic strength.
- As the distance between electron withdrawing substituent and $-\text{COOH}$ group increases acidic strength decreases.
- Direct attachment of phenyl or vinyl groups increase the acidity of acid due to resonance:



In general, acidity increases as the electronegativity of the carbon atom directly attached to $-\text{COOH}$ group increases or the hybridization of the carbon atom directly attached to $-\text{COOH}$ changes from $sp^3 \rightarrow sp^2 \rightarrow sp$.

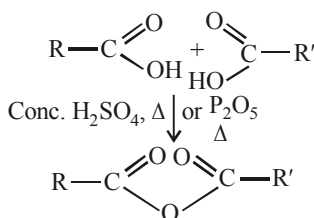
The order of acidity of various acids is as follows:



Note: o -Substituted benzoic acids are usually stronger acids than benzoic acid regardless of the nature of the substituent.

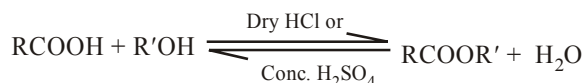
II. Cleavage of C – OH Bond

(i) Anhydride Formation



Acid anhydrides can also be obtained by treating acid chlorides with carboxylic acids.

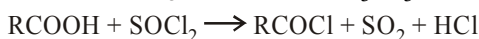
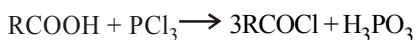
(ii) Esterification



Note: As the number and size of the substituents around the $-\text{COOH}$ or $-\text{OH}$ group increases, the rate of esterification decreases.

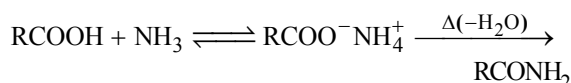
(iii) Formation of Acid Chlorides.

Reaction with PCl_5 , PCl_3 and SOCl_2



Note: In this reaction, SO_2 being a gas escapes out and HCl gets absorbed by basic pyridine and pure acyl chloride is left. So it is best method for preparing acyl chloride from acid.

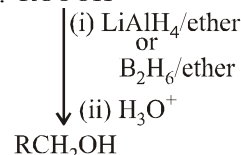
(iv) Reaction with NH_3



III. Reaction Involving $-\text{COOH}$ Group

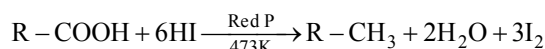
(i) Reduction:

(a) Reduction to alkanes: RCOOH

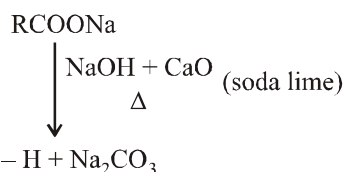


NaBH_4 does not reduce the carboxyl group B_2H_6 does not reduce groups like ester, $-\text{NO}_2$, halo, etc.

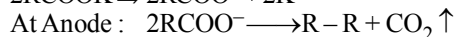
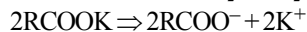
(b) Reduction to alkanes:



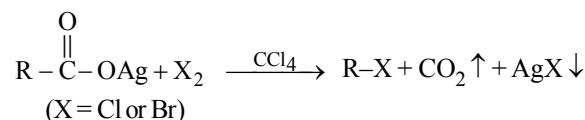
(ii) Decarboxylation



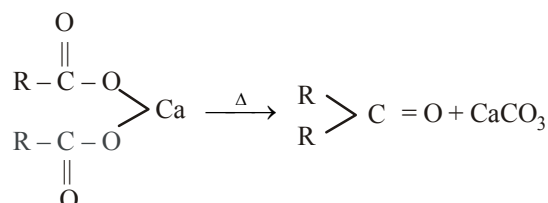
(iii) Kolbe's electrolytic synthesis :



(iv) Hunsdiecker reaction :

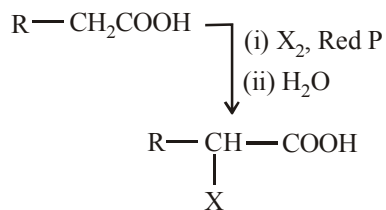


(v) Formation of carbonyl compounds [Dry Distillation of calcium salt] :



IV. Substitution in Hydrocarbon Part

(i) Halogenation

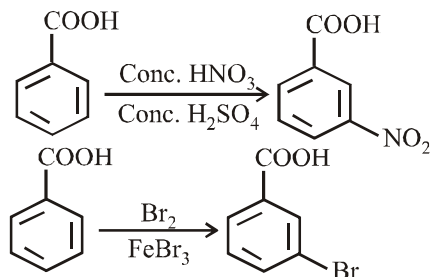


α - Halocarboxylic acid (X = Cl, Br)

This is **Hell-Volhard-Zelinsky (HVZ)** reaction

Acids which do not have α -hydrogens do not show HVZ reaction

(ii) Ring Substitution :



Note: – COOH group is m-directing. Aromatic acids do not undergo Friedal Crafts reaction.

DISTINCTION BETWEEN PHENOL AND CARBOXYLIC ACID

Test	Carboxylic acid	Phenol
1. Sodium bicarbonate test	R – COOH with NaHCO ₃ , give brisk effervescence due to evolution of CO ₂ gas	No reaction
2. Ferric chloride test	R – COOH give coloured ppt with neutral FeCl ₃ sol Ex: 3CH ₃ COOH + FeCl ₃ → (CH ₃ COO) ₃ Fe + 3HCl Buff coloured	C ₆ H ₅ OH give violet coloured ppt. with FeCl ₃ solution 3C ₆ H ₅ OH + FeCl ₃ → (C ₆ H ₅ O) ₃ Fe + 3HCl ferric phenoxide (violet coloured)

CONCEPT MAP

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Aldehydes and Ketones

Carboxylic acids

Preparation of aldehydes and ketones

- (a) 1° Alcohol $\xrightarrow{K_2Cr_2O_7 + H_2SO_4}$ Aldehyde
 2° Alcohol $\xrightarrow{K_2Cr_2O_7 + H_2SO_4}$ Ketone
- (b) Dehydrogenation of alcohols
 1° Alcohol $\xrightarrow{Cu, 573 K}$ Aldehyde
 2° Alcohol $\xrightarrow{Cu, 573 K}$ Ketone
- (c) Ozonolysis of alkenes
 $CH_3CH=CHCH_3 + O_3 \xrightarrow{H_2O, Zn} 2CH_3CHO$
- (d) Hydration of alkynes
 $CH \equiv CH + H_2O \xrightarrow{Dil. H_2SO_4} CH_3 - CHO$
 $CH_3C \equiv CH + H_2O \xrightarrow{Dil. H_2SO_4, HgSO_4} CH_3 - C(=O) - CH_3$

Preparation of aldehydes only

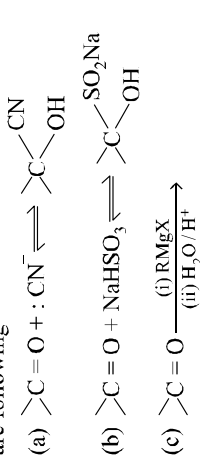
- Rosenmund reduction
 Acyl chloride $\xrightarrow{H_2 - Pd - BaSO_4}$ Aldehyde
- Stephen reaction
 $RCN + SnCl_2 + HCl \xrightarrow{H_3O^+} RCHO$
- Gatterman-Koch reaction
 Benzene $\xrightarrow[Anhy. AlCl_3/CuCl]{CO, HCl}$ Benzaldehyde

Preparation of ketones only

- Friedel crafts acylation
 $C_6H_6 + Ar' - C(=O) - Cl \rightarrow C_6H_5COC(=O)Ar'$
- $CH_3CH_2C \equiv N + C_6H_5MgBr \xrightarrow{ether} CH_3CH_2 - C(=O) - C_6H_5$

Properties of aldehydes and ketones

- Aldehydes are more reactive than ketones in nucleophilic addition reactions. These reactions are following



- Aldehydes + alcohols $\xrightarrow{dry HCl}$ Acetal

- Ketones + alcohols $\xrightarrow{dry HCl}$ Ketal

- $>C=O + H_2N - Z \rightarrow >C=N - Z + H_2O$
 (Z = Alkyl, aryl, $-NH_2$, $-OH$, $-NH-C_6H_5$, $-NHCONH_2$ etc.)

- Clemmensen reduction
 $>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$

- Wolff - kishner reduction
 $>C=O \xrightarrow[(ii) KOH/ethylene glycol]{(i) NH_2-NH_2} >CH_2 + N_2$

- Aldehydes gives positive test with Tollen's reagent and Fehling solution while ketones do not give such test

- Aldol condensation

Condensation of aldehydes and ketones having atleast one α -H atom.

- Cannizzaro reaction

Aldehydes with no α -hydrogen undergoes, self oxidation and reduction.

Preparation

- $RCH_2OH \xrightarrow[(ii) H_3O^+]{(i) Alk. KMnO_4} RCOOH$
- $RCN \xrightarrow[H_2O]{H^+/OH^-} R-C(=O)-NH_2 \xrightarrow[H^+]{OH^-} RCOOH$
- $R-Mg-X + CO_2 \xrightarrow[(ii) H_3O^+]{(i) Dry ether} RCOOH$
- $RCOCl \xrightarrow{H_2O} RCOOH + Cl^-$

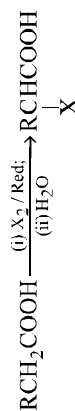
Properties

- Gives CO_2 with carbonates and $NaHCO_3$
- 2 Ethanoic acid $\xrightarrow[H^+]{P_2O_5, \Delta}$ Ethanoic anhydride

Esterification

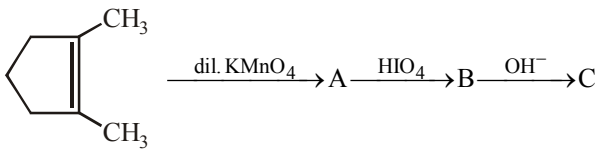
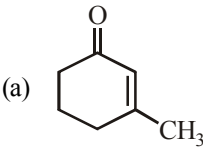
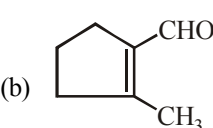
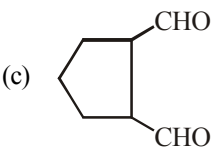
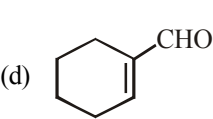
- $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$
- $RCOOH + PCl_5 \rightarrow RCOC(=O)Cl + PCl_3 + HCl$
- $RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$
- $RCOOH \xrightarrow[NH_3]{\Delta, H_2O} RCONH_2$
- $RCOOH \xrightarrow[(ii) H_3O^+]{(i) LiAlH_4} RCH_2OH$

- Hell - Volhard Zelinsky reaction



EXERCISE - 1

Conceptual Questions

- Benzaldehyde and alcohol KCN reacts to produce which of the following :
 (a) ethyl benzoate (b) benzyl alcohol
 (c) benzoin (d) benzyl benzoate
 - Reaction of phenylacetylene with dil. H_2SO_4 and HgSO_4 gives
 (a) acetophenone (b) 2-phenylethanol
 (c) phenylacetaldehyde (d) phenylacetic acid
 - A new C — C bond is formed in :
 (a) Cannizzaro's reaction
 (b) Reimer Tiemann reaction
 (c) Friedel Crafts reaction
 (d) both (b) and (c)
 - Two molecules of acetic acid on heating with phosphorous pentoxide produce :
 (a) ethyl alcohol
 (b) acetic anhydride
 (c) acetyl pentaoxide
 (d) pentaoxide of acetic acid
 - Which of the following gases does not form a ketone on treatment with dil H_2SO_4 and 1% HgSO_4 ?
 (a) C_4H_6 (b) C_2H_2
 (c) C_3H_4 (d) All of these
 - A compound X of formula $\text{C}_3\text{H}_8\text{O}$ yields a ketone $\text{C}_3\text{H}_6\text{O}$ on oxidation. To which of the following class of compounds would X belong?
 (a) Aldehyde (b) Tertiary alcohol
 (c) Secondary alcohol (d) Alkene
 - Clemmensen's reduction of ketones is carried out in :
 (a) LiAlH_4 in H_2O (b) glycol and KOH
 (c) Zn-Hg and HCl (d) H_2 and Pd catalyst
 - Suggest appropriate structures for the missing final compound. (The number of carbon atom remains the same throughout the reaction)
- 
- 

- 

- An unknown compound 'D' first oxidised to aldehyde and then acetic acid by a dilute solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 . The compound 'D' is :
 (a) CH_3OH (b) $\text{C}_2\text{H}_5\text{OH}$
 (c) $\text{CH}_3\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CH}_2\text{CHO}$
 - Identify the product C in the series

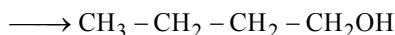
$$\text{CH}_3\text{CN} \xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}} \text{A} \xrightarrow{\text{HNO}_2} \text{B} \xrightarrow{\text{Cu/573K}} \text{C}$$

 (a) CH_3COOH (b) $\text{CH}_3\text{CH}_2\text{NOH}$
 (c) CH_3CONH_2 (d) CH_3CHO
 - Benzaldehyde can be prepared by oxidation of toluene by
 (a) Acidic KMnO_4 (b) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$
 (c) CrO_2Cl_2 (d) All of these
 - Formalin is an aqueous solution of
 (a) fluorescein (b) formic acid
 (c) formaldehyde (d) furfuraldehyde
 - The reagent (s) which can be used to distinguish acetophenone from benzophenone is (are)
 (a) 2,4- dinitrophenylhydrazine
 (b) aqueous solution of NaHSO_3
 (c) benedict reagent
 (d) I_2 and Na_2CO_3
 - The test used for the distinction of HCOOH and CH_3COOH is treatment with :
 (a) sodium (b) sodium hydroxide
 (c) Tollen's reagent (d) alcohol
 - Sodium formate on heating yields
 (a) oxalic acid and H_2 (b) sodium oxalate and H_2
 (c) CO_2 and NaOH (d) sodium oxalate.
 - $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ can be oxidized to $(\text{CH}_3)_2\text{C}=\text{CHCOOH}$ by
 (a) Chromic acid (b) NaOI
 (c) Cu at 300°C (d) KMnO_4
 - Pinacolone is
 (a) 2, 3-dimethyl-2 3-butanediol
 (b) 3, 3-dimethyl-2 butanone
 (c) 1-phenyl-2propanone
 (d) 1,1-diphenyl-2-ethandiol.
 - Urotropine is obtained when ammonia reacts with
 (a) HCHO (b) CH_3COCH_3
 (c) CH_3CHO (d) $\text{C}_6\text{H}_5\text{OH}$
 - Benzaldehyde reacts with ethanoic KCN to give
 (a) $\text{C}_6\text{H}_5\text{CHOHCN}$
 (b) $\text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_5$
 (c) $\text{C}_6\text{H}_5\text{CHOHCOOH}$
 (d) $\text{C}_6\text{H}_5\text{CHOHCHOHC}_6\text{H}_5$
 - Aldehydes and ketones will not form crystalline derivatives with
 (a) sodium bisulphite
 (b) phenylhydrazine
 (c) semicarbazide hydrochloride
 (d) dihydrogen sodium phosphate.

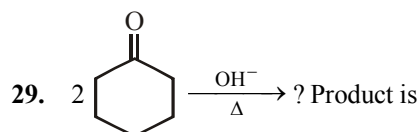
21. When formaldehyde is polymerised in the presence of dilute H_2SO_4 , the compound obtained is
 (a) paraldehyde (b) paraformaldehyde
 (c) metaldehyde (d) trioxymethylene
22. $(\text{CH}_3)_3\text{C}-\text{CHO}$ does not undergo Aldol condensation due to
 (a) three electron donating methyl groups
 (b) cleavage taking place between $-\text{C}-\text{CHO}$ bond
 (c) absence of α hydrogen atom in the molecule
 (d) bulky $(\text{CH}_3)_3\text{C}-$ group
23. In the reaction

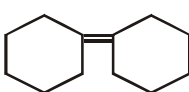
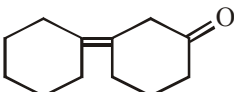
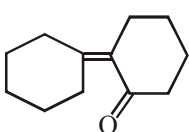
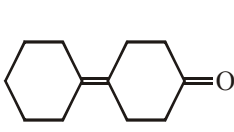
$$\text{CH}_3\text{CN} + 2\text{H} \xrightarrow[\text{Ether}]{\text{HCl}} \text{X} \xrightarrow[\text{H}_2\text{O}]{\text{Boiling}} \text{Y}; \text{ the term Y is :}$$

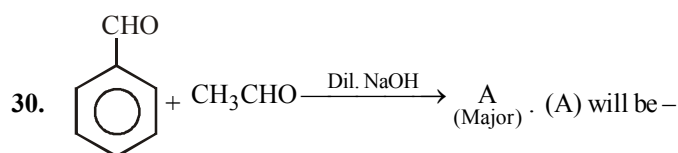
 (a) acetone (b) ethyl amine
 (c) acetaldehyde (d) dimethyl amine
24. Phenylmethyl ketone can be converted into ethylbenzene in one step by which of the following reagents?
 (a) LiAlH_4 (b) Zn-Hg/HCl
 (c) NaBH_4 (d) CH_3MgI
25. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?
 (a) Acetamide (b) Acetic acid
 (c) Ethyl acetate (d) Butan-2-one
26. Acetone reacts with bleaching powder to give
 (a) CCl_4
 (b) CHCl_3
 (c) $\text{CCl}_3-\text{COCH}_3$
 (d) none of these.
27. Appropriate reducing agent for the following conversion is—



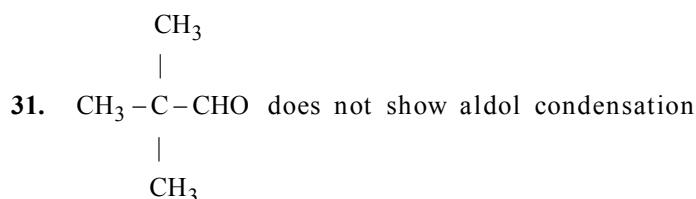
- (a) $\text{LiAlH}_4/\text{H}_2\text{O}$ (b) $\text{NaBH}_4/\text{H}_2\text{O}$
 (c) $\text{Na} + \text{C}_2\text{H}_5\text{OH}$ (d) $\text{B}_2\text{H}_6/\text{H}^+$
28. A compound called chloral whose formula is $\text{C}_2\text{Cl}_3\text{OH}$ is a/an
 (a) aldehyde (b) alcohol
 (c) ketone (d) alkanoyl chloride



- (a)  (b) 
 (c)  (d) 



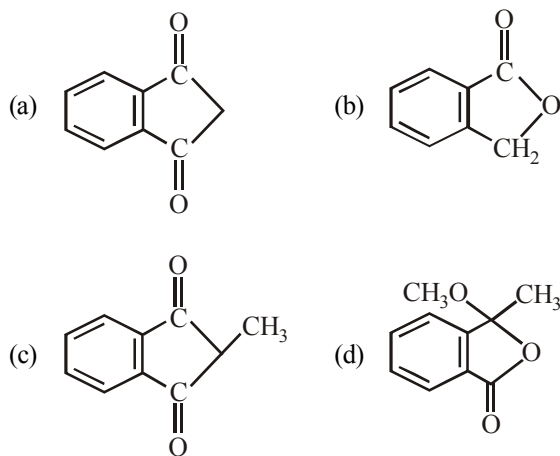
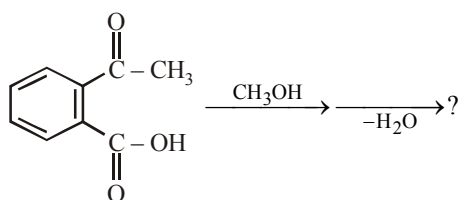
- (a) $\text{C}_6\text{H}_5\text{CH}(\text{OH})-\text{CH}_2\text{CHO}$ (b) $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{CHO}$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$ (d) Both (b) & (c)



because

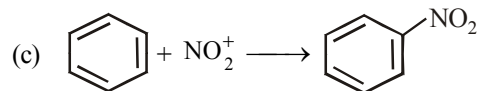
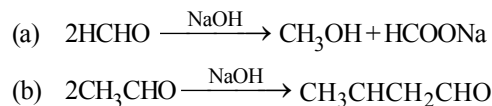
- (a) carbon is bounded by 3 heavy methyl group
 (b) due to absence of α -hydrogen
 (c) it is a neutral molecule
 (d) due to hindrance created by methyl for carbanion.
32. Which of the following is best method for reducing 3-bromopropanal to 1-bromopropane—
 (a) Wolf-Kishner reduction
 (b) Clemmensen reduction
 (c) Either (a) or (b)
 (d) Stephen's reduction
33. Cannizzaro reaction occurs with
 (a) $\text{CH}_3-\text{CH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CHO}$
 (c) CH_3CHO (d) $\text{CH}_3-\text{CO}-\text{CH}_3$
34. In an alkaline medium, acetaldehyde undergoes:
 (a) benzoin condensation (b) aldol condensation
 (c) polymerisation (d) Cannizzaro reaction
35. Which of the following compound will show positive silver mirror test?
 (a) HCOOH (b) $\text{CH}_3(\text{CHOH})_3\text{CHO}$
 (c) $\text{CH}_3\text{CO}(\text{CHOH})\text{CH}_3$ (d) Both (a) and (b)
36. Oxalic acid on heating with conc. H_2SO_4 produces
 (a) $\text{CO} + \text{CO}_2$ (b) $\text{CO}_2 + \text{H}_2$
 (c) $\text{C} + \text{H}_2\text{O}$ (d) $\text{CO} + \text{H}_2$
37. Aldehydes and ketones are generally reduced by :
 (a) Clemmensen reduction (b) H_2S
 (c) H_2/Ni (d) None of these
38. The product obtained by the reaction of an aldehyde and hydroxylamine is
 (a) hydrazone (b) aldoxime
 (c) primary amine (d) alcohol
39. In which reaction, $>\text{C}=\text{O}$ can be reduced to $>\text{CH}_2$?
 (a) Wolf-Kishner reaction
 (b) Reimer-Tiemann reaction
 (c) Wurtz reaction
 (d) None of these

40. In benzilic acid rearrangement,
 (a) benzoin is converted into benzilic acid
 (b) benzaldehyde is converted into benzoin
 (c) benzil is converted into benzilic acid
 (d) benzilic acid is converted into benzil
41. Which of the following does not show Cannizzaro reaction?
 (a) CH_3CHO (b) HCHO
 (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $(\text{CH}_3)_3\text{C}\cdot\text{CHO}$
42. A compound does not react with 2, 4-dinitrophenylhydrazine, the compound is :
 (a) Acetone (b) Acetaldehyde
 (c) CH_3OH (d) $\text{CH}_3\text{CH}_2\text{COCH}_3$
43. Which gives lactic acid on hydrolysis after reacting with HCN ?
 (a) HCHO (b) CH_3CHO
 (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) CH_3COCH_3
44. Ketones react with Mg-Hg over water to give :
 (a) pinacolone (b) pinacols
 (c) alcohols (d) none of these
45. Which of the following functional groups cannot be reduced to alcohol using NaBH_4 in ethanolic solution ?
 (a) R-O-R (b) RCOCl
 (c) R-COOH (d) R-CHO
46. What is the final product of the following reaction ?

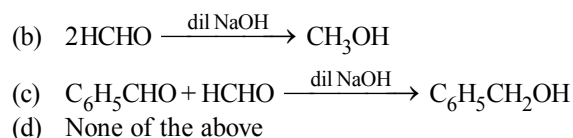
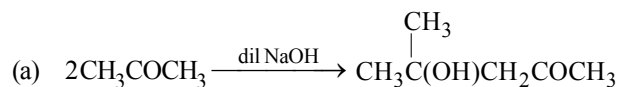


47. 2-pentanone and 3-pentanone can be distinguished by :
 (a) Cannizzaro's reaction
 (b) Aldol condensation
 (c) Iodoform reaction
 (d) Clemmensen's reduction
48. When dihydroxyacetone reacts with HIO_4 , the product is/are :
 (a) HCHO
 (b) HCOOH
 (c) HCHO and HCOOH
 (d) HCHO and CO_2

49. Which of the following is disproportionation reaction?



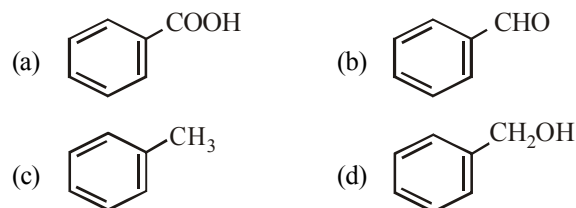
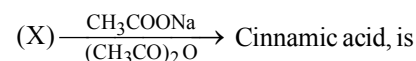
- (d) Both (a) & (b)
50. Formaldehyde reacts with ammonia to give urotropine is
 (a) $(\text{CH}_2)_6\text{N}_4$ (b) $(\text{CH}_2)_4\text{N}_3$
 (c) $(\text{CH}_2)_6\text{N}_6$ (d) $(\text{CH}_2)_3\text{N}_3$
51. The property which distinguishes formic acid from acetic acid is
 (a) only ammonium salt of formic acid on heating gives amide
 (b) when heated with alcohol/ H_2SO_4 only acetic acid forms ester
 (c) only acetic acid forms salts with alkali
 (d) only formic acid reduces Fehling's solution
52. Which of the following is an example of aldol condensation?



53. The reagent which does not give acid chloride on treating with a carboxylic acid is



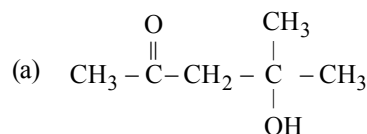
54. The reactant (X) in the reaction

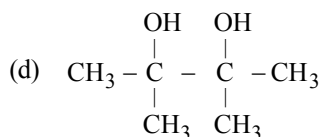
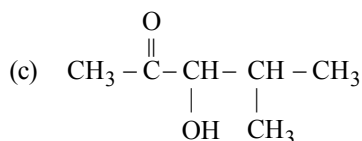
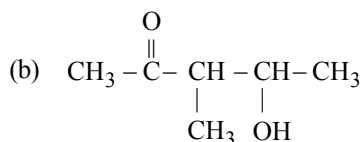


55. Main product obtained from the reaction of ammonia and formaldehyde is



56. Which of the products is formed when acetone is reacted with barium hydroxide solution?





57. Hydride ion transfer takes place in
 (a) Frankland method (b) Wurtz reaction
 (c) Cannizzaro's reaction (d) Wolf-Kishner reduction
58. Ketone upon treatment with Grignard Reagent gives
 (a) primary alcohol (b) secondary alcohol
 (c) tertiary alcohol (d) aldehyde
59. Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone?
 (a) $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CHO}$ (b) $\text{CH}_3\text{CH}=\text{CHCOCH}_3$
 (c) $(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CHO}$ (d) $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$
60. What is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl?
 (a) Acetamide (b) Acetic acid
 (c) Methyl cyanide (d) Acetic anhydride
61. Among acetic acid, phenol and *n*-hexanol, which of the following compounds will react with NaHCO_3 solution to give sodium salt and carbon dioxide?
 (a) acetic acid (b) *n*-Hexanol
 (c) acetic acid and phenol (d) phenol.
62. Formic acid is obtained when
 (a) calcium acetate is heated with conc. H_2SO_4
 (b) calcium formate is heated with calcium acetate
 (c) glycerol is heated with oxalic acid at 373 K
 (d) acetaldehyde is oxidised with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 .
63. Schotten-Baumann reaction is a reaction of phenols with
 (a) benzoyl chloride and sodium hydroxide
 (b) acetyl chloride and sodium hydroxide
 (c) salicylic acid and conc. H_2SO_4
 (d) acetyl chloride and conc H_2SO_4
64. Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis?
 (a) A secondary alcohol
 (b) A primary alcohol
 (c) Phenol
 (d) *tert*-Butyl alcohol
65. An ester is boiled with KOH. The product is cooled and acidified with concentrated HCl. A white crystalline acid separates. The ester is
 (a) methyl acetate (b) ethyl acetate
 (c) ethyl formate (d) ethyl benzoate
66. In the Friedel Craft's acylation reaction, the effective electrophile is
 (a) $\text{RCOCl}^\oplus$ (b) AlCl_3
 (c) RCOCl (d) $\text{RCO}^\oplus$
67. The compound which is not formed during the dry distillation of a mixture of calcium formate and calcium acetate is
 (a) methanal (b) propanal
 (c) propanone (d) ethanal
68. Which one of the following esters cannot undergo Claisen self-condensation?
 (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{COOC}_2\text{H}_5$
 (b) $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5$
 (d) $\text{C}_6\text{H}_{11}\text{CH}_2\text{COOC}_2\text{H}_5$
69. The cyanohydrin of a compound on hydrolysis gives an optically active α -hydroxy acid. The compound is
 (a) diethyl ketone (b) formaldehyde
 (c) acetaldehyde (d) acetone
70. The product of following reaction is
 $2\text{CH}_3\text{MgBr} + \text{CH}_2\text{O} \longrightarrow$
 (a) CH_3OH (b) $\text{C}_2\text{H}_5\text{OH}$
 (c) CH_4 (d) C_2H_6
71. $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{red P}]{\text{Cl}_2} \text{A} \xrightarrow{\text{alc. KOH}} \text{B}$. What is B?
 (a) $\text{CH}_3\text{CH}_2\text{COCl}$ (b) $\text{CH}_3\text{CH}_2\text{CHO}$
 (c) $\text{CH}_2=\text{CHCOOH}$ (d) $\text{ClCH}_2\text{CH}_2\text{COOH}$.
72. When dihydroxy acetone reacts with HIO_4 , the product is/
 are
 (a) HCHO
 (b) HCOOH
 (c) HCHO and HCOOH
 (d) HCHO and CO_2
73. When $\text{CH}_2=\text{CH}-\text{COOH}$ is reduced with LiAlH_4 , the compound obtained will be
 (a) $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ (b) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$
 (c) $\text{CH}_3-\text{CH}_2-\text{CHO}$ (d) $\text{CH}_3-\text{CH}_2-\text{COOH}$
74. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is
 (a) $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$
 (b) $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
 (c) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$
 (d) $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$
75. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives
 (a) 2-methyl-2-propanol (b) acetamide
 (c) acetone (d) acetyl iodide
76. Acetic anhydride reacts with diethyl ether in the presence of anhydrous AlCl_3 to give :
 (a) $\text{CH}_3\text{CH}_2\text{COOH}$ (b) $\text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5$
 (c) $\text{CH}_3\text{COOCH}_3$ (d) $\text{CH}_3\text{COOC}_2\text{H}_5$
77. An important reaction of acetone is auto condensation in presence of concentrated sulphuric acid to give the aromatic compound.....
 (a) Mesitylene (b) Mesityl oxide
 (c) Trioxan (d) Phorone

78. The acid(s) which do not contain $-\text{COOH}$ groups is/are :

- (a) palmitic acid
(b) lactic acid
(c) ethanoic acid
(d) picric acid and *p*-toluene sulphonic acid

79. The best combination of reagents for carrying out the conversion $\text{RCH}_2\text{CH}_2\text{OH} \rightarrow \text{RCH}_2\text{CH}_2\text{COOH}$ is

- (a) $\text{PBr}_3, \text{KCN}, \text{H}_3\text{O}^+$ (b) $\text{PBr}_3, \text{KCN}, \text{H}_2/\text{Pt}$
(c) $\text{KCN}, \text{H}_3\text{O}^+$ (d) $\text{PBr}_3, \text{H}_3\text{O}^+$

80. $\text{CH}_3\text{COOH} \xrightarrow{\text{A}} \text{CH}_3\text{COCl}$. What is A ?

- (a) PCl_5 (b) Cl_2
(c) HCl (d) COCl_2

81. Ethyl acetate on reaction with Grignard's reagent, forms a/an

- (a) alcohol (b) ketone
(c) ether (d) hydrocarbon

82. The compound not soluble in acetic acid is :

- (a) CaCO_3 (b) CaO
(c) CaC_2O_4 (d) $\text{Ca}(\text{OH})_2$

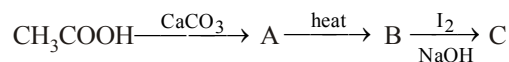
83. Among the following, the most acidic is :

- (a) CH_3COOH (b) ClCH_2COOH
(c) Cl_2CHCOOH (d) $\text{Cl}_2\text{CHCH}_2\text{COOH}$

84. The compound that neither forms semicarbazone nor oxime is

- (a) HCHO (b) $\text{CH}_3\text{COCH}_2\text{Cl}$
(c) CH_3CHO (d) $\text{CH}_3\text{CONHCH}_3$

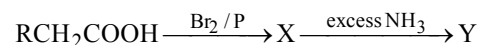
85. Consider the following transformations :



The molecular formula of C is

- (a) $\text{CH}_3-\overset{\text{OH}}{\underset{\text{I}}{\text{C}}}-\text{CH}_3$ (b) $\text{ICH}_2-\text{COCH}_3$
(c) CHI_3 (d) CH_3I

86. In the following reaction



The major compounds X and Y are

- (a) RCHBrCONH_2 ; $\text{RCH}(\text{NH}_2)\text{COOH}$
(b) RCHBrCOOH ; $\text{RCH}(\text{NH}_2)\text{COOH}$
(c) RCH_2COBr ; $\text{RCH}_2\text{COONH}_4$
(d) RCHBrCOOH ; $\text{RCH}_2\text{CONH}_2$

87. An organic compound $\text{C}_3\text{H}_6\text{O}$ neither gives precipitate with semicarbazide nor reacts with sodium. It could be

- (a) $\text{CH}_3\text{CH}_2\text{CHO}$ (b) CH_3COCH_3
(c) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$ (d) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$

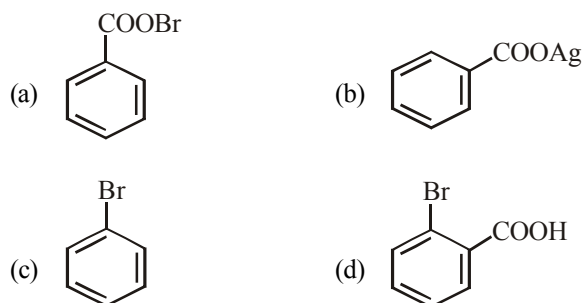
88. Which one of the following compounds will not react with CH_3MgBr ?

- (a) Ethyl acetate (b) Acetone
(c) Dimethyl ether (d) Ethanol

89. Some carboxylic acids and their IUPAC names are given below. Which of the following is not correctly matched?

- (a) Formic acid — Methanoic acid
(b) Acetic acid — Ethanoic acid
(c) *n*-Butyric acid — Butanoic acid
(d) *Iso*-butyric acid — 2-methylbutanoic acid

90. Silver benzoate will react with bromine in CCl_4 to form :



91. Which of the following pairs can be distinguished by sodium hypoiodite?

- (a) CH_3CHO and CH_3COCH_3
(b) $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3
(c) $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$
(d) CH_3OH and $\text{CH}_3\text{CH}_2\text{CHO}$

92. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called

- (a) Cope reduction
(b) Dow reduction
(c) Wolf-Kishner reduction
(d) Clemmensen reduction.

93. Which of the following represents the correct order of the acidity in the given compounds?

- (a) $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
(b) $\text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
(c) $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
(d) $\text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$

94. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?

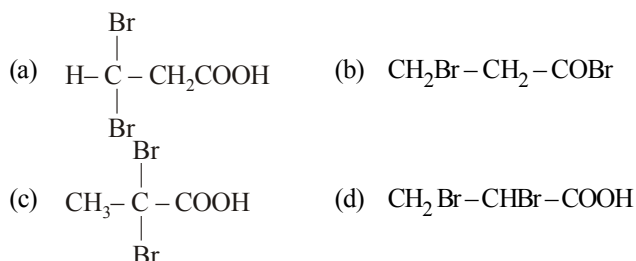
- (a) $\text{C}_6\text{H}_5\text{CHO}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

- (c) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$

95. The product formed in Aldol condensation is

- (a) a beta-hydroxy aldehyde or a beta-hydroxy ketone
(b) an alpha-hydroxy aldehyde or ketone
(c) an alpha, beta unsaturated ester
(d) a beta-hydroxy acid

96. Propionic acid with Br_2/P yields a dibromo product. Its structure would be:



97. Which of the following reactions will not result in the formation of carbon-carbon bonds?

- (a) Reimer-Tieman reaction (b) Cannizzaro reaction
(c) Wurtz reaction (d) Friedel-Crafts acylation

98. Following compounds are given:

- (i) $\text{CH}_3\text{CH}_2\text{OH}$ (ii) CH_3COCH_3
(iii) $\begin{array}{c} \text{CH}_3-\text{CHOH} \\ | \\ \text{CH}_3 \end{array}$ (iv) CH_3OH

Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

- (a) (i) and (ii) (b) (i), (iii) and (iv)
(c) Only (ii) (d) (i), (ii) and (iii)

99. Clemmensen reduction of a ketone is carried out in the presence of which of the following?

- (a) Glycol with KOH (b) Zn-Hg with HCl
(c) LiAlH_4 (d) H_2 and Pt as catalyst

100. Match the compounds given in List-I with List-II and select the suitable option using the code given below:

List I

- (A) Benzaldehyde
(B) Phthalic anhydride
(C) Phenyl benzoate
(D) Methyl salicylate

List-II

- (i) Phenolphthalein
(ii) Benzoin condensation
(iii) Oil of wintergreen
(iv) Fries rearrangement

Code:

(A)	(B)	(C)	(D)
(a) (iv)	(i)	(iii)	(ii)
(b) (iv)	(ii)	(iii)	(i)
(c) (ii)	(iii)	(iv)	(i)
(d) (ii)	(i)	(iv)	(iii)

EXERCISE - 2

Applied Questions

1. The catalyst used in the Wacker process of oxidation of ethyne to ethanal is

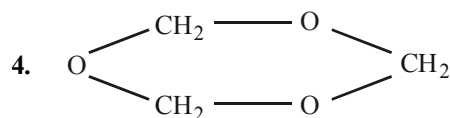
- (a) PdCl_2 (b) V_2O_5
(c) Nickel complexes (d) TiCl_4 and $\text{Al}(\text{CH}_3)_3$

2. Which one of the following reagents enables the purification of benzaldehydes?

- (a) HCN (b) CH_3MgBr
(c) NH_2OH (d) NaHSO_3

3. Which of the following is the correct decreasing order of acidic strength of

- (i) Methanoic acid (ii) Ethanoic acid
(iii) Propanoic acid (iv) Butanoic acid
(a) (i) > (ii) > (iii) > (iv) (b) (ii) > (iii) > (iv) > (i)
(c) (i) > (iv) > (iii) > (ii) (d) (iv) > (i) > (iii) > (ii)

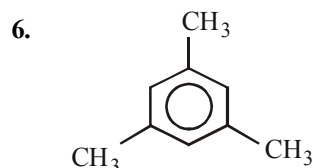


The above shown polymer is obtained when a carbonyl compound is allowed to stand. It is a white solid. The polymer is

- (a) Trioxane (b) Formose
(c) Paraformaldehyde (d) Metaldehyde

5. Which of the following gives reddish brown precipitate on heating with a solution of CuSO_4 and alkaline sodium potassium tartarate?

- (a) Ethanol (b) Ethanal
(c) Propanone (d) Ethanoic acid



The above compound describes a condensation polymer which can be obtained in two ways: either treating 3 molecules of acetone (CH_3COCH_3) with conc. H_2SO_4 or passing propyne ($\text{CH}_3\text{C}\equiv\text{CH}$) through a red hot tube. The polymer is

- (a) Phorone (b) Mesityl oxide
(c) Deacetyl alcohol (d) Mesitylene

7. In which of the following, the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation

- (a) CH_3COCH_3 (b) $\text{CCl}_3\text{CH}_2\text{CHO}$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) $\text{CH}_3\text{CH}_2\text{CHO}$

8. Aldehydes that do not undergo aldol condensation are

1. propanal 2. trichloroethanal
3. methanal 4. ethanal
5. benzaldehyde

- (a) 3 and 4 only (b) 3 and 5 only
(c) 1, 2 and 3 only (d) 2, 3 and 5 only

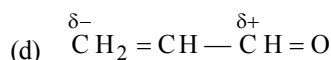
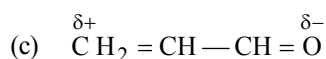
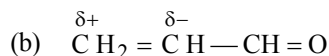
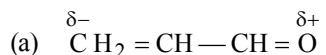
9. Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore X and Y are respectively

- (a) Soda-lime and copper (b) Zn dust and NaOH
(c) Zn dust and soda-lime (d) Soda-lime and zinc dust

10. An ester (A) with molecular formula, $\text{C}_9\text{H}_{10}\text{O}_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (B). Ozonolysis of (B) gave a ketone with molecular formula $\text{C}_8\text{H}_8\text{O}$ which shows positive iodoform test. The structure of (A) is

- (a) $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$
(b) $\text{C}_2\text{H}_5\text{COOC}_6\text{H}_5$
(c) $\text{H}_3\text{COCH}_2\text{COC}_6\text{H}_5$
(d) $\text{p}-\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{COCH}_3$

11. Polarization of electrons in acrolein may be written as:



12. Which compound among the following gives positive iodoform test?

1. Ethanol	2. Ethanal
3. 1-Butanol	4. 2-Butanol
5. Phenyl ethanol	

- (a) 1, 2 and 5 (b) 1, 3 and 4
(c) 1, 2 and 3 (d) 1, 2 and 4

13. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as

- (a) an amine (b) an imine
(c) an enamine (d) a schiff's base

14. The increasing order of the rate of HCN addition to compound A – D is

(A) HCHO	(B) CH_3COCH_3
(C) PhCOCH_3	(D) PhCOPh
(a) $\text{D} < \text{C} < \text{B} < \text{A}$	(b) $\text{C} < \text{D} < \text{B} < \text{A}$
(c) $\text{A} < \text{B} < \text{C} < \text{D}$	(d) $\text{D} < \text{B} < \text{C} < \text{A}$

15. Reaction of butanone with methylmagnesium bromide followed by hydrolysis gives

- (a) 2-methyl-2-butanol
(b) 2-butanol
(c) 3-methyl-2-butanol
(d) 2, 2-dimethyl-1-butanol

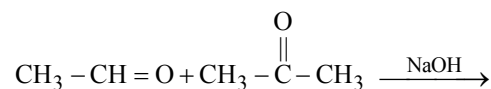
16. The correct order of increasing acid strength of the compounds

(A) $\text{CH}_3\text{CO}_2\text{H}$	(B) $\text{MeOCH}_2\text{CO}_2\text{H}$
(C) $\text{CF}_3\text{CO}_2\text{H}$	(D) $\text{Me}_2\text{C}(\text{Me})\text{CO}_2\text{H}$

is

- (a) $\text{D} < \text{A} < \text{B} < \text{C}$ (b) $\text{A} < \text{D} < \text{B} < \text{C}$
(c) $\text{B} < \text{D} < \text{A} < \text{C}$ (d) $\text{D} < \text{A} < \text{C} < \text{B}$

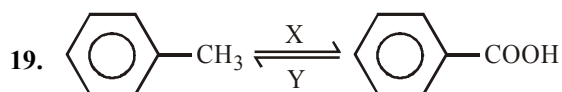
17. How many cross aldol products (without counting stereoisomers) are produced in the following reaction?



- (a) 5 (b) 2
(c) 3 (d) 1

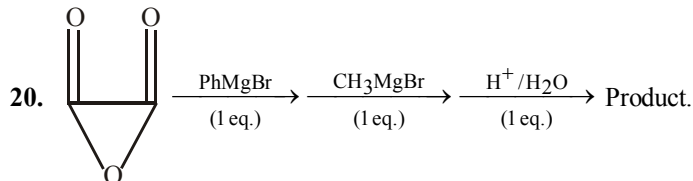
18. Monocarboxylic acids are functional isomers of:

- (a) Ethers (b) Amines
(c) Esters (d) Alcohols

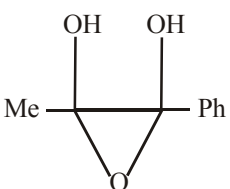
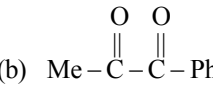
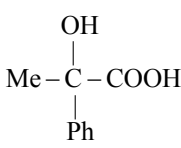
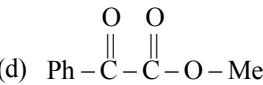


In the above sequence of reaction X and Y are respectively

- (a) H_2/Pt ; Br_2 (b) KMnO_4 ; H_2/Pt
(c) $\text{KMnO}_4(\text{aq})$; HI/P (d) $\text{NH}_2 - \text{NH}_2/\text{KOH}$, HI/P



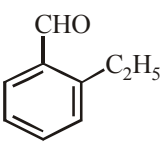
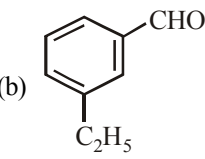
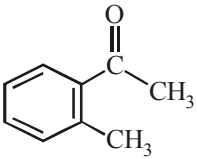
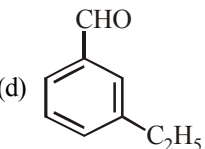
The product formed in the reaction is –

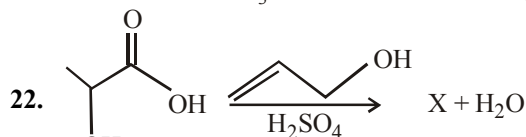
- (a)  (b) 
(c)  (d) 

21. An aromatic compound 'X' with molecular formula $\text{C}_9\text{H}_{10}\text{O}$ gives the following chemical tests. It

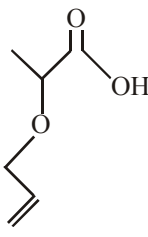
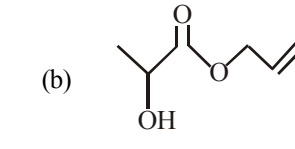
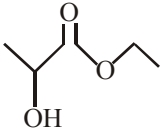
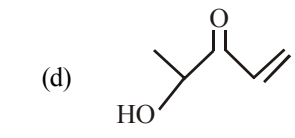
- (i) forms 2, 4-DNP derivative
(ii) reduces Tollen's reagent
(iii) undergoes Cannizzaro reaction and
(iv) on vigorous oxidation 1, 2-benzenedicarboxylic acid is obtained.

X is

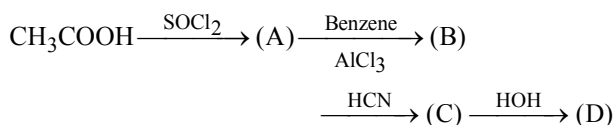
- (a)  (b) 
(c)  (d) 



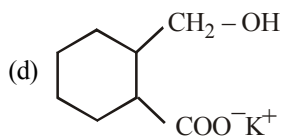
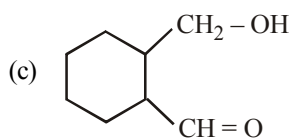
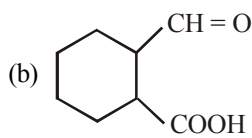
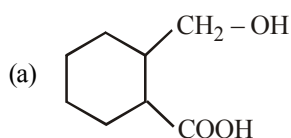
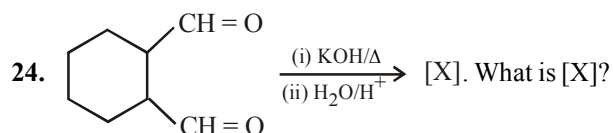
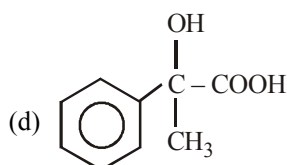
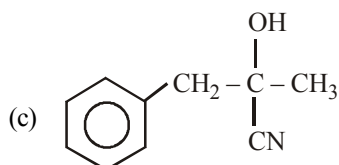
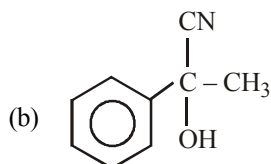
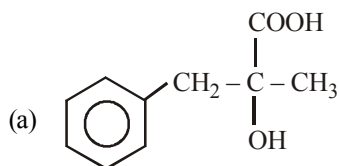
Product (X) of the reaction is–

- (a)  (b) 
(c)  (d) 

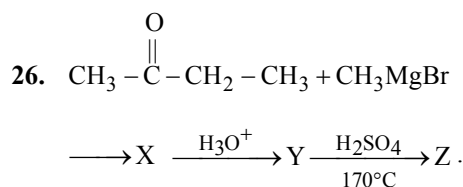
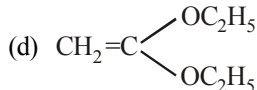
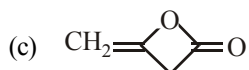
23. In a set of reactions acetic acid yielded a product D.



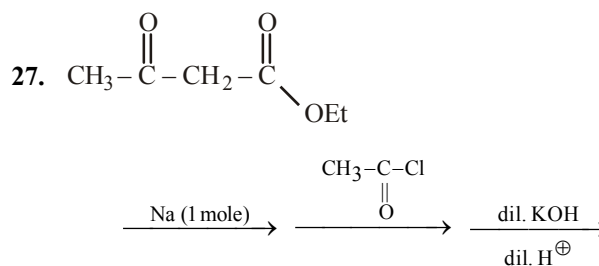
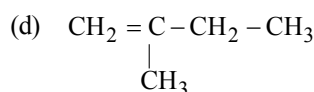
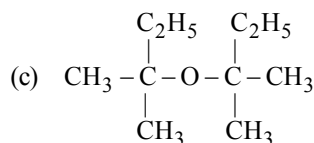
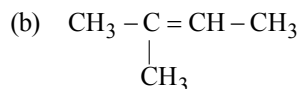
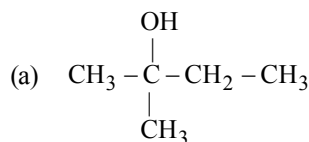
The structure of (D) would be –



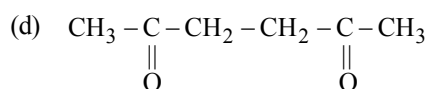
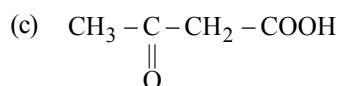
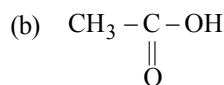
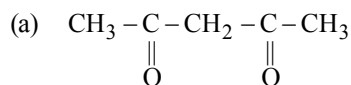
25. $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B. Compound B is :



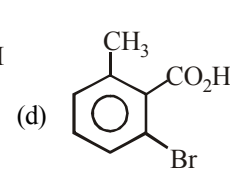
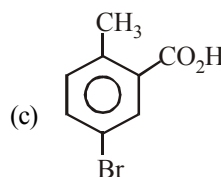
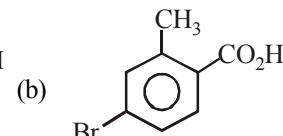
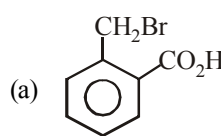
What is Z ?



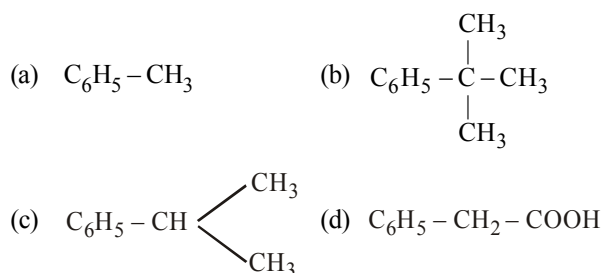
The final product is –



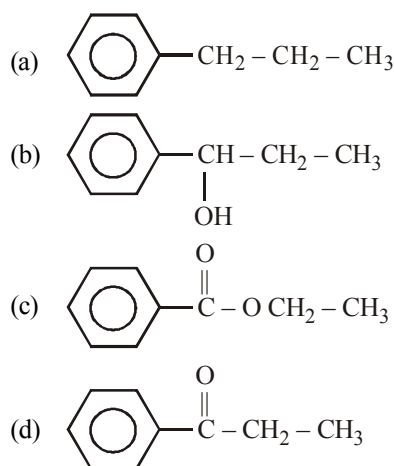
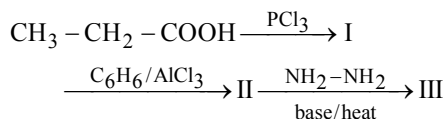
28. *o*-Toluic acid on reaction with $\text{Br}_2 + \text{Fe}$ gives



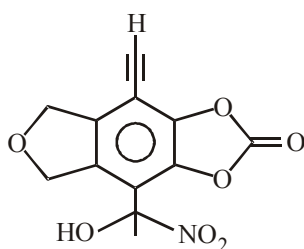
29. Which of the following compound will not give benzoic acid on oxidation with $\text{KMnO}_4/\text{OH}^-/\Delta$ –



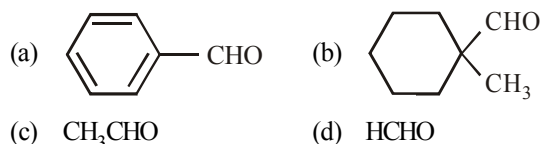
30. The final product (III) obtained in the reaction sequence –



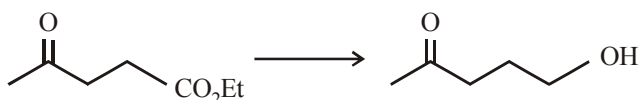
31. Calculate number of molecules of Grignard reagent consumed by 1 molecule of following compound.



- (a) 5 (b) 2
(c) 3 (d) 1
32. Cannizzaro's reaction is not given by :

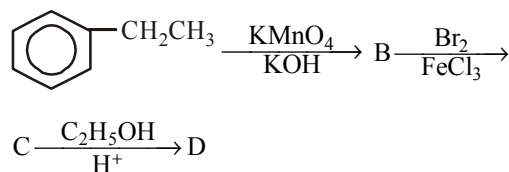


33. Which of the following reagent(s) used for the conversion?

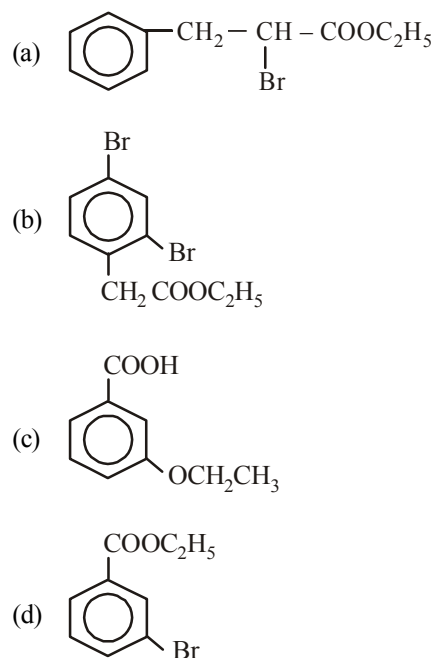


- (a) glycol/ $\text{LiAlH}_4/\text{H}_3\text{O}^+$ (b) glycol/ $\text{NaH}/\text{H}_3\text{O}^+$
(c) LiAlH_4 (d) NaBH_4

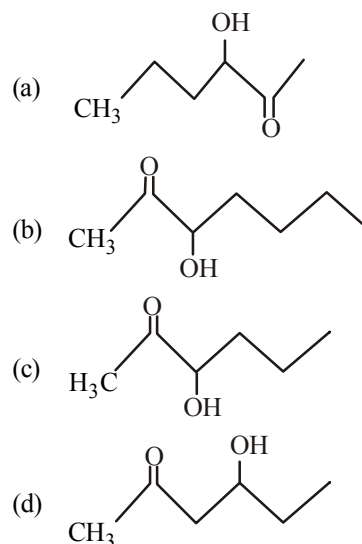
34. In a set of reactions, ethylbenzene yield a product D.



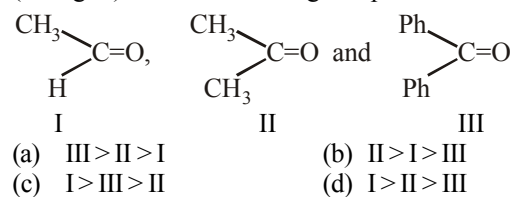
Identify D :



35. Which one of the following compounds will be most readily dehydrated?



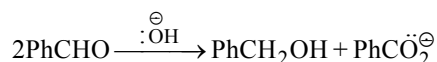
36. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds



37. An organic compound 'A' on treatment with NH_3 gives 'B' which on heating gives 'C', 'C' when treated with Br_2 in the presence of KOH produces ethylamine. Compound 'A' is:

- (a) CH_3COOH (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
 (c) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}}\text{COOH}$ (d) $\text{CH}_3\text{CH}_2\text{COOH}$

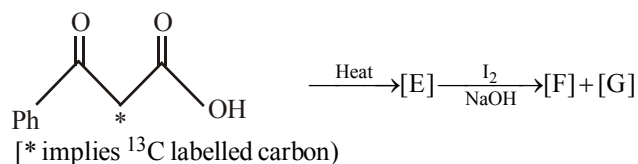
38. In Cannizzaro reaction given below



the slowest step is :

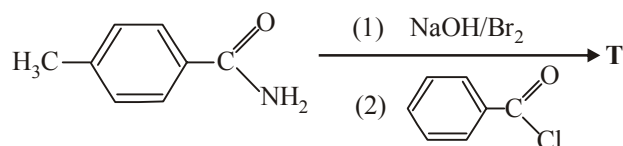
- (a) the transfer of hydride to the carbonyl group
 (b) the abstraction of proton from the carboxylic group
 (c) the deprotonation of PhCH_2OH
 (d) the attack of $:\text{OH}^-$ at the carboxyl group

39. In the following reaction sequence, the correct structures of E, F and G are



- (a) $\text{E} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{CH}_3$ $\text{F} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{O}^-\text{Na}^+$ $\text{G} = \text{CH}_3\text{I}$
 (b) $\text{E} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{CH}_3$ $\text{F} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{O}^-\text{Na}^+$ $\text{G} = \text{CH}_3\text{I}$
 (c) $\text{E} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{CH}_3$ $\text{F} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{O}^-\text{Na}^+$ $\text{G} = \text{CH}_3\text{I}$
 (d) $\text{E} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{CH}_3$ $\text{F} = \text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\overset{*}{\text{C}}-\text{O}^-\text{Na}^+$ $\text{G} = \text{CH}_3\text{I}$

40. In the reaction

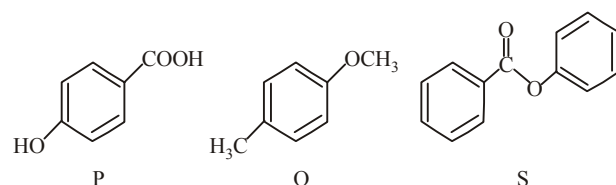


the structure of the product T is :

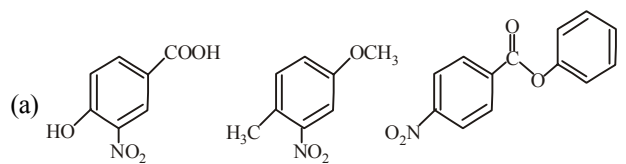
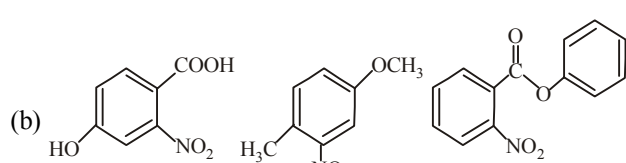
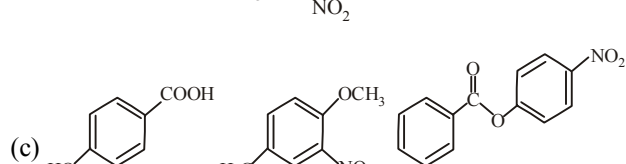
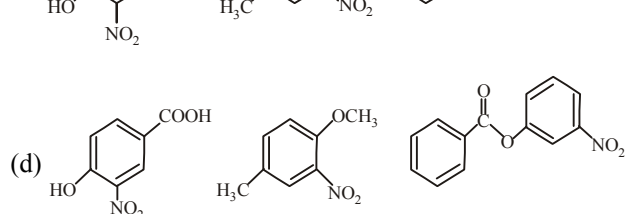
- (a) $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5$

- (b) $\text{C}_6\text{H}_5-\text{NH}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{CH}_3$
 (c) $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{NH}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5$
 (d) $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5$

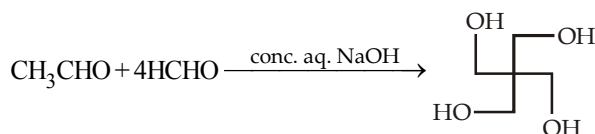
41. The compounds P, Q and S



were separately subjected to nitration using $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture. The major product formed in each case respectively, is :

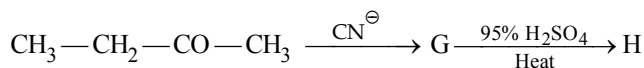
- (a) 
 (b) 
 (c) 
 (d) 

42. The number of aldol reaction(s) that occurs in the given transformation is :



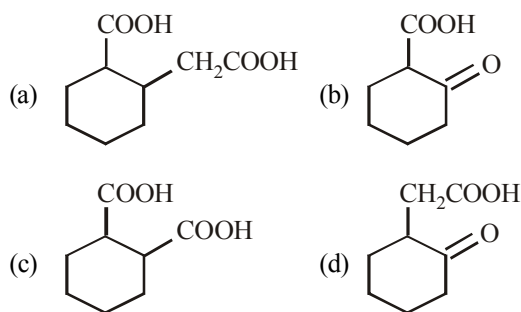
- (a) 1 (b) 2
 (c) 3 (d) 4

43. The major product **H** of the given reaction sequence is



- (a) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$
 (b) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CN}$
 (c) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{COOH}$
 (d) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}_2$

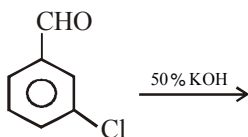
44. The compound that undergoes decarboxylation most readily under mild condition is

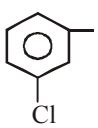
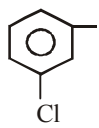
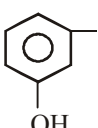
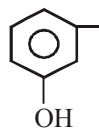


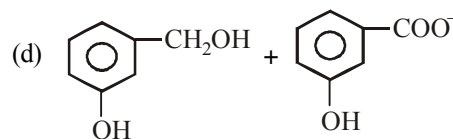
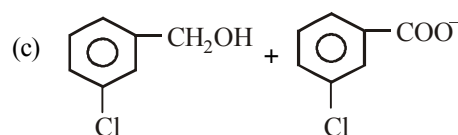
45. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to give $\text{CH}_3\text{CH}_2\text{NH}_2$. A is :

- (a) CH_3COOH (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
 (c) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{COOH}$ (d) $\text{CH}_3\text{CH}_2\text{COOH}$

46. Predict the product in the given reaction.



- (a)  + 
 (b)  + 



47. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is :

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_3$
 (c) $(\text{CH}_3)_2\text{C} \begin{matrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{matrix}$
 (d) $(\text{CH}_3)_2\text{C} \begin{matrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{matrix}$

DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: **Statement-1 (Assertion)** and **Statement-2 (Reason)**. Answer these questions from the following four options.

- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement -1
 (b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is True, Statement-2 is False
 (d) Statement-1 is False, Statement-2 is True

48. **Statement-1 :** Acetic acid does not undergo haloform reaction.

Statement-2 : Acetic acid has no alpha hydrogens.

49. **Statement-1 :** Benzaldehyde is more reactive than ethanol towards nucleophilic attack.

Statement-2 : The overall effect of -I and + R effect of phenyl group decreases the electron density on the carbon atom of $>\text{C}=\text{O}$ group in benzaldehyde.

50. **Statement-1 :** Lower aldehyde and ketones are soluble in water but the solubility decreases as molecular mass increases.

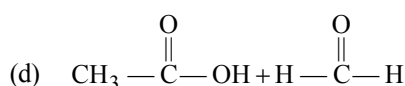
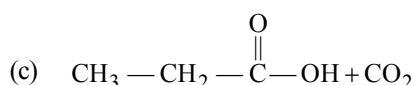
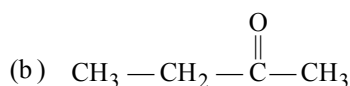
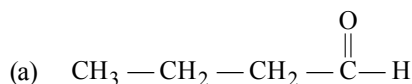
Statement-2 : Aldehydes and ketones can be distinguished by Tollen's reagent.

EXERCISE - 3

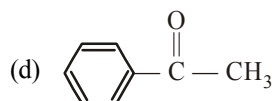
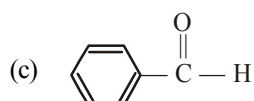
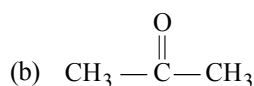
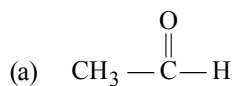
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but - 1-yne under these conditions?



2. Which of the following compounds is most reactive towards nucleophilic addition reactions?



3. The correct order of increasing acidic strength is

- (a) phenol < ethanol < chloroacetic acid < acetic acid
 (b) ethanol < phenol < chloroacetic acid < acetic acid
 (c) ethanol < phenol < acetic acid < chloroacetic acid
 (d) chloroacetic acid < acetic acid < phenol < ethanol

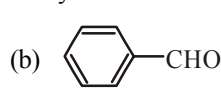
4. Compound $\text{Ph} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{Ph}$ can be prepared by the reactions of

- (a) phenol and benzoic acid in the presence of NaOH
 (b) phenol and benzoyl chloride in the presence of pyridine
 (c) phenol and benzoyl chloride in the presence of ZnCl_2
 (d) phenol and benzaldehyde in the presence of palladium

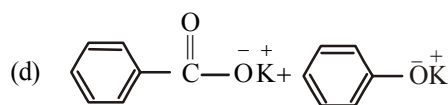
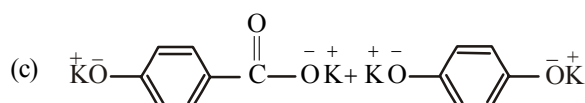
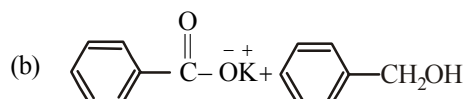
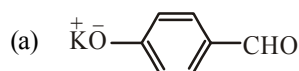
5. The reagent which does not react with both, acetone and benzaldehyde?

- (a) Sodium hydrogen sulphite
 (b) Phenyl hydrazine
 (c) Fehling's solution
 (d) Grignard reagent

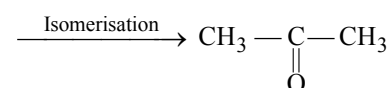
6. Cannizzaro's reaction is not given by



7. Which product is formed when the compound is treated with concentrated aqueous KOH solution?

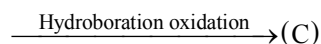
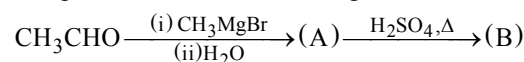


8. $\text{CH}_3 - \text{C} \equiv \text{CH} \xrightarrow[1\% \text{ HgSO}_4]{40\% \text{ H}_2\text{SO}_4} \text{A}$

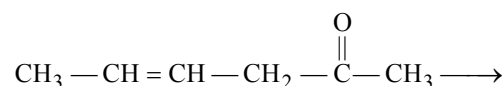


structure of 'A' and type of isomerism in the above reaction are respectively

- (a) Prop-1-en-2-ol, metamerism
 (b) Prop-1-en-1-ol, tautomerism
 (c) Prop-2-en-2-ol, geometrical isomerism
 (d) Prop-1-en-2-ol, tautomerism
9. Compounds A and C in following reaction are



- (a) identical (b) positional isomers
 (c) functional isomers (d) optical isomers
10. Which is the most suitable reagent for the following conversion?



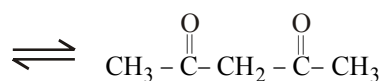
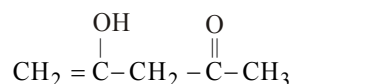
- (a) Tollen's reagent (b) Benzoyl peroxide
 (c) I_2 and NaOH solution (d) Sn and NaOH solution
11. Which of the following compounds will give butanone on oxidation with alkaline KMnO_4 solution?
- (a) Butan-1-ol (b) Butan-2-ol
 (c) Both (a) and (b) (d) None of these

12. In Clemmensen reduction, carbonyl compounds is treated with

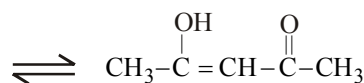
- (a) zinc amalgam + HCl
(b) sodium amalgam + HCl
(c) zinc amalgam + nitric acid
(d) sodium amalgam + HNO₃

NEET/AIPMT (2013-2017) Questions

13. The order of stability of the following tautomeric compounds is :



II

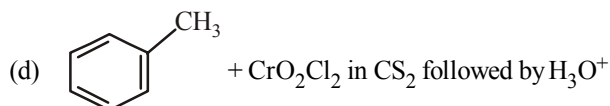
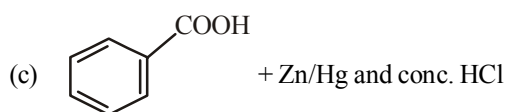
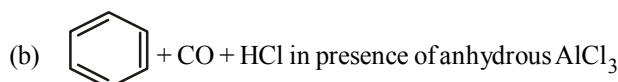
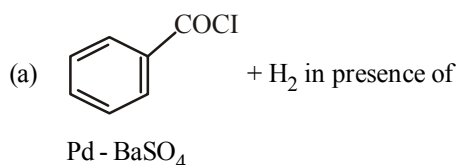


[2013]

- (a) III > II > I (b) II > I > III
(c) II > III > I (d) I > II > III

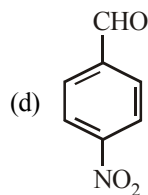
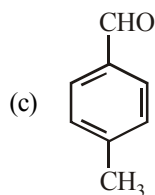
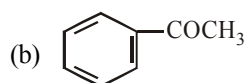
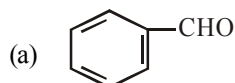
14. Reaction by which Benzaldehyde cannot be prepared :

[2013]



15. Which one is most reactive towards Nucleophilic addition reaction?

[2014]



16. An organic compound 'X' having molecular formula C₅H₁₀O yields phenyl hydrazone and gives negative response to the Iodoform test and Tollen's test. It produces n-pentane on reduction. 'X' could be :-

[2015]

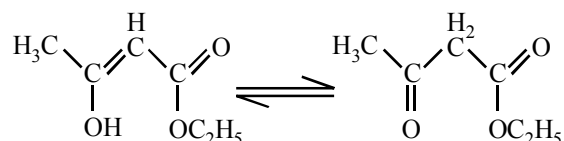
- (a) 2-pentanone (b) 3-pentanone
(c) n-amyl alcohol (d) pentanal

17. Treatment of cyclopentanone  with methyl lithium gives which of the following species?

[2015]

- (a) Cyclopentanonyl cation
(b) Cyclopentanonyl radical
(c) Cyclopentanonyl biradical
(d) Cyclopentanonyl anion

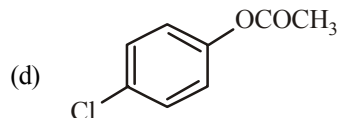
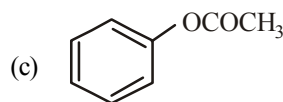
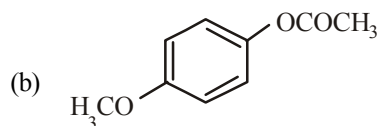
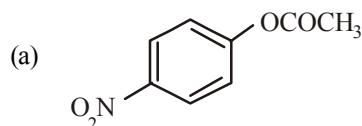
18. The enolic form of ethyl acetoacetate as below has: [2015]



- (a) 16 sigma bonds and 1 pi - bond
(b) 9 sigma bonds and 2 pi - bonds
(c) 9 sigma bonds and 1 pi - bond
(d) 18 sigma bonds and 2 pi - bonds

19. Which one of the following esters gets hydrolysed most easily under alkaline conditions?

[2015 RS]



20. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is :

[2015 RS]

- (a) a Grignard reagent
(b) hydrazine in presence of feebly acidic solution
(c) hydrocyanic acid
(d) sodium hydrogen sulphite

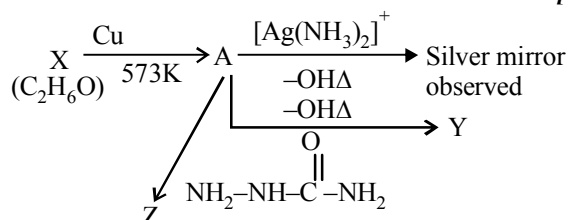
21. The correct statement regarding a carbonyl compound with a hydrogen atom on its alphacarbon, is : [2016]

- a carbonyl compound with a hydrogen atom on its alphacarbon never equilibrates with its corresponding enol.
- a carbonyl compound with a hydrogen atom on its alphacarbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.
- a carbonyl compound with a hydrogen atom on its alphacarbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation.
- a carbonyl compound with a hydrogen atom on its alphacarbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism.

22. The product formed by the reaction of an aldehyde with a primary amine is [2016]

- Schiff base
- Ketone
- Carboxylic acid
- Aromatic acid

23. Consider the reactions :- [2017]



Identify A, X, Y and Z

- A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.

- A - Ethanal, X-Ethanol, Y - But - 2-enal, Z-Semicarbazone
- A-Ethanol, X-Acetaldehyde, Y - Butanone, Z-Hydrazone
- A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine.

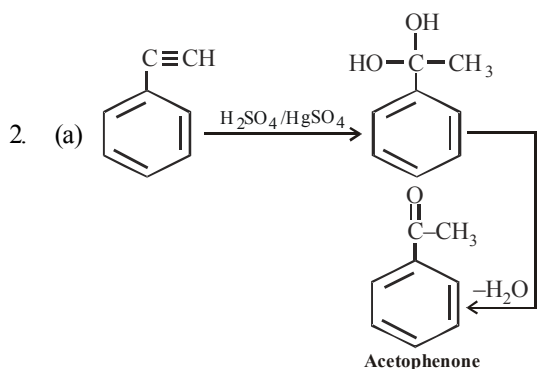
24. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating ? [2017]

-
-
-
-

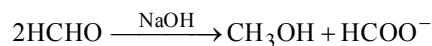
Hints & Solutions

EXERCISE - 1

1. (c) Benzaldehyde and alcoholic KCN react to form Benzoin. This is known as Benzoin condensation.

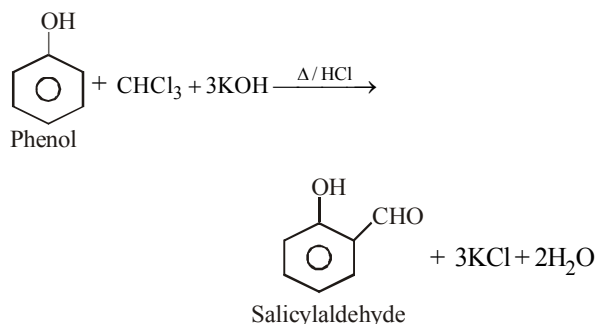


3. (d) (a) Cannizzaro reaction



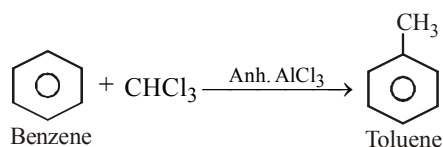
No new C—C bond is formed

(b) Reimer - Tiemann reaction :



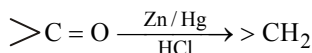
New C—C bond is formed

(c) Friedel-Craft reaction :

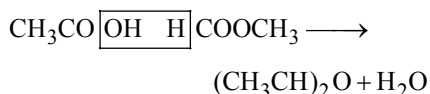


New C—C bond is formed

(d) Clemmensen reduction

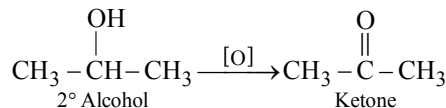


4. (b) Acetic Anhydride is produced due to dehydration of two molecules of acetic acid by P_2O_5



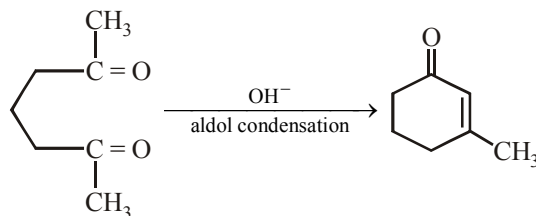
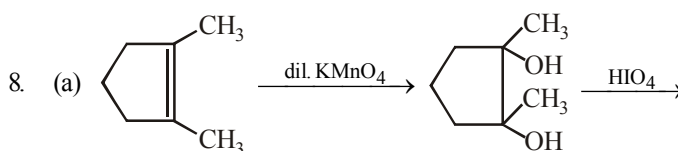
5. (b) $(\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\Delta} \text{CH}_3-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{CH}_3 + \text{CaCO}_3$
Calcium acetate Acetone

6. (c) $\text{C}_3\text{H}_8\text{O} \xrightarrow[\text{(x)}]{[\text{O}]} \text{C}_3\text{H}_6\text{O}$ (Ketone)

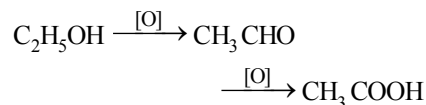


Ketones are oxidation products of 2° alcohols.

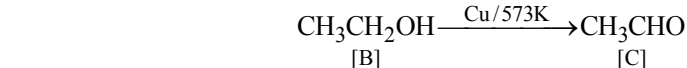
7. (c) Clemmensen's Reduction of ketones is carried out in Zn-Hg and HCl.



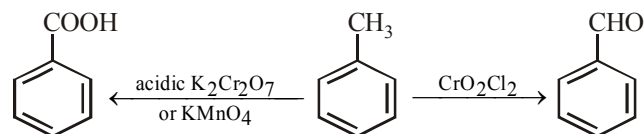
9. (b) The compound is $\text{C}_2\text{H}_5\text{OH}$.



10. (d) $\text{CH}_3\text{CN} \xrightarrow{\text{Na/C}_2\text{H}_5\text{OH}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{CH}_3\text{CHO}$
[A] [B] [C]



11. (c)



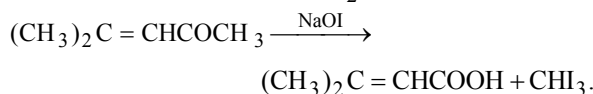
(Etard reaction)

Acidic KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ oxidise toluene to benzoic acid but CrO_2Cl_2 oxidises it to Benzaldehyde.

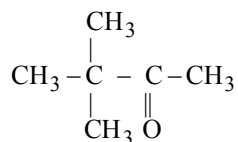
12. (c) Formalin is an aqueous solution (40%) of formaldehyde.
13. (d) I_2 and Na_2CO_3 react with acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) to give yellow ppt. of CHI_3 but benzophenone ($\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$) does not and hence can be used to distinguish between them.
14. (c) The test used for the distinction of HCOOH and CH_3COOH is treatment with Tollen's reagent because formic acid can reduce Tollen's reagent but acetic acid can not.

15. (b) $2\text{HCOONa} \xrightarrow[360^\circ]{\Delta} \begin{array}{c} \text{COONa} \\ | \\ \text{COONa} \end{array} + \text{H}_2$

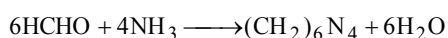
16. (b) Chromic acid and KMnO_4 will cleave the molecule at the site of double bond while Cu at 300°C cannot oxidise $\text{COCH}_3 \longrightarrow \text{COOH}$. The only reagent suitable for this conversion is NaOI or $\text{NaOH} + \text{I}_2$ (iodoform test):



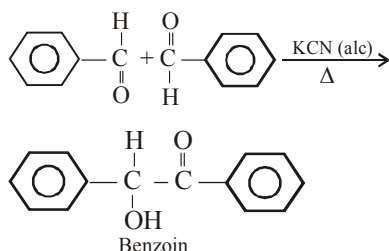
17. (b) Pinacolone is 3,3-dimethyl-2-butanone.



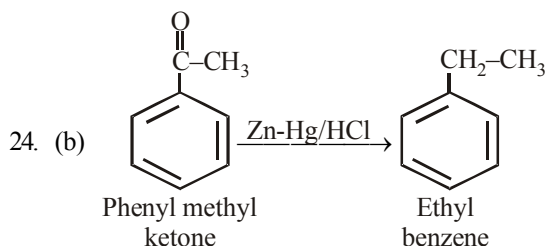
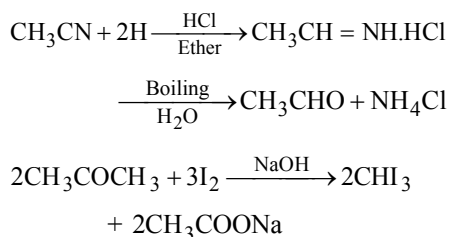
18. (a) Formaldehyde reacts with ammonia to form hexamethylene tetramine which is also known as urotropine. It is used as urinary tract antiseptic



19. (b) When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form benzoin

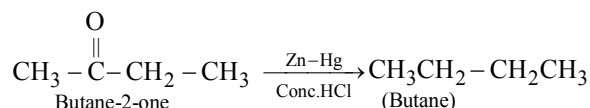


20. (d) Dihydrogen sodium phosphate (NaH_2PO_4) does not have a lone pair of electrons on the P atom. As such it can not act as a nucleophile and hence does not react with aldehydes and ketones.
21. (d) The compound formed is trioxo formaldehyde.
22. (c) Aldol condensation is given by the compounds which contain α hydrogen atom. As the given compound does not contain α hydrogen atom. Hence it does not undergo aldol condensation.
23. (c) Acetaldehyde is formed

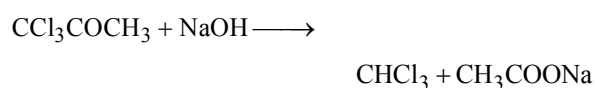


This reaction is known as Clemmensen's reduction.

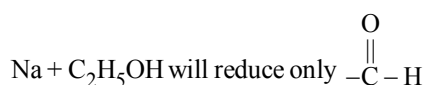
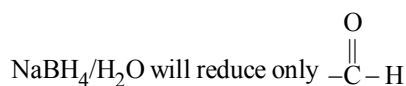
25. (d) It is Clemmensen's reduction



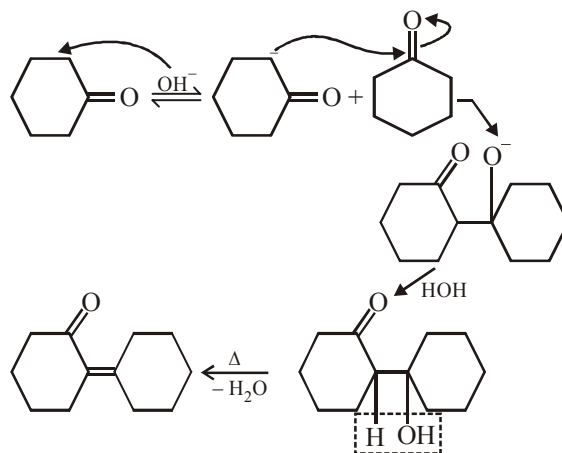
26. (b) $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_3 + 3\text{Cl}_2 \xrightarrow{\text{NaOH}} \text{CCl}_3\text{COCH}_3 + 3\text{HCl}$



27. (d) $\text{LiAlH}_4/\text{H}_2\text{O}$ will reduce only $\text{O}=\text{C}-\text{H}$

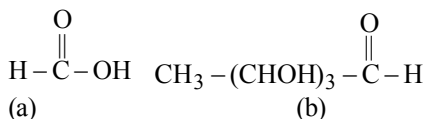


28. (a) Chloral is CCl_3CHO so, it is an aldehyde.
29. (c) In the presence of base, cyclohexanone show aldol condensation.

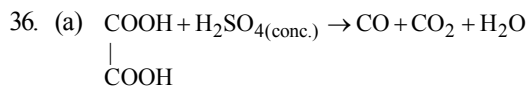


30. (b) Aldol formed in aromatic aldehydes itself loses water molecule without heating because double bond formed is more stable due to conjugation with benzene ring. $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ is commonly known as cinnamaldehyde.
31. (b) $(\text{CH}_3)_3\text{C}-\text{CHO}$ does not show aldol condensation because it does not contain α -hydrogen atom.
32. (b) In Wolf-Kishner reduction $\text{NH}_2\text{NH}_2/\text{OH}^-$ is used. Br^- can be replaced by OH^- .
33. (b) Cannizzaro reaction is given by aldehydes and ketones which do not have α -hydrogen atom. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) does not have α -H atom and hence gives Cannizzaro reaction.
34. (b) Acetaldehyde has α -H atoms. In alkaline medium it will undergo aldol condensation to produce aldol (β -hydroxyaldehyde).

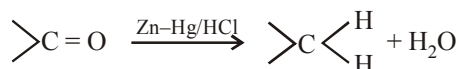
35. (d) Compounds having $-\text{CHO}$ group reduce Tollen's reagent to silver mirror. It is called silver mirror test.



Both (a) and (b) have $-\text{C}-\text{H}$ group so both of them give positive silver mirror test.

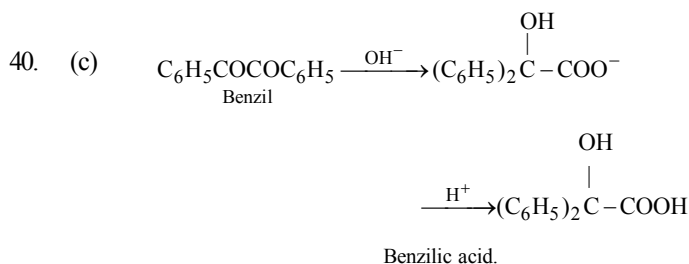
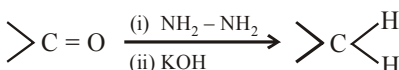


37. (a) Aldehydes and ketones are reduced to alkanes by Clemmensen reduction.

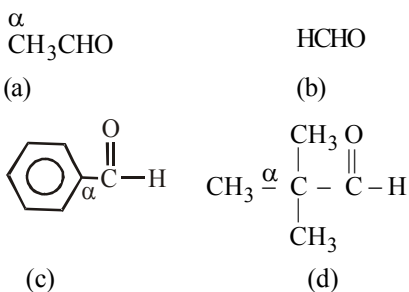


38. (b)

39. (a) Wolf-Kishner reduction

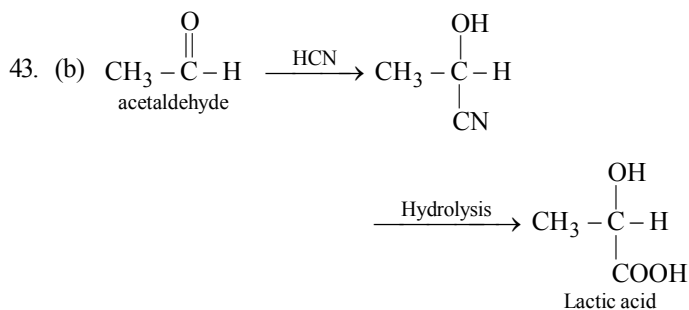


41. (a) Aldehydes having α -hydrogen atom do not show Cannizzaro reaction.

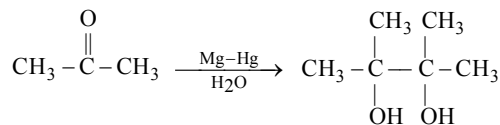


Thus only CH_3CHO has α -hydrogen atom and hence it will not show Cannizzaro reaction.

42. (c) Only aldehydes and ketones react with 2,4-dinitrophenylhydrazine.



44. (b) Example:

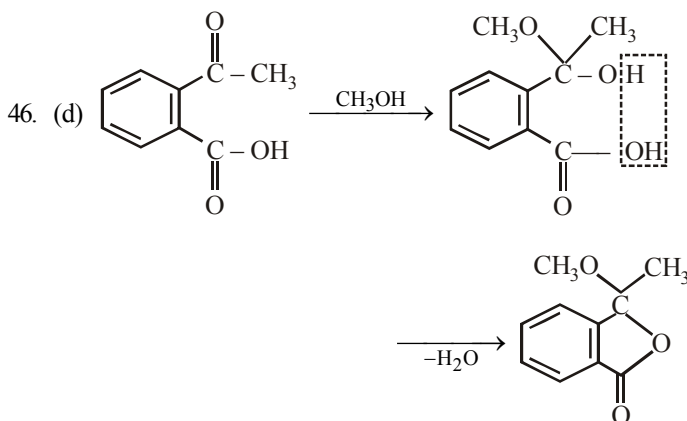


Pinacol

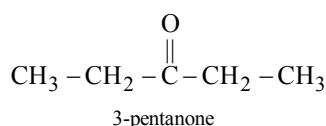
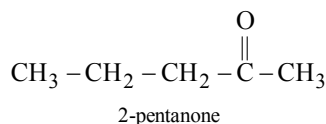
(Pinacols have adjacent hydroxyl groups)

45. (a) Compounds having $-\text{C}(=\text{O})-$ moiety in their structure are reduced to alcohols using NaBH_4 in ethanolic solution.

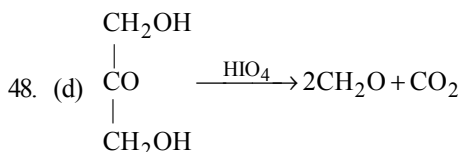
Thus $\text{R}-\text{C}(=\text{O})-\text{Cl}$, $\text{R}-\text{C}(=\text{O})-\text{OH}$ and $\text{R}-\text{C}(=\text{O})-\text{H}$ are reduced while, $\text{R}-\text{O}-\text{R}$ (ethers) are inert and can't be reduced by NaBH_4 .



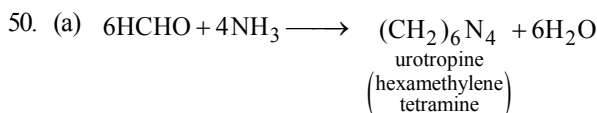
47. (c) Iodoform test is given by compounds which have CH_3CO group.



$\therefore$ 2-pentanone has CH_3CO group, so it gives iodoform test, while 3-pentanone does not have CH_3CO group, so it does not give iodoform test.



49. (a) In this reaction, one molecule is oxidised and other is reduced simultaneously.

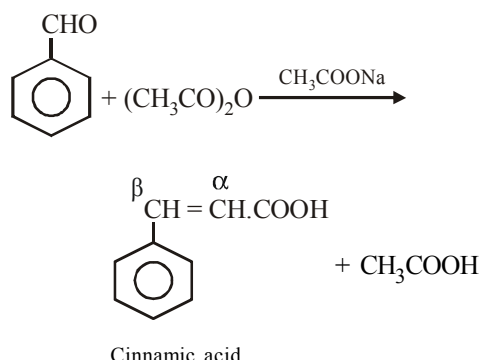


51. (d) We can distinguish between formic acid and acetic acid by their action on Fehling's solution. Formic acid gives a red ppt of cuprous oxide but acetic acid does not give red ppt.
52. (a) Aldol condensation involves an aldehyde or ketone having an α -hydrogen atom. This type of condensation occurs in presence of dilute base (i.e., dil NaOH).
Only CH_3COCH_3 will give aldol condensation (Both HCHO and $\text{C}_6\text{H}_5\text{CHO}$ lack α -hydrogen).
53. (b) Cl_2 does not give acid chloride on treating it with a carboxylic acid.

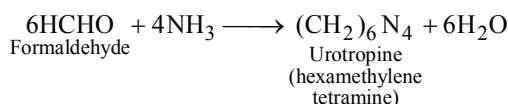
Only CH_3COCH_3 will give aldol condensation (Both HCHO and $\text{C}_6\text{H}_5\text{CHO}$ lack α -hydrogen).

53. (b) Cl_2 does not give acid chloride on treating it with a carboxylic acid.
- While PCl_3 , PCl_5 and SOCl_2 gives nucleophilic substitution reaction with carboxylic acid (Cl^- replaces OH^- group of $-\text{COOH}$)

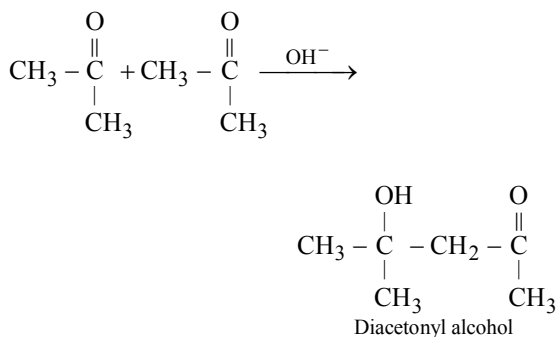
54. (b) Benzaldehyde forms cinnamic acid as follows.



55. (d) Formaldehyde on reaction with ammonia forms a crystalline compound, hexamethylene tetramine.

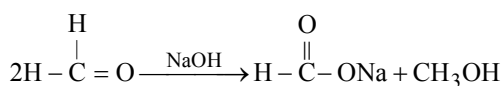


56. (a) Completing the given reaction.

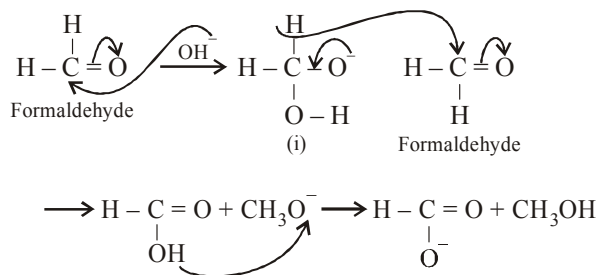


[**Note:** Carbonyl compounds having $\alpha - \text{H}$ atom undergoes **aldol condensation** in presence of dilute base {e.g., NaOH , $\text{Ba}(\text{OH})_2$ etc.} to form a class of compounds known as **aldol**].

57. (c) In the Cannizzaro reaction, two moles of carbonyl compounds having no α -hydrogen atom when treated with strong alkali undergo, redox or disproportionation reaction.

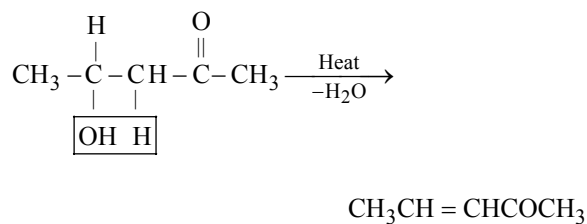
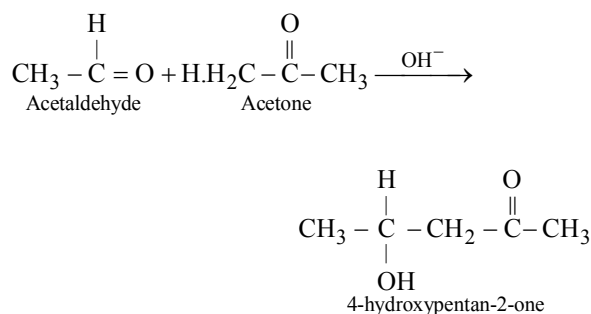


Mechanism : First of all base OH^- acts as a nucleophile and attack other one of carbonyl compound to generate a hydroxy alkoxide ion which acts as a hydride ion donor to the other molecule of carbonyl compounds. In the final step there is a exchange of proton from acid to alkoxide ion to get stable product.

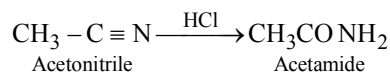


58. (c)
- $$\begin{array}{c}
 \text{R} \\
 \diagup \\
 \text{C} = \text{O} + \text{R}'\text{MgX} \longrightarrow \begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array} \begin{array}{c} \text{OMgX} \\ \\ \text{R}' \end{array} \\
 \diagdown \\
 \text{R}
 \end{array}$$
- $\downarrow \text{HOH}$
- $$\begin{array}{c}
 \text{R} \\
 \diagup \\
 \text{R}-\text{C}-\text{OH} + \text{Mg}(\text{OH})\text{X} \\
 \diagdown \\
 \text{R}'
 \end{array}$$
- 3° alcohol

59. (b) When aldehyde condensed with ketone, α -hydrogen of the ketone involved in condensation.



60. (a) When acetonitrile is hydrolysed partially with cold concentrated HCl it forms acetamide.

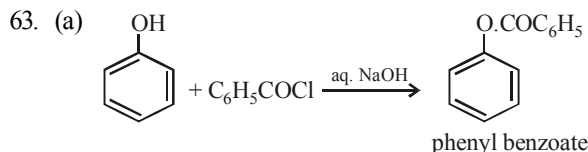
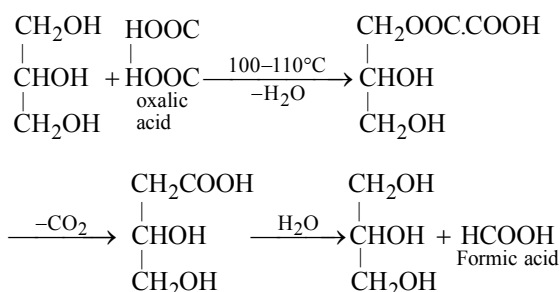


On further hydrolysis acetamide may give either CH_3COOH (acetic acid) or its salt.

61. (a) among acetic acid, phenol and n-hexanol only CH_3COOH reacts with NaHCO_3 to evolve CO_2 gas.

$$\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$$

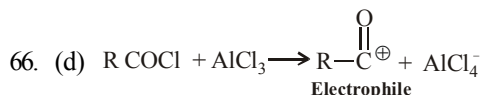
62. (c) When glycerol is heated with oxalic acid following reaction occurs.



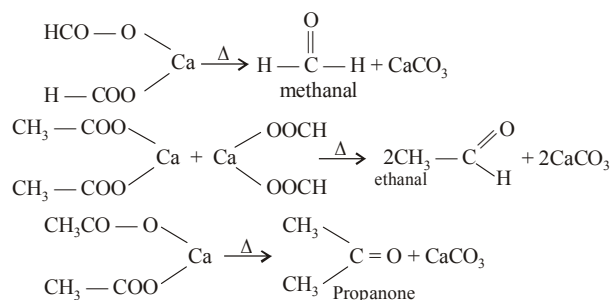
The function of NaOH is

- (i) To convert phenol to more stronger nucleophile PhO^-
 (ii) To neutralize the acid formed

64. (a) Aldehydes, other than formaldehyde, when treated with RMgX give 2° alcohols.
 65. (d) Methyl acetate and ethyl acetate on hydrolysis give CH_3COOH which is a liquid. Similarly ethyl formate on hydrolysis will give formic acid which is also a liquid. Only ethyl benzoate on hydrolysis will give benzoic acid which is a solid.

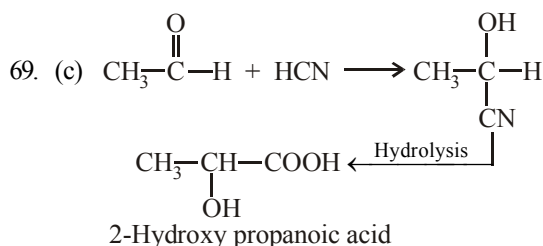


67. (b) Propanal is not formed during the dry distillation of a mixture of calcium formate and calcium acetate. While methanal, propanone and ethanal are formed as follows:

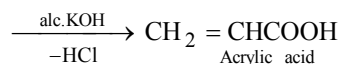
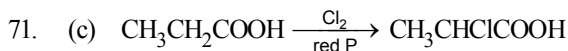
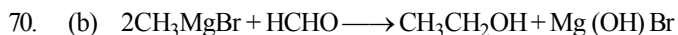


68. (b) The ester having α hydrogen atom show Claisen condensation reaction.

We know that ethyl benzoate ($\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$) does not contain α -hydrogen. Therefore $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ does not undergo Claisen self condensation.



(As it has a chiral C-atom thus it is optically active)

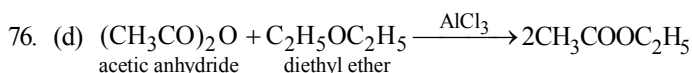
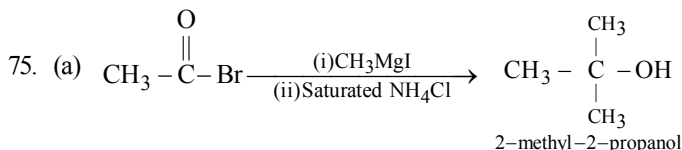


72. (d)

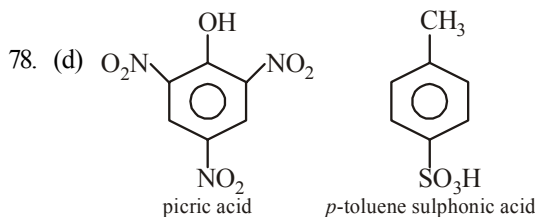
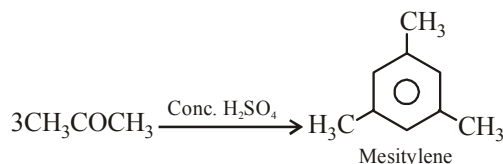
73. (a) LiAlH_4 can reduce COOH group and not the double bond.



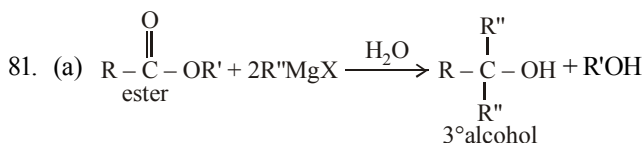
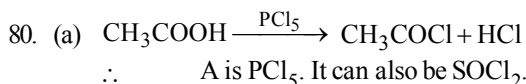
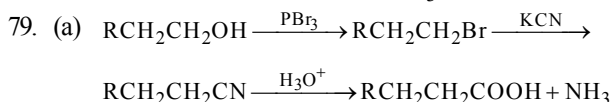
74. (c) There is no reaction hence the resultant mixture contains $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$.



77. (a) When distilled with conc. H_2SO_4 , three molecules of acetone condense to form mesitylene, i.e. 1, 3, 5-trimethylbenzene.



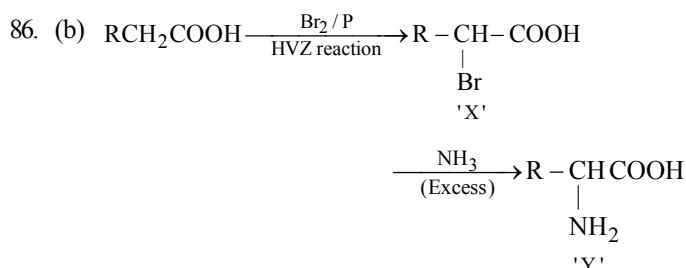
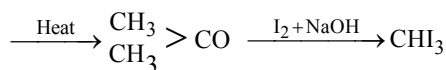
Other three acids contain $-\text{COOH}$ group.



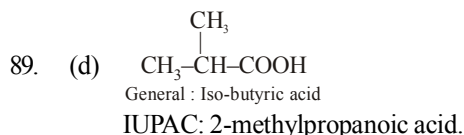
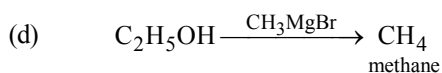
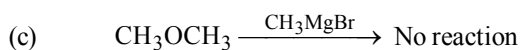
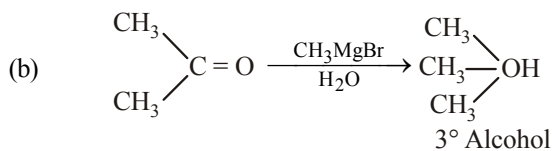
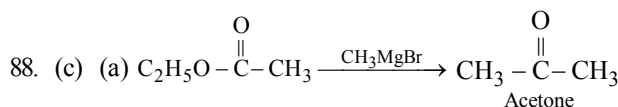
82. (c) CaC_2O_4 is the only compound of Ca which is not soluble in acetic acid. This property of Ca is used in inorganic salt analysis.

83. (c) Cl_2CHCOOH is most acidic because it has two chlorine at α -position.

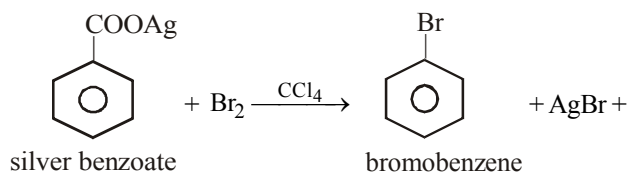
84. (d)



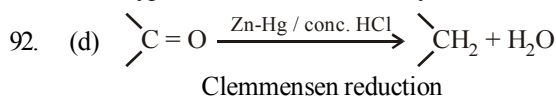
87. (d) Ethers neither react with sodium nor with semicarbazide.



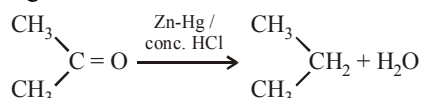
90. (c) This is Hunsdiecker's reaction.



91. (b) Oxidation of acetaldehydes and methyl ketones with sodium hypoiodite gives this test. So, here in option (b) ketone is having $(\text{CH}_3\text{CO}-)$ group and the other is having $(\text{CH}_3\text{CH}_2\text{CO}-)$ group which do not give hypoiodite test. So thus they can be distinguished.



e.g.



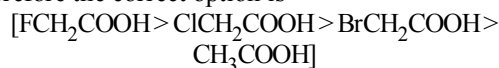
93. (c) Electron withdrawing substituent (like halogen, $-\text{NO}_2$, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative

charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.

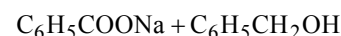
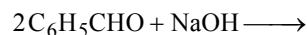
Electronegativity decreases in order



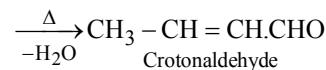
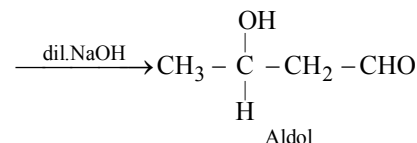
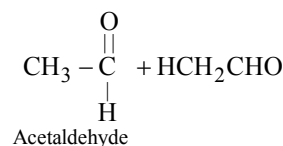
and hence $-I$ effect also decreases in the same order, therefore the correct option is



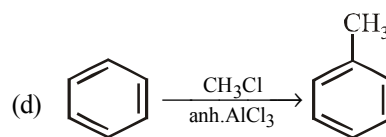
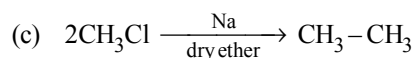
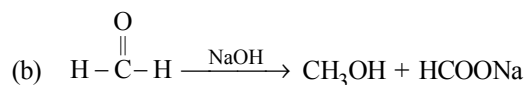
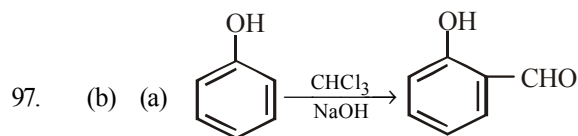
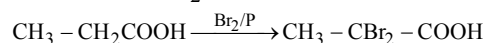
94. (a) Aldehydes containing no α -hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e., self oxidation - reduction known as cannizzaro's reaction.



95. (a) Aldehydes and ketones having at least one α -hydrogen atom in presence of dilute alkali give β -hydroxy aldehyde or β -hydroxy ketone



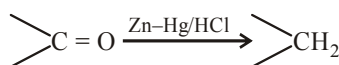
96. (c) This reaction is an example of Hell - Volhard Zelinsky reaction. In this reaction acids containing $\alpha - \text{H}$ on treatment with X_2/P give di-halo substituted acid.



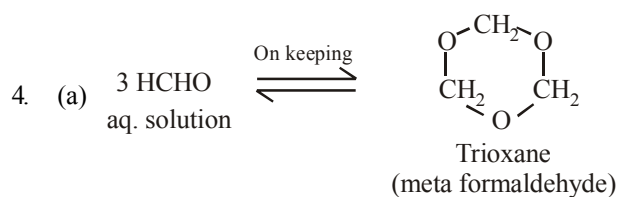
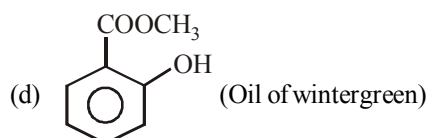
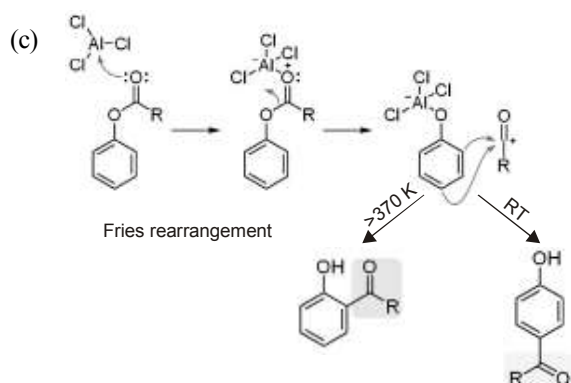
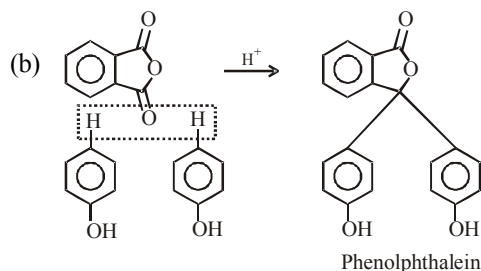
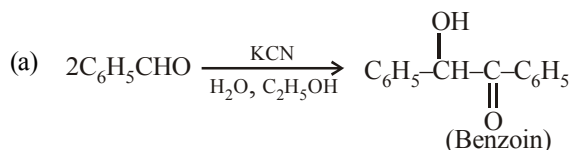
Note that new C-C bond is formed in a, c and d.

98. (d) Among the given compounds only CH_3OH does not give iodoform reaction.

99. (b) Clemmensen reduction is



100. (d)



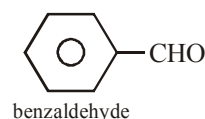
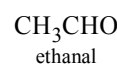
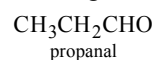
5. (b) Only aldehydes give reddish brown ppt. with Fehling's solution.

6. (d) Acetone or Propyne form mesitylene (1,3,5-trimethyl benzene) on distillation with conc. H_2SO_4 .

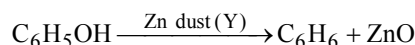
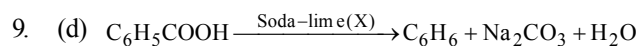
7. (a) Ketones on oxidation give carboxylic acids with lesser number of carbon atoms, i.e.,



8. (d) Structures of given aldehydes

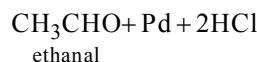
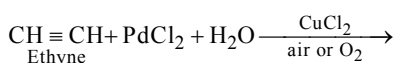


Trichloroethanal, methanal and benzaldehyde do not undergo aldol condensation. Aldol condensation is not given by aldehydes and ketones which do not contain α -hydrogen atom(s).

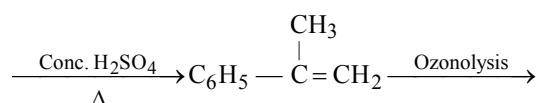
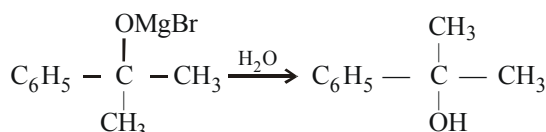
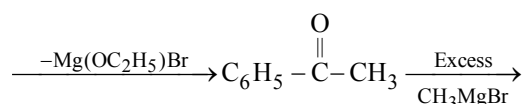
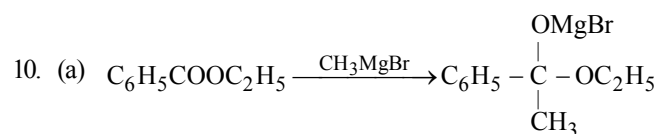


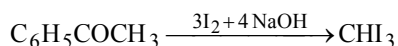
EXERCISE - 2

1. (a) Ethyne get converted to aldehydes and ketones when treated with an acidified aqueous solution of palladium chloride (PdCl_2) and cupric chloride (CuCl_2) in presence of air or oxygen. This method is known as Wacker's process.

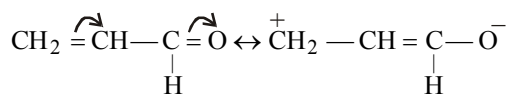


2. (d) Carbonyl compound form crystalline addition product with NaHSO_3 which on treatment with dilute acid or alkali regenerates the carbonyl compound.
3. (a) An electron releasing substituent (+I) intensify the negative charge on the anion resulting in the decrease of stability and thus decreases the acidity of the acid. Hence acid character decreases as the + I-effect of the alkyl group increases as
 $\text{CH}_3^- < \text{CH}_3\text{CH}_2^- < \text{CH}_3\text{CH}_2\text{CH}_2^- < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^-$
 Hence the order becomes : (i) > (ii) > (iii) > (iv)





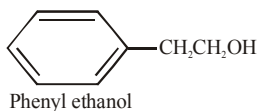
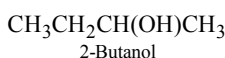
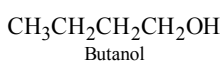
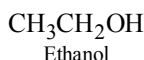
11. (c) In $\text{CH}_2 = \text{CH} - \text{CHO}$ due to — M effect of — CHO group polarization of electron takes place as follows



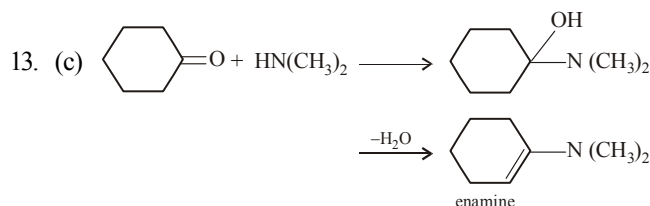
Hence partial polarization is represented as



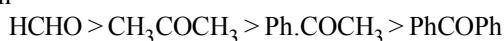
12. (d) Structures of given compounds



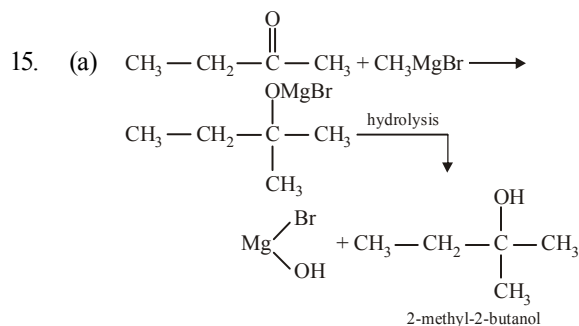
Compounds containing $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} -$ or $\text{CH}_3 - \text{CHOH} -$ group give positive iodoform test.



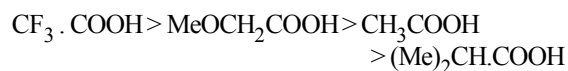
14. (a) Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is Aldehydes (smaller to higher) Ketones (smaller to higher), Then



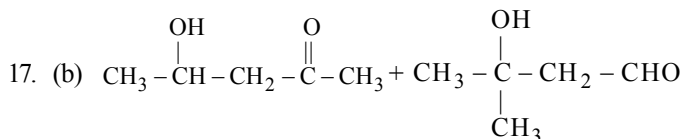
The lower reactivity of Ketones is due to presence of two alkyl group which shows +I effect. The reactivity of Ketones decreases as the size of alkyl group increases.



16. (a) The correct order of increasing acid strength

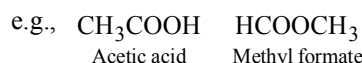


Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.

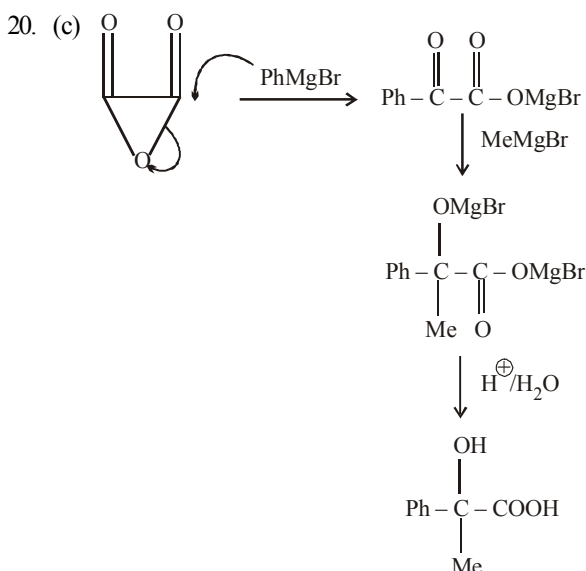


Two products are formed.

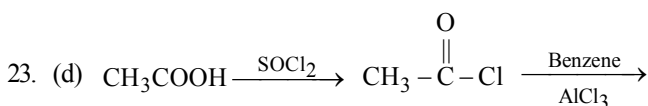
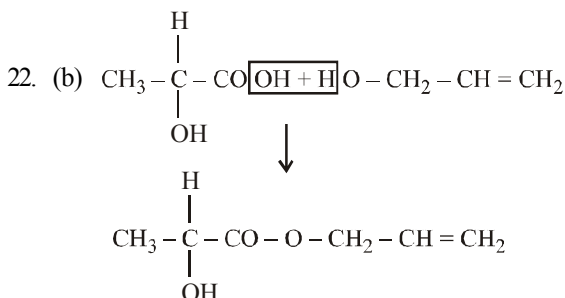
18. (c) Mono-carboxylic acids are functional isomers of esters.

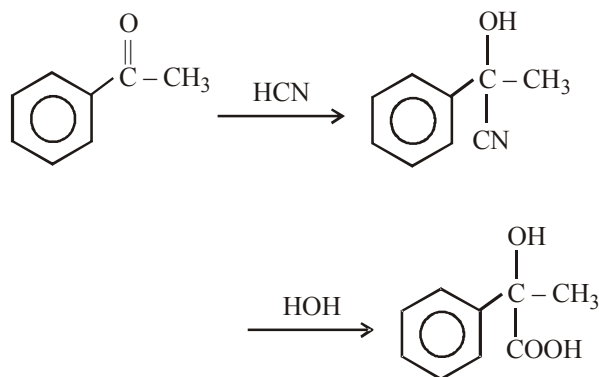


19. (c) KMnO_4 converts $-\text{CH}_3$ group of toluene into $-\text{COOH}$ while HI reduces $-\text{COOH}$ group into $-\text{CH}_3$ group.

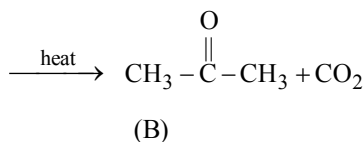
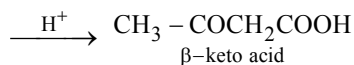
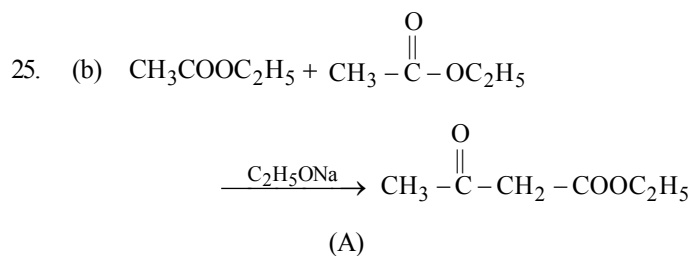
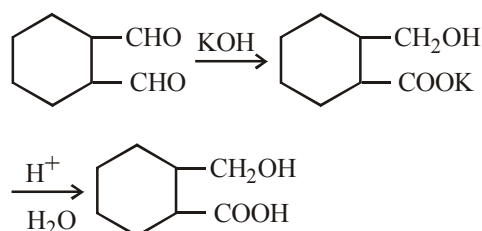


21. (a)

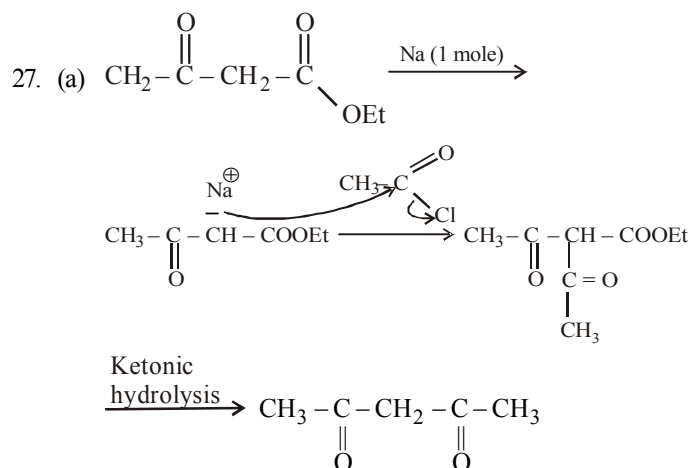
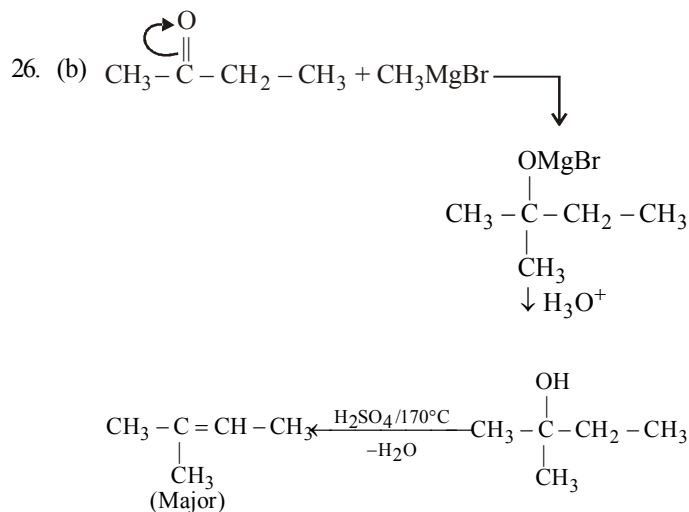




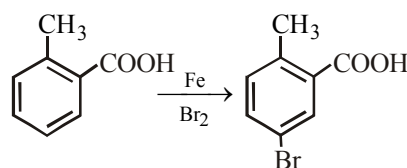
24. (a) It is an example of intramolecular cannizzaro reaction.



β-Keto acids, on heating, undergo decarboxylation.

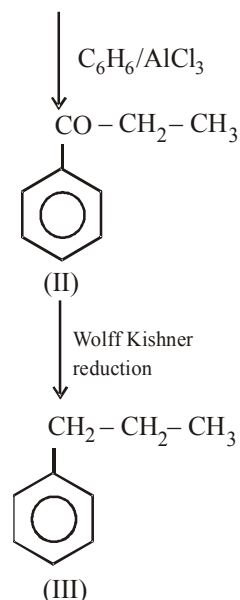
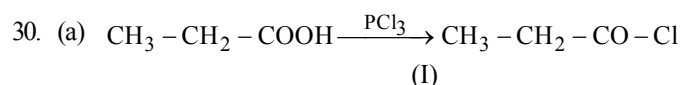
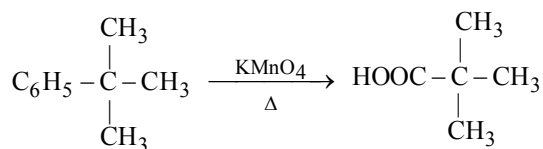


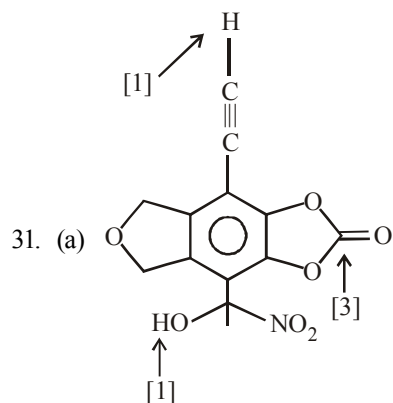
28. (c) In *o*-toluic acid, $-\text{CH}_3$ group is *ortho-para* directing



and $-\text{COOH}$ group is *meta*-directing. So, the resulting product will be (c) in which Br is attached at *para* to $-\text{CH}_3$ and *meta* to $-\text{COOH}$ group.

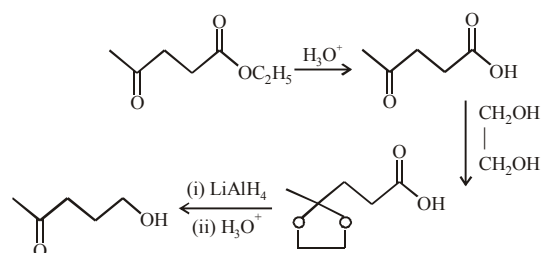
29. (b) Generally benzene ring is very resistant to oxidation thus side chain is always oxidised to $-\text{COOH}$ group. But if the side chain is tert-alkyl group, oxidation is difficult, but on vigorous oxidation benzene ring is oxidised.



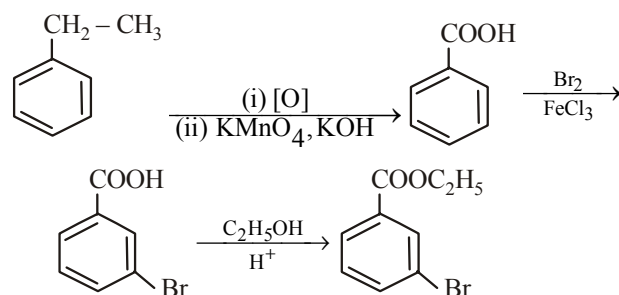


32. (c) Only those aldehydes which do not have α -H atom undergo Cannizzaro's reaction. Hence CH_3CHO will not undergo Cannizzaro's reaction as it has 3 α H atoms.

33. (a)

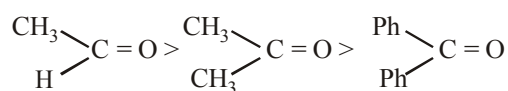


35. (d)



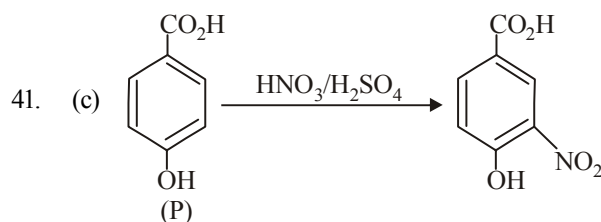
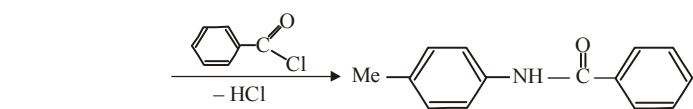
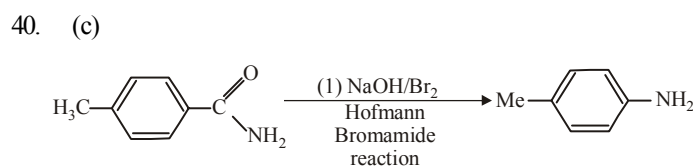
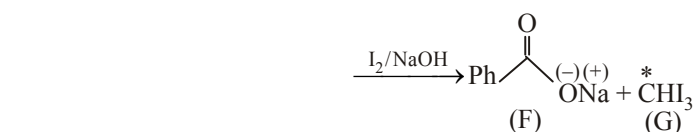
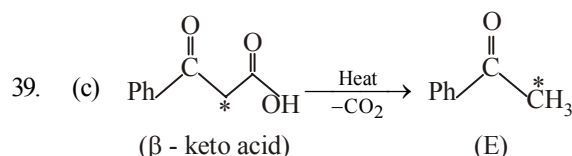
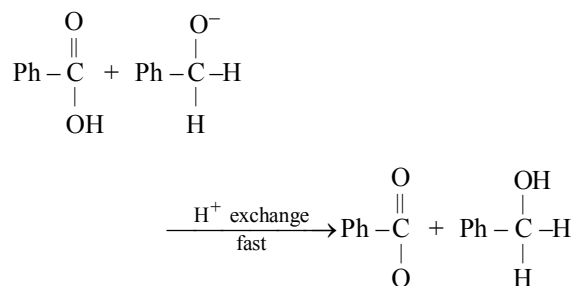
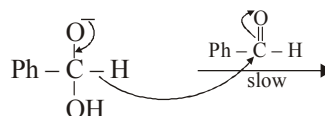
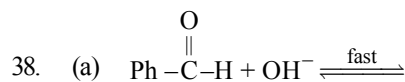
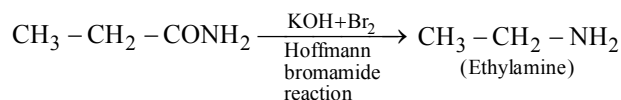
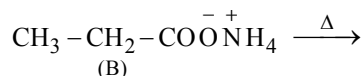
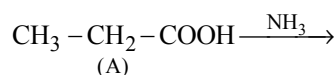
37. (d) The intermediate is carbocation which is destabilised by $\text{C}=\text{O}$ group in the first three cases. In (d), α -hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the $\text{C}=\text{O}$ group.

38. (d) The reactivity of the carbonyl group toward the nucleophilic addition reactions depend upon the magnitude of the positive charge on the carbonyl carbon atom (electronic factor) and also on the crowding around the carbonyl carbon atom in the transition state (steric factor). Both these factors predict the following order

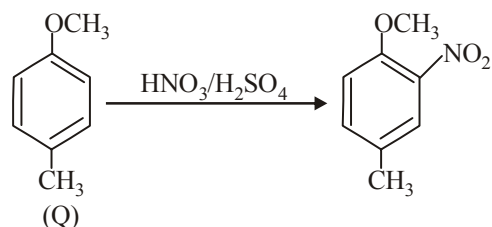


(due to steric crowding).

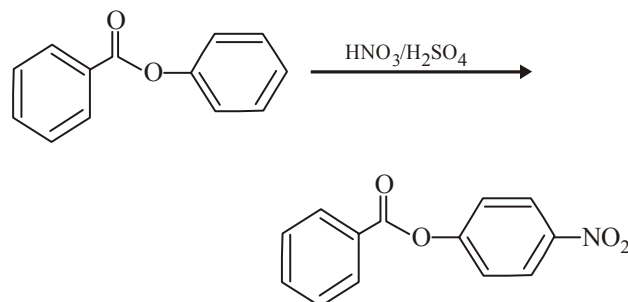
39. (d) Since, C when heated with Br_2 in presence of KOH produces ethylamine, hence it must be propanamide and hence the organic compound (A) will be propanoic acid. The reactions follows.



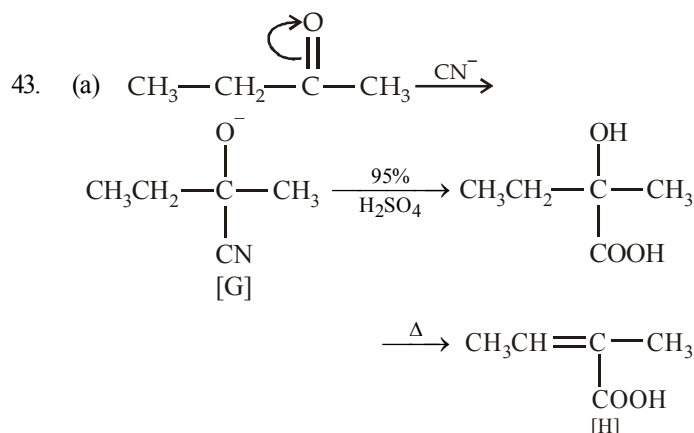
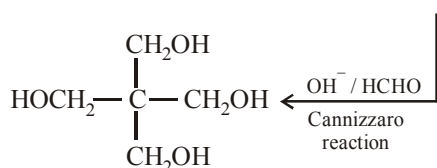
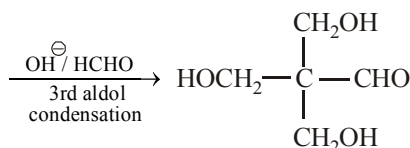
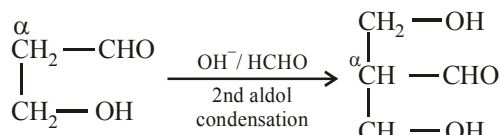
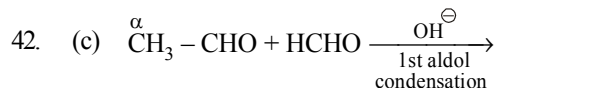
(OH group is activating)



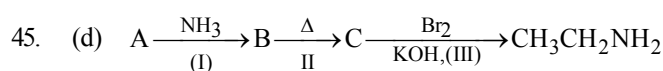
(OCH₃ group is more activating)



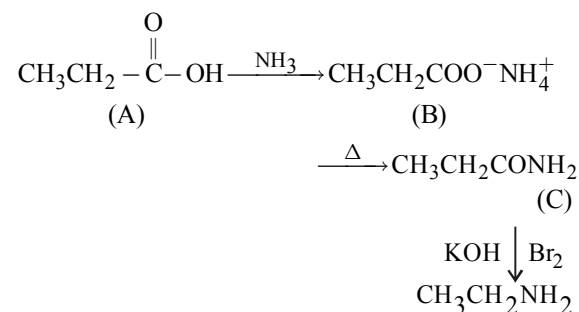
(Benzene ring having -O- is activated)



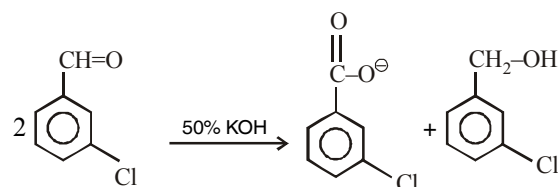
44. (b) β -Ketoacids undergo decarboxylation easily.



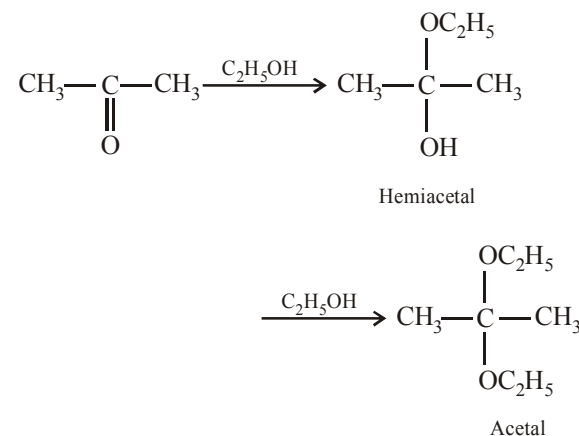
Reaction (III) is a Hofmann bromamide reaction. Now formation of CH₃CH₂NH₂ is possible only from a compound CH₃CH₂CONH₂ (C) which can be obtained from the compound CH₃CH₂COO⁻NH₄⁺ (B). Thus (A) should be CH₃CH₂COOH



46. (c) Cannizzaro reaction - when an aldehyde containing no α -H undergo reaction in presence of 50% KOH. It disproportionates to form a molecule of carboxylic acid and a molecule of alcohol.



47. (d) Anhydrous alcohols add to the carbonyl group of aldehydes in the presence of anhydrous hydrogen chloride to form acetals via hemiacetals.



48. (c)

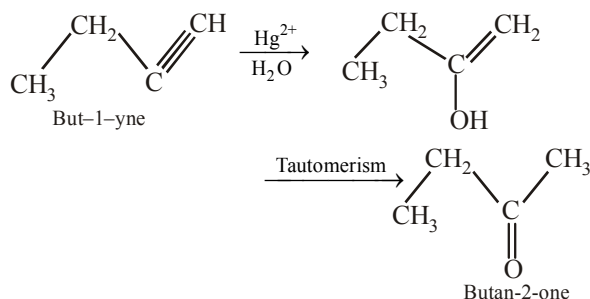
49. (d) Benzaldehyde is less reactive than ethanol towards nucleophilic attack. The combined effect of -I and +R effect of phenyl group is electron donating which increases the electron density on the carbon atom of the $>\text{C}=\text{O}$ in benzaldehyde.

50. (b) It is true that lower aldehyde and ketones are soluble in water but as the molecular mass increases their solubility decreases. On adding Tollen's reagent to a solution of Carbonyl compound if silver mirror is obtained then it is aldehyde. Therefore Tollen's reagent is used for the identification of aldehydes and ketones. Here, Statement-1 and Statement-2 both are true but the Statement-2 is not the correct explanation of Statement-1.

EXERCISE - 3

Exemplar Questions

1. (b) But-1-yne on reaction with water in presence of Hg^{2+} ions as a catalyst produces butan-2-one.



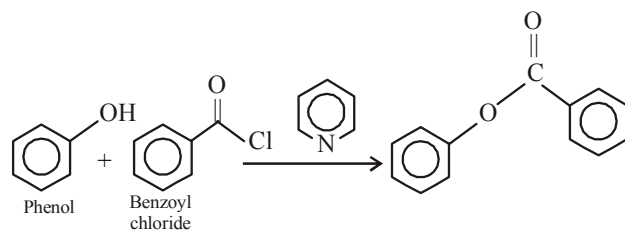
2. (a) The carbonyl group in ketones being influenced by two alkyl group is less reactive than in aldehydes where the carbonyl group is under the influence of one alkyl group only. As the number of alkyl group increases both the +I effect and the steric hindrance get increases preventing the attack of nucleophile.

Now among benzaldehyde and acetaldehyde former is less electrophilic than carbon atom of carbonyl group present in ethanal. The polarity of carbonyl group is reduced in benzaldehyde due to resonance hence it is less reactive than ethanal.

3. (c) Due to the electron withdrawing characteristic of $-\text{Cl}$, chloroacetic acid is more acidic than acetic acid further, in phenol phenoxide ion obtained on ionisation of phenol is stabilised due to resonance whereas no such stabilisation occurs in case of ethanol. Hence phenol is stronger acid than ethanol. Thus acidic strength increases in the order.

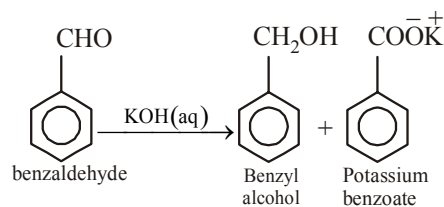
ethanol < phenol < acetic acid < chloroacetic acid

4. (b) Compound $\text{Ph} - \text{COO} - \text{Ph}$ can be prepared by the reaction of phenol & benzoyl chloride

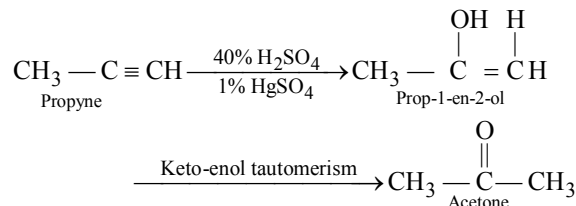


This is an example of **Schotten-Baumann reaction**.

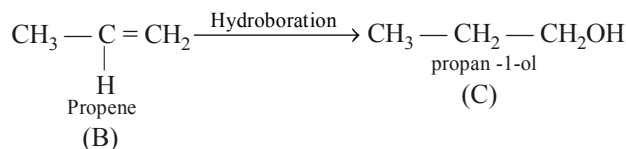
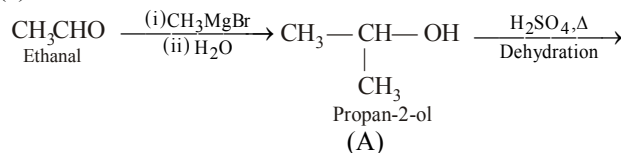
5. (c) Acetone and benzaldehyde both do not react with Fehling's solution.
6. (d) Cannizzaro reaction is given by those aldehydes which have absence of α -hydrogen atom. So, CH_3CHO will not give Cannizzaro reaction.
7. (b) Benzaldehyde having no α -hydrogen on reaction with aqueous KOH solution undergoes Cannizzaro reaction and produces benzyl alcohol and potassium benzoate.



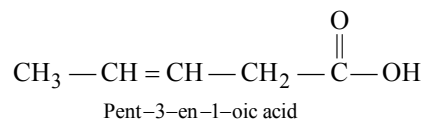
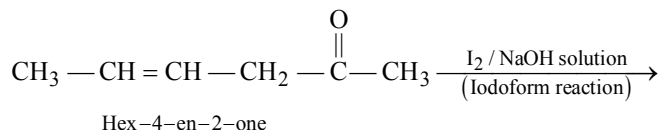
8. (d) Chemical reaction can be shown as



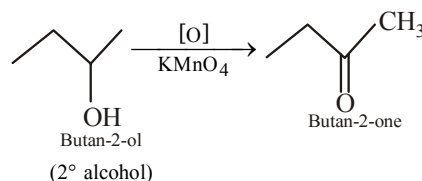
9. (b) Chemical reaction can be shown as



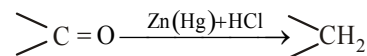
10. (c)



11. (b) 2° alcohols on oxidation with alkaline KMnO_4 solution produce ketones.



12. (a) Clemmensen reduction is used to convert carbonyl group as follows



Zinc amalgam and HCl act as reagent in this reaction.

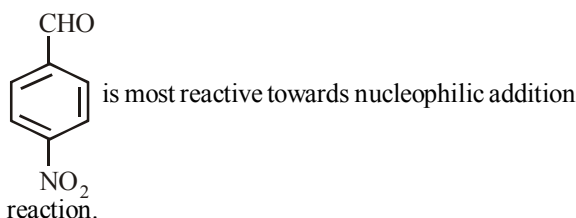
NEET/AIPMT (2013-2017) Questions

13. (a) Enolic form predominates in compounds containing two carbonyl groups separated by a $-\text{CH}_2-$ group. This is due to following two factors.
- Presence of conjugation which increases stability.
 - Formation of intramolecular hydrogen bond between enolic hydroxyl group and second

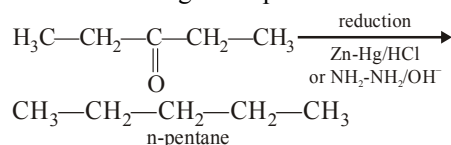
carbonyl group which leads to stabilisation of the molecule. Hence the correct answer is $\text{III} > \text{II} > \text{I}$.

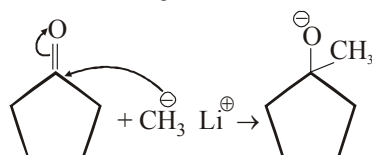
14. (c) Zn/Hg and conc. HCl reduce carboxyl group to methylene group (Clemmensen reduction).
 15. (d) Any substituent in the carbonyl compound that increases the positive charge on the carbonyl carbon will increase reactivity towards nucleophilic addition.

$-\text{NO}_2$ shows $-M$ effect hence

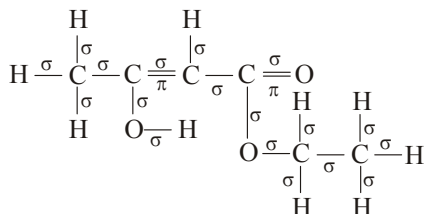


16. (b) $\text{H}_3\text{C}-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3$
 does not give iodoform test due to absence of $(\text{CH}_3-\text{C}(=\text{O})-)$ group. It also does not give Tollen's test. On reduction it gives n-pentane

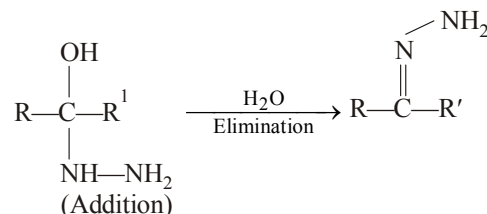
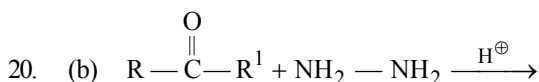
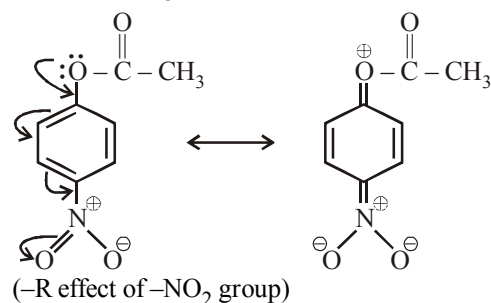


17. (d) 
 Cyclopentanoyl anion

18. (d) Enolic form of ethyl acetoacetate has 18 sigma and 2 pi bonds as shown below:

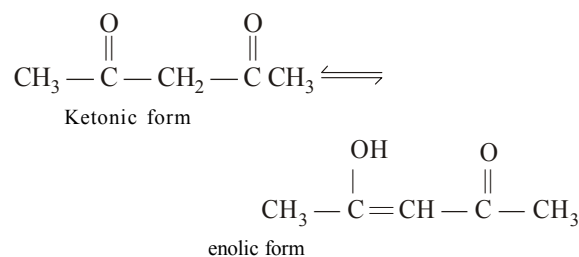


19. (a) Among the substituent attached to the benzene ring, $-\text{NO}_2$ group is the most electron withdrawing, thus withdraws electron density from carbonyl carbon thus facilitate the attack of OH^- ion.

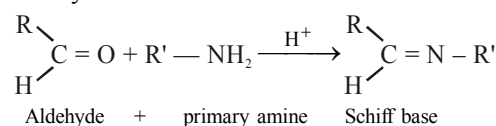


While in all other case no elimination take place.

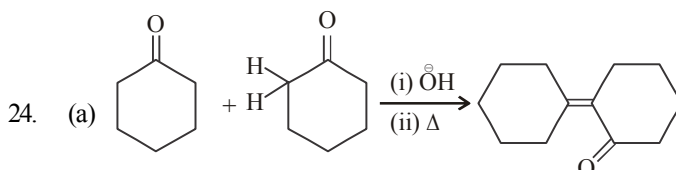
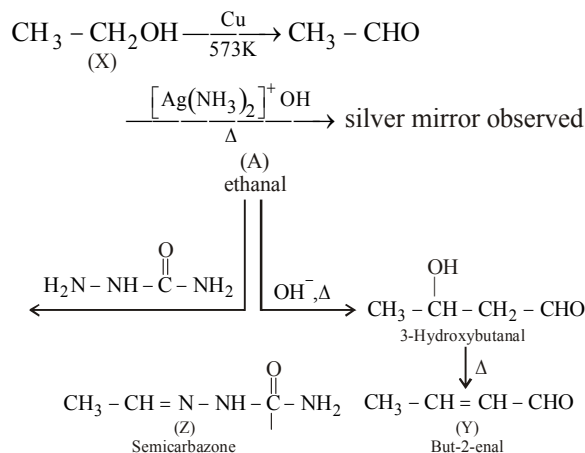
21. (d) Keto-enol tautomerism is possible only in those aldehydes and ketones which have at least one α -hydrogen atom, which can convert the ketonic group to the enolic group. e.g.



22. (a) Schiff base is formed when 1° amine reacts with aldehydes.



23. (b) Since 'A' gives positive silver mirror test therefore, it must be an aldehyde of α -Hydroxyketone. Also, reaction with OH^- i.e., aldol condensation (by assuming alkali to be dilute) indicates that A is aldehyde as aldol reaction of ketones is reversible and carried out in special apparatus. It indicates that A is an aldehyde



Chapter 27

Amines

(A) AMINES

They are derivatives of ammonia and are obtained by replacement of one, two or all three H-atoms of NH_3 by alkyl or aryl groups.

For Ex: CH_3NH_2 , $\text{CH}_3-\text{NH}-\text{CH}_3$, etc.

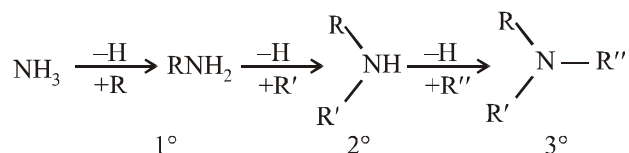
STRUCTURE OF AMINES

N in amines is sp^3 -hybridised and the geometry of amines is pyramidal.

The fourth orbital of N contains an unshared pair of e^- s, due to which the bond angle decreases from the tetrahedral angle of 109.28° to 107° in 1° and 2° amines. However in 3° amines bond angle increased upto 108° due to steric hindrance.

CLASSIFICATION OF AMINES

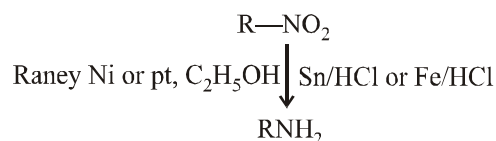
Amines are classified as 1° , 2° and 3° depending upon the number of H-atoms replaced by alkyl or aryl groups in NH_3 .



Amines are said to be simple if all the alkyl or aryl groups are same and mixed if they are different.

PREPARATION OF AMINES

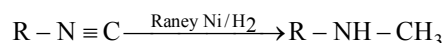
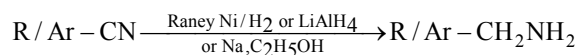
(i) Reduction of Nitro Compounds



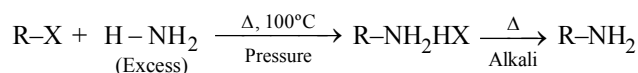
Note:

The yield can be increased to about 90% by using more powerful reductant like LiAlH_4 or NaBH_4 .

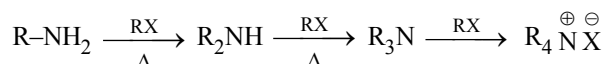
(ii) By the Reduction of Nitriles: (Mendius reduction)



(iii) Ammonolysis of Alkyl Halides (Hofmann's Method) :



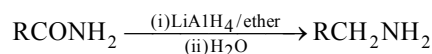
On taking the alkyl halides in excess, the primary amines gets further alkylated to form 2° & 3° amines and finally quaternary ammonium salt.



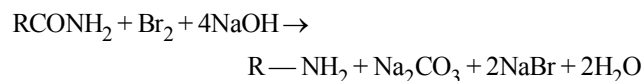
Note:

- This reaction is an example of a nucleophilic substitution reaction in which ammonia molecule (NH_3) acts as a nucleophile.
- The order of reactivity of haloalkanes in ammonolysis reaction is $\text{RI} > \text{RBr} > \text{RCl}$.
- This method cannot be used for preparing aryl amines because simple aryl halides do not undergo nucleophilic substitution easily.

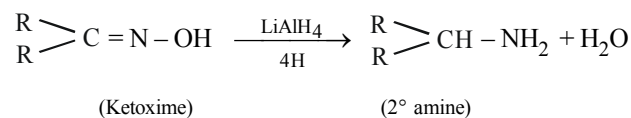
(iv) Reduction of amides

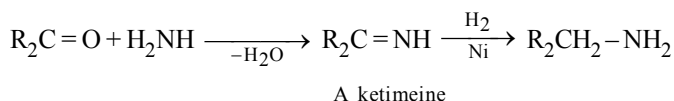
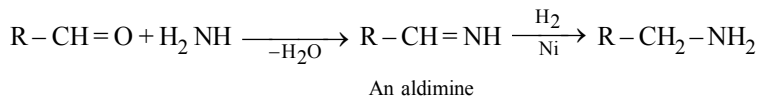
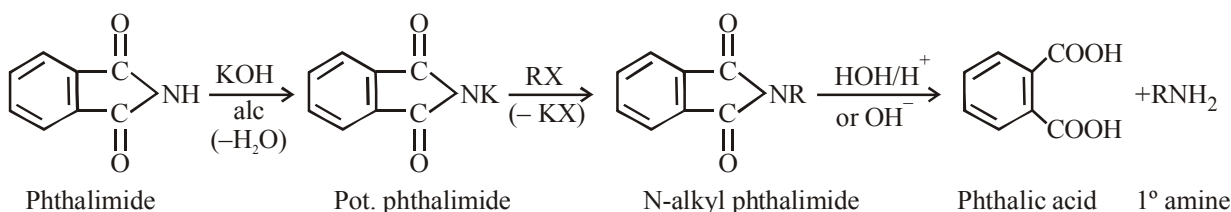
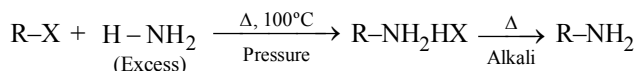


(v) Hoffmann Bromamide Degradation

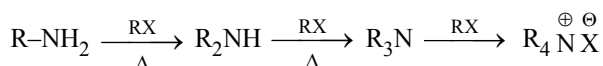


(vi) By Oximes:



(vii) By Reductive Amination of carbonyl compounds :**(viii) Gabriel Phthalimide Synthesis****(ix) Ammonolysis of Alkyl Halides (Hofmann's Method) :**

On taking the alkyl halides in excess, the primary amines gets further alkylated to form 2° & 3° amines and finally quaternary ammonium salt.



This reaction is an example of a nucleophilic substitution reaction in which ammonia molecule (NH₃) acts as a nucleophile. The order of reactivity of haloalkanes in ammonolysis reaction is RI > RBr > RCl. This method cannot be used for preparing aryl amines because simple aryl halides do not undergo nucleophilic substitution easily.

Note:

- In reduction of nitro compounds, Fe + HCl is preferred because FeCl₂ formed gets hydrolysed to release HCl during the reaction. Thus, only a small amount of HCl is required to initiate the reaction.
- Ammonolysis yields a mixture of 1°, 2°, 3° amines and quaternary ammonium salt. 1° amine is obtained as a major product by taking large excess of ammonia.
- Reduction of nitriles to amines results in ascent of amine series i.e. for preparation of amine with one carbon atom more than the starting amine.
- The amines formed by Hofmann bromamide degradation method contain one carbon atom less than the parent amide.

PHYSICAL PROPERTIES OF AMINES

- Pure amines are almost colourless but develop colour on keeping in air due to atmospheric oxidation.
- Lower aliphatic amines are gases with fishy odour. 1° amines with 3 or more C-atoms are liquid and higher ones are solid.
- Lower aliphatic amines are soluble in H₂O due to H-bonding. Solubility decreases with increase in size of hydrophobic alkyl part. Alcohols are more soluble than amines in H₂O.
- Boiling point :** b.p. of alcohols & carboxylic acids > b.p. of amines > b.p. of alkanes and, b.p. of 1° amine > 2° amine > 3° amine

Explanation :

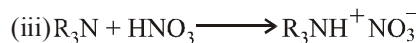
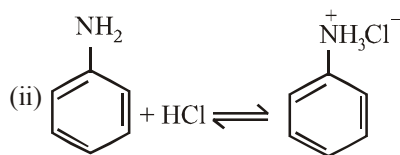
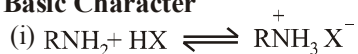
- Primary and secondary amines form inter molecular H-bonds, while tertiary amines do not form inter-molecular H-bonds. As a result, 1° & 2° amines show high B.P. than 3° amines.
- H-bonding in amines is through nitrogen atoms while in alcohols and carboxylic acids, it is through oxygen atoms and nitrogen is less electronegative than oxygen. So H-bonding in amines is weaker than that in carboxylic acids and alcohols.

CHEMICAL PROPERTIES OF AMINES

Amines are reactive due to (i) difference in electronegativity between N and H, (ii) presence of lone pair of e⁻ of N.

Chemical reactions are as follows:

→ **Basic Character**

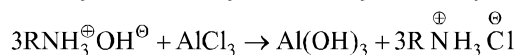
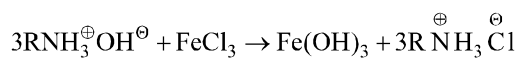


These amine salts are ionic compounds.

(iv) **Reaction with water** : Give alkaline solution in water.

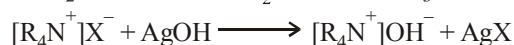


Aqueous solution of alkylamine precipitate hydroxides of heavy metals

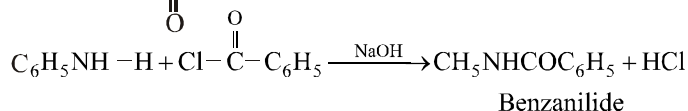
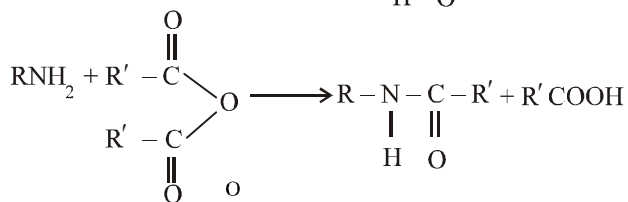
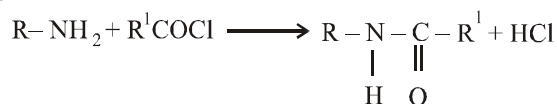


→ **Reactions With Electrophiles**

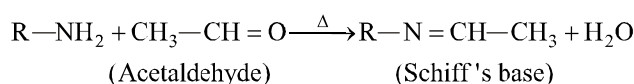
(i) **Alkylation:**



(ii) **Acylation:**

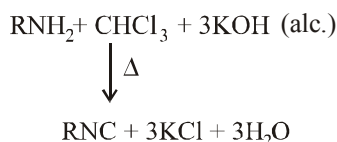


(iii) **With aldehydes:**

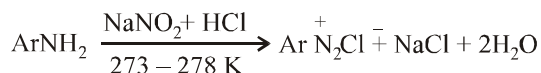
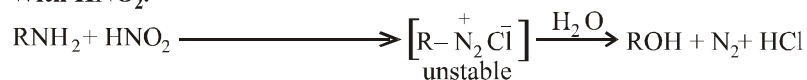
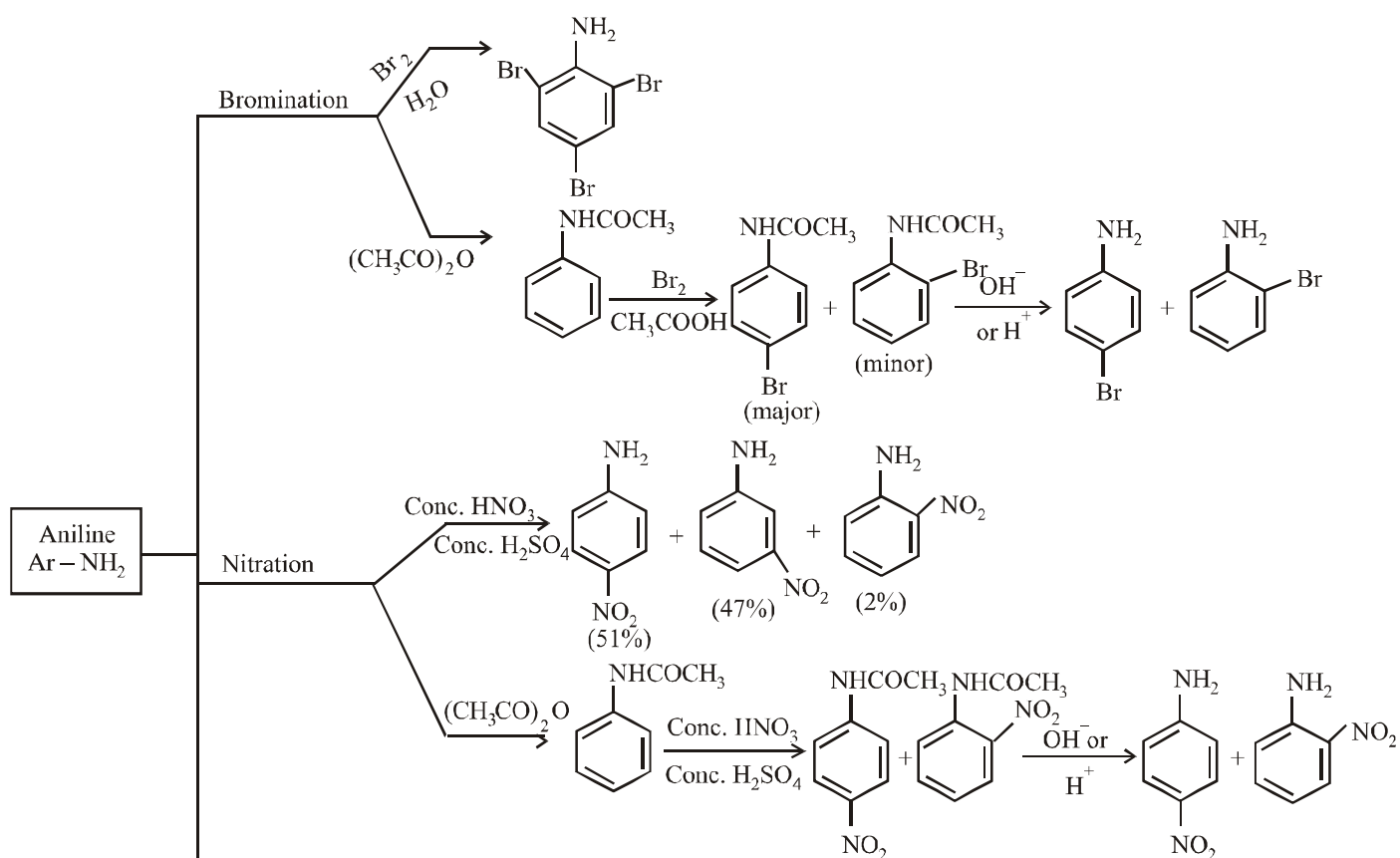
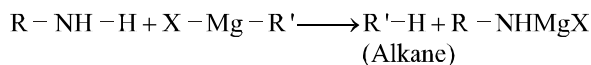


(iv) **Schotten- Baumann reaction** : Benzoylation of compounds containing an active hydrogen atom such as alcohols, phenols, and amines with benzoyl chloride in presence of dil. aq NaOH.

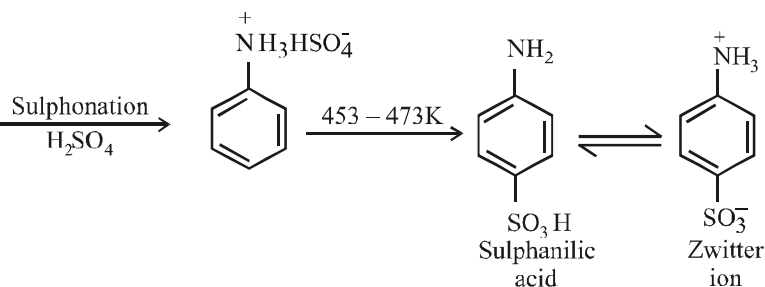
(v) **Carbylamine Reaction** :



Amines
R/NH₂

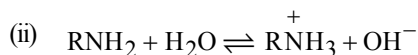
Miscellaneous Reactions(i) **With HNO_2 :**(ii) **Hinsberg's Reaction :** (See distinguish between 1° , 2° and 3° amines)(iii) **With Grignard's reagent:**

Under strongly acidic conditions, most of aniline is converted into anilinium ion and since $-\text{NH}_3^+$ is a *m*-directing group thus an unexpected large amount of *m*-nitroaniline is obtained. To avoid this, the amino group is first protected by acetylation and the acetyl group is finally removed by hydrolysis to give a mixture of *o*- and *p*-nitroaniline.



BASIC CHARACTER OF AMINES

- (i) Amines have an unshared pair of e^- s on nitrogen due to which they behave as Lewis base.



$$K_{\text{eq}} = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2][\text{H}_2\text{O}]} \Rightarrow K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

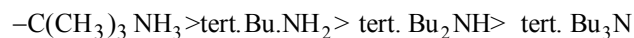
$$\Rightarrow K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} \quad (K_{\text{eq}}[\text{H}_2\text{O}] = K_b)$$

also, $\text{p}K_b = -\log K_b$.

Larger the value of K_b or smaller the value of $\text{p}K_b$, stronger is the base.

- (iii) Aliphatic amines are stronger bases than NH_3 due to + I - effect of alkyl groups leading to high e^- - density on N - atom.
- (iv) Aromatic amines are weaker bases than NH_3 due to e^- with - drawing nature of aryl group resulting is decreased e^- density on N.
- (v) The order of basicity of amines in gaseous phase is:
 $3^\circ \text{ amine} > 2^\circ \text{ amine} > 1^\circ \text{ amine}$
 This is because with increase in the number of alkyl groups + I - effect increases and thus e^- - density on N - atom also increases.
- (vi) In aqueous solution, besides I-effect, solvation and steric effects also play a role. Thus in aqueous medium, basic strength increases. Order for different alkyl groups is:

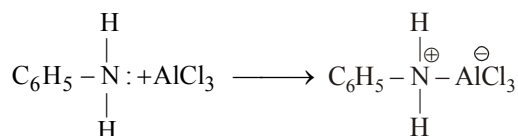
Alkyl group	Relative strength
$-\text{CH}_3$	$\text{Me}_2\text{NH} > \text{MeNH}_2 > \text{Me}_3\text{N} > \text{NH}_3$
$-\text{C}_2\text{H}_5$	$\text{Et}_2\text{NH} > \text{EtNH}_2 > \text{NH}_3 > \text{Et}_3\text{N}$
$-\text{CH}(\text{CH}_3)_2$	$\text{Iso Pr. NH}_2 > \text{NH}_3 > \text{Iso Pr}_2\text{NH} > \text{Iso Pr}_3\text{N}$



- (vii) An electron releasing group such as $-\text{CH}_3$, $-\text{OH}$, etc., present in the benzene ring at ortho and para positions increases the basic strength of aromatic amines. This is due to the stabilization of the ammonium cation formed after protonated of amine.
- (viii) An electron withdrawing group such as $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{X}$, etc. present in the benzene ring at ortho and para positions decreases the basic strength of aromatic amines. This due to the destabilization of the ammonium cation formed after protonation of amine.

Note:

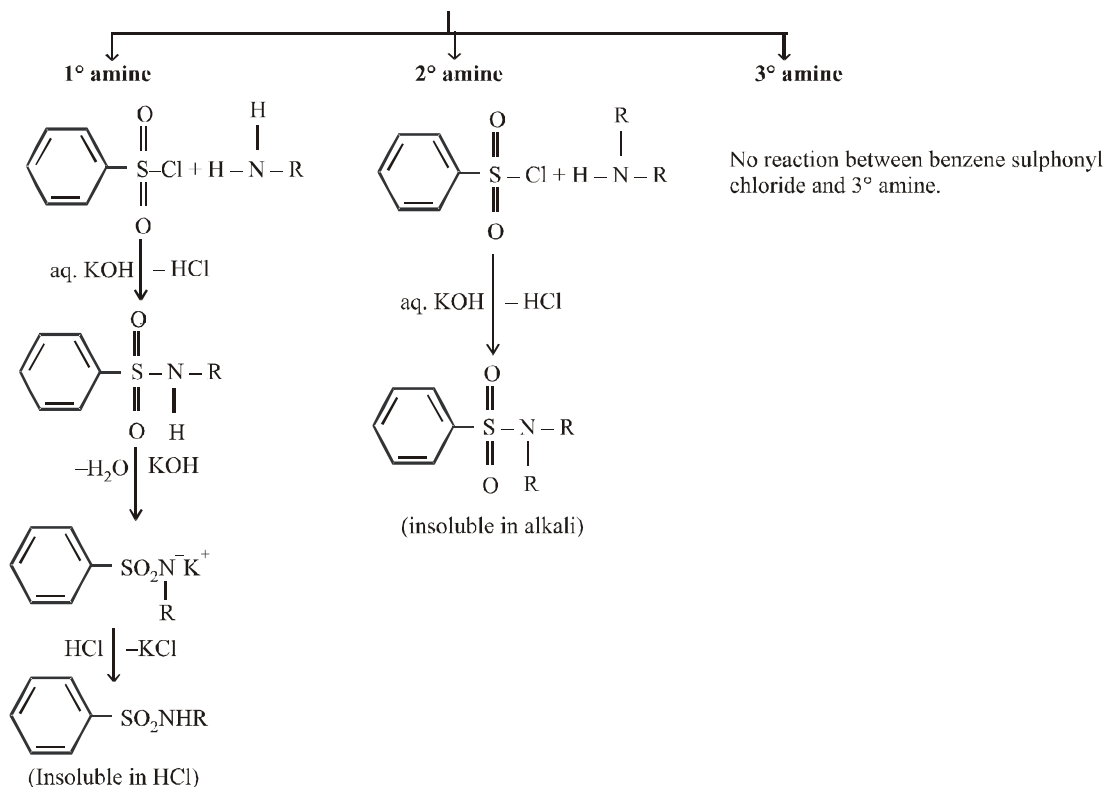
- (a) Carbylamine reaction is used to distinguish between 1° (aliphatic and aromatic) and $2^\circ / 3^\circ$ amines.
- (b) Reaction with HNO_2 is used to distinguish between 1° aliphatic and 1° aromatic amines.
- (c) In aniline, $-\text{NH}_2$ is a strong activating group. Thus, it gives trisubstituted bromine derivative. To avoid this, the $-\text{NH}_2$ group is protected by acetylation and then carrying out the desired substitution. Electron attracting group ($>\text{C}=\text{O}$) present in acetanilide decreases availability of lone pair on nitrogen atom and hence decreases electron density on benzene ring of aniline.
- (d) Aniline does not undergo Friedel - Crafts reaction due to salt formation with AlCl_3 (a Lewis acid) which is used as a catalyst.



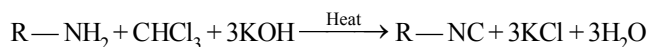
DISTINCTION BETWEEN 1°, 2° AND 3° AMINES

(i) Hinsberg's Test:

Hinsberg's reagent is benzene sulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).



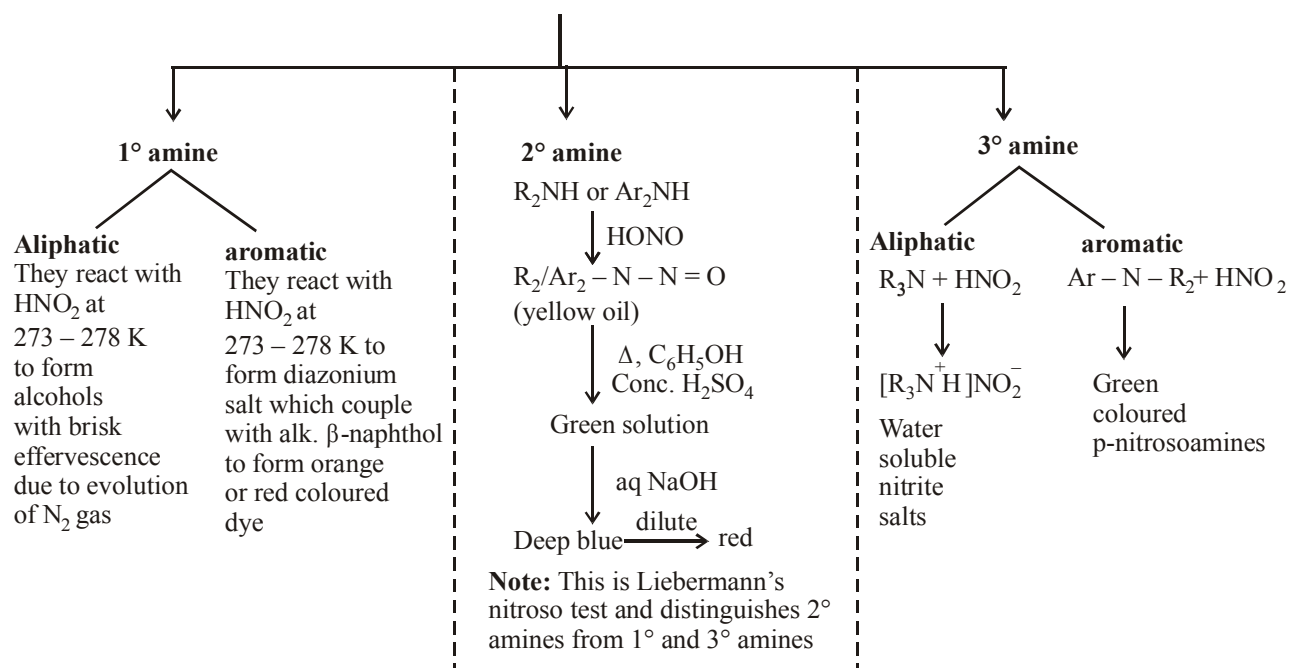
(ii) Carbylamine or Isocyanide Test



Shown only by 1°, 2° and 3° amines do not show this reaction.

(iii)

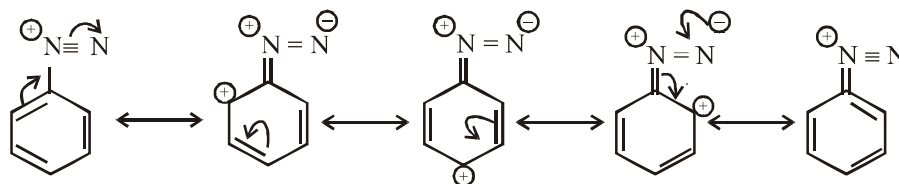
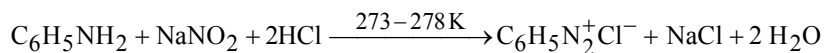
Nitrous Acid Test:



(B) DIAZONIUM SALTS

They have the general formula $\text{RN}_2^+ \text{X}^-$ where $\text{R} \rightarrow$ aryl group $\text{X}^- \rightarrow \text{Cl}^-, \text{Br}^-, \text{HSO}_4^-, \text{BF}_4^-$

The stability of arenediazonium ion is explained on the basis of resonance:

**PREPARATION OF DIAZONIUM SALT**

The process is called diazotisation. Due to its instability, diazonium salt is not stored and is used immediately after its preparation.

PHYSICAL PROPERTIES OF DIAZONIUM SALTS

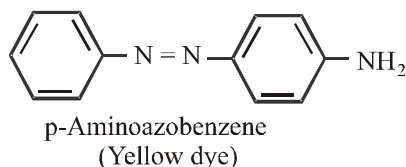
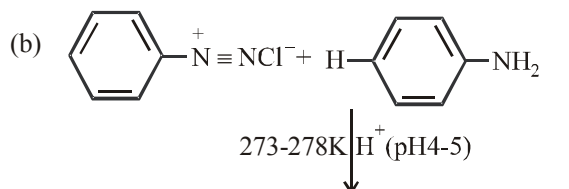
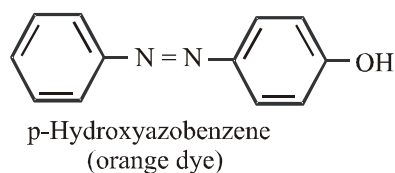
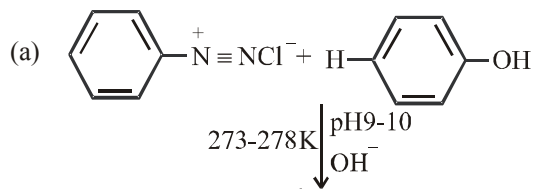
- (i) It is a colourless crystalline solid.
- (ii) Soluble in water, stable in cold reacts with warm H_2O .
- (iii) Decomposes in dry state.
- (iv) Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

CHEMICAL PROPERTIES OF DIAZONIUM SALTS

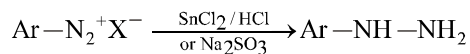
Studied under two categories

Reactions in which diazo group is retained

(i) Coupling reactions

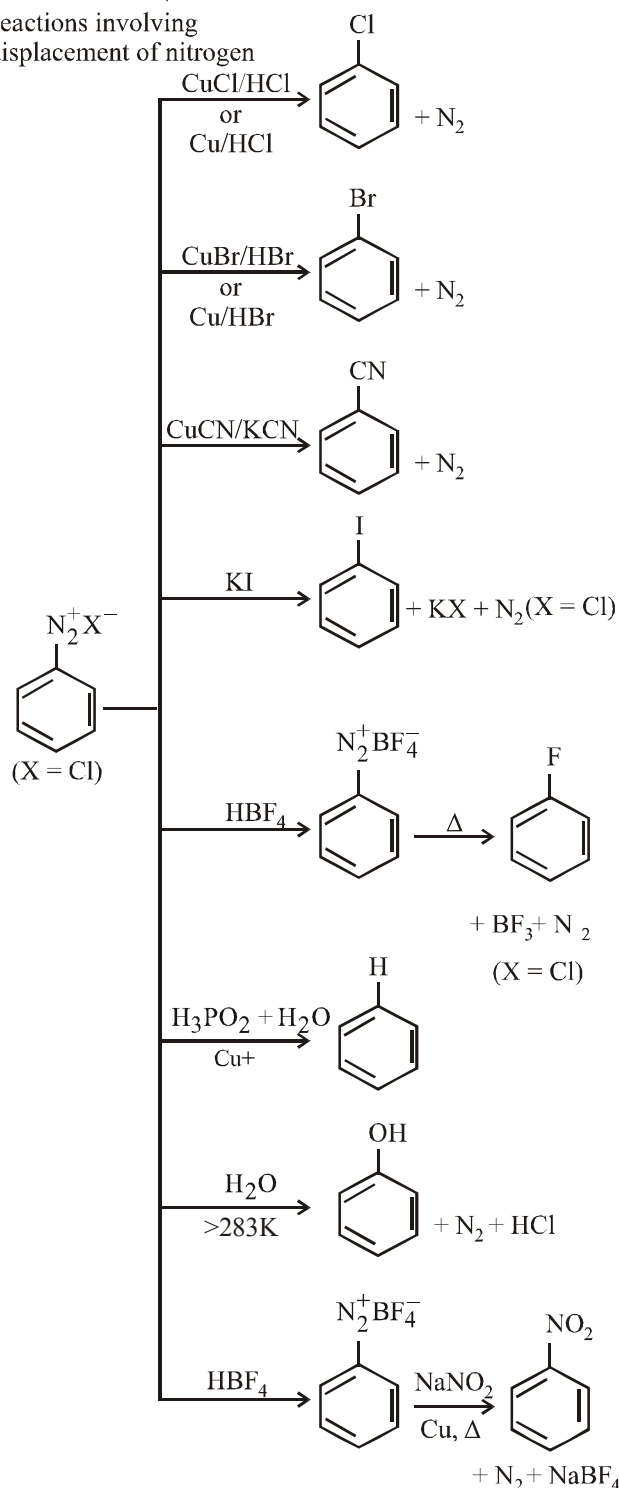


(ii) Reduction to arylhydrazines:



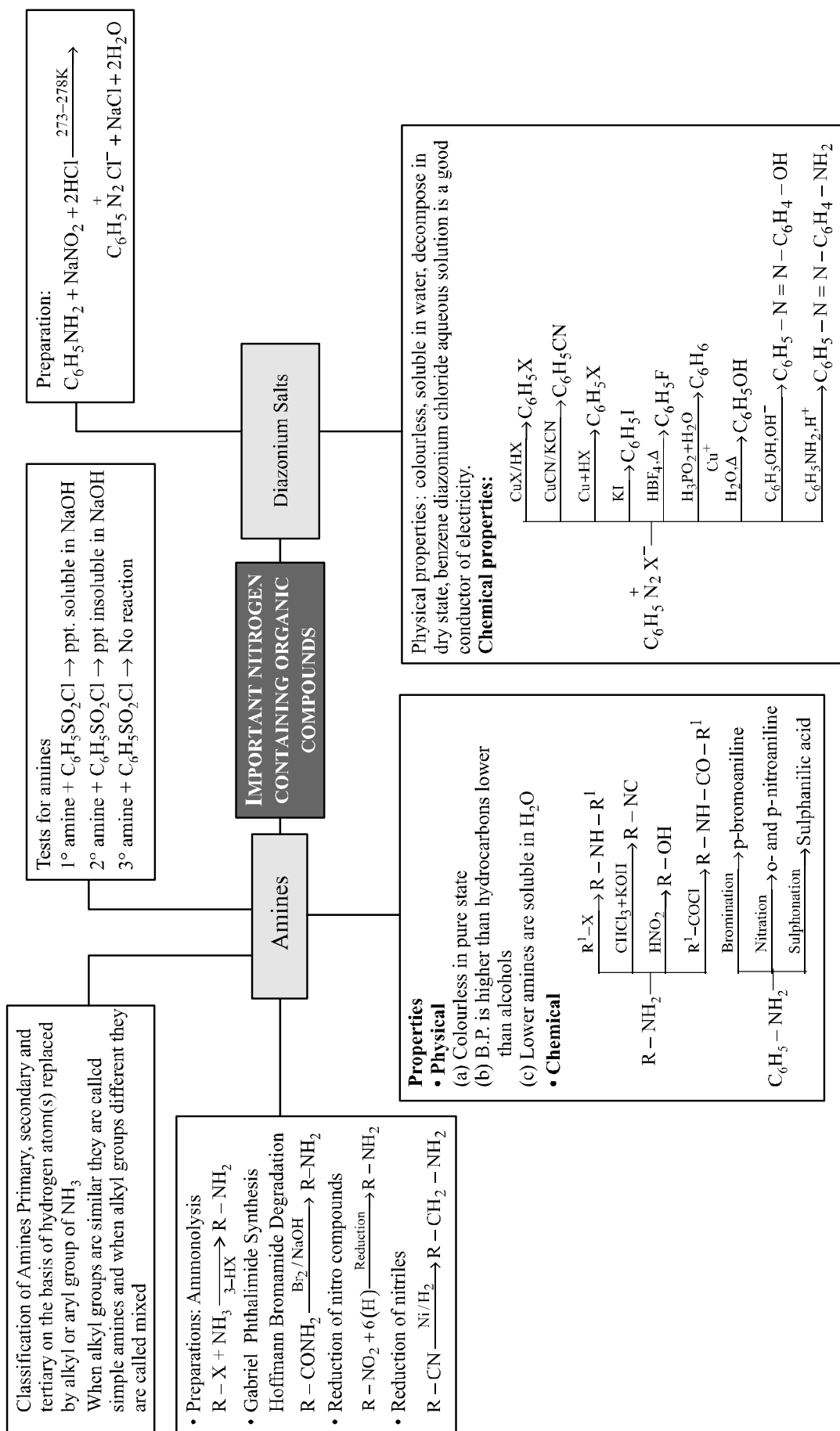
Note: Coupling usually occurs at p-position w.r.t. to $-\text{OH}$ or $-\text{NH}_2$ group. If p-position is blocked, it occurs at o-position.

Reactions involving displacement of nitrogen



Note: Conversion of diazonium salt to haloarenes by using CuX/HX is called sandmeyer reaction whereas if Cu/HX is used reaction is called Gattermann reaction.

CONCEPT MAP



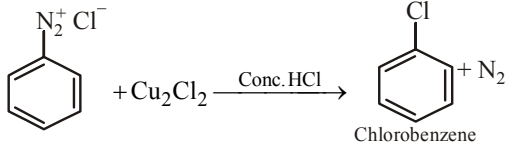
EXERCISE - 1

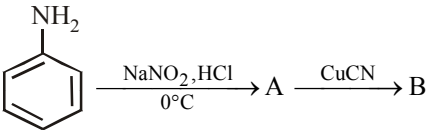
Conceptual Questions

- Acetaldoxime reacts with P_2O_5 to produce
 - ethyl cyanide
 - propyl cyanide
 - methyl cyanide
 - none of these
- Acetamide and ethylamine can be distinguished by reacting with
 - aqueous HCl and heat
 - aqueous NaOH and heat
 - acidified $KMnO_4$
 - bromine water.
- The compound obtained by heating a mixture of a primary amine and chloroform with ethanolic potassium hydroxide (KOH) is
 - an alkyl cyanide
 - a nitro compound
 - an alkyl isocyanide
 - an amide
- Which of the following reagents will convert *p*-methylbenzenediazonium chloride into *p*-cresol?
 - Cu powder
 - H_2O
 - H_3PO_2
 - C_6H_5OH
- C_3H_9N can not represent the following
 - primary amine
 - secondary amine
 - tertiary amine
 - quaternary ammonium salt
- Which one of the following methods is neither meant for the synthesis nor for separation of amines?
 - Curtius reaction
 - Wurtz reaction
 - Hofmann method
 - Hinsberg method
- Benzamide on reaction with $POCl_3$ gives
 - aniline
 - chlorobenzene
 - benzylamine
 - benzonitrile
- Which of the following will produce isopropyl amine –
 - $(CH_3)_2CO \xrightarrow{NH_2OH} X \xrightarrow{LiAlH_4} \text{product}$
 - $CH_3 - CH_2 - CHO \xrightarrow[\text{heat}]{NH_3} X \xrightarrow{LiAlH_4} \text{product}$
 - $(CH_3)_2CH - OH + PCl_5 \longrightarrow X \xrightarrow{NH_3} \text{product}$
 - $CH_3 - CH_2 - CH_2 - NH_2 \xrightarrow{\text{heat}} \text{product}$
 - I, II
 - II, III
 - I, III
 - IV only
- Reaction of $R - \overset{\overset{O}{\parallel}}{C} - NH_2$ with a mixture of Br_2 and KOH produces RNH_2 . During the reaction, which of the intermediate product is formed :
 - $R - NH - Br$
 - $H - CO - NBr_2$
 - $R - N = C = O$
 - all of these
- $$\begin{array}{c} R \\ \diagdown \\ C = N - OH \\ \diagup \\ R' \end{array} \xrightarrow{H^+} [X], \text{ the product and name of this reaction is -}$$
 - $R - \overset{\overset{O}{\parallel}}{C} - NHR'$; Pinnacole rearrangement
 - $R' - \overset{\overset{O}{\parallel}}{C} - NHR$; Fries rearrangement
 - $R - \overset{\overset{O}{\parallel}}{C} - NHR'$; Beckmann's rearrangement
 - $R - \overset{\overset{O}{\parallel}}{C} - NHR'$, Allylic rearrangement
- Which of the following reactions can produce aniline as main product?
 - $C_6H_5NO_2 + Zn/KOH$
 - $C_6H_5NO_2 + Zn/NH_4Cl$
 - $C_6H_5NO_2 + LiAlH_4$
 - $C_6H_5NO_2 + Zn/HCl$
- $R - NH_2 + CH_3COCl \longrightarrow A$.
(excess)
The product (A) will be –
 - $RNHCOCH_3$
 - $RN(COCH_3)_2$
 - $RN^+(COCH_3)_3 Cl^-$
 - $R - CONH_2$
- $$\begin{array}{c} NH_2 \\ | \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow[0^\circ C]{NaNO_2/HCl} (P) \xrightarrow[HB\ddot{r}]{CuBr} (Q)$$
 The compound Q is –
 - bromo benzene
 - chlorobenzene
 - benzyl bromide
 - benzyl chloride
- Identify Z in the following sequence of reactions –

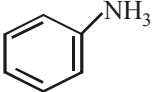
$$CH_3 - COONH_4 \xrightarrow{\Delta} X \xrightarrow{P_2O_5} Y \xrightarrow{H_2O/H^+} Z$$
 - $CH_3 - CH_2 - CO - NH_2$
 - $CH_3 - CN$
 - $(CH_3CO)_2O$
 - $CH_3 - COOH$
- Among the following which one does not act as an intermediate in Hofmann rearrangement ?
 - $RNCO$
 - $R\ddot{C}ON$
 - $R\ddot{C}ONHBr$
 - RNC
- Propionamide on Hofmann degradation gives –
 - methyl amine
 - ethyl amine
 - propyl amine
 - ethyl cyanide

17. The basicity of aniline is less than that of cyclohexylamine. This is due to
 (a) +R effect of —NH_2 group
 (b) —I effect of —NH_2 group
 (c) —R effect of —NH_2 group
 (d) hyperconjugation effect
18. When phenol and benzene diazonium chloride are coupled, the main product is :
 (a) aniline (b) *p*-hydroxyazobenzene
 (c) azobenzene (d) chlorobenzene
19. Ethylamine can be prepared by the action of bromine, caustic potash and :
 (a) acetamide (b) propionamide
 (c) formamide (d) methyl cyanide
20. The number of primary amines of formula $\text{C}_4\text{H}_{11}\text{N}$ is :
 (a) 1 (b) 3 (c) 4 (d) 2
21. In the diazotization of arylamines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to
 (a) Suppress the concentration of free aniline available for coupling
 (b) Suppress hydrolysis of phenol
 (c) Ensure a stoichiometric amount of nitrous acid
 (d) Neutralise the base liberated
22. *p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by :
 (a) Sandmeyer reaction (b) Carbylamine reaction
 (c) Hinsberg's reaction (d) AgNO_3
23. The conversion of acetophenone to acetanilide is best accomplished by using :
 (a) Beckmann rearrangement
 (b) Curtius rearrangement
 (c) Lossen rearrangement
 (d) Hofmann rearrangement
24. High basicity of Me_2NH relative to Me_3N is attributed to :
 (a) effect of solvent (b) inductive effect of Me
 (c) shape of Me_2NH (d) shape of Me_3N
25. In the reaction,

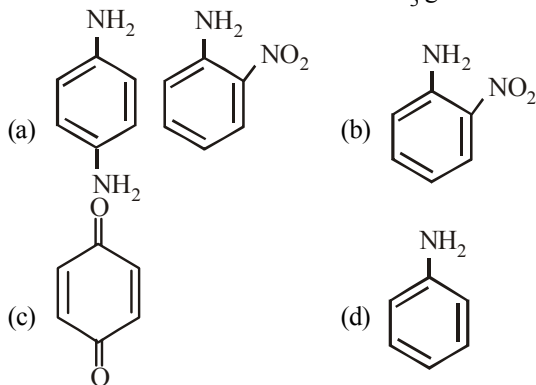
$$\text{RNH}_2 \xrightarrow{\text{HNO}_2} \text{A} + \text{B} + \text{C} \uparrow ; \text{C is}$$
 (a) NH_3 (b) N_2 (c) O_2 (d) CO_2
26. 
 Above reaction is known as:
 (a) Strecker's reaction (b) Sandmeyer's reaction
 (c) Wohl-Ziegler reaction (d) Stephen's reaction
27. Nitrobenzene and hydrogen in presence of zinc combines to form :
 (a) azobenzene (b) benzene
 (c) azoxybenzene (d) aniline
28. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine. The compound is
 (a) CH_3NH_2 (b) $\text{CH}_3\text{CH}_2\text{NH}_2$
 (c) $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$ (d) $(\text{CH}_3\text{CH}_2)_3\text{N}$
29. In the following sequence of reactions, the compound C formed would be

$$\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_3 \xrightarrow[\text{H}_2\text{O}]{\text{HNO}_2} \text{A} \xrightarrow{[\text{O}]} \text{B} \xrightarrow[\text{H}^+/\text{H}_2\text{O}]{\text{CH}_3\text{MgI}} \text{C}$$
 (a) 1,1-dimethyl ethanol
 (b) butanol-1
 (c) butanol-2
 (d) 2-methyl-propanol-1
30.
$$\text{CH}_3\text{COOH} \xrightarrow[\text{Heat}]{\text{NH}_3} \text{A} \xrightarrow[(-\text{H}_2\text{O})]{\text{P}_2\text{O}_5} \text{B} \xrightarrow[(-\text{H}_2\text{O})]{\text{P}_2\text{O}_5} \text{C}$$
 The compound 'C' is :
 (a) acetamide (b) ammonium acetate
 (c) methyl cyanide (d) aniline
31. Azo dye is prepared by the coupling of phenol and
 (a) diazonium chloride
 (b) *o*-nitroaniline
 (c) benzoic acid
 (d) chlorobenzene
32. Nitrosoamines ($\text{R}_2\text{N} - \text{N} = \text{O}$) are soluble in water. On heating them with concentrated H_2SO_4 , they give secondary amines. This reaction is called
 (a) Perkin reaction
 (b) Sandmeyer's reaction
 (c) Fitting reaction
 (d) Liebermann nitroso reaction
33. Primary amines react with benzaldehyde to form:
 (a) diazonium salts (b) azo dyes
 (c) anilides (d) schiff's base
34. In the reaction sequence

 the product 'C' is:
 (a) benzonitrile (b) benzaldehyde
 (c) benzoic acid (d) benzylamine
35. The end product (Y) in the reaction sequence

$$\text{CH}_3\text{CONH}_2 \xrightarrow[\Delta]{\text{P}_2\text{O}_5} \text{X} \xrightarrow{\text{Sn/HCl}} \text{Y}, \text{ is :}$$
 (a) ethane nitrile (b) acetic acid
 (c) ethanamine (d) chloroethane
36. The structural formula of methyl aminomethane is
 (a) $(\text{CH}_3)_2\text{CHNH}_2$ (b) $(\text{CH}_3)_3\text{N}$
 (c) $(\text{CH}_3)_2\text{NH}$ (d) CH_3NH_2
37. The end product of the reactions is

$$\text{C}_2\text{H}_5\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{A} \xrightarrow{\text{PCl}_5} \text{B} \xrightarrow{\text{H.NH}_2} \text{C}$$
 (a) ethyl cyanide (b) ethyl amine
 (c) methyl amine (d) acetamide
38. Which of the following is strongest base :
 (a)  (b) 
 (c)  (d) 

39. Aniline when treated with conc. HNO_3 gives



40. If methyl is alkyl group, then which order of basicity is correct

- (a) $\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$
 (b) $\text{R}_2\text{NH} > \text{R}_3\text{N} > \text{RNH}_2 > \text{NH}_3$
 (c) $\text{RNH}_2 > \text{NH}_3 > \text{R}_2\text{NH} > \text{R}_3\text{N}$
 (d) $\text{NH}_3 > \text{RNH}_2 > \text{R}_3\text{N} > \text{R}_2\text{NH}$

41. Among the following, the strongest base is

- (a) $\text{C}_6\text{H}_5\text{NH}_2$ (b) $p\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$
 (c) $m\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

42. A primary amine is formed an amide by the treatment of bromine and alkali. The primary amine has :

- (a) 1 carbon atom less than amide
 (b) 1 carbon atom more than amide
 (c) 1 hydrogen atom less than amide
 (d) 1 hydrogen atom more than amide

43. Benzene diazonium chloride reacts with hypophosphorous acid to produce:

- (a) phenol
 (b) benzene
 (c) p -hydroxyazobenzene
 (d) benzonitrile

44. Nitration of aniline also gives m -nitro aniline, in strong acidic medium because

- (a) in electrophilic substitution reaction amino group is meta directing
 (b) inspite of substituents nitro group always goes to m -position
 (c) in strong acidic medium, nitration of aniline is a nucleophilic substitution reaction
 (d) in strong acidic medium aniline present as anilinium ion

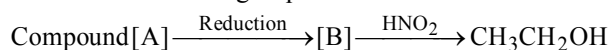
45. Which is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl ?

- (a) Acetic acid (b) Acetamide
 (c) Methyl cyanide (d) Acetic anhydrides

46. $\text{C}_6\text{H}_5\text{NH}_2 + \text{CS}_2 \xrightarrow{\text{HgCl}_2} \text{C}_6\text{H}_5\text{NCS} + \text{HgS} + 2\text{HCl}$
 the above reaction is:

- (a) Libermann's nitroso reaction
 (b) Carbylamine reaction
 (c) Hinsberg's reaction
 (d) Hoffmann mustard oil reaction

47. Consider the following sequence of reactions :



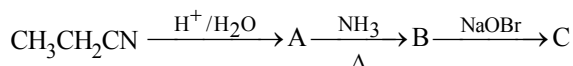
The compound [A] is

- (a) $\text{CH}_3\text{CH}_2\text{CN}$ (b) CH_3NO_2
 (c) CH_3NC (d) CH_3CN

48. Ethyl isocyanide on hydrolysis in acidic medium generates

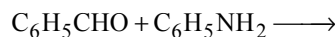
- (a) propanoic acid and ammonium salt
 (b) ethanoic acid and ammonium salt
 (c) methylamine salt and ethanoic acid
 (d) ethylamine salt and methanoic acid

49. What will be the final product in the following reaction sequence –



- (a) $\text{CH}_3\text{CH}_2\text{CONH}_2$ (b) $\text{CH}_3\text{CH}_2\text{COBr}$
 (c) $\text{CH}_3\text{CH}_2\text{NH}_2$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

50. In the reaction :



The compound, $\text{C}_6\text{H}_5\text{N} = \text{CHC}_6\text{H}_5$ is known as

- (a) aldol (b) Schiff's base
 (c) Schiff's reagent (d) Benedict's reagent

51. Methyl cyanide is less basic than methylamine because:

- (a) there is a triple bond between carbon and nitrogen atoms
 (b) molecular weight is higher than methylamine
 (c) the lone pair of electrons in nitriles belongs to sp -orbital and lone pair of electrons in amines belongs to sp^3 -orbital
 (d) None of these

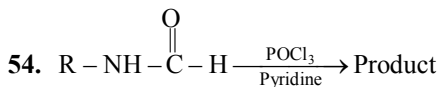
52. In the reaction : $\text{R} - \text{C} \equiv \text{N} + 4(\text{H}) \xrightarrow{\text{X}} \text{RCH}_2\text{NH}_2$

X can be :

- (a) LiAlH_4 (b) H_2SO_4 (c) Ni (d) 2KBr

53. Aromatic nitriles (ArCN) are not prepared by reaction :

- (a) $\text{ArX} + \text{KCN}$ (b) $\text{ArN}_2^+ + \text{CuCN}$
 (c) $\text{ArCONH}_2 + \text{P}_2\text{O}_5$ (d) $\text{ArCONH}_2 + \text{SOCl}_2$



In the given reaction what will be the product

- (a) $\text{R} - \text{N} = \text{C} = \text{O}$ (b) $\text{R} - \overset{+}{\text{N}} \equiv \text{C}^-$
 (c) $\text{R} - \text{C} \equiv \text{N}$ (d) None of these.

55. When primary amine is heated with CS_2 in presence of excess mercuric chloride, it gives isothiocyanate. This reaction is called

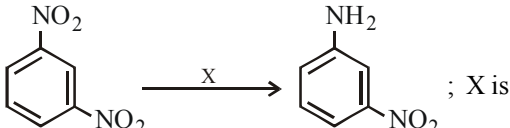
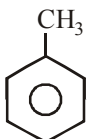
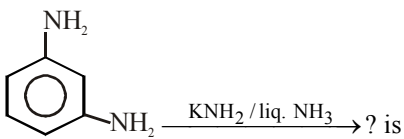
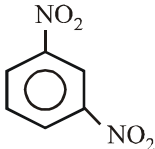
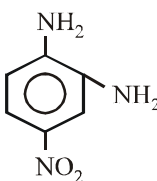
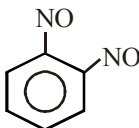
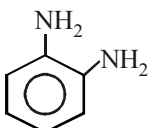
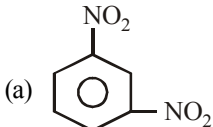
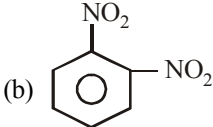
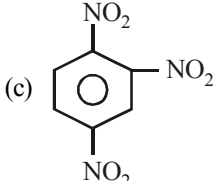
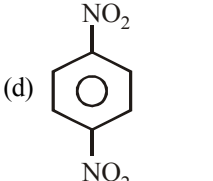
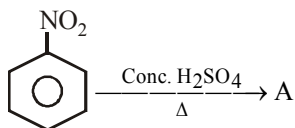
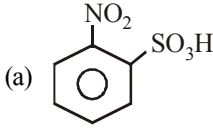
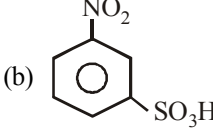
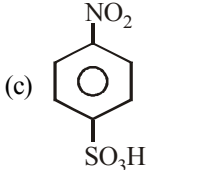
- (a) Hoffmann bromide reaction
 (b) Hoffmann mustard oil reaction
 (c) Carbylamine reaction
 (d) Perkin reaction

56. Hydrolysis of phenyl isocyanide forms

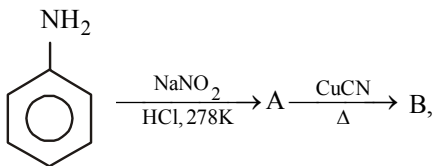
- (a) Benzoic acid (b) Formic acid
 (c) Acetic acid (d) None of these

57. Nitrobenzene on treatment with zinc dust and aqueous ammonium chloride gives:

- (a) $\text{C}_6\text{H}_5\text{N} = \text{NC}_6\text{H}_5$ (b) $\text{C}_6\text{H}_5\text{NH}_2$
 (c) $\text{C}_6\text{H}_5\text{NO}$ (d) $\text{C}_6\text{H}_5\text{NHOH}$

58. *n*-Propylamine yields a volatile compound *X* on warming with alc. alkali and chloroform. *X* has an offensive odour. The structure of *X* is
 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ (b) $(\text{CH}_3)_2\text{CHCN}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NC}$ (d) $(\text{CH}_3)_2\text{CHNC}$
59. $\text{CH}_3 - \text{CH}_2\text{C} \equiv \text{N} \xrightarrow{X} \text{CH}_3\text{CH}_2\text{CHO}$. The compound *X* is
 (a) $\text{SnCl}_2 / \text{HCl} / \text{H}_2\text{O}$, boil (b) $\text{H}_2 / \text{Pd} - \text{BaSO}_4$
 (c) $\text{LiAlH}_4 / \text{ether}$ (d) $\text{NaBH}_4 / \text{ether} / \text{H}_3\text{O}^+$
60. Benzamide and benzyl amine can be distinguished by
 (a) cold dil. NaOH
 (b) cold dil. HCl
 (c) both a & b
 (d) NaNO_2 , HCl , 0°C , then β -naphthol
61. Acetanilide on nitration followed by alkaline hydrolysis mainly gives –
 (a) *o*-Nitroaniline (b) *p*-Nitroaniline
 (c) *m*-Nitroaniline (d) 2, 4, 6-Trinitroaniline
62. In the reaction :
 ; *X* is
 (a) SiC (b) H_2SO_4
 (c) KMnO_4 (d) $\text{Fe} + \text{HCl}$
63. Amine that cannot be prepared by Gabriel phthalimide synthesis is
 (a) aniline (b) benzylamine
 (c) methylamine (d) *iso*-butylamine
64. Which of the following will be easily nitrated?
 (a)  (b)
 (c) CH_3NO_2 (d) $\text{C}_6\text{H}_5\text{NO}_2$
65. Nitrobenzene is reduced to azoxybenzene using
 (a) Sn/HCl (b) $\text{Zn}/\text{NH}_4\text{Cl}$
 (c) $\text{As}_2\text{O}_3/\text{NaOH}$ (d) Zn/NaOH
66. Product of the reaction
 ? is
 (a)  (b)
 (c)  (d)
67. Nitrobenzene, on reaction with fuming nitric acid at 90°C , gives
 (a)  (b)
 (c)  (d)
68. In the series of reaction
 $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[0-5^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} \text{X} \xrightarrow[\text{H}_2\text{O}]{\text{HNO}_2} \text{Y} + \text{N}_2 + \text{HCl}$ *X* and *Y* are respectively
 (a) $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$
 (b) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_5$
 (c) $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, $\text{C}_6\text{H}_5\text{NO}_2$
 (d) $\text{C}_6\text{H}_5\text{NO}_2$, C_6H_6
69. A primary amine that can be obtained both by the reduction of cyanides and amides is
 (a) methyl amine (b) benzyl amine
 (c) aniline (d) *iso*-propyl amine
70.  Product '*A*' in above reaction is
 (a)  (b)
 (c) (d) None of these
71. Anilinium hydrogensulphate on heating with sulphuric acid at $453-473\text{ K}$ produces
 (a) benzene sulphonic acid (b) anthranilic acid
 (c) aniline (d) sulphanilic acid
72. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine?
 (a) Methyl isocyanide (b) Acetamide
 (c) Methyl cyanide (d) Nitroethane
73. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 in the mixture, nitric acid acts as a/an :
 (a) acid (b) base
 (c) catalyst (d) reducing agent
74. Acetamide is treated with the following reagents separately. Which one of these would yield methylamine?
 (a) $\text{NaOH} - \text{Br}_2$ (b) Sodalime
 (c) Hot conc. H_2SO_4 (d) PCl_5

75. In the chemical reactions :



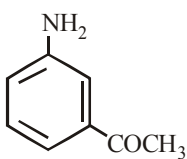
the compounds A and B respectively are :

- benzene diazonium chloride and benzonitrile
- nitrobenzene and chlorobenzene
- phenol and bromobenzene
- fluorobenzene and phenol

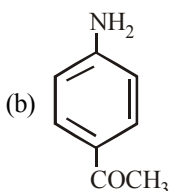
EXERCISE - 2

Applied Questions

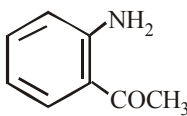
- Aniline is treated with bromine water to give an organic compound 'X' which when treated with NaNO_2 and HCl at 0°C gives a water soluble compound 'Y'. Compound 'Y' on treatment with Cu_2Cl_2 and HCl gives compound 'Z'. Compound 'Z' is
 - o*-bromochlorobenzene
 - p*-bromochlorobenzene
 - 2, 4, 6-tribromophenol
 - 2, 4, 6-tribromochlorobenzene
- Which one of the following statements is not correct?
 - pK_b of aniline is greater than that of methyl amine
 - Aniline does not undergo Friedel-Crafts reaction
 - Dimethyl amine is capable of forming intermolecular hydrogen bonding
 - NH_3 is a stronger base than ethanamine
- When aniline reacts with oil of bitter almonds ($\text{C}_6\text{H}_5\text{CHO}$) condensation takes place and benzal derivative is formed. This is known as
 - Million's base
 - Schiff's reagent
 - Schiff's base
 - Benedict's reagent
- Aniline is an activated system for electrophilic substitution. The compound formed on heating aniline with acetic anhydride is



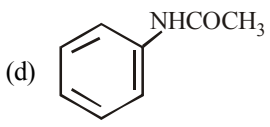
(a)



(b)

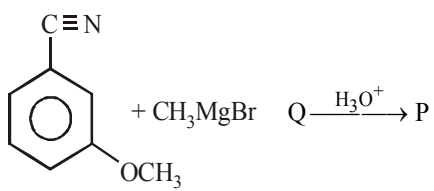


(c)

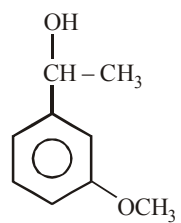


(d)
- Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. The final product is
 - 1,3,5-tribromobenzene
 - p*-bromofluorobenzene
 - p*-bromoaniline
 - 2,4,6-tribromofluorobenzene
- Choose the amide which on reduction with LiAlH_4 yields a secondary amine
 - Ethanamide
 - N-Methylethanamide
 - N,N-dimethylethanamide
 - Phenylmethanamide
- $$[\text{A}] \xrightarrow{\text{reduction}} [\text{B}] \xrightarrow{\text{CHCl}_3 + \text{KOH}} [\text{C}] \xrightarrow{\text{reduction}} \text{N-Methylaniline, A is}$$
 - Formaldehyde
 - Trichloromethane
 - Nitrobenzene
 - Toluene
- Intermediates formed during reaction of RCNH_2 with Br_2 and KOH are

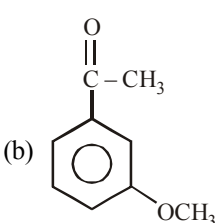


 - RNHBr and RCONHBr
 - RNHCOBr and RNCO
 - RCONHBr and RNCO
 - RCONBr_2
- 

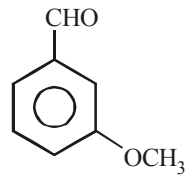
Product 'P' in the above reaction is



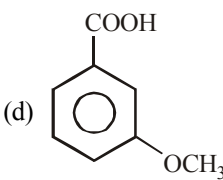
(a)



(b)

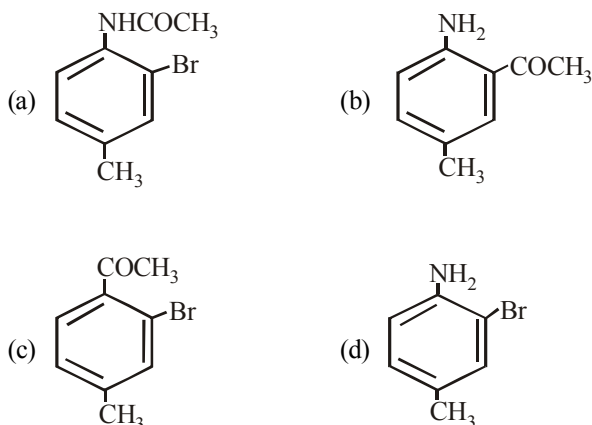
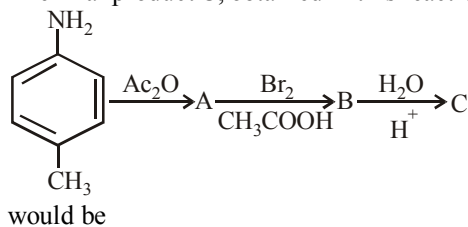


(c)



(d)

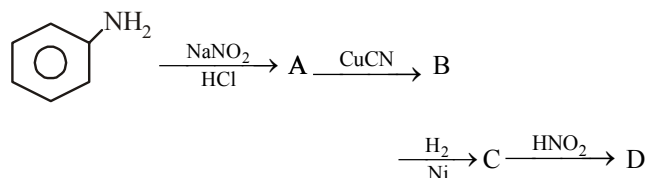
10. The final product C, obtained in this reaction



11. Choose the incorrect statement

- (a) Primary amines show intermolecular hydrogen bonds
 (b) Tert-butylamine is a primary amine.
 (c) Tertiary amines do not show intermolecular hydrogen bonds.
 (d) Isopropylamine is a secondary amine.

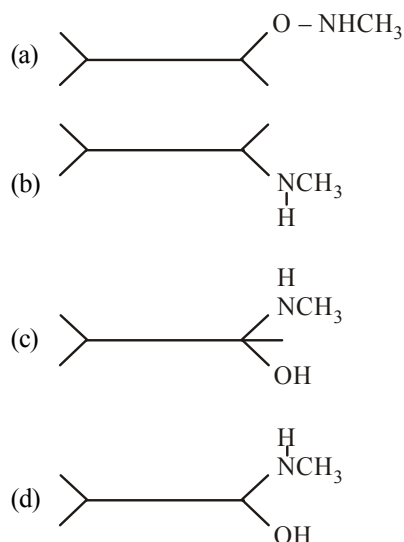
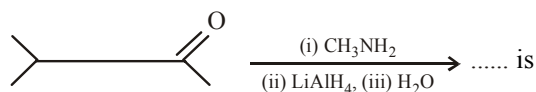
12. Aniline in a set of reactions yielded a product D.



The structure of the product D would be:

- (a) $\text{C}_6\text{H}_5\text{NHOH}$ (b) $\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_3$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
13. Ethanoic acid on heating with ammonia forms compound A which on treatment with bromine and sodium hydroxide gives compound B. Compound B on treatment with $\text{NaNO}_2/\text{dil. HCl}$ gives compound C. The compounds A, B and C respectively are
- (a) ethanamide, methanamine, methanol
 (b) propanamide, ethanamine, ethanol
 (c) N-ethylpropanamide, methanisonitrile, methanamine
 (d) ethanamine, bromoethane, ethanedia-zonium chloride
 (e) methanamine, ethanamide, methanol

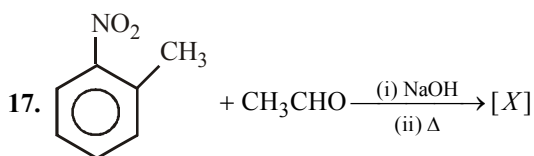
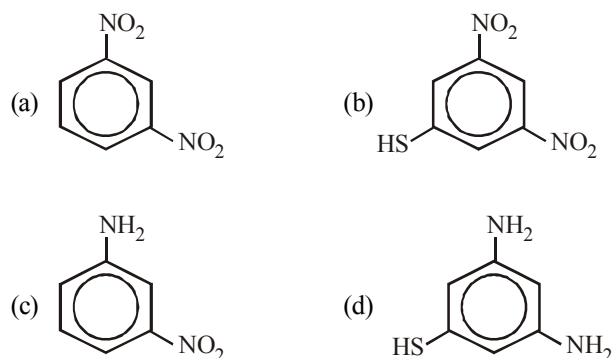
14. The major organic product formed from the following reaction:



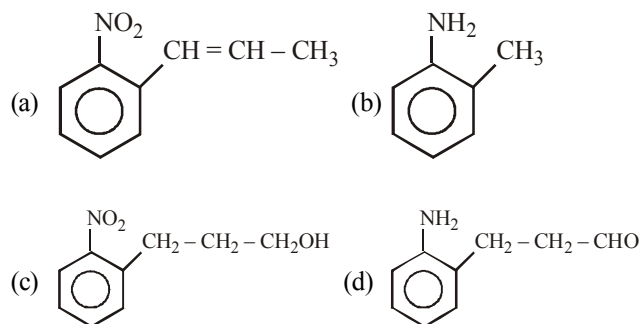
15. Among the following amines, which one has the highest pK_b value in aqueous solution?

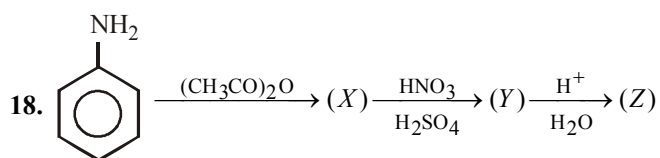
- (a) Methanamine (b) N,N-Dimethylaniline
 (c) Ethanamine (d) Benzenamine

16. The major product (70% to 80%) of the reaction between *m*-dinitrobenzene with NH_4HS is

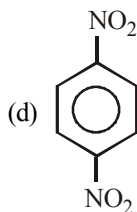
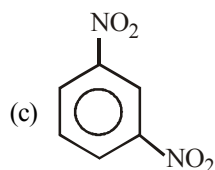
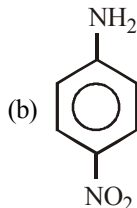
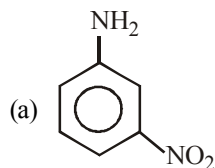


In this reaction [X] will be –

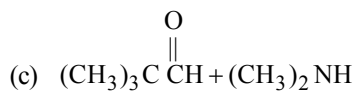
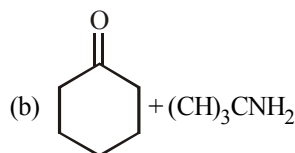
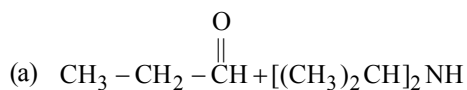




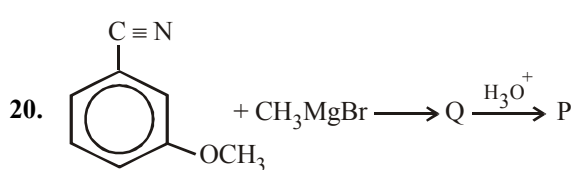
Product Z of the reaction



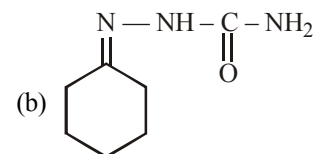
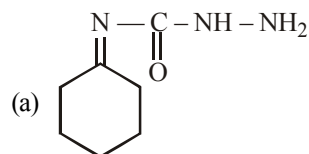
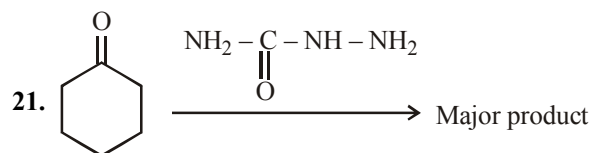
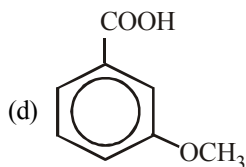
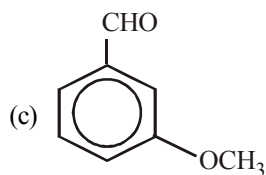
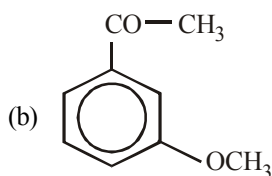
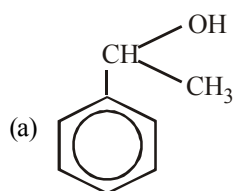
19. In which of the following pairs of reactants is most effective in forming an enamine



(d) None of these forms an enamine

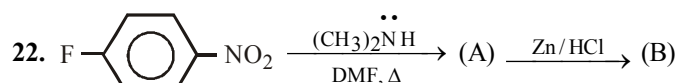


The product 'P' in the above reaction is

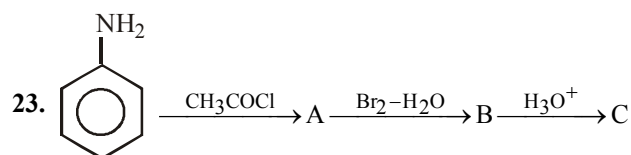
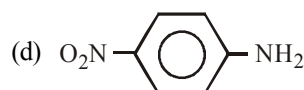
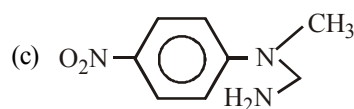
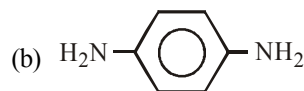
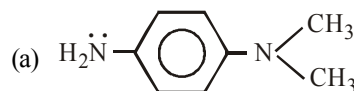


(c) Both of these

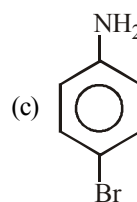
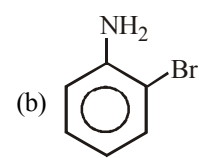
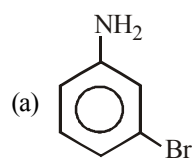
(d) None of these



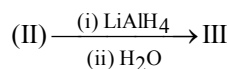
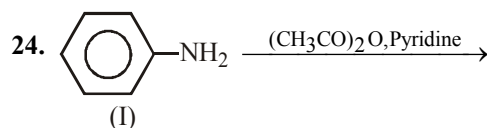
(B) is –



C (major product) is –

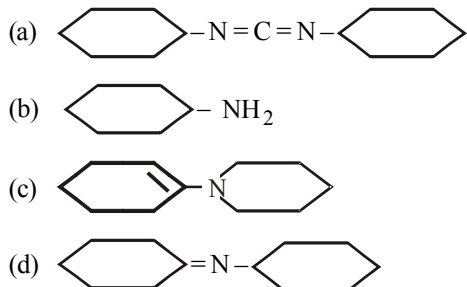


(d) None of these

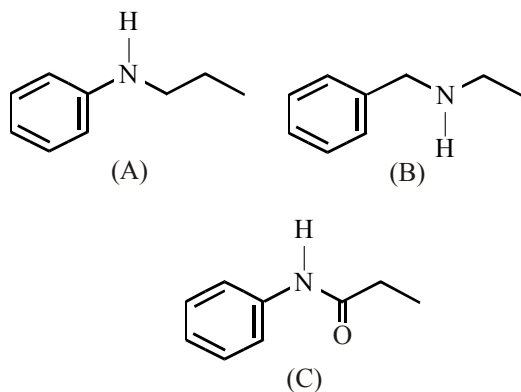


The basicity order of I, II and III is –

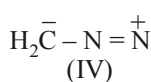
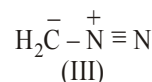
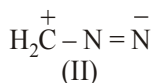
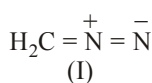
- (a) III > I > II (b) I > II > III
(c) III > II > I (d) II > III > I
25. Which of the following compounds is an enamine ?



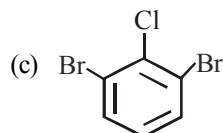
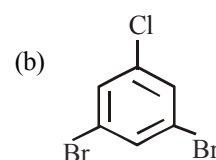
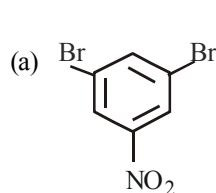
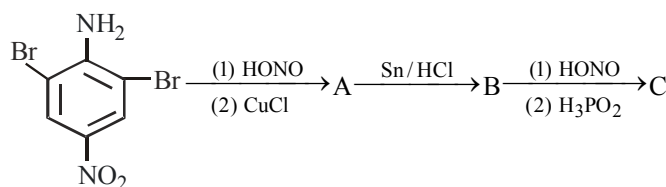
26. Which one of the following compound is most basic?



- (a) (A) (b) (B)
(c) (C) (d) All are equally basic
27. The correct stability order of the following resonance structures is

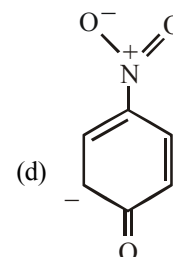
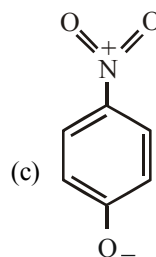
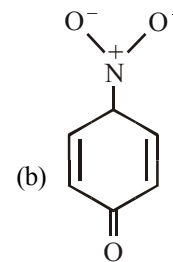
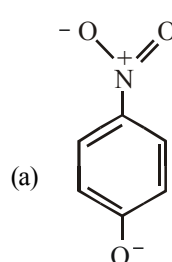


- (a) (I) > (II) > (IV) > (III) (b) (I) > (III) > (II) > (IV)
(c) (II) > (I) > (III) > (IV) (d) (III) > (I) > (IV) > (II)
28. The product – (C) obtained in the following sequence of reactions is

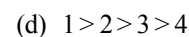
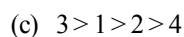
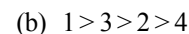
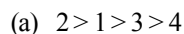
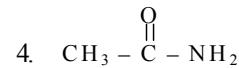
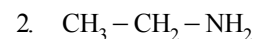
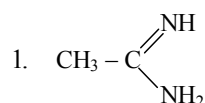


(d) None of these

29. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is



30. The correct order of basicities of the following compounds is

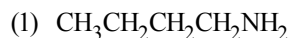


31. An organic compound A containing nitrogen, on acid catalysed hydrolysis produces a water soluble organic compound B and a gaseous compound C. When methyl magnesium bromide is slowly added to A in 1 : 1 ratio and hydrolysed, it produces a compound which can be obtained by dry distillation of the calcium salt of B. The compound A is
- (a) N-methylmethanamide
(b) N-ethylmethanamide
(c) acetonitrile
(d) N,N-dimethylmethanamide

32. Match the compounds given in List - I with their characteristic reactions given in List - II. Select the correct option.

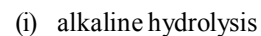
List - I

Compounds



List - II

Reactions

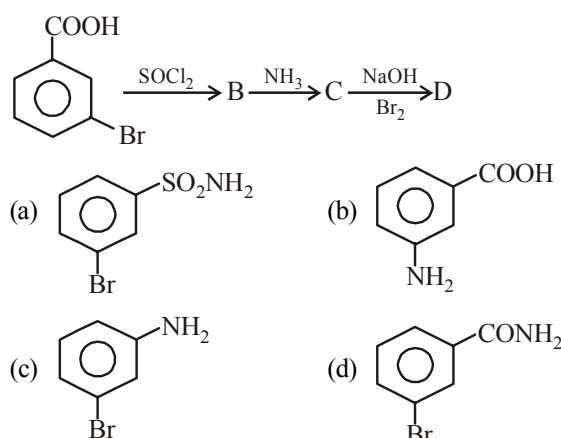


- (2) $\text{CH}_3\text{C}\equiv\text{CH}$ (ii) with KOH (alcohol) and CHCl_3 produces bad smell
 (3) $\text{CH}_3\text{CH}_2\text{COOCH}_3$ (iii) gives white ppt. with ammonical AgNO_3
 (4) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ (iv) with Lucas reagent cloudiness appears after 5 minutes

Options :

- (1) (2) (3) (4)
 (a) (iv) (ii) (iii) (i)
 (b) (ii) (i) (iv) (iii)
 (c) (iii) (ii) (i) (iv)
 (d) (ii) (iii) (i) (iv)

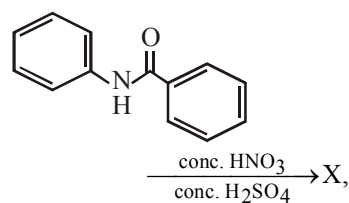
33. In a set of reactions *m*-bromobenzoic acid gave a product D. Identify the product D.



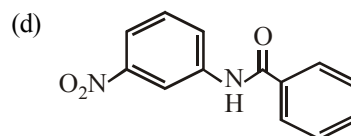
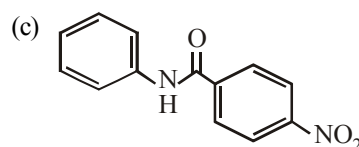
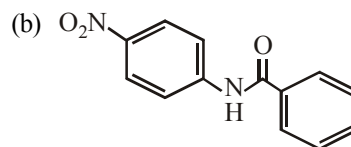
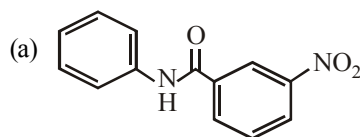
34. An organic compound ($\text{C}_3\text{H}_9\text{N}$) (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with CHCl_3 and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A).

- (a) (b) (c) (d)

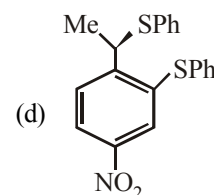
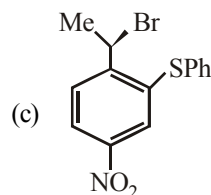
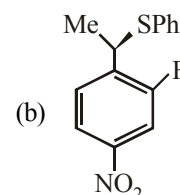
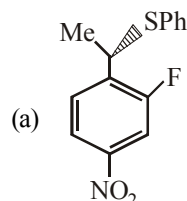
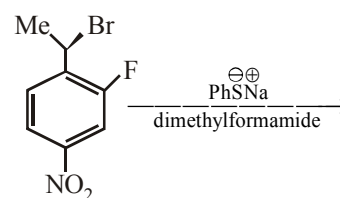
35. In the following reaction



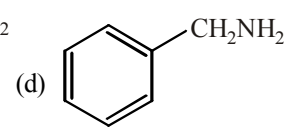
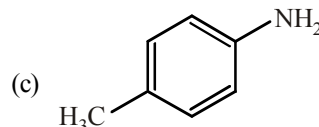
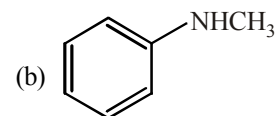
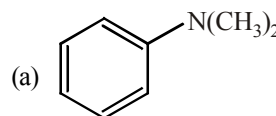
the structure of the major product 'X' is



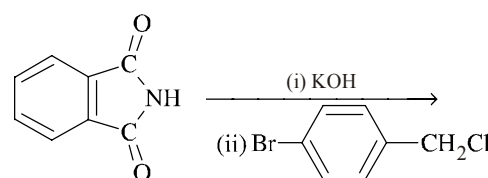
36. The major product of the following reaction is

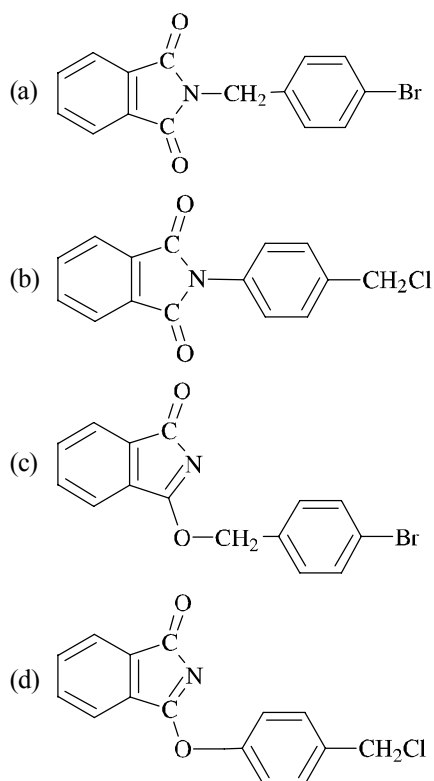


37. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with NaNO_2 in dil. HCl followed by addition to an alkaline solution of β -naphthol is



38. The major product of the following reaction is

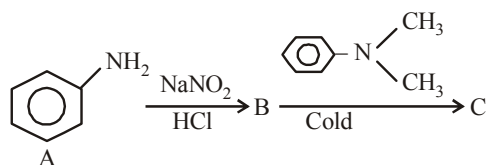




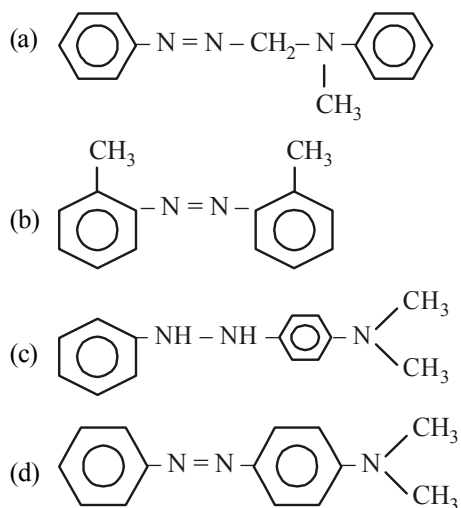
39. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is :

- (a) 2 (b) 5
(c) 4 (d) 6

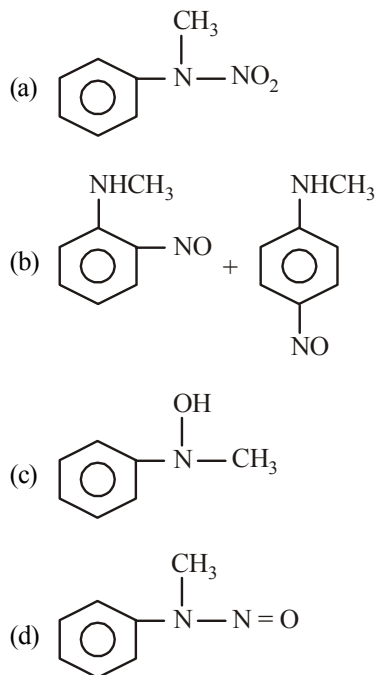
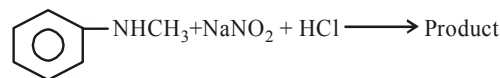
40. In a reaction of aniline a coloured product C was obtained.



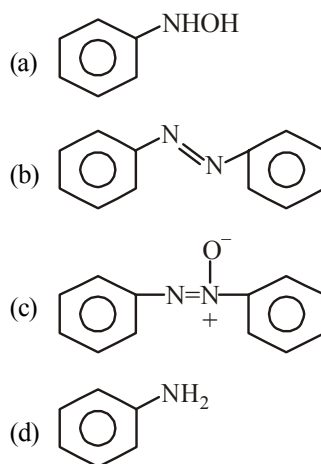
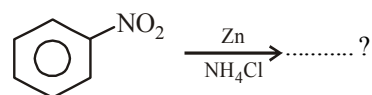
The structure of C would be :



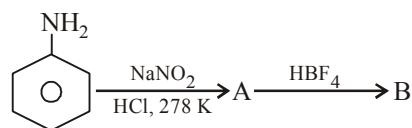
41. Predict the product:



42. What is the product obtained in the following reaction :



43. In the chemical reactions,



the compounds 'A' and 'B' respectively are

- (a) nitrobenzene and fluorobenzene
(b) phenol and benzene
(c) benzene diazonium chloride and fluorobenzene
(d) nitrobenzene and chlorobenzene

44. Which one of the following is the strongest base in aqueous solution ?

- (a) Methylamine (b) Trimethylamine
(c) Aniline (d) Dimethylamine

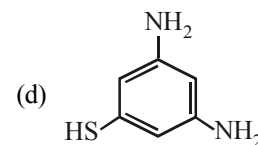
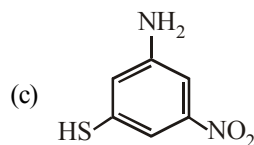
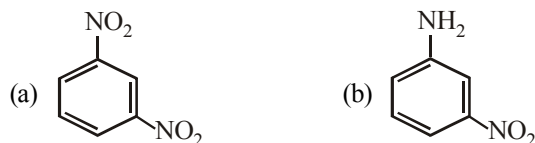
45. Which of the following statements about primary amines is 'False' ?

- (a) Alkyl amines are stronger bases than aryl amines
(b) Alkyl amines react with nitrous acid to produce alcohols
(c) Aryl amines react with nitrous acid to produce phenols
(d) Alkyl amines are stronger bases than ammonia

46. Ortho-Nitrophenol is less soluble in water than *p*- and *m*-Nitrophenols because :

- (a) *o*-Nitrophenol is more volatile than those of *m*- and *p*-isomers.
(b) *o*-Nitrophenol shows intramolecular H-bonding
(c) *o*-Nitrophenol shows intermolecular H-bonding
(d) Melting point of *o*-Nitrophenol is lower than those of *m*- and *p*-isomers.

47. The major product (70% to 80%) of the reaction between *m*-dinitrobenzene with NH_4HS is



DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement -1
(b) Statement -1 is true, Statement-2 is true ; Statement-2 is NOT a correct explanation for Statement -1
(c) Statement -1 is true, Statement-2 is false
(d) Statement -1 is false, Statement-2 is true

48. **Statement-1** : Amines are basic in nature.

Statement-2 : Presence of lone pair of electron on nitrogen atom.

49. **Statement-1** : Nitrating mixture used for carrying out nitration of benzene consists of conc. HNO_3 + conc. H_2SO_4 .

Statement-2 : In presence of H_2SO_4 , HNO_3 acts as a base and produces NO_2^+ ions.

50. **Statement-1** : CN^- ion is an ambident nucleophile.

Statement-2 : Nucleophiles are electron rich species.

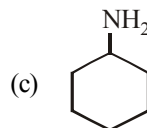
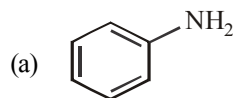
EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

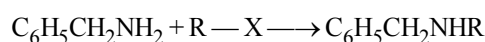
Exemplar Questions

- Which of the following is a 3° amine?
(a) 1-methylcyclohexylamine
(b) Triethylamine
(c) tert-butylamine
(d) N-methylaniline
- The correct IUPAC name for $\text{CH}_2=\text{CHCH}_2\text{NHCH}_3$ is
(a) allyl methylamine
(b) 2-amino-4-pentene
(c) 4-aminopent-1-ene
(d) N-methylprop-2-en-1-amine
- Amongst the following, the strongest base in aqueous medium is
(a) CH_3NH_2 (b) NCCH_2NH_2
(c) $(\text{CH}_3)_2\text{NH}$ (d) $\text{C}_6\text{H}_5\text{NHCH}_3$

4. Which of the following is the weakest Bronsted base?

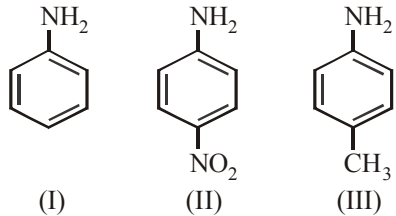
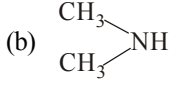
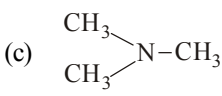
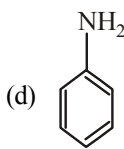


5. Benzylamine may be alkylated as shown in the following equation?

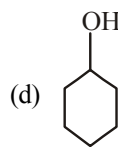
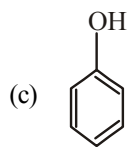
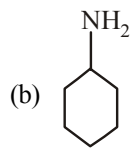
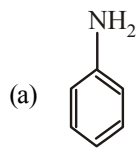


Which of the following alkyl halides is best suited for this reaction through $\text{S}_{\text{N}}1$ mechanism?

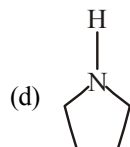
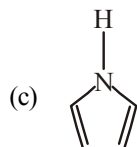
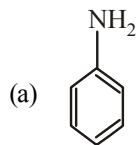
- (a) CH_3Br (b) $\text{C}_6\text{H}_5\text{Br}$
(c) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (d) $\text{C}_2\text{H}_5\text{Br}$

6. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?
 (a) $\text{H}_2(\text{excess}) / \text{Pt}$ (b) LiAlH_4 in ether
 (c) Fe and HCl (d) Sn and HCl
7. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as a source of nitrogen is
 (a) sodium amide, NaNH_2
 (b) sodium azide, NaN_3
 (c) potassium cyanide, KCN
 (d) potassium phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}^-\text{K}^+$
8. The source of nitrogen in Gabriel synthesis of amines is
 (a) sodium azide, NaN_3
 (b) sodium nitrite, NaNO_2
 (c) potassium cyanide, KCN
 (d) potassium phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}^-\text{K}^+$
9. Amongst the given set of reactants, the most appropriate for preparing 2° amine is
 (a) $2^\circ \text{R}-\text{Br} + \text{NH}_3$
 (b) $2^\circ \text{R}-\text{Br} + \text{NaCN}$ followed by H_2/Pt
 (c) $1^\circ \text{R}-\text{NH}_2 + \text{RCHO}$ followed by H_2/Pt
 (d) $1^\circ \text{R}-\text{Br}(2 \text{ mol}) + \text{potassium phthalimide}$ followed by $\text{H}_3\text{O}^+/\text{heat}$
10. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is
 (a) excess H_2
 (b) Br_2 in aqueous NaOH
 (c) iodine in the presence of red phosphorus
 (d) LiAlH_4 in ether
11. The best reagent for converting 2-phenylpropanamide into 1-phenylethanamine is
 (a) excess H_2 / Pt (b) $\text{NaOH} / \text{Br}_2$
 (c) $\text{NaBH}_4 / \text{methanol}$ (d) $\text{LiAlH}_4 / \text{ether}$
12. Hoffmann bromamide degradation reaction is shown by
 (a) ArNH_2 (b) ArCONH_2
 (c) ArNO_2 (d) ArCH_2NH_2
13. The correct increasing order of basic strength for the following compounds is

 (I) (II) (III)
14. Methylamine reacts with HNO_2 to form
 (a) $\text{CH}_3-\text{O}-\text{N}=\text{O}$ (b) $\text{CH}_3-\text{O}-\text{CH}_3$
 (c) CH_3OH (d) CH_3CHO
15. The gas evolved when methylamine reacts with nitrous acid is
 (a) NH_3 (b) N_2
 (c) H_2 (d) C_2H_6
16. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3 , the species which initiates the reaction is
 (a) NO_2 (b) NO^+
 (c) NO_2^+ (d) NO_2^-
17. Reduction of aromatic nitro compounds using Fe and HCl gives
 (a) aromatic oxime (b) aromatic hydrocarbon
 (c) aromatic primary amine (d) aromatic amide
18. The most reactive amine towards dilute hydrochloric acid is
 (a) CH_3-NH_2 (b) 
 (c)  (d) 
19. Acid anhydrides on reaction with primary amines give
 (a) amide (b) imide
 (c) secondary amine (d) imine
20. The reaction $\text{ArN}_2\text{Cl}^- \xrightarrow{+\text{Cu/HCl}} \text{ArCl} + \text{N}_2 + \text{CuCl}$ is named as
 (a) Sandmeyer reaction (b) Gattermann reaction
 (c) Claisen reaction (d) Carbylamine reaction
21. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is
 (a) Hoffmann bromamide reaction
 (b) Gabriel phthalimide synthesis
 (c) Sandmeyer reaction
 (d) reaction with NH_3
22. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride?
 (a) Aniline (b) Phenol
 (c) Anisole (d) Nitrobenzene

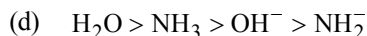
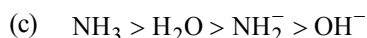
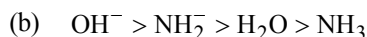
23. Which of the following compounds is the weakest Bronsted base?



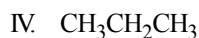
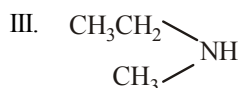
24. Among the following amines, the strongest Bronsted base is



25. The correct decreasing order of basic strength of the following species is H_2O , NH_3 , OH^- , NH_2^-

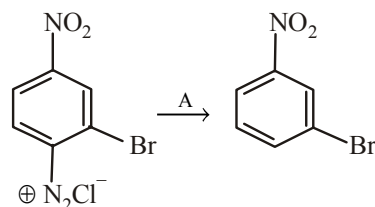


26. Which of the following should be most volatile?

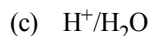
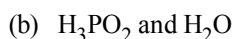
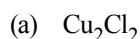


NEET/AIPMT (2013-2017) Questions

27. In the reaction



A is :



[2013]

28. Nitrobenzene on reaction with conc. $\text{HNO}_3/\text{H}_2\text{SO}_4$ at $80-100^\circ\text{C}$ forms which one of the following products?



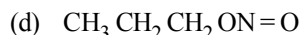
[2013]



29. On hydrolysis of a "compound", two compounds are obtained. One of which on treatment with sodium nitrite and hydrochloric acid gives a product which does not respond to iodoform test. The second one reduces Tollen's reagent and Fehling's solution. The "compound" is

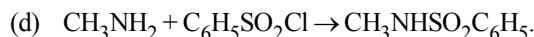
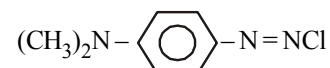
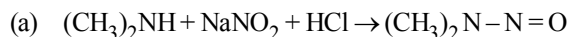


[NEET Kar. 2013]



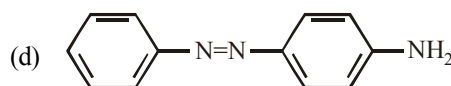
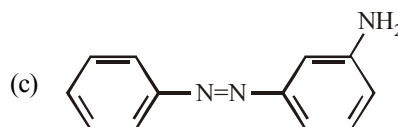
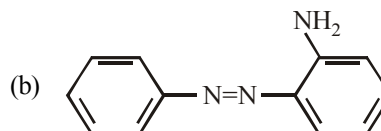
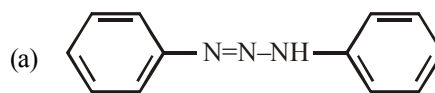
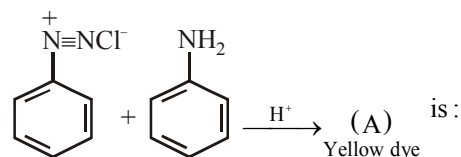
30. Some reactions of amines are given. Which one is not correct?

[NEET Kar. 2013]



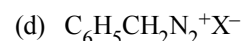
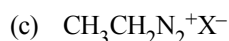
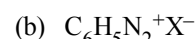
31. In the following reaction, the product (A)

[2014]



32. Which of the following will be most stable diazonium salt RN_2^+X^- ?

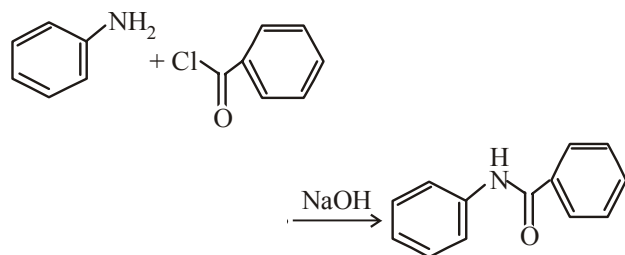
[2014]



33. The electrolytic reduction of nitrobenzene in strongly acidic medium produces : [2015]

- (a) Azoxybenzene (b) Azobenzene
(c) Aniline (d) p-Aminophenol

34. The following reaction



is known by the name :

[2015 RS]

- (a) Friedel-Craft's reaction
(b) Perkin's reaction
(c) Acetylation reaction
(d) Schotten-Baumen reaction

35. The number of structural isomers possible from the molecular formula C_3H_9N is: [2015 RS]

- (a) 4 (b) 5
(c) 2 (d) 3

36. Method by which Aniline cannot be prepared is:

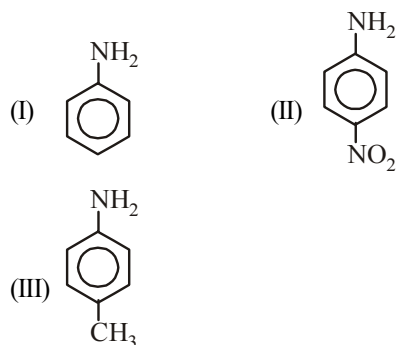
[2015 RS]

- (a) hydrolysis of phenylisocyanide with acidic solution
(b) degradation of benzamide with bromine in alkaline solution
(c) reduction of nitrobenzene with H_2/Pd in ethanol
(d) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

37. The correct statement regarding the basicity of arylamines is [2016]

- (a) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring π electron system.
(b) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring π electron system.
(c) Arylamines are generally more basic than alkylamines because of aryl group.
(d) Arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is sp -hybridized.

38. The correct increasing order of basic strength for the following compounds is: [2017]



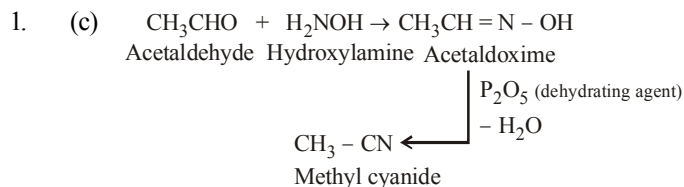
- (a) $III < I < II$ (b) $III < II < I$
(c) $II < I < III$ (d) $II < III < I$

39. Which of the following reactions is appropriate for converting acetamide to methanamine ? [2017]

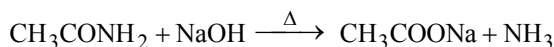
- (a) Hoffmann hypobromamide reaction
(b) Stephens reaction
(c) Gabriel phthalimide synthesis
(d) Carbylamine reaction

Hints & Solutions

EXERCISE - 1



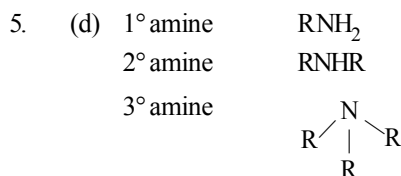
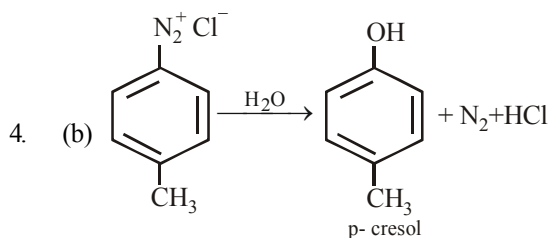
2. (b) Acetamide and ethylamine can be distinguished by heating with NaOH solution. Acetamide evolves NH_3 but ethylamine does not.



3. (c) We know that

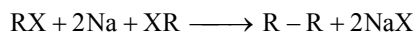


In this reaction, bad smelling compound ethyl isocyanide ($\text{CH}_3\text{CH}_2\text{NC}$) is produced. This equation is known as **carbylamine reaction**.

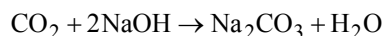
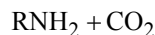
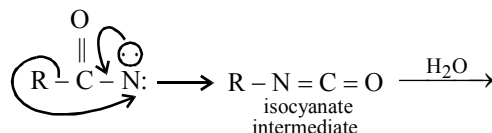
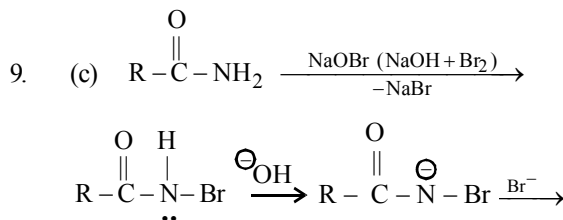
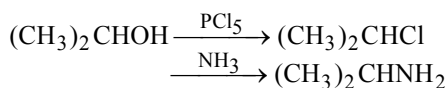
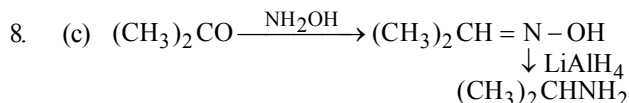
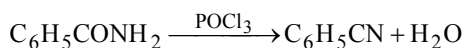


quaternary ammonium salt is R_4N^+ .

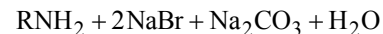
6. (b) Wurtz reaction is for the preparation of hydrocarbons from alkyl halide



7. (d) POCl_3 is a dehydrating agent. Hence



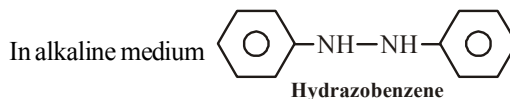
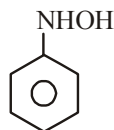
Overall reaction



10. (c) Backmann rearrangement is used to form N-alkyl amide.
 11. (d) Various products are formed when nitroarenes are reduced. These are given below for $\text{C}_6\text{H}_5\text{NO}_2$.

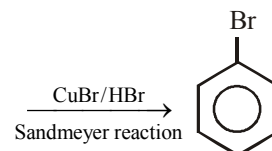
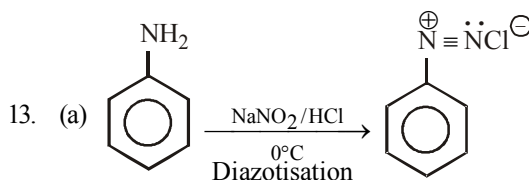
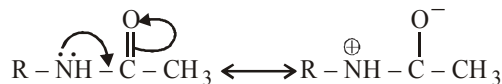
Medium Main product

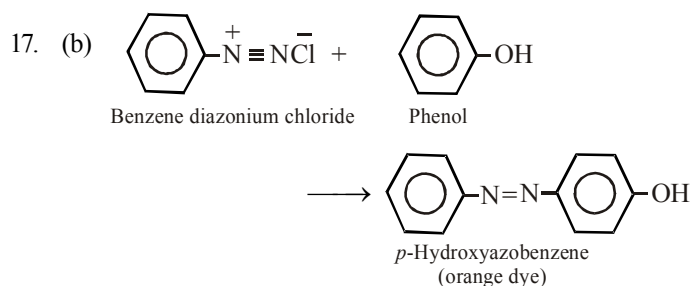
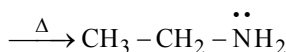
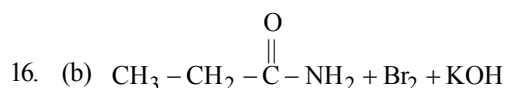
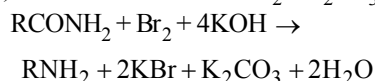
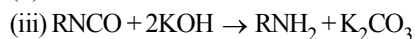
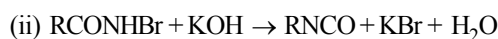
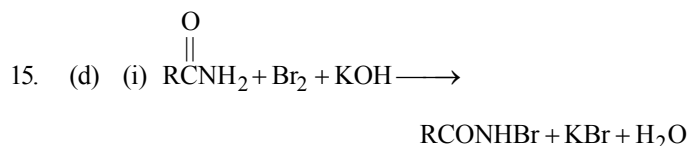
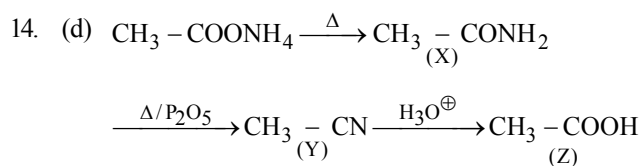
In acidic medium Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) (metal/HCl)
 In neutral medium Phenyl hydroxylamine, ($\text{Zn}/\text{NH}_4\text{Cl}$)



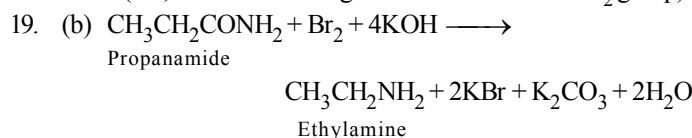
Thus, Aniline will be main product in case of (d).

12. (a) Acylation occurs in one step only because lone pair of nitrogen is delocalized with acyl group.



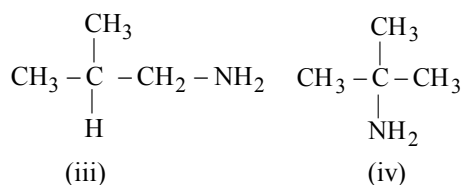
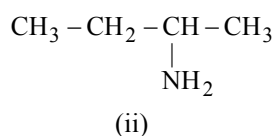
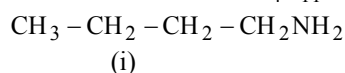


18. (a) The reason for the lesser basicity of aniline as compared to that of cyclohexylamine is +R effect of $-\text{NH}_2$ group (*i.e.*, electron releasing resonance effect of $-\text{NH}_2$ group).



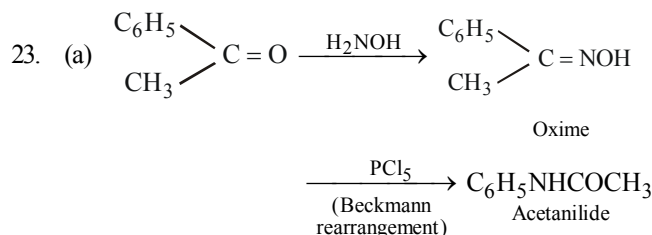
This is Hofmann bromamide reaction in which amide is converted into amine having one carbon atom less than amide.

20. (c) 1° amines have -NH_2 group in their structure. 4 primary amines are possible by $\text{C}_4\text{H}_{11}\text{N}$.

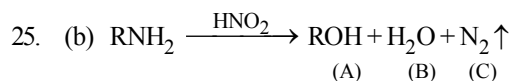


21. (a) Excess of HCl is used to convert free aniline to aniline hydrochloride otherwise free aniline would undergo coupling reaction with benzenediazonium chloride.

22. (d) *p*-Chloroaniline and anilinium hydrogen chloride can be distinguished by AgNO_3 . Anilinium hydrogen chloride will give white ppt of AgCl on reaction with AgNO_3 but *p*-chloroaniline will not react with it because Cl is directly attached to benzene nucleus.

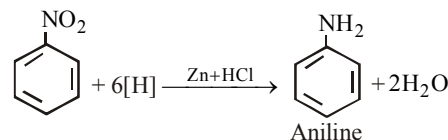


24. (a) Secondary amines are more basic than tertiary amines due to stabilisation of 2° amine by hydrogen bonding with solvent molecule.



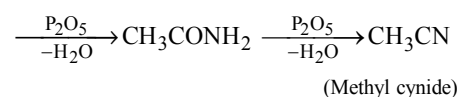
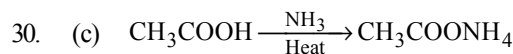
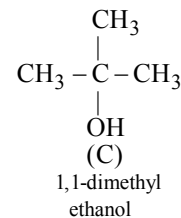
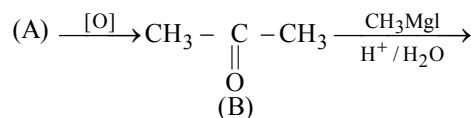
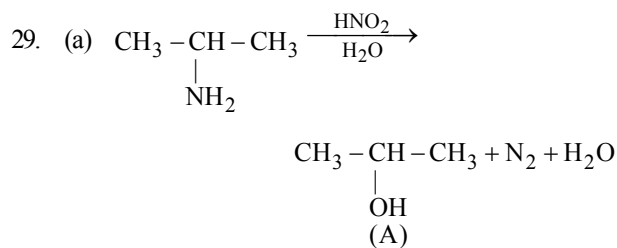
26. (b) The given reaction is known as Sandmeyer's reaction.

27. (d) Aniline is formed

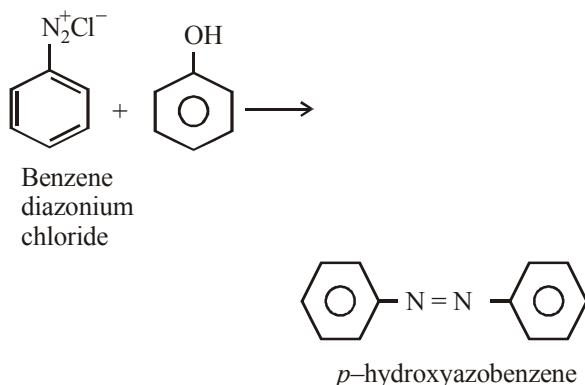


This is reduction in acidic medium.

28. (c) Since the organic amino compound on reaction with nitrous acid at low temperature produces an oily nitrosoamine so the organic amino compound is a secondary aliphatic amines.

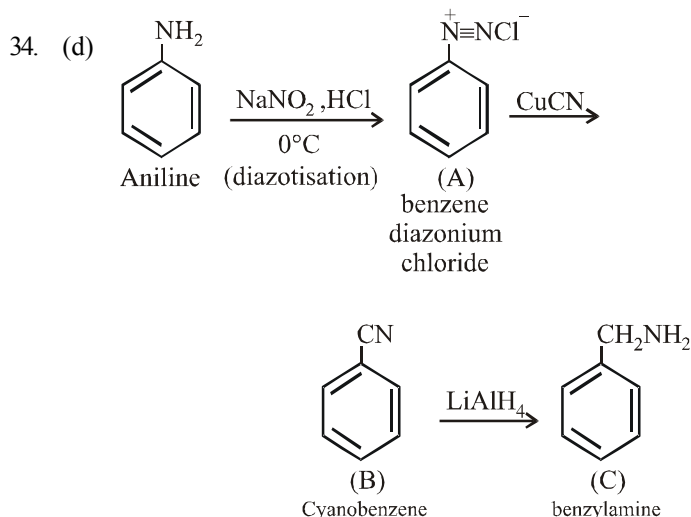
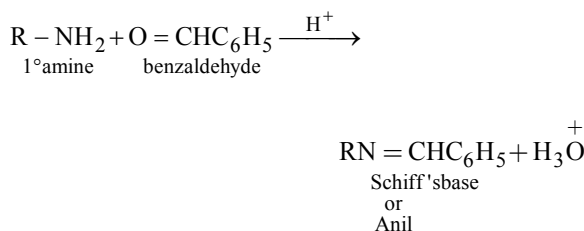


31. (a) Azo dye is prepared by diazo coupling reaction of phenol with diazonium salt.

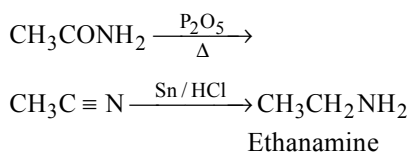


(-N=N-) group is called azo-group.

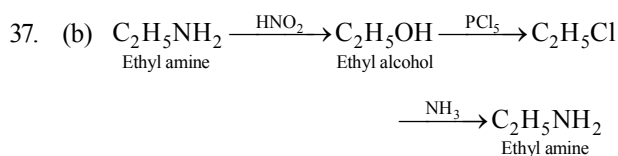
32. (d) The given reaction is known as Liebermann Nitroso reaction.
33. (d) Primary amines react with benzaldehyde in presence of a trace of an acid as catalyst to form Schiff's base or Anil



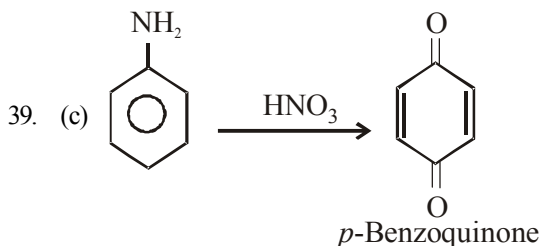
35. (c) Completing the given reaction we get



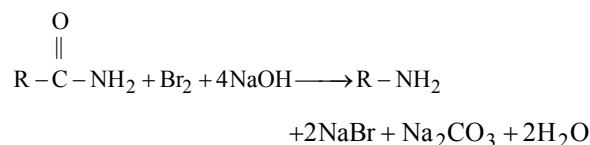
36. (c)



38. (a) In (b), (c) and (d) lone pair of nitrogen is linked with sp^2 hybridised carbon which is acidic in nature therefore it attracts the electron pair towards itself. In (a) lone pair of nitrogen is free because it is attached with carbon which is sp^3 hybridised. So it is most basic.

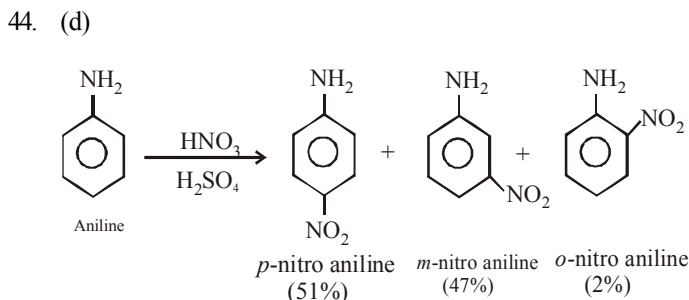


40. (a) $\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$.
41. (d)
42. (a) The reaction is Hoffmann bromamide reaction



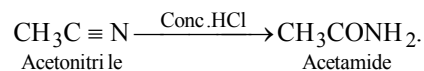
$\text{R}-\text{NH}_2$ contains one carbon less than $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$

43. (b) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_6 + \text{N}_2 + \text{HCl} + \text{H}_3\text{PO}_3$

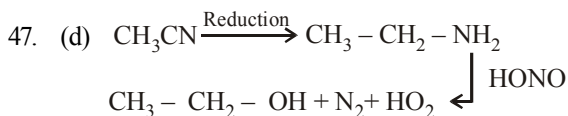


The reason for this is that, in acidic condition protonation of $-\text{NH}_2$ group gives anilinium ion (NH_3^+), which is of **deactivating nature and of *m*-directing nature**.

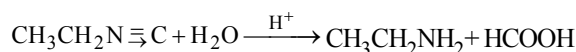
45. (b) Methyl cyanide on treatment with conc. HCl give acetamide.

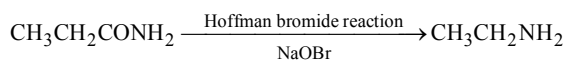
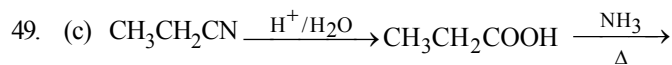


46. (d) The reaction is known as Hoffmann's mustard oil reaction.

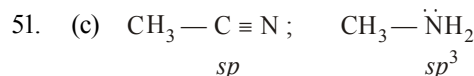
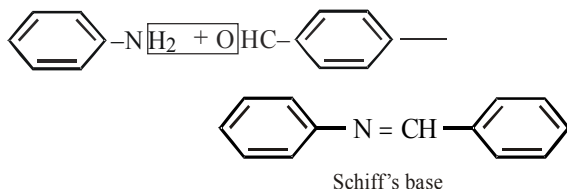


48. (d) Ethyl isocyanide on hydrolysis form primary amines.





50. (b) Primary amines react with aldehydes or ketones to form compound known as Schiff's base



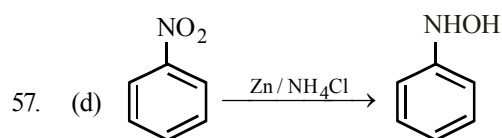
52. (a) Among the given reagents, only LiAlH_4 is the reducing agent.

53. (a) Aryl halide (ArX) does not undergo nucleophilic substitution because they have strong $\text{C}-\text{X}$ bond due to resonance.

54. (b) N-alkyl formamides when dehydrated with POCl_3 in presence of pyridine give isocyanides.

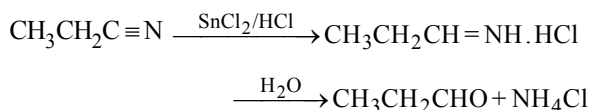
55. (b)

56. (b) Hydrolysis of phenyl isocyanide forms formic acid.

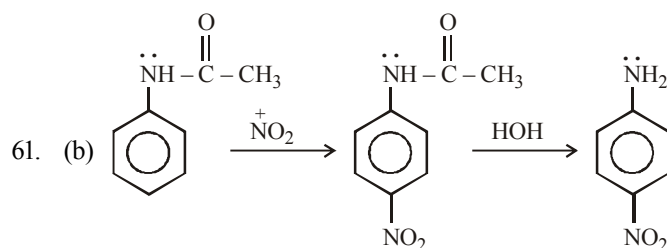


58. (c)

59. (a) It is Stephen's reaction.

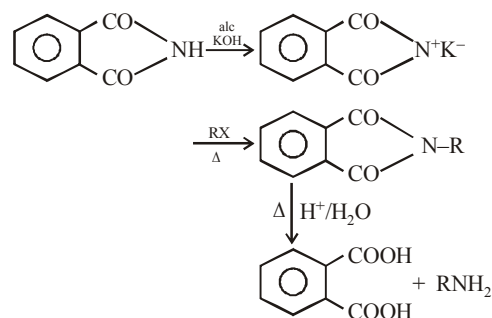


60. (b) Cold dil. NaOH does not attack to either of the compound, while cold dil. HCl reacts only with benzyl amine $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$.



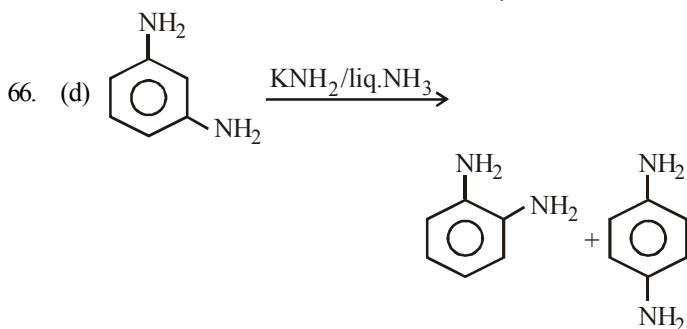
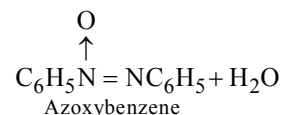
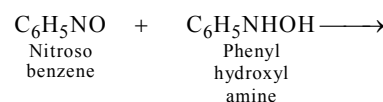
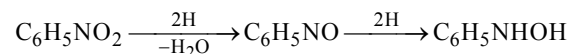
62. (d) The reaction involves the conversion of $-\text{NO}_2$ to $-\text{NH}_2$ group (reduction) which occurs in presence of Fe/HCl .

63. (a) Aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with potassium phthalimide under ordinary conditions to give N-phenyl phthalimide (i.e., cleavage of $\text{C}-\text{X}$ bond in haloarenes is quite difficult).

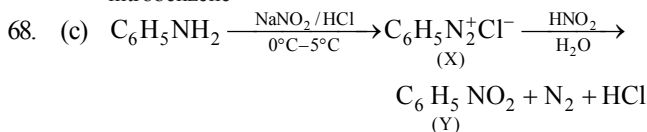
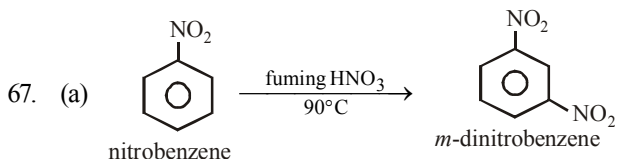


64. (a) Of the given compounds toluene which contains an electron donating group in the ring will be nitrated easily.

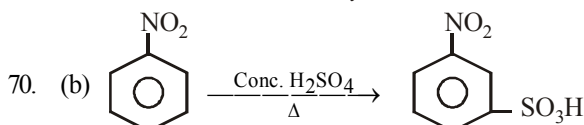
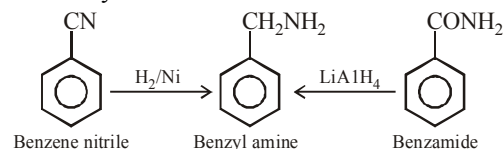
65. (c) When nitrobenzene is reduced in alkaline medium like Na_3AsO_3 / NaOH or glucose / NaOH , azoxybenzene is formed as the reduction product.

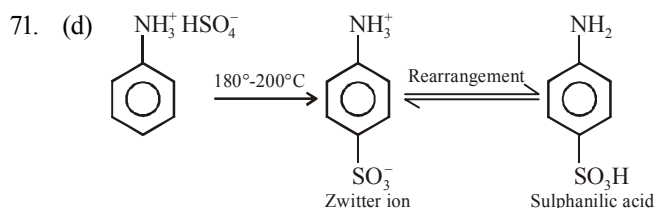


It is an example of nucleophilic aromatic substitution. It proceeds via the formation of an intermediate benzyne.

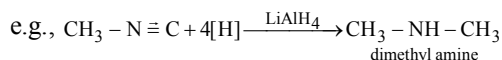
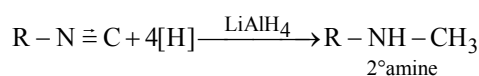


69. (b) Out of the given options, only benzyl amine can be obtained by both the methods.

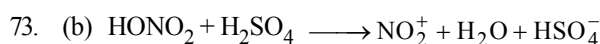




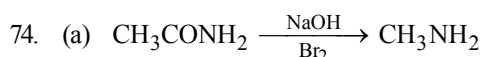
72. (a) Reduction of alkyl isocyanides in presence of LiAlH_4 yields secondary amines containing methyl as one of the alkyl group.



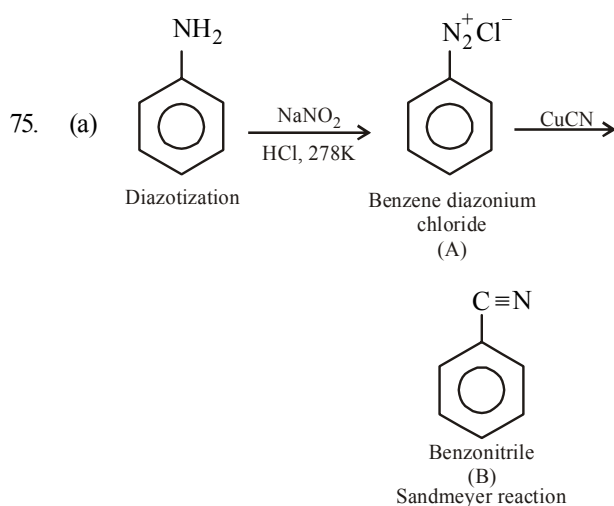
whereas, alkyl cyanides give 1° amine on reduction.



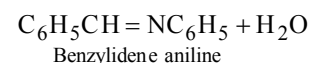
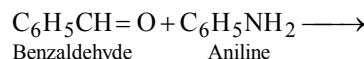
Nitric acid acts as a base by accepting a proton.



(Hofmann bromamide reaction)

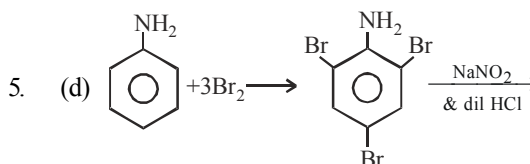
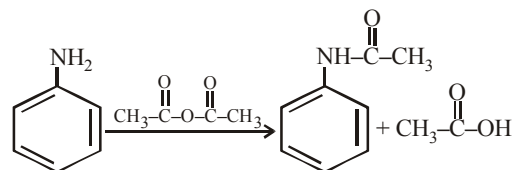


3. (c) Benzaldehyde reacts with primary aromatic amine to form schiff's base

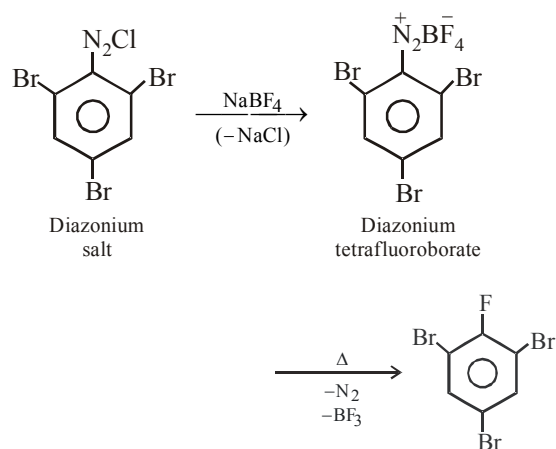


This is known as Schiff's base reaction.

4. (d) Aniline when treated with acetic anhydride forms acetanilide.

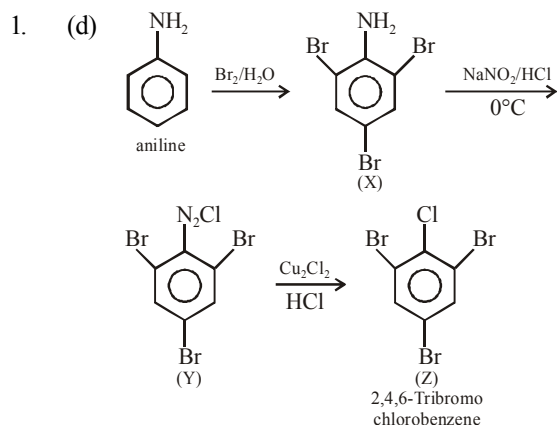


(2, 4, 6 tribromoaniline)



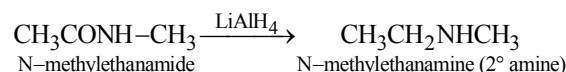
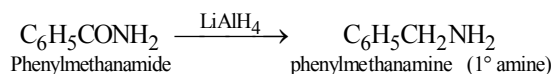
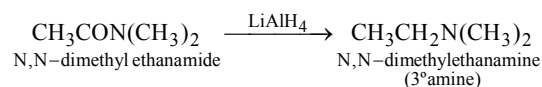
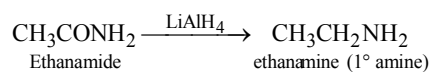
2,4,6 tribromofluorobenzene

EXERCISE - 2

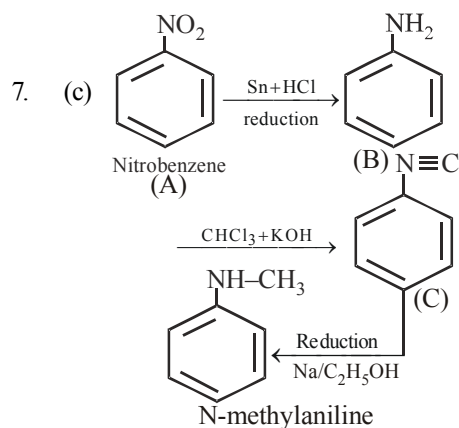


2. (d) NH_3 is a weaker base than ethanamine.

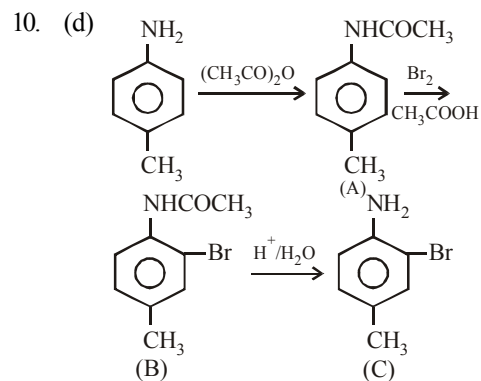
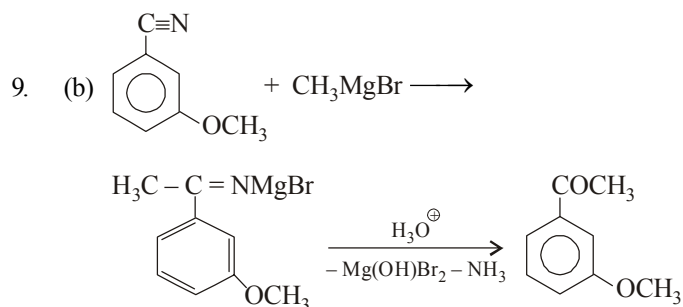
6. (b) Reduction reactions of given amines are following



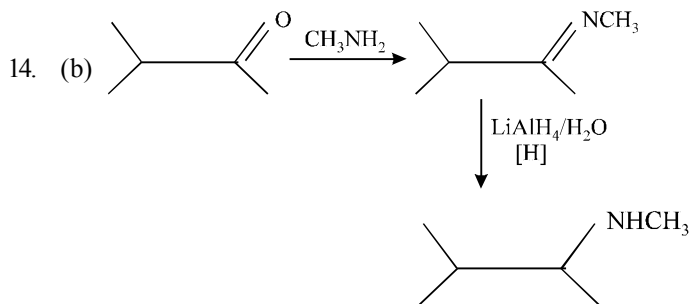
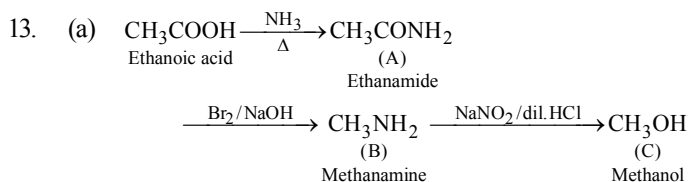
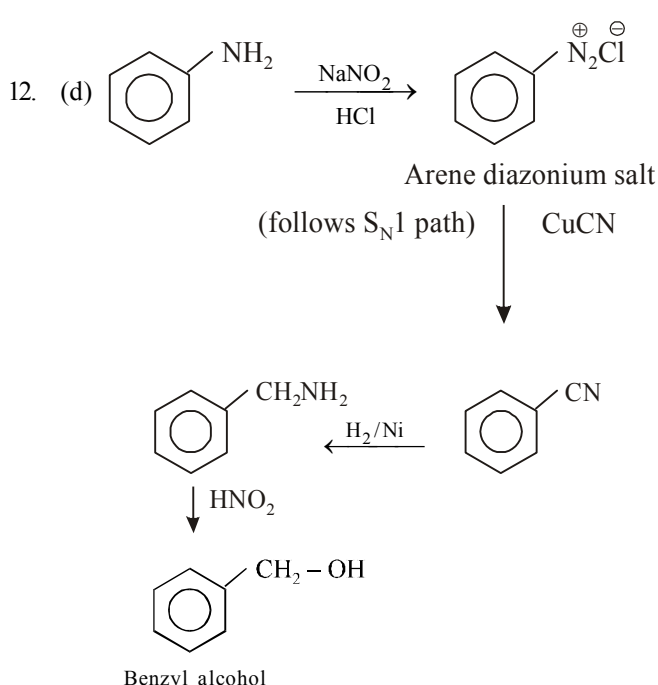
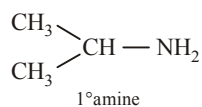
Thus N-methyl ethanamide gives 2° amine on reduction.



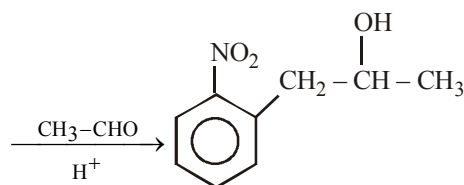
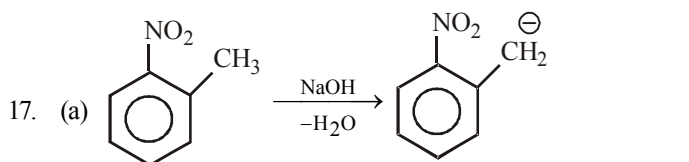
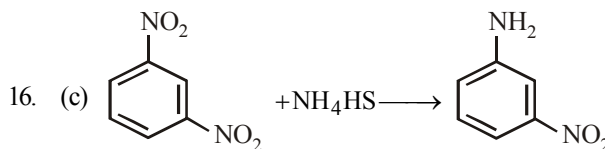
8. (c) The mechanism of Hoffmann bromide reaction is
- $\text{RCONH}_2 + \text{Br}_2 \rightarrow \text{RCONHBr} + \text{HBr}$
 - $\text{RCONHBr} + \text{HBr} \xrightarrow{\text{OH}^-} \text{R}-\text{CO}-\ddot{\text{N}}^-\text{Br} + \text{H}_2\text{O}$
 - $\text{R}-\text{C}(=\text{O})-\ddot{\text{N}}^-\text{Br} \xrightarrow{\text{K}^+} \text{R}-\text{C}(=\text{O})-\ddot{\text{N}} + \text{KBr}$
 - $\text{O}=\text{C}-\ddot{\text{N}} \rightleftharpoons \text{R}-\ddot{\text{N}}=\text{C}=\text{O}$ (rearrangement)
 - $\text{R}-\ddot{\text{N}}=\text{C}=\text{O} + 2\text{KOH} \rightarrow \text{RNH}_2 + \text{K}_2\text{CO}_3$

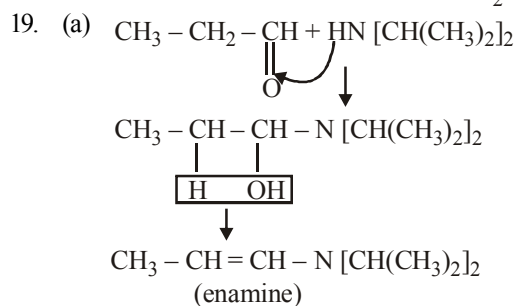
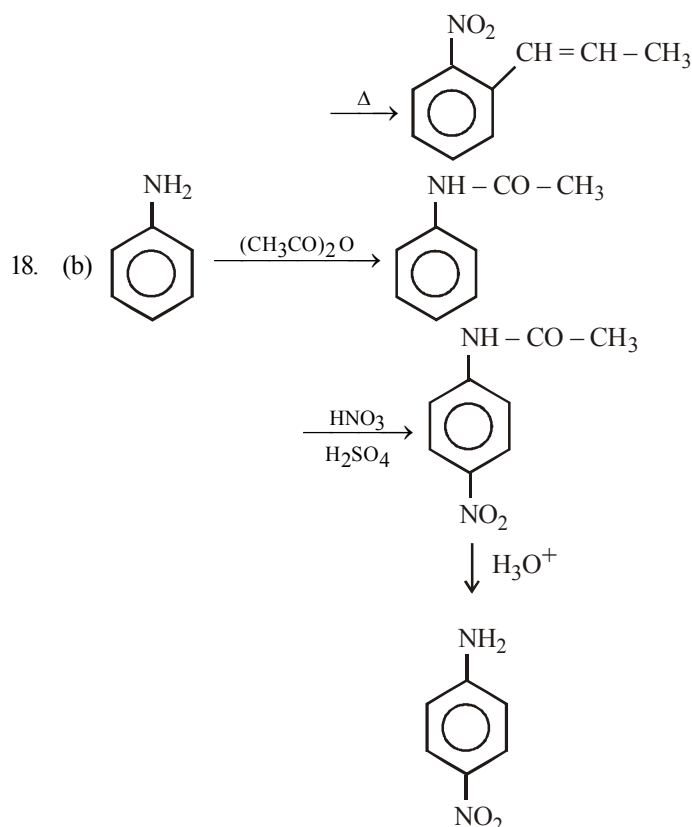


11. (d) Isopropylamine is a primary amine.

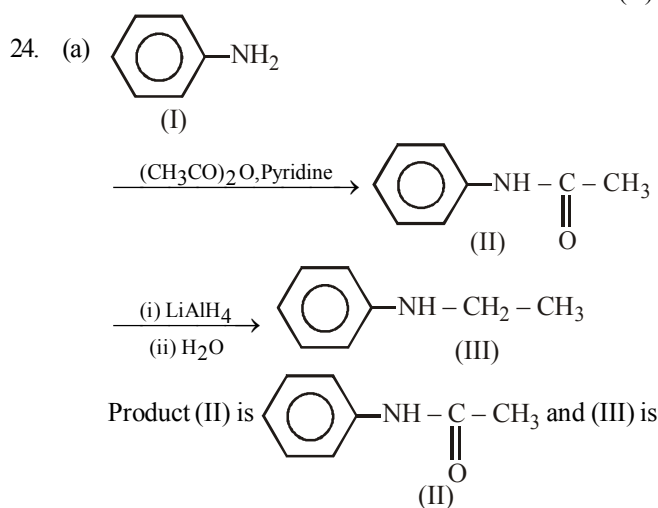
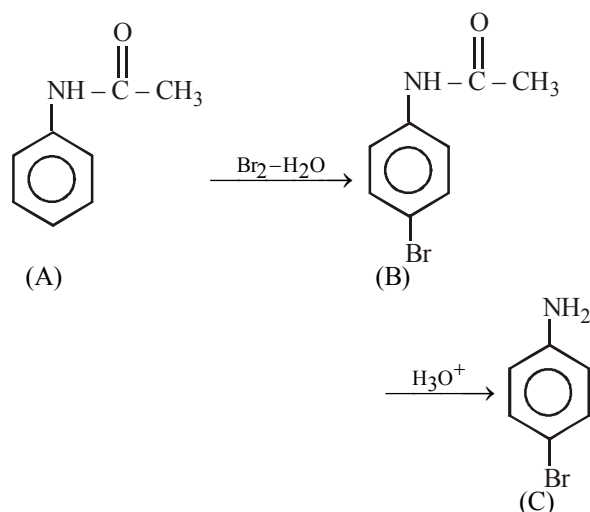
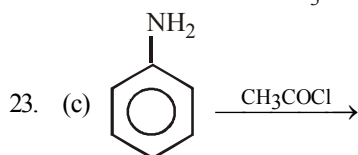
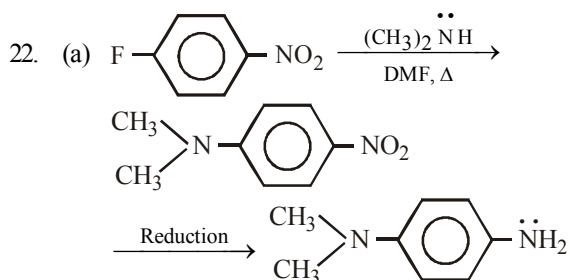
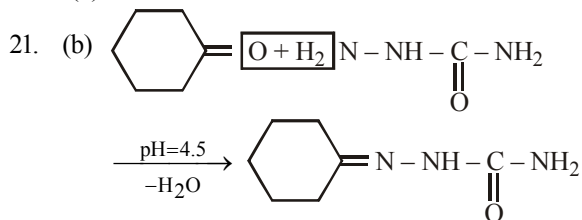


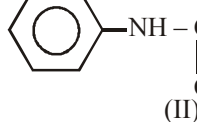
15. (d) Weak base has high pK_b value. Benzenamine (aniline) is the weakest base among the given amines. Therefore it has highest pK_b value.

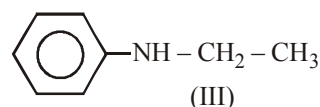




20. (b)



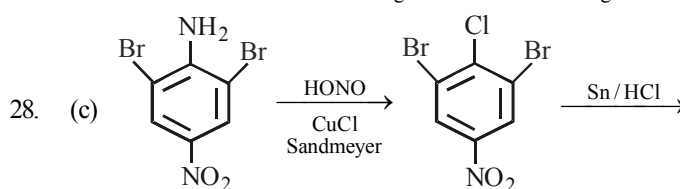
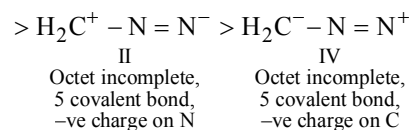
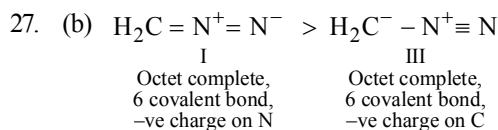
Product (II) is  and (III) is

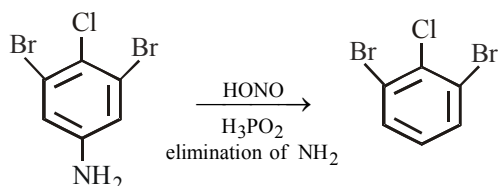


$\therefore \text{III} > \text{I} > \text{II}$, As +I effect increases the basic strength and -R, -I effect shown by $-\text{COCH}_3$ reduces the basic strength.

25. (c) Enamine (ene for carbon-carbon double bond and amine for amine group). $>\text{C}=\text{C}-\text{N}<$

26. (b) In (b) the lone pair of electrons on N is not in conjugation with benzene ring, hence it is not involved in resonance causing the compound to be most basic.



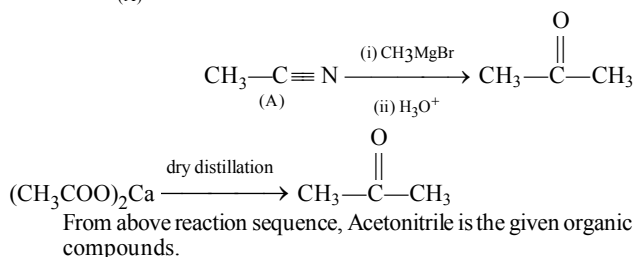


29. (c) N can't have more than 8 electrons in its valence shell as it does not have any d orbital. In (c), N has 10 electrons.

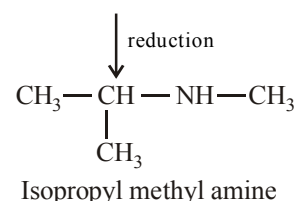
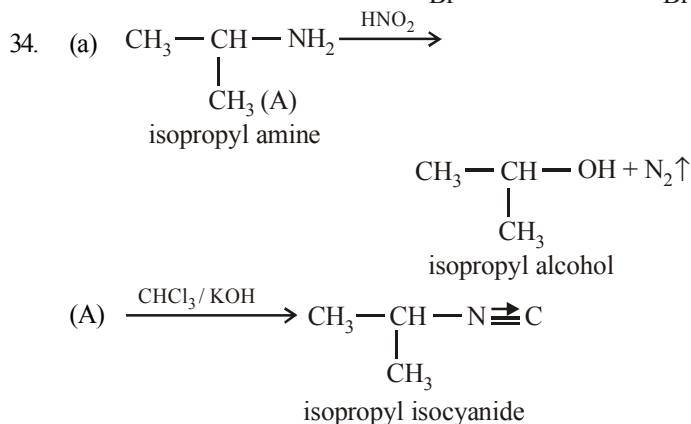
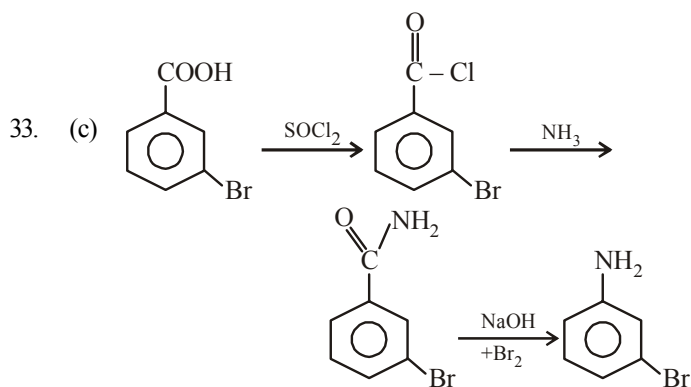
30. (d) $\text{CH}_3-\text{C}(\text{NH}_2)_2$ is most basic

$(\text{CH}_3)_2\text{NH}$ is less basic than $\text{CH}_3\text{CH}_2\text{NH}_2$ due to steric hindrance because of two bulky $-\text{CH}_3$ groups on nitrogen atom.

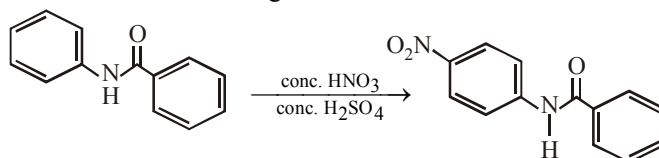
31. (c) $\text{CH}_3-\text{C}\equiv\text{N} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3-\text{COOH} + \text{NH}_3$
 Acetonitrile (A) (B) (C)



32. (d) (1) $\text{CH}_3\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$
 (ii) with KOH (alcohol) and CHCl_3 produces bad smell
- (2) $\text{CH}_3\text{C}\equiv\text{CH}$
 (ii) gives white ppt with ammonical AgNO_3
- (3) $\text{CH}_3\text{CH}_2\text{COOCH}_3$
 (i) alkaline hydrolysis
- (4) $\text{CH}_3\text{CHOH}-\text{CH}_3$
 (iv) with Lucas reagent cloudiness appears after 5 minutes

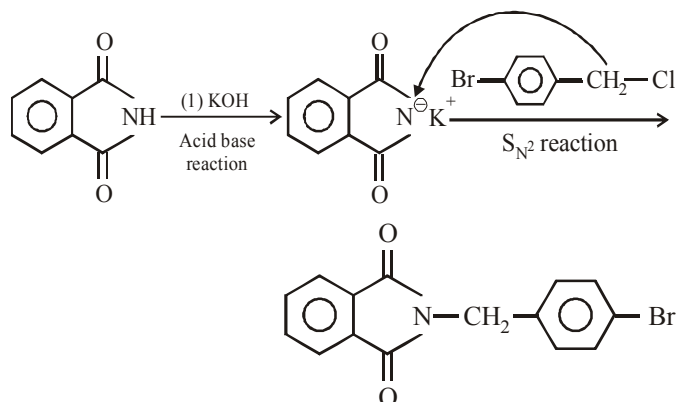


35. (b) The benzene ring which is directly attached with nitrogen atom of acidamide group is more activated than the other, so nitration will take place at para position of this activated ring.



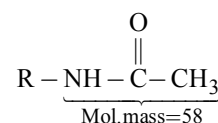
36. (a)
 $\text{S}_{\text{N}}2$ Mechanism $\therefore$ Inversion takes place

37. (c) Only primary aromatic amines undergo diazotisation followed by coupling.
38. (a)



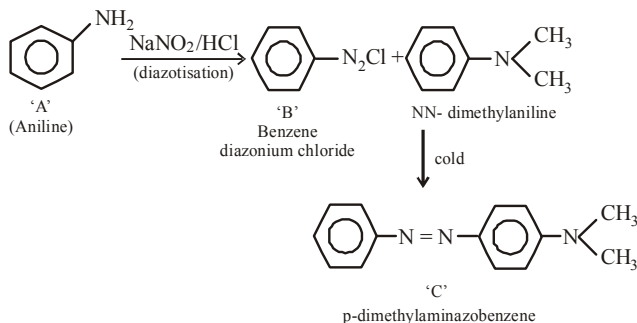
Due to resonance $\text{C}-\text{Br}$ bond shows partial double bond character. Therefore nucleophile does not replace Br in above reaction.

39. (b) $\text{R}-\text{NH}_2 + \text{CH}_3-\text{C}(=\text{O})-\text{Cl} \xrightarrow{-\text{HCl}}$
 Mol. Mass = 16

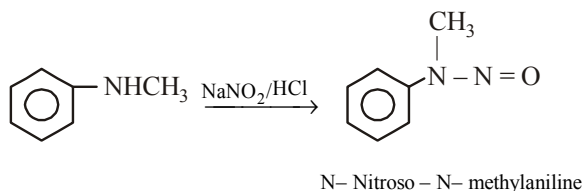


Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH_3COCl with one $-\text{NH}_2$ group and the given increase in mass is 210. Hence the number of $-\text{NH}_2$ groups is $= 210/42 = 5$.

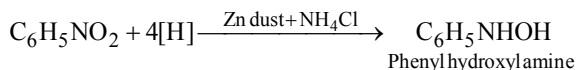
40. (d) The reaction can be completed as follows:



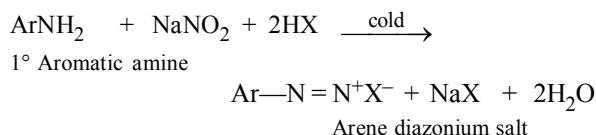
41. (d) Secondary amine with ($\text{NaNO}_2 + \text{HCl}$) gives a nitroso product



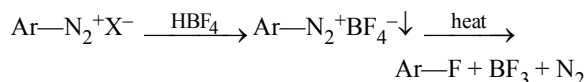
42. (a) When nitro compound is reduced with a neutral reducing agent (Zn dust + NH_4Cl) the corresponding hydroxyl amine is formed



43. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.



The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF_4). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as Balz-Schiemann reaction.



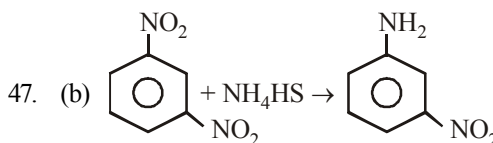
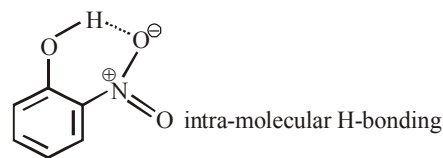
44. (d) Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is $2^\circ > 1^\circ > 3^\circ$. The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show $-I$ effect, thus decreases the electron density on nitrogen atom and hence the basicity.

$\therefore$ dimethylamine (2° aliphatic amine) is strongest base among given choices.

$\therefore$ The correct order of basic strength is
Dimethylamine > Methyl amine > Trimethyl amine > Aniline.

45. (c) Aryl amines do not produce phenol on treatment with nitrous acid

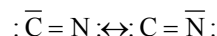
46. (b) *o*-nitrophenol shows intramolecular H-bonding and forms chelate. Compounds involved in chelation become non-polar. Consequently such compounds are soluble in non-polar solvents like ether, benzene etc. and are only sparingly soluble in water whereas meta and para isomers are more soluble in water & less soluble in non-polar solvents.



48. (a) Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.



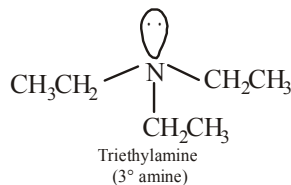
50. (b) Nucleophilic species which have more than one site of reaction are called ambident nucleophiles.



EXERCISE - 3

Exemplar Questions

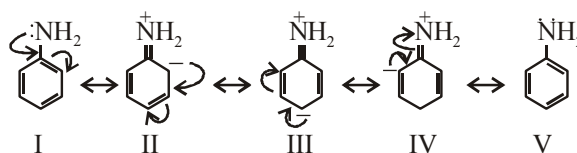
1. (b) 3° amine is the amine in which nitrogen is attached to three alkyl groups whether they are same or different.



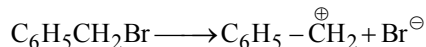
2. (d) IUPAC name of $\text{CH}_2=\overset{3}{\text{CH}}\overset{2}{\text{CH}}\overset{1}{\text{CH}_2}\text{NHCH}_3$ is N-methylprop-2-en-1-amine.

3. (c) More the hydrogen bonding more will be the basicity in gaseous phase but in aqueous solution solvation effect also play the role. By combining both the effects order of basicity in aqueous medium is $2^\circ > 3^\circ > 1^\circ > \text{NH}_3$. The inductive effect comes to play when order of amines is same as in case of (c) & (d) where both the amines are secondary. $+I$ group increase the basicity and $-I$ group will decrease the basicity of amines.

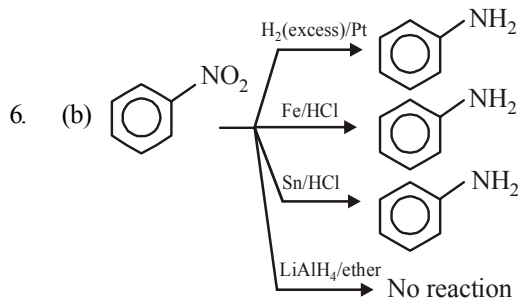
4. (a) In aniline, lone pair of nitrogen is not available for donation to the acid as it is involved in the resonance. Thus, it will act as the weakest Bronsted base amongst the given compounds.



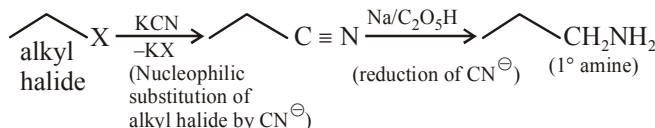
5. (c) S_N1 reaction involves the formation of carbocation, so, more stable carbocation will have higher reactivity towards S_N1 mechanism.



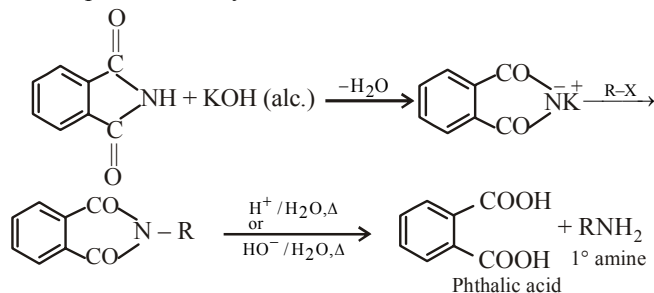
As $C_6H_5\overset{\oplus}{CH_2}$ is the most stabilised carbocation due to resonance, hence it will be most reactive towards S_N1 mechanism.



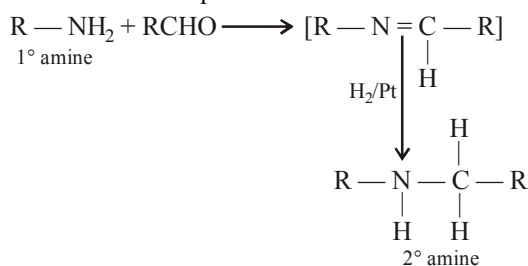
7. (c) 1° amine with increased $-CH_2$ group can be achieved by following the given steps:



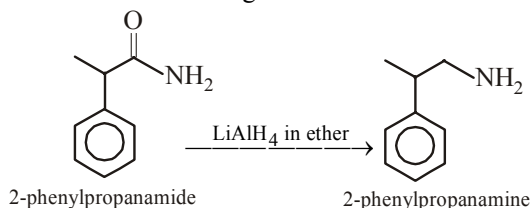
8. (d) Potassium phthalimide is the source of nitrogen in Gabriel phthalimide synthesis.



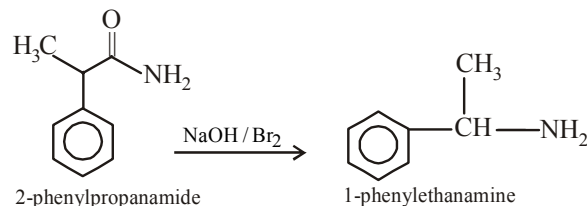
9. (c) Reaction can be represented as



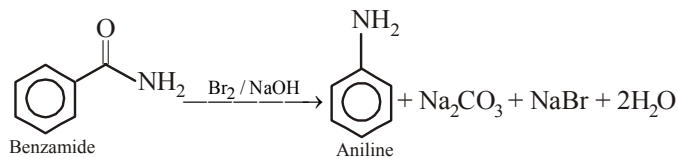
10. (d) $LiAlH_4$ in ether is the best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine because $LiAlH_4$ will reduce carbonyl group but does not reduce benzene ring.



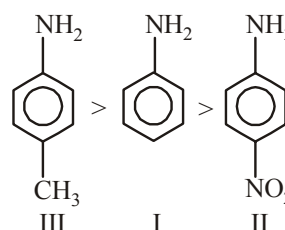
11. (b) Hoffmann bromamide reaction.



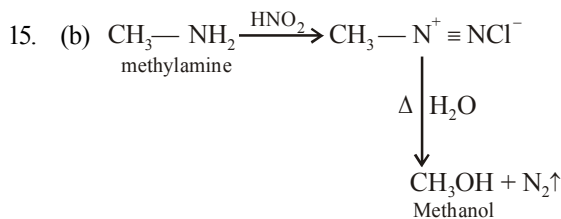
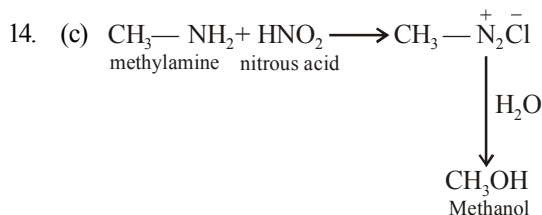
12. (b) Hoffmann bromamide degradation reaction:



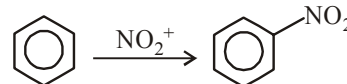
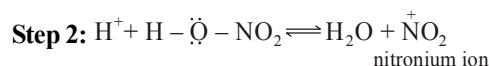
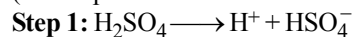
13. (d)



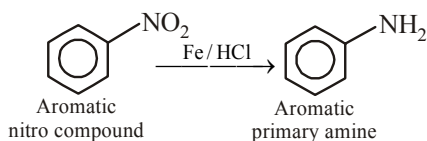
Higher the electron density towards ring, higher will be its basic strength. Electron donating group increases the basic strength while electron withdrawing group decreases the basic strength.



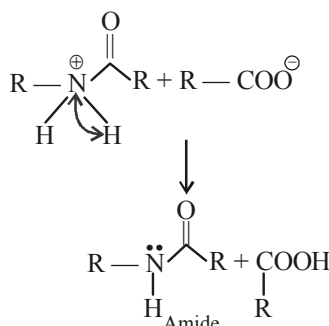
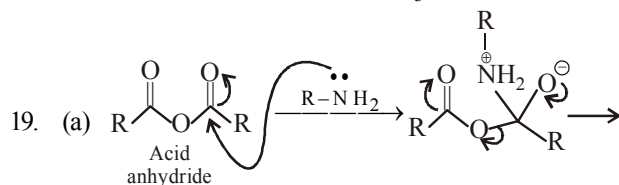
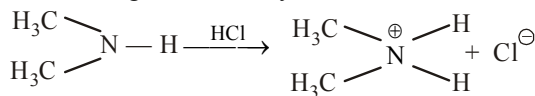
16. (c) For the nitration of benzene, NO_2^+ acts as an electrophile (electrophilic substitution reaction).



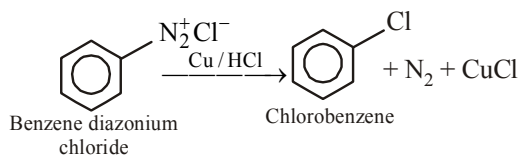
17. (c) Reduction of aromatic nitro compounds gives aromatic 1° amine.



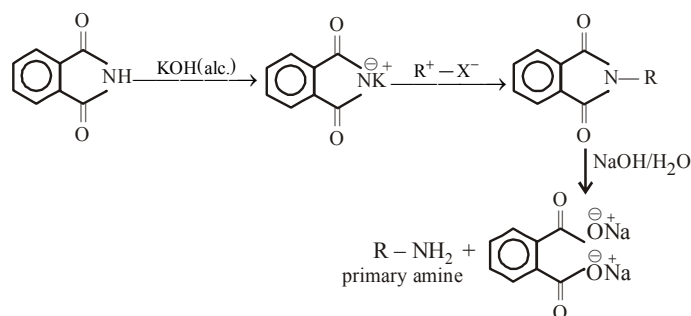
18. (b) Reactivity of a base towards dilute HCl is directly proportional to the strength of the base. Thus, as $(\text{CH}_3)_2\text{NH}$ has the highest basic strength, so it will have highest reactivity.



20. (b) Gattermann reaction:

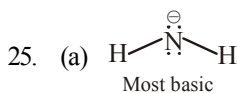


21. (b) Gabriel phthalimide synthesis is the best method of preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain.



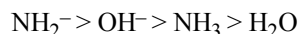
22. (d) Diazonium cation is a weak E^+ so it will not react with compound containing electron withdrawing group. Also, NO_2 group is an electron withdrawing group thus, nitrobenzene will not undergo azo coupling reaction with benzene diazonium chloride.
23. (c) Phenol has the least tendency to accept a proton and also exhibit acidic character due to polar O-H bond hence, it is a weak Bronsted base.

24. (d) Pyrrolidine will be the strongest base as the lone pair on nitrogen are not involved in resonance and are easily available for the donation. So, basic strength becomes high.



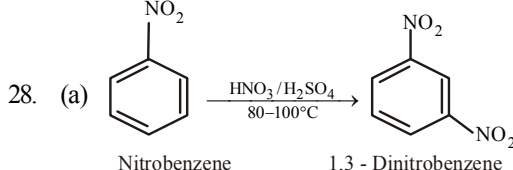
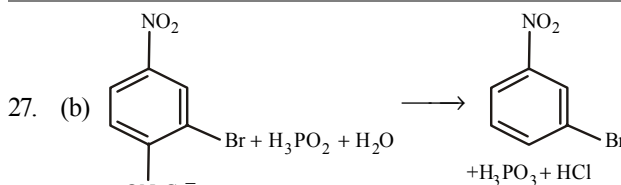
Amide ion is the most basic among the given species due to the presence of negative charge and two lone pairs of electron on nitrogen atom. The species which are having lone pair of electrons are more basic than neutral species. So, NH_3 and H_2O are less basic than NH_2^- and OH^- . Also, nitrogen is less electronegative than oxygen hence it can easily donate e^- s.

$\therefore$ The correct order of basic strength will be:



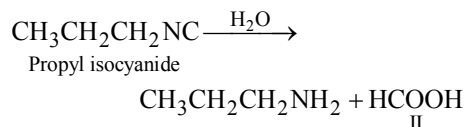
26. (b) On comparison to amines, hydrocarbons have lower boiling point, hence they are more volatile whereas amines are having higher boiling point due to H-bonding.

NEET/AIPMT (2013-2017) Questions

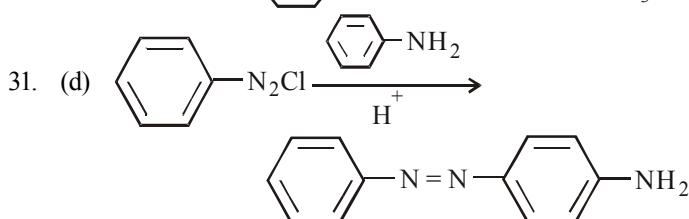
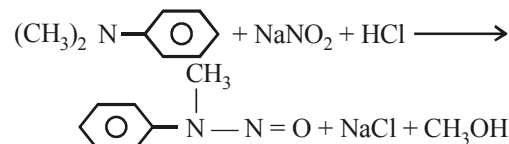


29. (b) Hydrolysis of propyl isocyanide ($\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$) gives $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HCOOH}$.

On treatment with NaNO_2 and HCl I gives $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ which does not give iodoform test. II (HCOOH) reduces Tollen's reagent and Fehling's solution.

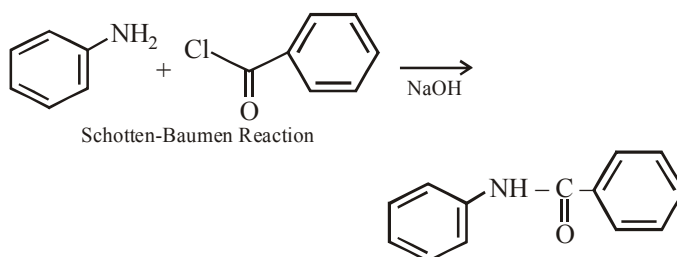
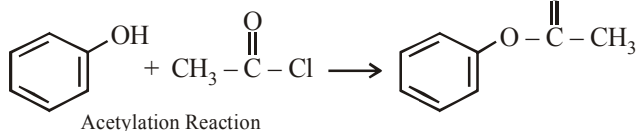
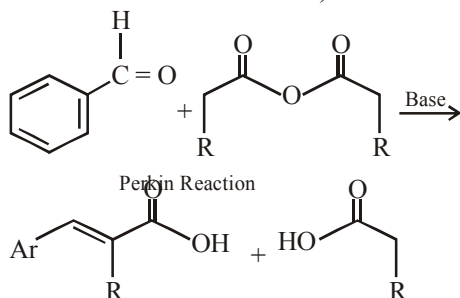
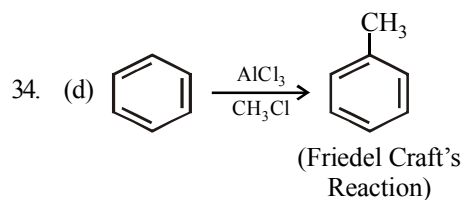
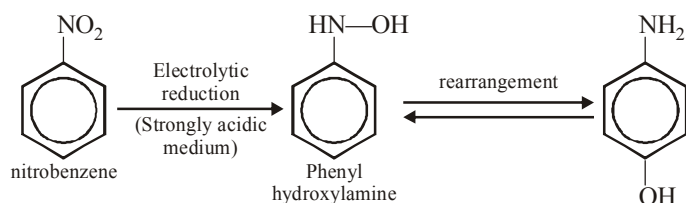


30. (b) Secondary amine react with nitrous acid to give N-Nitrosoamines.



32. (b) Arene diazonium salts are most stable among the given options because of the dispersal of +ve charge on the benzene ring due to resonance.

33. (d)



35. (a) $\text{C}_3\text{H}_9\text{N}$
 $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$
 $\text{CH}_3-\text{NH}-\text{CH}_2-\text{CH}_3$
 $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_3$, $\text{CH}_3-\underset{\text{CH}_3}{\text{N}}-\text{CH}_3$
36. (d) Because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide easily.
37. (a) Arylamines are generally less basic than alkylamines due to following factors
 (a) Due to resonance in aromatic amines.
 (b) Lower stability of anilinium ion
38. (c) $-\text{NO}_2$ group has strong $-R$ effect and $-\text{CH}_3$ shows $+R$ effect.
 $\therefore$ Order of basic strength is

 $\text{p-NO}_2\text{C}_6\text{H}_4\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{p-CH}_3\text{C}_6\text{H}_4\text{NH}_2$
39. (a) $\text{CH}_3-\overset{\text{O}}{\underset{\text{acetamide}}{\text{C}}}-\text{NH}_2 + \text{Br}_2 + 4\text{NaOH} \xrightarrow{\Delta}$
 $\text{CH}_3-\underset{\text{methanamine}}{\text{NH}_2} + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}$
 It is called Hoffmann Bromamide reaction.

Chapter 28

Biomolecules

Biomolecules may be defined as complex lifeless chemical substances which form the basis of life i.e. they not only build up living system but are also responsible for their growth, maintenance and their ability to reproduce.

CARBOHYDRATES

Carbohydrates are a major source of energy to our body. They are defined as optically active polyhydroxy aldehydes or polyhydroxy ketones or substances which give these on hydrolysis.

They are also called saccharides (meaning sugar)

Classification of Carbohydrates

They are classified in number of ways

(I) Based on molecular size :

- Monosaccharides:** It cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone. For ex: glucose, fructose, ribose, etc.
- Oligosaccharides:** They yield 2-10 monosaccharide units on hydrolysis. They are further classified as di-, tri, tetra-, saccharides etc. depending upon the number of monosaccharides formed by them on hydrolysis ex: sucrose on hydrolysis gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose only.
- Polysaccharides:** They yield a large number of monosaccharide units (more than ten) upon hydrolysis. For ex: starch, cellulose, glycogen, gums etc.

(II) Based on nature :

Carbohydrates are also classified as reducing and non-reducing sugars depending on whether they reduce Fehling's and Tollen's reagent or not.

- All monosaccharides whether aldose or ketose are reducing sugars.
- In disaccharides, if reducing groups of monosaccharides, i.e., aldehydic or ketone groups are bonded, these are non-reducing sugars, ex:- sucrose. If, however these groups are free in the sugar, then it is reducing sugar ex: maltose and lactose

(III) Based on taste :

Carbohydrates with sweet taste are called sugars while those without a sweet taste are called non-sugars. Mono and oligosaccharides are sugars while polysaccharides are non-sugars.

Monosaccharides

Monosaccharides are further classified as : aldose and ketose.

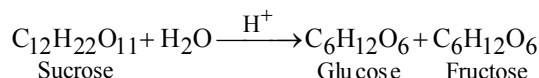
If a monosaccharide contains an aldehyde group, it is called an aldose and if it contains a keto group, it is called a ketose.

Glucose

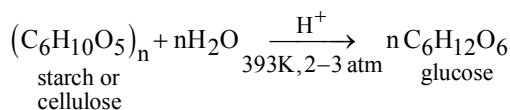
Glucose is an aldohexose. It is a monomer of many of the larger carbohydrates such as starch, cellulose.

Preparation

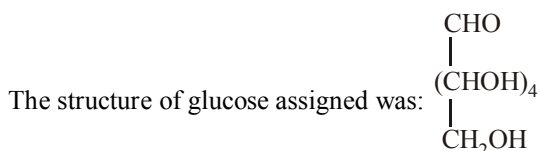
- By hydrolysis of sucrose:



- By hydrolysis of starch:

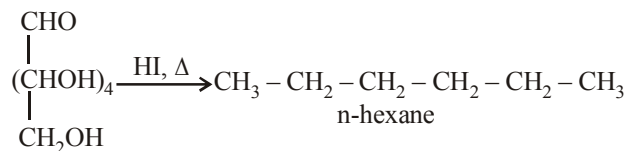


Structure of glucose:



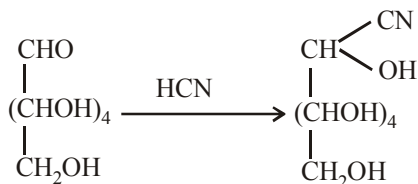
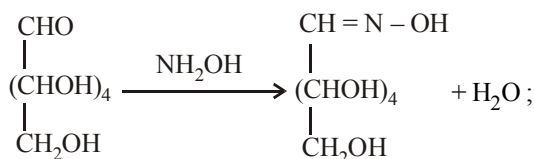
It was on the basis of following evidences :

- Its molecular formula was found to be $\text{C}_6\text{H}_{12}\text{O}_6$
- On prolonged heating with HI, it forms n-hexane, suggesting that all six C-atoms are linked in a straight chain.

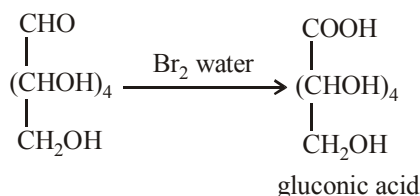


(iii) Relation due to -CHO group

- It reacts with hydroxylamine to form an oxime and adds a molecule of HCN to give cyanohydrin. These reactions confirm the presence of carbonyl group ($>\text{C}=\text{O}$) in glucose

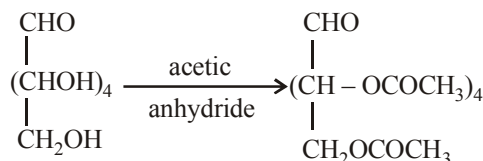


- (b) On reaction with bromine water, it gives gluconic acid. This shows that carbonyl group is present as aldehydic group.

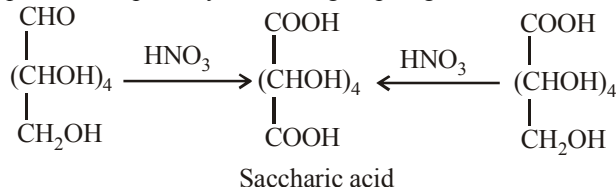


(iv) Reactions due to -OH group

- (a) Formation of glucose pentaacetate with acetic anhydride confirms the presence of five -OH groups.

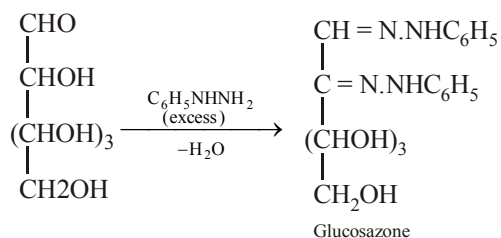


- (b) On oxidation with nitric acid, glucose and gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of primary alcoholic group in glucose.

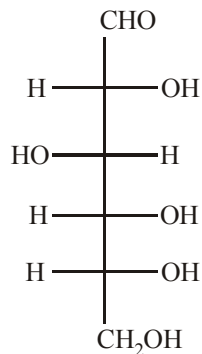


(v) Formation of osazone

Like the normal aldehydes, glucose reacts with phenylhydrazine in equimolecular proportion to form phenylhydrazone but unlike the normal aldehydes, glucose reacts with excess of phenylhydrazine (three molecular proportions) to form glucosazone.



Fischer projection for glucose is :



D-(+)-glucose

Here 'D' represents the configuration while (+) implies rotation of the plane polarised to the right.

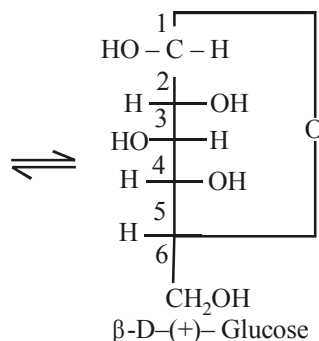
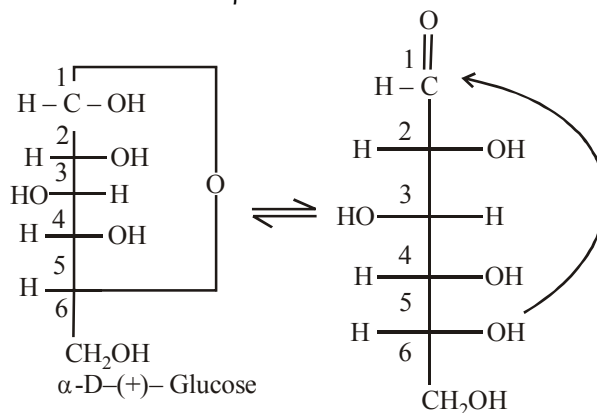
Limitation of open chain structure of D (+) glucose :

The following reactions of glucose could not be explained on the basis of its open chain structure.

- Glucose does not give, 2, 4-DNP test, Schiff's test and does not form addition product with NaHSO_3 .
- The penta acetate of glucose does not react with hydroxylamine indicating the absence of free -CHO group.
- It is found to exist in 2 forms: α and β .

Cyclic structure of D (+) glucose :

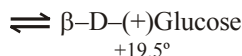
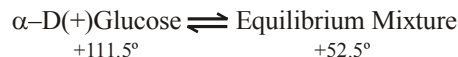
In this structure, the aldehyde (-CHO) group is involved in the form of a ring with the -OH group attached to C_5 carbon. It is a six membered ring, often called δ -oxide ring. The ring accounts for the two isomeric forms α and β as shown below :



The two cyclic hemi acetal forms of glucose differ only in configuration of -OH at C_1 . Such isomers (α and β) are called **anomers**.

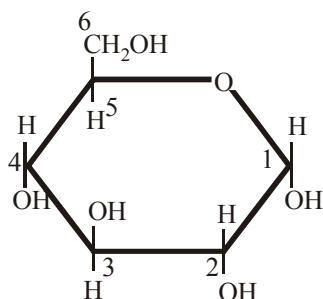
Note : Both the forms are optically active, α -D- glucose has specific rotation $+111.5^\circ$ and β -D-glucose has specific rotation $+19.5^\circ$.

Mutarotation - When either of the two forms of glucose is dissolved in water there is change in rotation till the equilibrium value of $+52.5^\circ$. This is known as mutarotation.

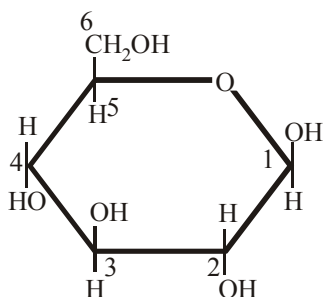


Haworth structure of glucose

The two cyclic structures for D (+) glucose shown in the pyranose form as :



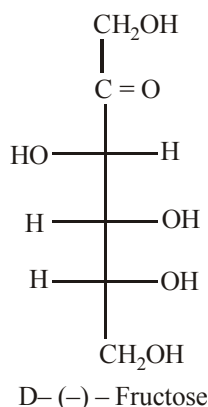
$\alpha\text{-D-(+)-Glucopyranose}$



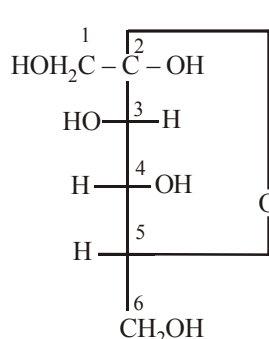
$\beta\text{-D-(+)-Glucopyranose}$

Fructose (Laevulose)

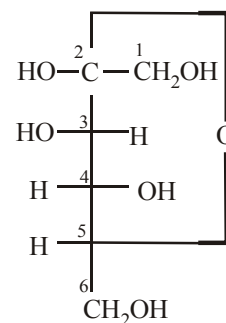
- (i) Its molecular formula is $\text{C}_6\text{H}_{12}\text{O}_6$.
- (ii) It is isomeric with glucose. However it is a ketohexose
- (iii) It consists of a keto group at C-2 and 6 C-atoms in a straight chain
- (iv) Its open chain structure is:



- (v) It exists in 2 cyclic forms obtained by addition of $-\text{OH}$ at C-5 to $\text{>C}=\text{O}$ group. The ring thus formed is a five membered ring and is named as furanose.

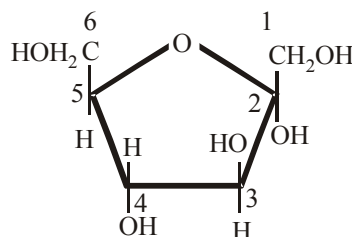


$\alpha\text{-D-(-)-Fructofuranose}$

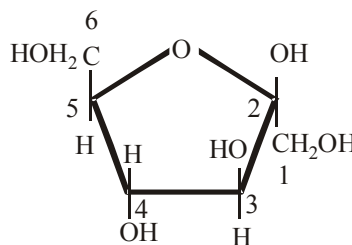


$\beta\text{-D-(-)-Fructofuranose}$

- (vi) The **Haworth structures** of the two anomers are :



$\alpha\text{-D-(-)-Fructofuranose}$



$\beta\text{-D-(-)-Fructofuranose}$

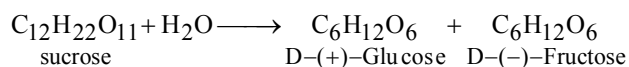
Epimer

Carbohydrates which differ in configuration at any carbon other than glycosidic carbon are called **epimers**. For example glucose and mannose are called epimers since they differ in configuration at C_2 (glycosidic carbon)

Disaccharides

Sucrose

- (i) On hydrolysis, it gives an equimolar mixture of D-(+)- glucose and D-(-) fructose, i.e.,



- (ii) The two monosaccharides are held together by glycosidic linkage between C_1 of α -glucose and C_2 of β -fructose.
- (iii) It is a non-reducing sugar.
- (iv) It is an invert sugar because on hydrolysis, it brings a change in the sign of rotation, from dextro (+) to laevo (-).

Maltose

- (i) It is composed of two α -D-glucose units in which C_1 of one glucose unit is linked to C_4 of another glucose unit.
- (ii) It is a reducing sugar.

Lactose

- (i) Also known as milk sugar as it is found in milk.
- (ii) It is composed of β -D-galactose and β -D-glucose with a linkage between C_1 of galactose and C_4 of glucose.
- (iii) It is a reducing sugar.

Polysaccharides

Starch

It is a polymer of α -glucose and consists of two components - **amylose** and **amylopectin**.

Amylose is water soluble component with 200-1000 α -D-(+) glucose units held by C_1 - C_4 glycosidic linkage.

Amylopectin is insoluble in water and is a branched chain polymer of α -D-glucose.

Cellulose

It is a straight chain polysaccharide composed only of β -D-glucose units joined by C_1 - C_4 glycosidic linkages.

Glycogen

It is also known as animal starch because its structure is similar to amylopectin. It is present in liver, muscles and brain.

Importance of Carbohydrates

- (i) Used as storage molecules as starch in plants and glycogen in animals.
- (ii) Cell wall of bacteria and plants is made up of cellulose.
- (iii) Provide raw materials for many important industries like textiles, paper, lacquers and breweries.

LIPIDS

Lipids are organic compounds soluble in non-polar fat solvents such as acetone, ether, chloroform, benzene, etc. and insoluble in water. The most important role of lipids is that of biological fuel. Lipids supply more energy than carbohydrates, excess of lipids is stored in the body and used at the time of starvation. Lipids are of three types.

- (i) **Simple lipids:** They yield fatty acids and an alcohol on hydrolysis. Fats, oils and waxes are examples of this type.
- (ii) **Compound lipids:** These yield fatty acids, alcohol and other compound like phosphoric acid, sugar, etc. on hydrolysis. Phospholipids are the most common examples.
- (iii) **Derived lipids:** These lipids do not contain any ester linkage. These are those hydrolysis products of simple or compound lipids which still retain the properties of lipids. Fatty acids, alcohols (e.g., sterols), vitamins D, E and K are examples of this type.

PROTEINS

All proteins are polymers of α -amino acids.

Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat etc. They are required for growth and maintenance of body.

Amino acids

- (i) They contain amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) functional groups.

- (ii) Depending upon the relative position of $-\text{NH}_2$ group with respect to the carboxyl group, amino acids are classified as α , β , γ , δ and so on.
- (iii) Only α -amino acids are obtained on hydrolysis of proteins.



Classification of Amino Acids

Acidic, basic and neutral amino acid

They are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in the molecule.

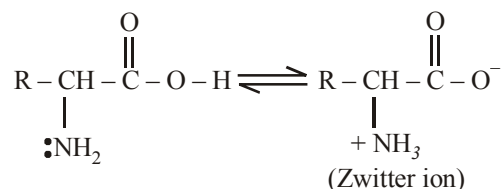
Equal number of amino and carboxyl groups make it neutral; more amino than carboxyl make it basic while more carboxyl groups than amino make it acidic.

Essential and non essential amino acids - Human body can synthesise ten amino acids called non essential amino acids. The remaining ten amino acids required for protein synthesis are called essential amino acids. They are

(i) Phenylalanine	(ii) Histidine
(iii) Tryptophane	(iv) Valine
(i) Methionine	(vi) Theonine
(vii) Arginine	(viii) Leucine
(ix) Isoleucine	(x) Lysine

Properties of Amino Acids

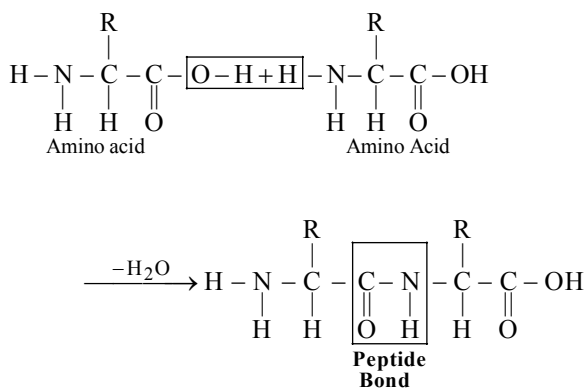
- (i) They are usually colourless, crystalline solids.
- (ii) They are water-soluble, high melting solids and behave like solids rather than simple amines or carboxylic acids.
- (iii) This behaviour is due to the presence of both acidic ($-\text{COOH}$) and basic ($-\text{NH}_2$) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as **zwitter ion**.
- (iv) The zwitter ion is neutral but contains both positive and negative charges. In zwitter ionic form, amino acids show amphoteric behaviour.



- (v) Except glycine, all naturally occurring α -amino acids are optically active.
- (vi) Amino acids have been assigned notations D or L depending upon the configuration about the chiral carbon atom most of the naturally occurring amino acids have L configuration.

Peptide Bond

- (i) Two or more than two amino acids link to form a peptide.
- (ii) The bond present between peptides is called peptide bond.
- (iii) Peptide linkage ($-\text{CO}-\text{NH}-$) is formed by combination of $-\text{NH}_2$ of one group and $-\text{COOH}$ of the other with the elimination of H_2O .



- (iv) When a large number of amino acid (>10) combine, polypeptide is formed. A polypeptide with more than 100 amino acid residues, having molecular mass higher than $10,000 \mu$ is called a protein.

Types of Proteins

Classification of proteins is based upon three general properties: shape, solubility and chemical composition.

Classification on the basis of hydrolysis products

- Simple proteins:** The simple proteins are those which yield only amino acids on hydrolysis.
- Conjugated proteins:** Conjugated proteins on hydrolysis yield α -amino acids and other non-proteinous substances in addition to α -amino acids. The non-proteinous moiety is usually referred to prosthetic group.
- Derived proteins:** Derived proteins are the products formed by the action of physical (such as heat), chemical or enzymatic agents on natural proteins. The derived proteins are thus intermediate hydrolysis products of proteins.

On the basis of their composition, proteins are classified as :

- Fibrous proteins:** These have thread like molecules which lie side by side to form fibres. The various molecules are held together by hydrogen bonds. These are insoluble in water but soluble in concentrated acids and alkalis. Examples are keratin of hair, nails, wood, feathers and horn, myosin of muscles, and fibroin of silk.
- Globular proteins:** This type of protein has molecule folded into compact units which often acquire spheroidal shape. Such proteins are soluble in water, dilute acids and alkalis. Examples are insulin, haemoglobin, albumin, etc.

Structure and shape of proteins are studied at four different levels:

- Primary structure:** Each polypeptide chain in a protein has amino acids linked to each other in a specific sequence and this sequence is called primary structure of protein. Any change in primary structure results in a different protein. In primary structure all amino acids are attached in a straight chain by peptide bond. It is important as the replacement of just one amino acid in the sequence of a protein destroys its biological activity.
- Secondary structure:** It refers to the shape in which a long polypeptide chain can exist. The regular folding of the

backbone of the polypeptide chain (due to H-bonding

between $\text{C}=\text{O}$ and $-\text{NH}-$ groups of peptide bond) gives rise to two structures : α helix and β -pleated sheet.

(a) α -helix

Polypeptide chains twist into a right handed screw (helix) with $-\text{NH}$ of each amino acid residue H-bonded to $\text{C}=\text{O}$ of an adjacent turn of the helix.

Example : Myosin, Keratin, etc.

(b) β -pleated

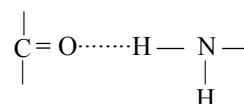
All peptide chains stretch out to the maximum extension and then lay side by side and are held together by intermolecular H-bonds.

Example : Silk fibres.

- (iii) **Tertiary Structure:** It represents the overall folding of the polypeptide chains. It gives rise to two major molecular shapes: fibrous and globular.

The main forces which stabilise 3° structure of protein are H-bonds, disulphide linkages, ionic bond and hydrophobic interactions. Which can be explained as :

(a) Hydrogen bond :



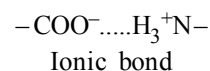
Hydrogen bond

They are formed between oxygen of acidic amino acid and $-\text{H}$ of basic amino acid.

(b) Hydrophobic bond -

- Non - polar side chains of neutral amino acid tends to be closely associated with one another in proteins.
- Present in between the amino acids.
- These are not true bonds.

(c) Ionic bond :

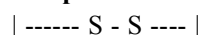


These are salt bonds formed between oppositely charged groups in side chains of Amino acids

Eg. Aspartic acid

Glutamic acid

(d) Disulphide bonds :



- Relatively stable bond and thus is not broken readily under usual conditions of denaturation.
 - Formed between the $-\text{SH}$ group of Amino acid Ex. Cystine and Methionine .
- (iv) **Quaternary Structure:** Some proteins are composed of 2 or more polypeptide chains referred to as sub-units. The spatial arrangement of these sub-units wrt each other is known as quaternary structure.

Denaturation of Proteins

When a protein in its native form is subjected to a change in temperature or pH, H-bonds are disturbed. Due to this, globules unfold, helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact.
ex: coagulation of egg white on boiling; curdling of milk

Tests for Proteins

- (i) **Biuret** - Protein solution + NaOH + dil. $\text{CuSO}_4 \rightarrow$ Pink or violet colour
- (ii) **Ninhydrin** - Protein solution + Ninhydrin $\rightarrow$ blue colour
- (iii) **Hopkin's cole** - Protein solution + glyoxalic acid + conc. $\text{H}_2\text{SO}_4 \rightarrow$ Blue - violet
- (iv) **Millon's** - Protein solution + Millon's reagent $\rightarrow$ Pink colour.
Millon's reagent - Solution of mercuric nitrate and nitrite in nitric acid containing traces of nitrous acid.
- (v) **Iodine reaction** - Protein solution + iodine in potassium iodide solution $\rightarrow$ yellow colour
- (vi) **Xanthoproteic test** - Protein solution + conc $\text{HNO}_3 \rightarrow$ yellow colour $\xrightarrow{\text{NaOH}}$ orange colour

ENZYMES

Enzymes are biological catalysts which catalyse biological reactions by providing alternate lower activation energy pathways thereby increasing rate of reaction.

Chemically, all enzymes are globular proteins. Some enzymes are associated with some non-protein component called cofactor for their activity. These cofactors can be inorganic ions or organic molecules.

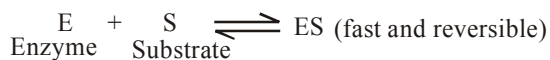
Characteristics of Enzymes

- (i) **Specificity**, i.e., each enzyme catalysis only one chemical reaction.
- (ii) **Efficiency**, i.e., they can speed up the rate of a reaction by a factor of 10^{20} .
- (iii) **Small quantity** i.e., only small quantity of enzymes can be highly efficient.
- (iv) Enzymes function best at an optimum temperature ($25^\circ\text{C} - 40^\circ\text{C}$) and show maximum efficiency at an optimum pH (6 – 7.7)

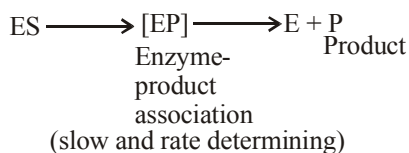
Mechanism of Enzyme Catalysis

It is known as 'lock and key' Mechanism

Step 1: Formation of enzyme-substrate complex



Step 2: Dissociation of the complex to form products



VITAMINS

They are regarded as organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) Fat soluble vitamins:

Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) Water soluble vitamins:

B-complex and Vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and can not be stored (except vitamin B_{12}) in our body.

Some Important Vitamins

	Name of Vitamin	Sources	Deficiency Diseases
1.	vit. A (Retinal)	fish, liver oil, carrots, butter, milk	Xerophthalmia, night blindness
2.	vit B ₁ (Thiamine)	yeast, milk, green vegetables, cereals	Beri beri
3.	vit B ₂ (Riboflavin)	milk, eggwhite, liver, kidney	chielosis, digestive disorders, burning sensation of skin
4.	vit B ₆ (pyridoxine)	yeast, milk, egg yolk, cereals, grams	convulsions
5.	vit B ₁₂ (Cyanocobalamine)	meat, fish, egg, curd	pernicious anaemia
6.	vit. C (Ascorbic acid)	citrus fruits, amla, green leafy vegetables.	scurvy
7.	vit. D (Calciferol)	sunlight, fish, egg yolk	Rickets, osteomalacia
8.	vit. E (Tocopherol)	vegetable oils	increased fragility of RBC's and muscular weakness.
9.	vit. K (Phylloquinone)	green leafy vegetables	increased blood clotting time

NUCLEIC ACIDS

Nucleic acids are long chain polymers of nucleotides and are hence also called polynucleotides.

Nucleic acids are made up of three units : bases, sugar and phosphoric acid. They are required for the storage and expression of genetic information.

Nucleic acids are of two types:

- (i) **Deoxyribonucleic acid (DNA)**
- (ii) **Ribonucleic acid (RNA)**

Chemical Composition of Nucleic Acids

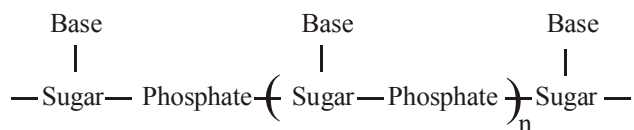
Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases).

Sugars: Two sugars are found to be present in nucleic acids, namely D-ribose in R.N.A. and 2-deoxyribose in D.N.A.

Bases: Two types of bases have been isolated from the

hydrolysis products of nucleosides; viz. purines and pyrimidines. Important purine bases are adenine and guanine; while pyrimidine bases are uracil, thymine and cytosine. Adenine, guanine and cytosine are present in RNA as well as in DNA, while thymine is present only in DNA and uracil only in RNA.

A simplified version of nucleic acid chain is



Nucleosides and Nucleotides

Nucleosides: These are condensation products of a base with sugar. The five important nucleosides are named as adenosine, guanosine, cytidine, uridine and thymidine.

Nucleotides: These are condensation products of nucleosides with phosphoric acid. The five important nucleotides are named as adenylic acid, guanylic acid, cytidylic acid, uridylic acid and thymidylic acid.

Structure of DNA

Primary structure tells about the sequence of nucleotides in DNA. The two polynucleotide chains of DNA molecule are twisted around a common axis but run in opposite directions to form a right bonded helix.

In secondary structure of DNA, the nucleic acid chains wound about each other and are held by H-bonds between specific pairs of bases. The two strands are complementary to each other. 'A'

forms two H-bonds with 'T' while 'C' form three H-bonds with 'G'.

Structure of RNA

In RNA, only single stranded helices are present. RNA molecules are of 3 types and perform different functions. They are m-RNA, r-RNA and t-RNA.

Biological Functions of Nucleic Acids

- (i) DNA is responsible for maintaining identity of different species of organisms. A DNA molecule is capable of self duplication during cell division and identical DNA strands are transferred to daughter cells.
- (ii) They help in protein synthesis in the cell.

Gene

The portion of DNA carrying information about a specific protein is called gene.

Genetic Code

The relation between the amino acid and the nucleotide triplet is called genetic code.

Codons

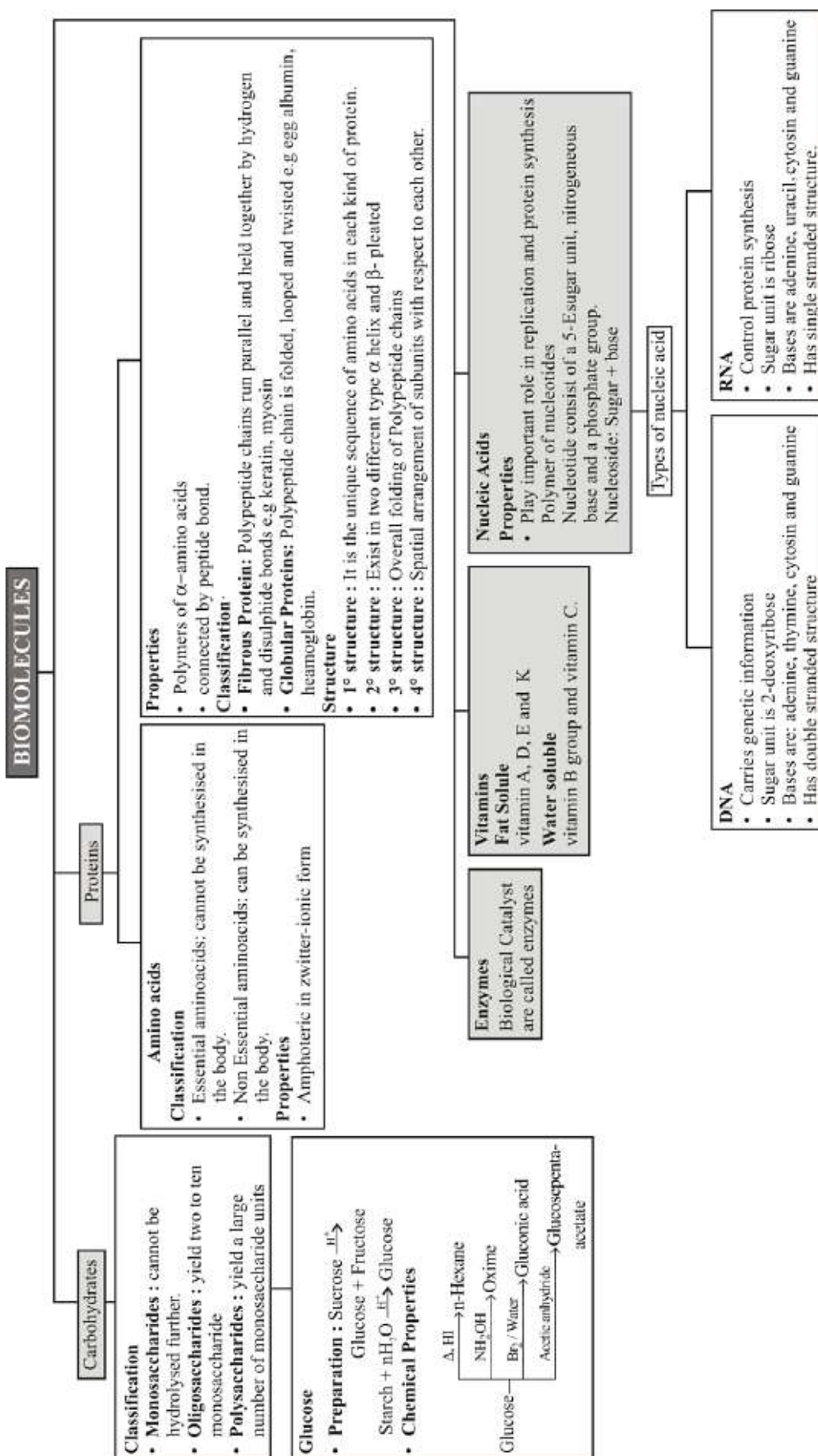
The nucleotide bases in RNA function in groups of three (triplet) in coding amino acids. These base triplets are called codons.

Mutation

A chemical change in DNA molecule that could lead to the synthesis of proteins with an altered sequence of amino acids.

Mutation leads to the formation of defective genes which causes abnormalities or disease.

CONCEPT MAP

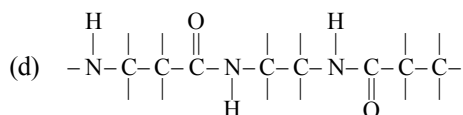
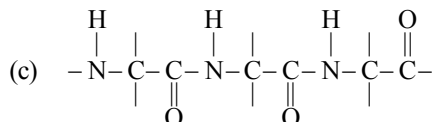
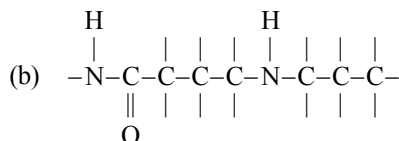
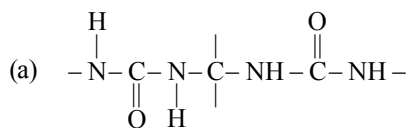


EXERCISE - 1

Conceptual Questions

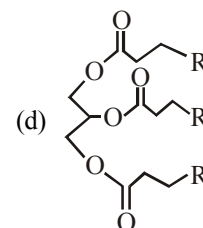
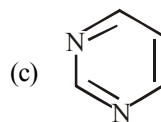
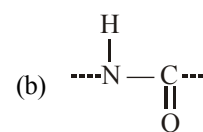
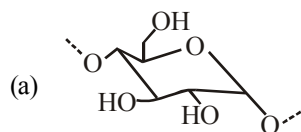
- Which one of the following metals is required as co-factor by all enzymes utilizing ATP in phosphate transfer?
(a) K (b) Ca (c) Na (d) Mg
- Which of the following is the sweetest sugar?
(a) Sucrose (b) Glucose (c) Fructose (d) Maltose
- In cells the net production of ATP molecules generated from one glucose molecule is
(a) 46 (b) 32 (c) 36 (d) 40
- In aqueous solution, an amino acid exists as
(a) cation (b) anion (c) dianion (d) zwitter ion
- Which is correct statement?
(a) Starch is a polymer of α -glucose
(b) In cyclic structure of fructose, there are four carbons and one oxygen atom
(c) Amylose is a component of cellulose
(d) Proteins are composed of only one type of amino acids
- Glycolysis is
(a) conversion of glucose to haem
(b) oxidation of glucose to glutamate
(c) conversion of pyruvate to citrate
(d) oxidation of glucose to pyruvate
- Phospholipids are esters of glycerol with
(a) three phosphate groups
(b) three carboxylic acid residues
(c) two carboxylic acid residues and one phosphate group
(d) one carboxylic acid residue and two phosphate groups
- Glucose does not react with
(a) $\text{Br}_2/\text{H}_2\text{O}$ (b) H_2NOH (c) HI (d) NaHSO_3
- α -D- Glucose and β - D-glucose differ from each other due to difference in one carbon with respect to its
(a) size of hemiacetal ring (b) number of OH groups
(c) configuration (d) conformation
- The glycosidic linkage involved in linking the glucose units in amylose part of starch is
(a) $\text{C}_1 - \text{C}_4$ β linkage (b) $\text{C}_1 - \text{C}_6$ α linkage
(c) $\text{C}_1 - \text{C}_5$ α linkage (d) $\text{C}_1 - \text{C}_4$ α linkage
- In fructose, the possible optical isomers are
(a) 12 (b) 8 (c) 16 (d) 4
- Which of the following does not reduce Benedict's solution?
(a) Glucose (b) Fructose
(c) Sucrose (d) Aldehyde
- Sucrose on hydrolysis gives
(a) fructose+ribose (b) glucose + fructose
(c) glucose+glucose (d) fructose + fructose
- Pick out the one which does not belong to the same family:
(a) pepsin (b) cellulose
(c) ptyalin (d) lipase
- The change in optical rotation, with time, of freshly prepared solution of sugar is known as
(a) rotatory motion (b) inversion
(c) specific rotation (d) mutarotation
- Anaemia is caused by the deficiency of vitamin
(a) B_6 (b) B_1 (c) B_2 (d) B_{12}
- Which of the following monosaccharide is a pentose ?
(a) Galactose (b) Glucose
(c) Fructose (d) Arabinose
- Glucose gives silver mirror with Tollen's reagent. It shows the presence of
(a) an acidic group (b) an alcoholic group
(c) a ketonic group (d) an aldehydic group
- Hydrolysis of sucrose is called
(a) esterification (b) saponification
(c) inversion (d) hydration
- Glucose on oxidation with bromine water gives
(a) gluconic acid (b) tartaric acid
(c) saccharic acid (d) mesoxalic acid
- The highest calorific value is found in
(a) proteins (b) fats
(c) vitamins (d) carbohydrates
- The number of essential amino acids in man is
(a) 8 (b) 10 (c) 18 (d) 20
- Number of chiral carbon atoms in glucose and fructose are
(a) 4 in each
(b) 3 in each
(c) 4 in glucose and 3 in fructose
(d) 3 in glucose and 4 in fructose
- For $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\ddot{\text{N}}\text{H}- \end{array}$ (peptide bond)
(a) C — N bond length in proteins is longer than usual bond length of the C — N bond
(b) Spectroscopic analysis shows planar structure of the $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{NH}- \end{array}$ group
(c) C — N bond length in proteins is smaller than usual bond length of the C—N bond
(d) None of the above
- Which is not a true statement?
(a) α -Carbon of α -amino acid is asymmetric
(b) All proteins are found in L-form
(c) Human body can synthesize all proteins they need
(d) At pH = 7 both amino and carboxylic groups exist in ionised form
- The metal present in vitamin B_{12} is :
(a) cobalt (b) iron
(c) manganese (d) magnesium

27. Which one of the following structures represents the peptide chain?



28. A sequence of how many nucleotides in messenger RNA makes a codon for an amino acid?
 (a) Three (b) Four (c) One (d) Two
29. Glucose molecule reacts with X number of molecules of phenylhydrazine to yield osazone. The value of X is
 (a) three (b) two (c) one (d) four
30. The helical structure of protein is stabilized by
 (a) dipeptide bonds (b) hydrogen bonds
 (c) ether bonds (d) peptide bonds
31. A triglyceride can have how many different acyl groups?
 (a) 3 (b) 2 (c) 1 (d) 4
32. Which functional group participates in disulphide bond formation in proteins?
 (a) Thioester (b) Thioether
 (c) Thiol (d) Thiolactone
33. Which of the following is not an amino acid?
 (a) Glycine (b) Adenine
 (c) Histidine (d) Benzidine
34. Which of the following is not a function of proteins?
 (a) Nail formation
 (b) Skin formation
 (c) Muscle formation
 (d) Providing energy for metabolism
35. The structural feature which distinguishes proline from natural α -amino acids?
 (a) Proline is optically inactive
 (b) Proline contains aromatic group
 (c) Proline is a dicarboxylic acid
 (d) Proline is a secondary amine
36. Pepsin enzyme hydrolyses
 (a) proteins to amino acids
 (b) fats to fatty acids
 (c) glucose to ethyl alcohol
 (d) polysaccharides to monosaccharides
37. Which of the following tests is not used for testing proteins?
 (a) Millon's test (b) Molisch's test
 (c) Biuret test (d) Ninhydrin test

38. The process by which synthesis of protein takes place based on the genetic information present in m-RNA is called
 (a) Translation (b) Transcription
 (c) Replication (d) Messenger hypothesis
39. The bond that determines the secondary structure of proteins is
 (a) coordinate bond (b) covalent bond
 (c) hydrogen bond (d) peptide bond
40. DNA has deoxyribose, a base and the third component which is
 (a) phosphoric acid (b) ribose
 (c) adenine (d) thymine
41. Enzymes take part in a reaction and
 (a) decrease the rate of a chemical reaction
 (b) increase the rate of a chemical reaction
 (c) Both (a) and (b)
 (d) None of these
42. Lysine is least soluble in water in the pH range:
 (a) 3 to 4 (b) 5 to 6 (c) 6 to 7 (d) 8 to 9
43. Which one of the following chemical units is certainly to be found in an enzyme?



44. When adenine is attached to ribose sugar, it is called adenosine. To make a nucleotide from it, it would require
 (a) oxygenation (b) addition of a base
 (c) addition of phosphate (d) hydrogenation
45. Fructose on reduction gives a mixture of two alcohols which are related as
 (a) diastereomers (b) epimers
 (c) both (a) and (b) (d) anomers.
46. Which of the following is correct about H-bonding in nucleotide?
 (a) A --- A and T --- T (b) G --- T and A --- C
 (c) A --- G and T --- C (d) A --- T and G --- C
47. Chargaff's rule states that in an organism
 (a) Amounts of all bases are equal
 (b) Amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C)
 (c) Amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C)
 (d) Amount of adenine (A) is equal to that of cytosine (C) and the amount of thymine (T) is equal to that of guanine (G)
48. The enzyme which hydrolyses triglycerides to fatty acids and glycerol is called
 (a) maltase (b) lipase (c) zymase (d) pepsin

49. Of the following statements about enzymes which ones are true?
 (i) Enzymes lack in nucleophilic groups
 (ii) Enzymes are highly specific both in binding chiral substrates and in catalysing their reactions
 (iii) Enzymes catalyse chemical reactions by lowering the energy of activation
 (iv) Pepsin is a proteolytic enzyme
 (a) (i) and (iv) (b) (i) and (iii)
 (c) (ii), (iii) and (iv) (d) (i)
50. Which of the following is not present in a nucleotide?
 (a) Guanine (b) Cytosine
 (c) Adenine (d) Tyrosine
51. If one strand of DNA has the sequence ATGCTTGA, the sequence in the complimentary strand would be
 (a) TCCGAAC (b) TACGTAGT
 (c) TACGAAC (d) TAGCTAGT
52. Vitamin K is associated with the disease:
 (a) Scurvy (b) Beri-beri
 (c) Blood coagulation (d) Sore throat
53. Which of the following is a steroid hormone?
 (a) Cholesterol (b) Adrenaline
 (c) Thyroxine (d) Progesterone
54. Which one is a female sex hormone?
 (a) Estrogen (b) Estradiol
 (c) Progesterone (d) All of these
55. For osazone formation, the effective structural unit necessary is
 (a) $\begin{array}{c} \text{CH}_2\text{OCH}_3 \\ | \\ \text{CO} \\ | \end{array}$ (b) $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CO} \\ | \end{array}$
 (c) $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHOCH}_3 \\ | \end{array}$ (d) $\begin{array}{c} \text{CHO} \\ | \\ \text{CHOCH}_3 \\ | \end{array}$
56. Vitamin B₁₂ contains
 (a) Ca(II) (b) Fe(II) (c) Co(III) (d) Zn(II)
57. The human body does not produce
 (a) vitamins (b) hormones (c) enzymes (d) DNA
58. Biotin is an organic compound present in yeast. Its deficiency in diet causes dermatitis and paralysis. It is also known as
 (a) Vitamin H (b) Vitamin B₃
 (c) Vitamin B₁₂ (d) Vitamin D
59. The chemical change in DNA molecule that could lead to synthesis of protein with an altered amino acid sequence is called
 (a) replication (b) lipid formation
 (c) cellular membrane (d) mutation
60. Which one of the following is a non-steroidal hormone?
 (a) Estradiol (b) Prostaglandin
 (c) Progesterone (d) Estrone
61. Vitamin B₆ is known as
 (a) pyridoxine (b) thiamine
 (c) tocopherol (d) riboflavin
62. Which one of the following is a peptide hormone?
 (a) Testosterone (b) Thyroxin
 (c) Adrenaline (d) Glucagon
63. Secondary structure of protein refers to
 (a) mainly denatured proteins and structure of prosthetic groups
 (b) three -dimensional structure, especially the bond between amino acid residues that are distinct from each other in the polypeptide chain
 (c) linear sequence of amino acid residues in the polypeptide chain
 (d) regular folding patterns of continuous portions of the polypeptide chain
64. RNA and DNA are chiral molecules, their chirality is due to
 (a) chiral bases
 (b) chiral phosphate ester units
 (c) D-sugar component
 (d) L-sugar component
65. Which one of the following is an amine hormone?
 (a) Thyroxine (b) Oxypurin
 (c) Insulin (d) Progesterone
66. In DNA, the complimentary bases are:
 (a) adenine and thymine; guanine and cytosine
 (b) adenine and thymine; guanine and uracil
 (c) adenine and guanine; thymine and cytosine
 (d) uracil and adenine; cytosine and guanine
67. The segment of DNA which acts as the instrumental manual for the synthesis of the protein is:
 (a) ribose (b) gene
 (c) nucleoside (d) nucleotide
68. Fructose reduces Tollen's reagent due to:
 (a) enolisation of fructose followed by conversion to glucose (having aldehydic group) by the base present in Tollen's reagent
 (b) asymmetric carbons
 (c) primary alcoholic group
 (d) secondary alcoholic group
69. Which one of the following statements is incorrect about enzyme catalysis?
 (a) Enzymes are mostly proteinous in nature.
 (b) Enzyme action is specific.
 (c) Enzymes are denatured by ultraviolet rays and at high temperature.
 (d) Enzymes are least reactive at optimum temperature.
70. Deficiency of vitamin B₁ causes the disease
 (a) Convulsions (b) Beri-Beri
 (c) Cheilosis (d) Sterility
71. Which of the following acids does not exhibit optical isomerism?
 (a) Maleic acid (b) α -amino acids
 (c) Lactic acid (d) Tartaric acid
72. α -D-(+)-glucose and β -D-(+)-glucose are
 (a) conformers (b) epimers
 (c) anomers (d) enantiomers
73. The two functional groups present in a typical carbohydrate are:
 (a) $-\text{CHO}$ and $-\text{COOH}$ (b) $>\text{C}=\text{O}$ and $-\text{OH}$
 (c) $-\text{OH}$ and $-\text{CHO}$ (d) $-\text{OH}$ and $-\text{COOH}$
74. Biuret test is **not** given by
 (a) carbohydrates (b) polypeptides
 (c) urea (d) proteins
75. The presence or absence of hydroxyl group on which carbon atom of sugar differentiates RNA and DNA?
 (a) 1st (b) 2nd
 (c) 3rd (d) 4th

EXERCISE - 2

Applied Questions

- Match the vitamin of column I with deficiency disease given in column II

Column I	Column II
1. Vitamin A	a. Scurvy
2. Vitamin B ₁₂	b. Hemorrhagic condition
3. Vitamin C	c. Sterility
4. Vitamin E	d. Xerophthalmia
5. Vitamin K	e. Pernicious anaemia
(a) 1-e, 2-d, 3-a, 4-b, 5-c	(b) 1-d, 2-e, 3-a, 4-b, 5-c
(c) 1-d, 2-e, 3-a, 4-c, 5-b	(d) 1-e, 2-d, 3-a, 4-c, 5-b
- The base adenine occurs in
 - DNA only
 - RNA only
 - DNA and RNA both
 - Protein
- Glucose is converted into alcohol by the action of the enzyme
 - invertase
 - maltase
 - zymase
 - diastase
- Which one of the following forms the constituent of cell wall of plant cells?
 - Starch
 - Glycogen
 - Cellulose
 - Amylose
- Starch is converted into maltose by the
 - maltase
 - invertase
 - zymase
 - diastase
- The disaccharide present in milk is
 - maltose
 - lactose
 - sucrose
 - cellobiose
- How many amino acids are present in insulin?
 - 25
 - 51
 - 20
 - 22
- On heating glucose with Fehling's solution we get a precipitate whose colour is
 - yellow
 - red
 - black
 - white
- Which of the following gives maximum energy in metabolic processes?
 - Proteins
 - Carbohydrates
 - Lipids
 - Vitamins
- A distinctive and characteristic functional group of fats is
 - an ester group
 - a peptide group
 - a ketonic group
 - an alcoholic group
- Which one of the following is NOT correct?
 - D(-) Fructose exists in furanose structure
 - D(+) Glucose exists in pyranose structure
 - In sucrose the two monosaccharides are held together by peptide linkage
 - Maltose is a reducing sugar
- Hydrolytic reaction of fats, with caustic soda, is known as
 - acetylation
 - carboxylation
 - saponification
 - esterification
- Vitamin A is present in
 - cod liver oil
 - carrot
 - milk
 - in all of these
- The base present in DNA, but not in RNA is
 - guanine
 - adenine
 - uracil
 - thymine
- Energy is stored in our body in the form of
 - ATP
 - ADP
 - Fats
 - carbohydrates
- Which of the following is a non-reducing sugar?
 - Sucrose
 - Maltose
 - Lactose
 - Fructose
- Glycosidic linkage is actually an :
 - Carbonyl bond
 - Ether bond
 - Ester bond
 - Amide bond
- When α -D-glucose and β -D-glucose are dissolved in water in two separate beakers I and II respectively and allowed to stand, then –
 - specific rotation in beaker I will decrease while in II will increase upto a constant value
 - the specific rotation of equilibrium mixture in two beakers will be different
 - the equilibrium mixture in both beakers will be laevorotatory
 - the equilibrium mixture in both beakers will contain only cyclic form of glucose
- Nucleotide in DNA are linked by –
 - hydrogen bond
 - 3'-5' phosphodiester bond
 - glycosidic bond
 - peptide bond
- Natural glucose is termed D-glucose because :
 - OH on the second carbon is on the right side in Fischer projection
 - OH on the sixth carbon is on the right side in Fischer projection.
 - OH on the fifth carbon is on the right side in Fischer projection.
 - It is dextrorotatory.
- The dipeptide, Gly. Ala has structure –

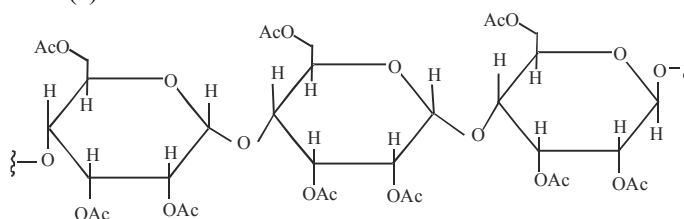
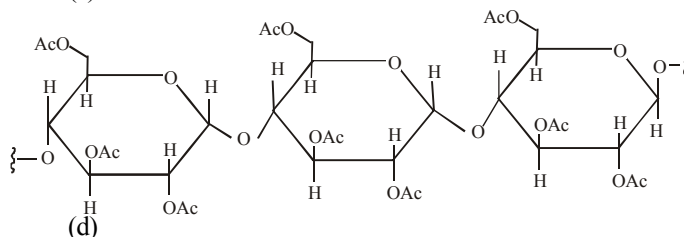
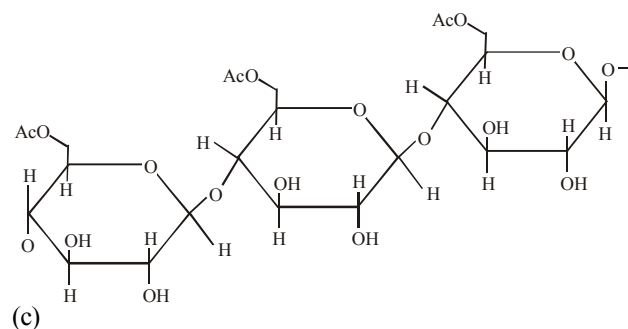
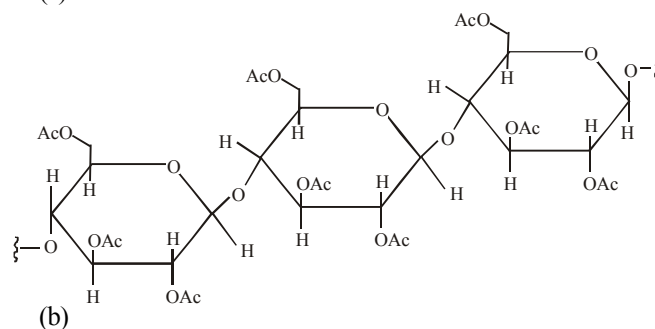
$$\text{(a) } \text{H}_3\text{N}^+\text{CH}_2\text{C}(=\text{O})\text{NHCH}(\text{CH}_3)\text{CO}_2^-$$

$$\text{(b) } \text{H}_3\text{N}^+\text{CH}_2\text{C}(=\text{O})\text{NHCH}(\text{CH}_3)\text{CO}_2^-$$

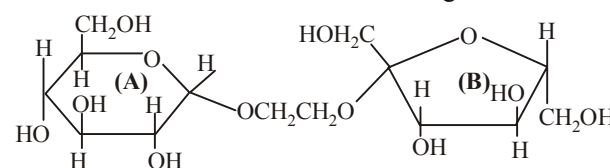
$$\text{(c) } \text{O}_2\text{CCH}(\text{CH}_3)\text{NH}^+ - \text{CH}_2\text{NH}_3^+$$

$$\text{(d) } \text{O}_2\text{CCH}_2\text{NH}^+ - \text{C}(\text{CH}_3)(\text{NH}_3^+)\text{CO}_2^-$$

22. The pair of compounds in which both the compounds give positive test with Tollen's reagent is
 (a) glucose and sucrose
 (b) fructose and sucrose
 (c) acetophenone and hexanal
 (d) glucose and fructose
23. The two forms of D-glucopyranose obtained from the solution of D-glucose are called
 (a) isomers (b) anomers
 (c) epimers (d) enantiomers
24. Double stranded DNA virus with 20,000 base pairs has nucleotides
 (a) 20,000 (b) 10,000
 (c) 666 (d) 40,000
25. Which of the following statement is not correct ?
 (a) Amylopectin is a branched polymer of α -glucose.
 (b) Cellulose is a linear polymer of β -glucose
 (c) Glycogen is the food reserve of plants
 (d) All proteins are polymers of α -amino acids.
26. Which of the following hormones contains iodine?
 (a) Testosterone (b) Adrenaline
 (c) Thyroxine (d) Insulin
27. Which one of the following does not exhibit the phenomenon of mutarotation ?
 (a) (+) – Sucrose (b) (+) – Lactose
 (c) (+) – Maltose (d) (–) – Fructose
28. Which one of the following statements is not true regarding (+) Lactose ?
 (a) On hydrolysis (+) Lactose gives equal amount of D(+) glucose and D(+) galactose.
 (b) (+) Lactose is a β -glycoside formed by the union of a molecule of D(+) glucose and a molecule of D(+) galactose.
 (c) (+) Lactose is a reducing sugar and does not exhibit mutarotation.
 (d) (+) Lactose, $C_{12}H_{22}O_{11}$ contains 8-OH groups.
29. Which of the statements about "Denaturation" given below are correct ?
 (A) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
 (B) Denaturation leads to the conversion of double strand of DNA into single strand
 (C) Denaturation affects primary structure which gets distorted
 Options :
 (a) (B) and (C) (b) (A) and (C)
 (c) (A) and (B) (d) (A), (B) and (C)
30. The secondary structure of a protein refers to
 (a) fixed configuration of the polypeptide backbone
 (b) α -helical backbone
 (c) hydrophobic interactions
 (d) sequence of α -amino acids.
31. Which one of the following statements is correct?
 (a) All amino acids except lysine are optically active
 (b) All amino acids are optically active
 (c) All amino acids except glycine are optically active
 (d) All amino acids except glutamic acids are optically active
32. Cellulose upon acetylation with excess acetic anhydride/ H_2SO_4 (catalytic) gives cellulose triacetate whose structure is
 (a)

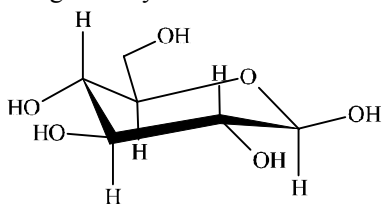


33. The correct statement about the following disaccharide is



- (a) Ring (A) is pyranose with α -glycosidic link
 (b) Ring (A) is furanose with α -glycosidic link
 (c) Ring (B) is furanose with α -glycosidic link
 (d) Ring (B) is pyranose with β -glycosidic link

34. The following carbohydrate is



- (a) a ketohexose (b) an aldohexose
(c) an α -furanose (d) an α -pyranose
35. Synthesis of each molecule of glucose in photosynthesis involves :
(a) 18 molecules of ATP (b) 10 molecules of ATP
(c) 8 molecules of ATP (d) 6 molecules of ATP
36. Which of the following compounds can be detected by Molisch's Test ?
(a) Nitro compounds (b) Sugars
(c) Amines (d) Primary alcohols
37. The glycosidic linkage involved in linking the glucose units in amylose part of starch is
(a) $C_1 - C_4$ β linkage (b) $C_1 - C_6$ α linkage
(c) $C_1 - C_5$ α linkage (d) $C_1 - C_4$ α linkage
38. Which of the following are neutral amino acids?
(a) Glycine (b) Valine
(c) Proline (d) All of these
39. Glucose on oxidation with bromine water gives
(a) gluconic acid (b) tartaric acid
(c) saccharic acid (d) mesoxalic acid
40. Number of chiral carbon atoms in glucose and fructose are
(a) 4 in each
(b) 3 in each
(c) 4 in glucose and 3 in fructose
(d) 3 in glucose and 4 in fructose
41. Glucose does not react with
(a) Br_2/H_2O (b) H_2NOH
(c) HI (d) $NaHSO_3$
42. The vitamin that is not soluble in water is
(a) Vitamin B_1 (b) Vitamin B_2
(c) Vitamin B_6 (d) Vitamin D

43. Which one of the following metals is required as co-factor by all enzymes utilizing ATP in phosphate transfer?
(a) K (b) Ca
(c) Na (d) Mg
44. Secondary structure of protein is mainly governed by
(a) hydrogen bonds (b) covalent bonds
(c) ionic bonds (d) disulphide bonds
45. The linkage between the two monosaccharide units in lactose is
(a) C_1 of β -D-glucose and C_4 of β -D-galactose
(b) C_1 of β -D-galactose and C_4 of β -D-glucose
(c) C_1 of α -D-galactose and C_4 of β -D-glucose
(d) C_1 of β -D-galactose and C_4 of α -D-glucose

DIRECTIONS for Qs. 46 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True
46. **Statement-1** : Glycine is amphoteric in nature.
Statement-2 : Glycine contains both acid and basic groups.
47. **Statement-1** : Hydrolysis of sucrose is known as inversion of cane sugar.
Statement-2 : Sucrose is a disaccharide.
48. **Statement-1** : Proteins on hydrolysis produce amino acids.
Statement-2 : Amino acids contain $-NH_2$ and $-COOH$ groups.
49. **Statement-1** : Sequence of bases in DNA is TGAACCTT and sequence of bases in m-RNA is CATTAAACC.
Statement-2 : In DNA, nitrogenous bases have hydrogen bonds.
50. **Statement-1** : Vitamin B_5 is also called as pyridoxin.
Statement-2 : Deficiency of vitamin B_5 causes dermatitis and dementia.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

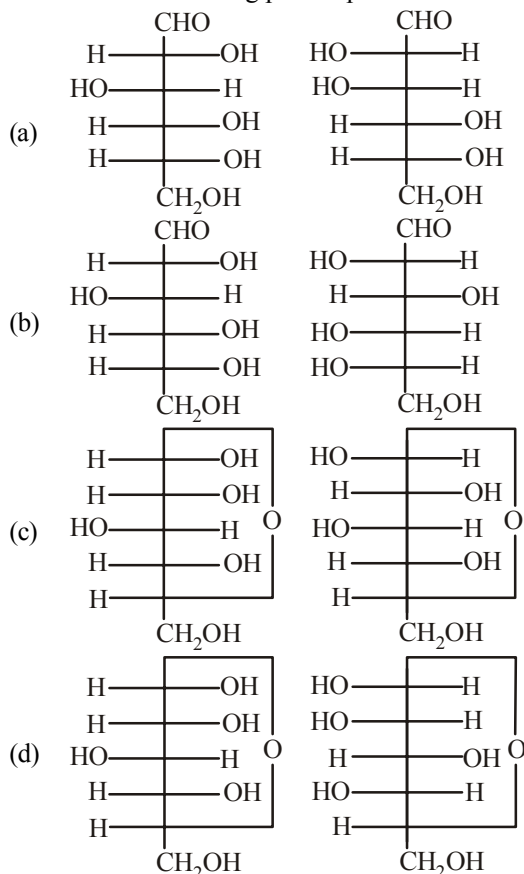
Exemplar Questions

1. Glycogen is a branched chain polymer of α -D glucose units in which chain is formed by $C_1 - C_4$ glycosidic linkage where as branching occurs by the formation of $C_1 - C_6$ glycosidic linkage. Structure of glycogen is similar to
(a) amylose (b) amylopectin
(c) cellulose (d) glucose
2. Which of the following polymer is stored in the liver of animals?
(a) Amylose (b) Cellulose
(c) Amylopectin (d) Glycogen

3. Sucrose (Cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives

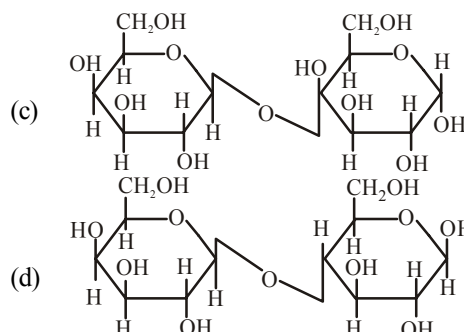
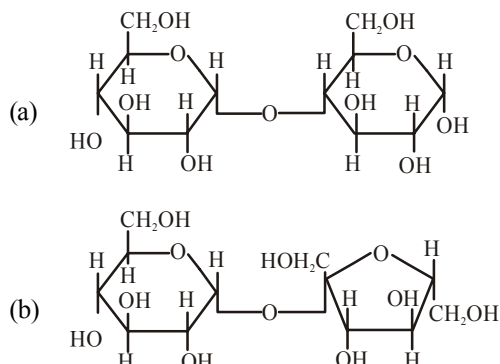
- 2 molecules of glucose
- 2 molecules of glucose + 1 molecule of fructose
- 1 molecule of glucose + 1 molecule of fructose
- 2 molecules of fructose

4. Which of the following pairs represents anomers?

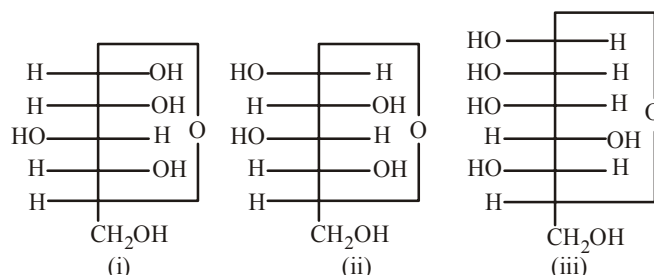


5. Proteins are found to have two different types of secondary structures viz. α -helix and β -pleated sheet structure. α -helix structure of protein is stabilised by:

- peptide bonds
 - van der Waal's forces
 - hydrogen bonds
 - dipole-dipole interactions
6. In disaccharides, if the reducing groups of monosaccharides, i.e., aldehydic or ketonic groups are bonded, these are non-reducing sugars. Which of the following disaccharide is a non-reducing sugar?

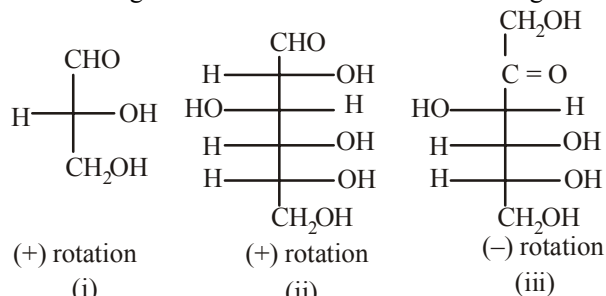


7. Which of the following acids is a vitamin?
- Aspartic acid
 - Ascorbic acid
 - Adipic acid
 - Saccharic acid
8. Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present?
- 5' and 3'
 - 1' and 5'
 - 5' and 5'
 - 3' and 3'
9. Nucleic acids are the polymers of.....
- nucleosides
 - nucleotides
 - bases
 - sugars
10. Which of the following statements is not true about glucose?
- It is an aldohexose
 - On heating with HI it forms n-hexane
 - It is present in furanose form
 - It does not give 2, 4-DNP test
11. Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be
- primary structure of proteins
 - secondary structure of proteins
 - tertiary structure of proteins
 - quaternary structure of proteins
12. DNA and RNA contain four bases each. Which of the following bases is not present in RNA?
- Adenine
 - Uracil
 - Thymine
 - Cytosine
13. Which of the following B group vitamins can be stored in our body?
- Vitamin B₁
 - Vitamin B₂
 - Vitamin B₆
 - Vitamin B₁₂
14. Which of the following bases is not present in DNA?
- Adenine
 - Thymine
 - Cytosine
 - Uracil
15. Three cyclic structures of monosaccharides are given below which of these are anomers.

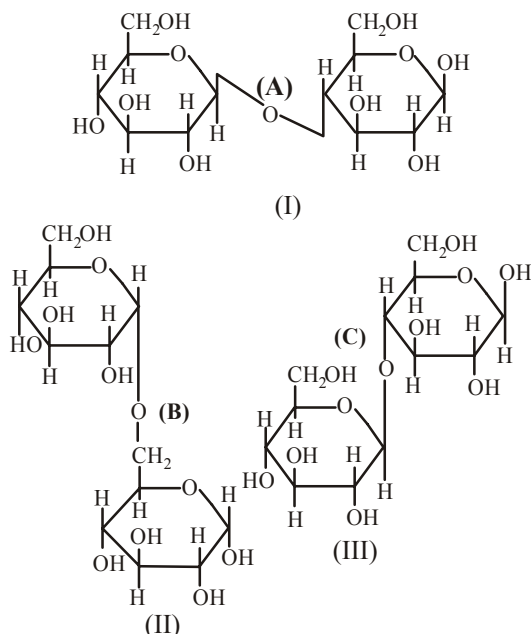


- I and II
- II and III
- I and III
- III is anomer of I and II

16. Which of the following reactions of glucose can be explained only by its cyclic structure?
- Glucose forms pentaacetate
 - Glucose reacts with hydroxylamine to form an oxime
 - Pentaacetate of glucose does not react with hydroxylamine
 - Glucose is oxidised by nitric acid to gluconic acid
17. Optical rotations of some compounds along with their structures are given below which of them have D configuration.



- I, II, III
 - II, III
 - I, II
 - III
18. Structure of disaccharide formed by glucose and fructose is given below. Identify anomeric carbon atoms in monosaccharide units.
-
- 'a' carbon of glucose and 'a' carbon of fructose
 - 'a' carbon of glucose and 'e' carbon of fructose
 - 'a' carbon of glucose and 'b' carbon of fructose
 - 'f' carbon of glucose and 'f' carbon of fructose
19. Three structures are given below in which two glucose units are linked. Which of these linkages between glucose units are between C1 and C4 and which linkages are between C1 and C6?



- (A) is between C1 and C4, (B) and (C) are between C1 and C6

- (A) and (B) are between C1 and C4, (C) is between C1 and C6
- (A) and (C) are between C1 and C4, (B) is between C1 and C6
- (A) and (C) are between C1 and C6, (B) is between C1 and C4

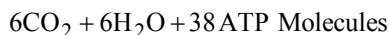
NEET/AIPMT (2013-2017) Questions

20. In DNA the linkages between different nitrogenous bases are: [NEET Kar. 2013]
- peptide linkage
 - phosphate linkage
 - H-bonding
 - glycosidic linkage
21. D (+) glucose reacts with hydroxylamine and yields an oxime. The structure of the oxime would be : [2014]
- | | |
|--|--|
| $\begin{array}{c} \text{CH} = \text{NOH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ | $\begin{array}{c} \text{CH} = \text{NOH} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{HO} - \text{C} - \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ |
| (c) | (d) |
22. Which of the following hormones is produced under the condition of stress which stimulates glycogenolysis in the liver of human beings?
- Thyroxine
 - Insulin
 - Adrenaline
 - Estradiol
23. In a protein molecule various amino acids are linked together by [2016]
- α -glycosidic bond
 - β -glycosidic bond
 - peptide bond
 - dative bond
24. The correct statement regarding RNA and DNA, respectively is [2016]
- The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose.
 - The sugar component in RNA is ribose and the sugar component in DNA is 2'-deoxyribose.
 - The sugar component in RNA is arabinose
 - The sugar component in RNA is 2'-deoxyribose and the sugar component in DNA is arabinose
25. Which one given below is a non-reducing sugar? [2016]
- Maltose
 - Lactose
 - Glucose
 - Sucrose
26. Which of the following statements is not correct : [2017]
- Ovalbumin is a simple food reserve in egg-white
 - Blood proteins thrombin and fibrinogen are involved in blood clotting
 - Denaturation makes the proteins more active
 - Insulin maintains sugar level in the blood of a human body

Hints & Solutions

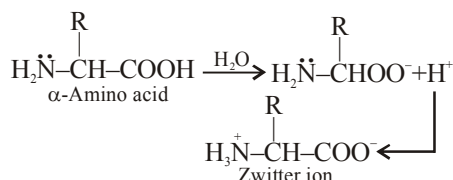
EXERCISE - 1

- (d) Mg acts as a cofactor to the enzyme as it forms complex with phosphate group of ATP that is utilized in the transfer of ATP phosphate.
- (c) Fructose is the sweetest sugar.
- (c) $C_6H_{12}O_6 + 6O_2 + 2ATP \longrightarrow$

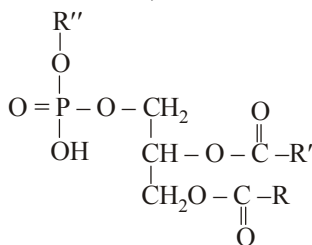


Net total number of ATP molecules evolved = 36 molecules.

- (d) In neutral solution, amino acids exist as dipolar ion (also known as zwitter ions or inner salts) where the proton of $-COOH$ group is transferred to the $-NH_2$ group to form inner salt, known as dipolar ion.

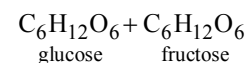
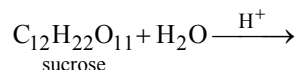


- (a) Starch is also known as amyllum which occurs in all green plants. A molecule of starch $(C_6H_{10}O_5)_n$ is built of a large number of α -glucose ring joined through oxygen-atom.
- (d) It is a common pathway for both the aerobic & anaerobic respiration in which 1 glucose molecule is converted to 2 molecules of pyruvate.
- (c) Phospholipids are derivatives of glycerol in which two of the hydroxyl groups are esterified with fatty acids while the third is esterified with some derivative of phosphoric acid with some alcohol such as choline, ethanolamine, serine or inositol.



- (d) Weak reagent like $NaHSO_3$ is unable to open the chain and can't react with glucose. This explains the inability of glucose to form aldehyde bisulphite compound.
- (c) α and β -D-glucoses differ in the arrangement of groups around one carbon atom (C_1) i.e., they differ in configuration at C_1 , hence these are also known as anomers.
- (d)
- (b) Fructose has 3 chiral centres and hence number of optical isomers are $2^3 = 8$

- (c) Sucrose, being a non-reducing sugar, does not reduce Benedict's solution. Remember that fructose has an α -hydroxy ketonic group, which is also reducing group (difference from ordinary ketonic group)
- (b) Sucrose is a disaccharide which on hydrolysis gives one molecule of glucose (monosaccharide) and fructose (monosaccharide).



- (b) Cellulose is a type of carbohydrate while pepsin, ptyalin and lipase are the enzymes which help in digestion.
- (d) $\alpha\text{-D-Glucose} \rightleftharpoons \text{Equilibrium mixture} \rightleftharpoons \beta\text{-D-Glucose}$

$$\begin{array}{ccc}
 [\alpha]_D^{+112^\circ} & & [\alpha]_D^{+52^\circ} \\
 (36\%) & & (0.02\%)
 \end{array}$$

$$\begin{array}{c}
 \beta\text{-D-Glucose} \\
 [\alpha]_D^{+19^\circ} \\
 (64\%)
 \end{array}$$

Glucose has two forms α and β . When either of these two is dissolved in water and allowed to stand, it gets converted to an equilibrium mixture of α and β forms.

- (d)

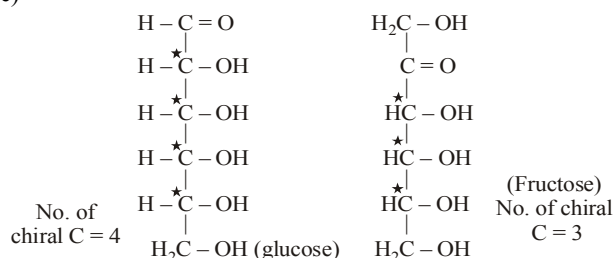
Vitamin	Disease caused by deficiency
B_6	Dermatitis
B_1	Beri-beri
B_2	Photophobia, glossitis
B_{12}	Pernicious anaemia
C	Scurvy
- (d) Arabinose is an aldopentose $HOCH_2-(CHOH)_3-CHO$
- (d) Glucose + Tollen's reagent $\rightarrow$ Gluconic acid + Ag-mirror
- (c)
- (a) $CH_2OH(CHOH)_4CHO + [O] \xrightarrow{Br_2/H_2O}$

Glucose

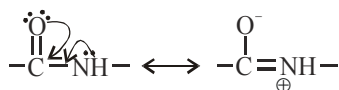
$$CH_2OH(CHOH)_4COOH$$

Gluconic acid
- (b) 1 g fat provides 37 kJ of energy on oxidation while 1 g carbohydrate on oxidation gives 17 kJ of energy. Hence, fat has highest calorific value.
- (b) There are 20 amino acids in man out of which 10 amino acids are essential amino acids. These essential amino acids are supplied to our bodies by food which we take because they cannot be synthesised in the body. These are (1) Valine (2) Leucine (3) Isoleucine (4) Phenylalanine (5) Threonine (6) Methionine (7) Lysine (8) Tryptophan (9) Arginine (10) Histidine.

23. (c)



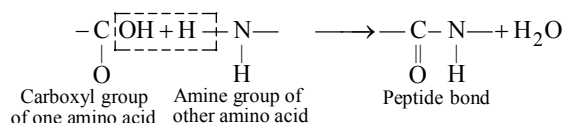
24. (c) Due to resonance C—N bond in protein acquires double bond character and is smaller than usual double bond.



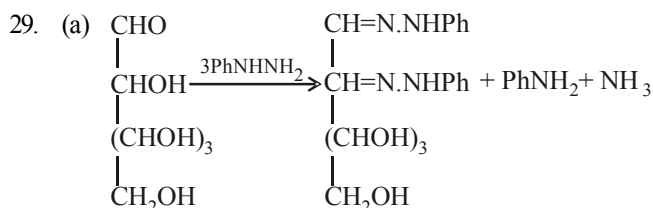
25. (b) All proteins are not found in L-form but they may be present in form of D or L

26. (a) Metal present in vitamin B₁₂ is Co (cobalt).

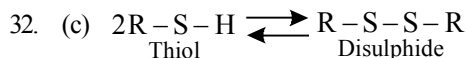
27. (c) The bond formed between two amino acids by the elimination of a water molecule is called a peptide linkage or bond. The peptide bond is simply another name for amide bond.



The product formed by linking amino acid molecules through peptide linkages. —CO—NH—, is called a peptide.

28. (a) The sequence of bases in mRNA are read in a serial order in groups of three at a time. Each triplet of nucleotides (having a specific sequence of bases) is known as codon. Each codon specifies one amino acid. Further since, there are four bases. therefore, $4^3 = 64$ triplets or codons are possible.30. (b) The α -helix structure is formed when the chain of α -amino acids coils as a right handed screw (called α -helix) because of the formation of hydrogen bonds between amide groups of the same peptide chain, i.e., NH group in one unit is linked to carbonyl oxygen of the third unit by hydrogen bonding. This hydrogen bonding between different units is responsible for holding helix in a position.

31. (a) Since glycerol has three —OH groups, it can have three acyl (similar or different) groups



33. (d) Benzidine is 4,4'-diaminodiphenyl

34. (d) Proteins do not provide energy for metabolism.

35. (d) 36. (a) 37. (b)

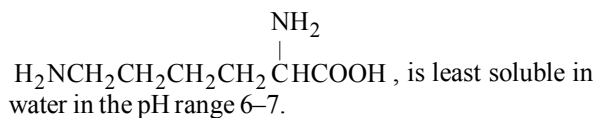
38. (a) Synthesis of polypeptide is known as translation. For this process three type of RNA are essential.

39. (c)

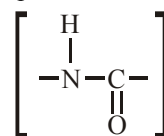
40. (a)

41. (b) Enzymes can increase the rate of a reaction upto 10 million times. Even very small amount can accelerate a reaction.

42. (c) Lysine

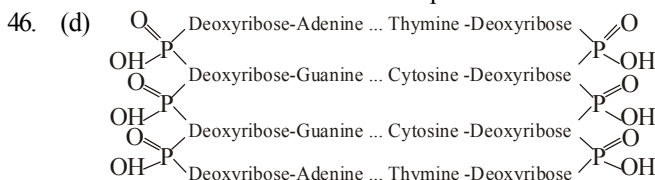


43. (b) Peptide bonds are present in enzyme.



44. (c)

45. (c) Ketoses on reduction produce a new chiral carbon leading to the formation of two isomeric alcohols which are diastereomeric as well as C–2 epimers.



The hydrogen bonds are formed between the base (shown by dotted lines). Because of size and geometries of the bases, the only possible pairing in DNA is between G(Guanine) and C(Cytosine) through three H-bonds and between A (Adenosine) and T (Thymine) through two H-bonds.

$$\frac{A}{T} = \frac{G}{C} = 1$$

Amount of A = T and that of G = C.

48. (b) Triglycerides are lipids, hence these are hydrolysed by *lipases* to glycerol and fatty acids.

49. (c)

50. (d) Tyrosine is an α -amino acid, and not a purine

51. (c) In a DNA molecule, A = T (Two H-bond)

C $\equiv$ G (Three H-bond)

Purine $\rightarrow$ Adenine (A), Guanine (G)

Pyrimidine $\rightarrow$ Cytosine (C), Thymine (T)

So the complimentary sequence of ATGCTTGA is TACGAAC.

52. (c)

53. (d) Progesterone (Gestogens) is a steroid hormone, which controls the development and maintenance of pregnancy. Thyroxine and Adrenaline are Amine hormones.

54. (d)

55. (b)

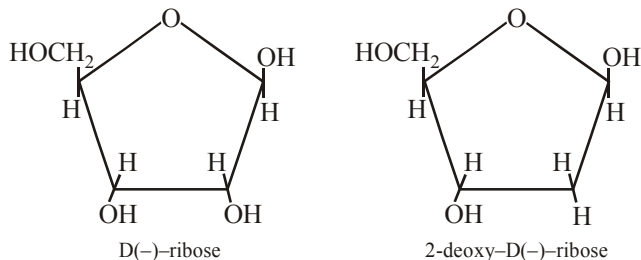
56. (c) Vitamin B₁₂ also called cyanocobaltamine, is anti-pernicious anaemia vitamin. It is C₆₃H₈₄O₁₄N₁₄PCo.

57. (a) The human body does not produce vitamins.

58. (a)

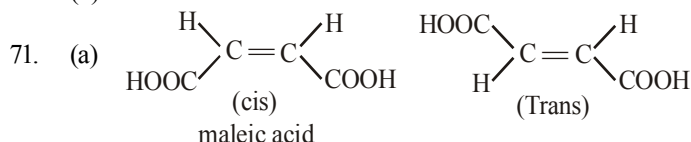
59. (d)

60. (b) Prostaglandin is a non-steroidal hormone.
 61. (a) Vitamin B₆ is called pyridoxine. It is found in fruits, green-vegetables, milk, etc.
 62. (d) Testosterone and Adrenaline are steroid hormone, Thyroxine is non-steroidal hormone glucagon is peptide hormone.
 63. (d)
 64. (c) Each nucleic acid consists of a pentose sugar a heterocyclic base, and phosphoric acid. The sugar present in DNA is 2-deoxy-D (-) ribose and the sugar present in RNA is D (-)- ribose. The chirality of DNA and RNA molecules are due to the presence of sugar components.



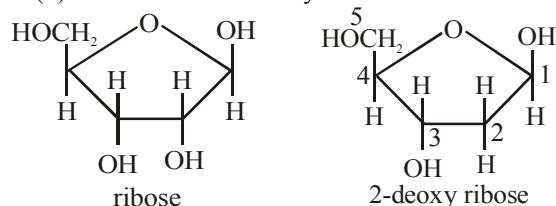
65. (a) Thyroxine is an amine hormone.
 66. (a) In DNA the complementary base are Adenine and thymine.
 Guanine and cytosine
 The genetic information for cell is contained in the sequence of bases A, T, G and C in DNA molecule.
 67. (b) The DNA sequence that codes for a specific protein is called a Gene and thus every protein in a cell has a corresponding gene.
 68. (a)
 69. (d) Enzymes are most reactive at optimum temperature. The optimum temperature for enzyme activity lies between 40°C to 60°C.

70. (b) Beri-Beri.



It shows geometrical isomerism but does not show optical isomerism.

72. (c) Since α -D-(+)-glucose and β -D-(+)-glucose differ in configuration at C-1 atom so they are anomers. Anomers are those diastereomers that differ in configuration at C-1 atom.
 73. (c) Glucose is considered as a typical carbohydrate which contains -CHO and -OH group.
 74. (a) Biuret test produces violet colour on addition of dilute CaSO₄ to alkaline solution of a compound containing peptide linkage.
 75. (b) RNA has D (-) - Ribose and the DNA has 2-Deoxy D (-) - ribose as the carbohydrate unit.

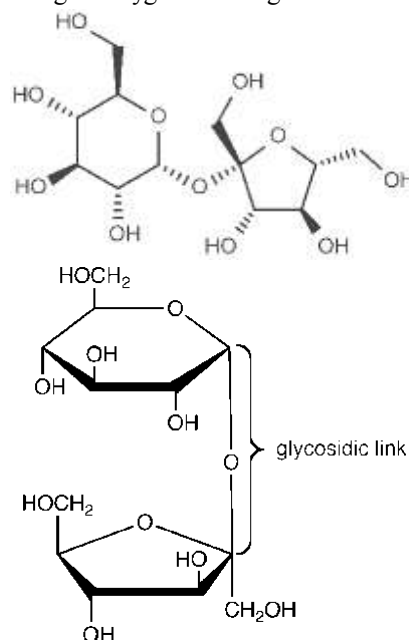


From the structures it is clear that 2nd carbon in DNA do not have OH group.

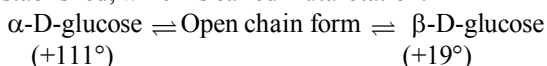
EXERCISE - 2

- (c) Vitamin A - Xerophthalmia
 Vitamin B₁₂ - Pernicious anaemia
 Vitamin C - Scurvy
 Vitamin E - Sterility
 Vitamin K - Haemorrhage
- (c) Adenine is a purine base which is present in RNA and DNA both.
- (c) Glucose is converted into alcohol by the action of zymase.

$$\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{zymase}} \text{C}_2\text{H}_5\text{OH}$$
- (c) Cellulose is the constituent of cell wall of plant cells.
- (d) Diastase enzyme converts starch into maltose.
- (b) Lactose is present in milk (Glucose + Galactose).
- (b) Insulin contains 51 amino acids.
- (b) Glucose + Fehling solution $\rightarrow$ Gluconic acid + Cu₂O (Red ppt)
- (c) 10. (a)
- (c) In sucrose the two monosaccharides are held together by glycosidic linkage and not by peptide linkage.
- (c) Oil / fat + Alkali $\xrightarrow{\text{Saponification}}$ Soap + Glycerol.
- (d)
- (d) Thymine is present in DNA while in RNA there is Uracil.
- (a) Energy is stored in our body in the form of A.T.P
- (a) Sucrose is formed by 1-2 linking of glucose and fructose. Thus both reducing groups are involved in glycosidic linkage.
- (b) Glycosidic linkage is actually an ether bond as the linkage forming the rings in an oligosaccharide or polysaccharide is not just one bond, but the two bonds sharing an oxygen atom e.g. sucrose



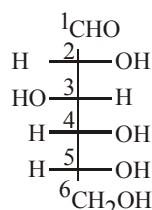
18. (a) α -D-glucose or β -D-glucose when dissolved in water and allowed to stand, following equilibrium is established, which is called mutarotation.



Specific rotation of α -form falls until a constant value of +52.5° is reached. On the other hand, specific rotation of β form increases. Specific rotation of equilibrium mixture is 52.5°.

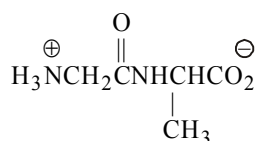
19. (b) Phosphate is linked to 3rd & 5th carbon of corresponding sugar
20. (c) Fischer gave the prefix "D" to compounds whose bottom chiral has its OH to the right. So natural glucose is called D-glucose or dextrose.

Structure of D-Glucose :

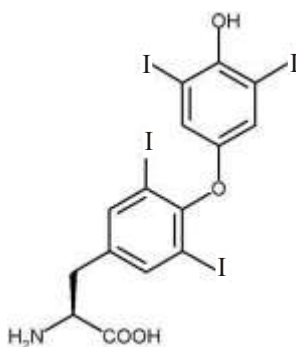


D-Glucose

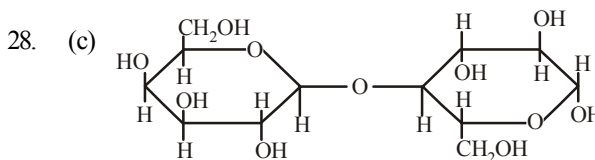
21. (a) By convention, the amino acid with the free amino group (N-terminal) is written at the left end and the one with the unreacted carboxyl group (C-terminal) at the right end. Thus, the structure of Gly. Ala is



22. (d) Glucose being an aldose responds to Tollen's test while fructose, although a ketose, undergoes rearrangement in presence of basic medium (provided by Tollen's reagent) to form glucose, which then responds to Tollen's test.
23. (b) The two isomeric forms (α - and β -) of D-glucopyranose differ in configuration only at C-1; hence these are called anomers.
24. (d)
25. (c) Glycogen is called animal starch and is found in all animal cells. It constitutes the reserve food material.
26. (c) Thyroxine is the only hormone among the given choices that contains iodine. Its structure is as follows:



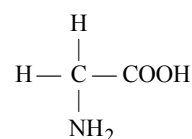
27. (a) Sucrose does not have free —CHO or CO group, hence it does not undergo mutarotation.



(Lactose)

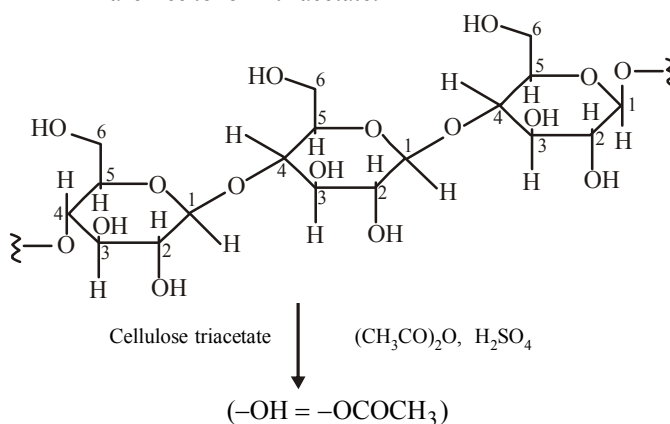
All reducing sugar shows mutarotation.

29. (c) When the proteins are subjected to the action of heat, mineral acids or alkali, the water soluble form of globular protein changes to water insoluble fibrous protein. This is called denaturation of proteins. During denaturation secondary and tertiary structures of protein destroyed but primary structures remains intact.
30. (b) The secondary structure of a protein refers to the shape in which a long peptide chain can exist. There are two different conformations of the peptide linkage present in protein, these are α -helix and β -conformation. The α -helix always has a right handed arrangement. In β -conformation all peptide chains are stretched out to nearly maximum extension and then laid side by side and held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β -pleated sheet.
31. (c) With the exception of glycine all the 19 other common amino acids have a uniquely different functional group on the central tetrahedral alpha carbon.

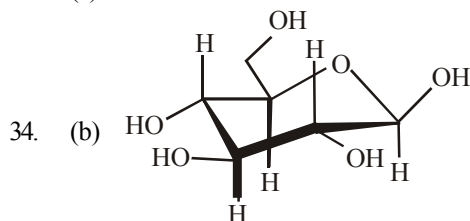
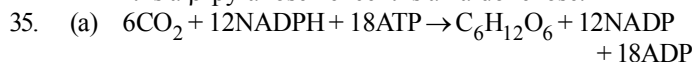


glycine

32. (a) Cellulose is a polysaccharide composed of only D-glucose units. Every adjacent glucose units are joined by β -glycosidic linkage between C₁ of one glucose and C₄ of the next.
- Thus in every glucose units only three —OH groups are free to form triacetate.

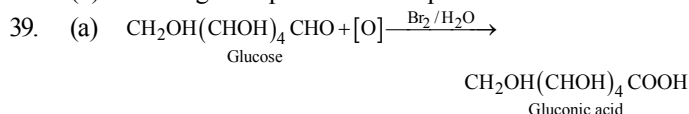


33. (a)

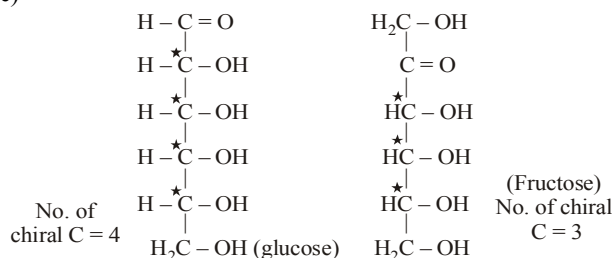
34. (b) It is a β -pyranose hence it is an aldohexose.36. (b) Molisch's Test : This is a general test for carbohydrates. One or two drops of alcoholic solution of α -naphthol is added to 2 ml glucose solution. 1 ml of conc. H_2SO_4 solution is added carefully along the sides of the test-tube. The formation of a violet ring at the junction of two liquids confirms the presence of a carbohydrate or sugar.

37. (d)

38. (d) All the given options are example of neutral amino acids.



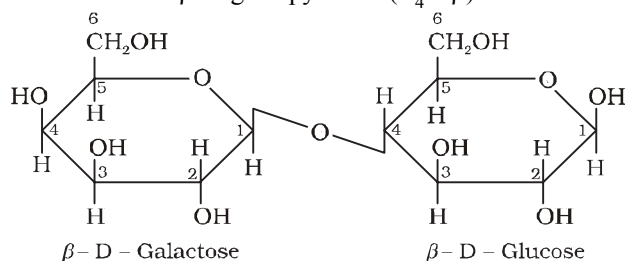
40. (c)

41. (d) Weak reagent like NaHSO_3 is unable to open the chain and can't react with glucose. This explains the inability of glucose to form aldehyde bisulphite compound.

42. (d) Vitamin D is a fat soluble vitamin.

43. (d) Mg acts as a cofactor to the enzyme as it forms complex with phosphate group of ATP that is utilized in the transfer of ATP phosphate.

44. (a) The arrangement of polypeptide chains formed as a result of hydrogen bonding is called secondary structure of proteins.

45. (b) Lactose is obtained by the condensation of one molecule of β -D-galactopyranose ($\text{C}_1-\beta$) unit and one molecule of β -D-glucopyranose ($\text{C}_4-\beta$) unit. β -D-Galactose β -D-Glucose46. (a) Glycine is an amino acid, it contains both NH_2 as well as $-\text{COOH}$ groups and therefore, its aqueous solution form Zwitter ion which is amphoteric in nature.

47. (b) Hydrolysis of sucrose is known as inversion of cane sugar because sucrose produce equimolecular mixture of glucose and fructose. Sucrose is dextrorotatory while glucose and fructose mixture is laevorotatory. Sucrose is disaccharide.

48. (b) **Proteins on hydrolysis gives α -amino acid** because amino acids are the building blocks of proteins. It is also fact that amino acids contain both $-\text{NH}_2$ and $-\text{COOH}$ group.

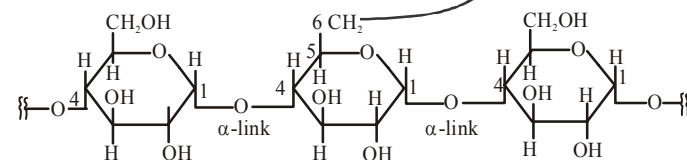
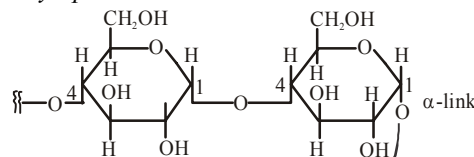
Here statement-1 and statement-2 both are correct but statement-2 is not a correct explanation of statement-1.

49. (d) Sequence of bases in DNA is TGAACCCTT, since according to base-pairing principle, T in DNA faces A in *m*-RNA, while G faces C and A faces U. Therefore, sequence of bases in *m*-RNA is ACUUGGGAA.50. (d) Vitamin B_3 is also called as nicotinic acid. Nicotinic acid in the form of nicotinamide is found usually in all living cells in small amounts.

EXERCISE - 3

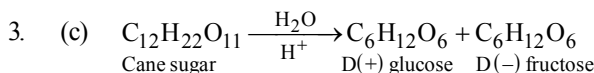
Exemplar Questions

1. (b) Structure of glycogen is similar to the structure of amylopectin.

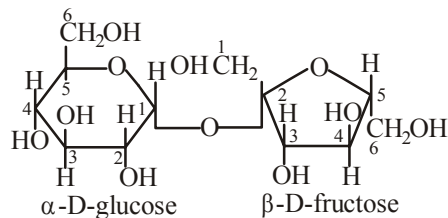


Structure of amylopectine

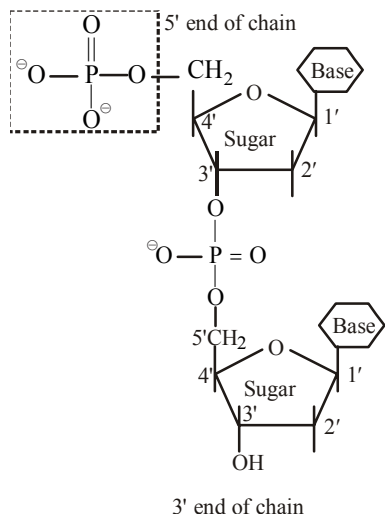
2. (d) Glycogen is stored in the liver, brain and muscles of animals.



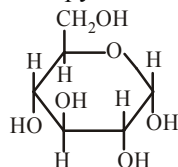
4. (c) Structures having different configuration at C-1 are known as anomers

5. (c) In α -helix structure, $-\text{NH}$ group of one amino acid is hydrogen bonded to $>\text{C}=\text{O}$ group of adjacent amino acid, forming a helix.6. (b) Reducing groups of glucose and fructose are involved in glycosidic bond formation $40 \text{ H}_2\text{C}$. α -D-glucose β -D-fructose

7. (b) Ascorbic acid is the chemical name of vitamin C.
 8. (a) Dinucleotides are formed by phosphodiester linkage between 5' and 3' carbon atom of pentose sugar.

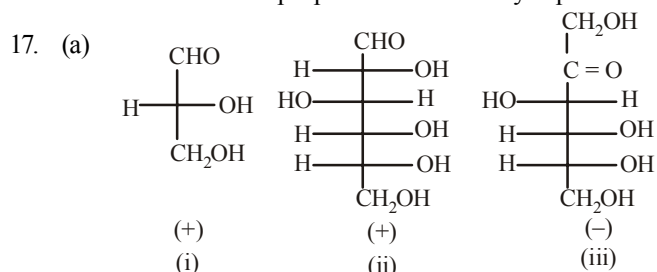


9. (b) The polymer of nucleotides in which nucleic acids are linked together by phosphodiester linkage are known as nucleic acid.
 10. (c) Glucose is present in pyranose form,



Pyranose means six membered ring containing oxygen.

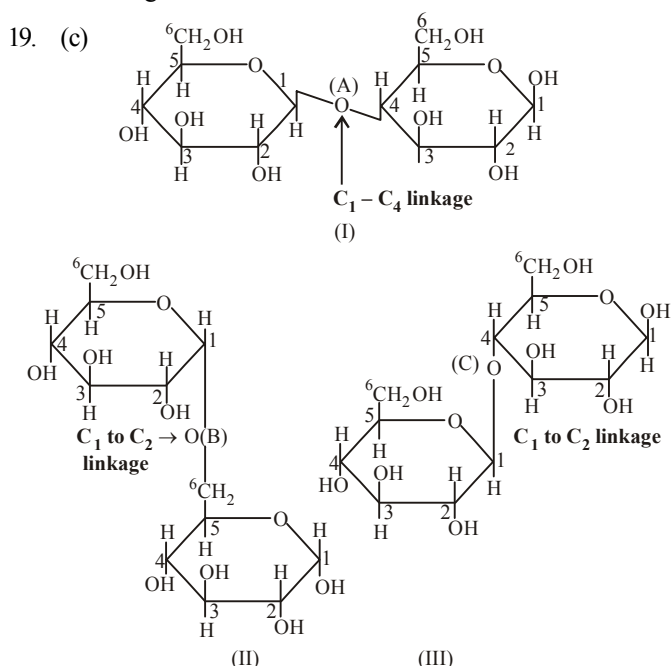
11. (a) Primary structure of proteins. When each polypeptide in a protein has amino acids linked with each other in a specific sequence.
 12. (c) RNA does not contain thymine.
 13. (d) Vitamin B₁₂ can be stored in our body because it is not water soluble.
 14. (d) DNA does not contain uracil.
 15. (a) Cyclic structures of monosaccharides which differ in structure at carbon -1 are known as anomers. Here, I and II are anomer because they differ from each other at carbon-1 only.
 16. (c) "Pentaacetate of glucose does not react with hydroxylamine" showing absence of free CHO group. This can not be explained by open structure of glucose while all other properties can be easily explained.



When OH on lowest asymmetric carbon is written at right hand side, it is represented as D configuration

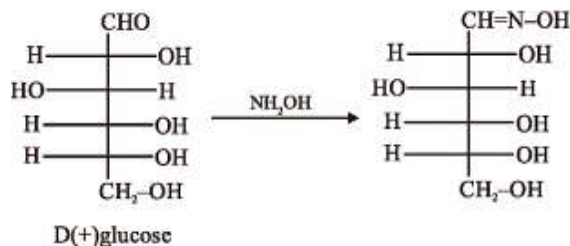
and when OH is written on left hand side, it is represented as L configuration.

18. (c) Carbon adjacent to oxygen atom in the cyclic structure of glucose or fructose is known as anomeric carbon.

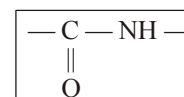


NEET/AIPMT (2013-2017) Questions

20. (c) The base pairs of the two strands of DNA are linked together through H-bonds.
 21. (d) Glucose reacts with hydroxyl amine to form an oxime.



22. (c) Adrenaline is a hormone produced by adrenal glands during high stress or exciting situations. This powerful hormone is part of the human body's acute stress response system, also called the fight or flight response.
 23. (c) Peptide bond



24. (b) Sugar in DNA is 2-deoxyribose whereas sugar in RNA is ribose.
 25. (d) Sucrose is non-reducing disaccharide as the two monosaccharide units are linked through their respective carbonyl groups.
 26. (c) Due to denaturation of proteins, helix get uncoiled and protein loses its biological activity.

Chapter 29

Polymers

Polymer is defined as very large molecule having high molecular mass ($10^3 - 10^7 \mu$). They are also referred to as macromolecules, which are formed by joining repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerisation.

CLASSIFICATION OF POLYMERS

Based on Source

Natural polymers :

Found in nature and generally obtained from plants and animals. For examples : proteins, cellulose, starch, resins, rubber, etc.

Semi-synthetic polymers

These are mostly derived from naturally occurring polymers by chemical modifications.

For examples : cellulose acetate (rayon) and cellulose nitrate

Synthetic polymers

Polymers prepared by synthesis (man made), are known as synthetic polymers.

For examples : plastics like polyethene, synthetic fibres like nylon 6, 6 and synthetic rubbers like Buna-S

Based on Structure of Polymers

Linear polymers

These polymers consist of long and straight chains. As a result of close packing of polymer chains, linear polymers have high melting points densities and tensile strength.

For examples : HDPE, PVC, etc.

Branched chain polymers

These polymers contain linear chains having some branches. As a result of branching these polymers do not pack well thus have low melting points, densities and tensile strength.

For examples : LPDE, etc.

Cross-linked or Network polymers

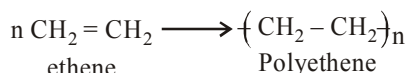
These polymers are formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. Because of presence of crosslinks these polymers are hard, rigid and brittle.

For examples : bakelite, melamine, etc.

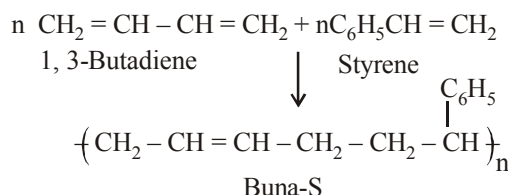
Based on Mode of Polymerisation

Addition polymers

- These polymers are formed by repeated addition of monomer molecules possessing double or triple bond.
For examples : polyethene, polypropene, Buna-S, Buna-N, etc.
- If only one type of monomeric species are present, the addition polymer is called **homopolymer**.
ex: polythene, polyvinylchloride, etc.



- If the monomers are different, the addition polymer is called **copolymer**.
ex: Buna-S, Buna - N etc.



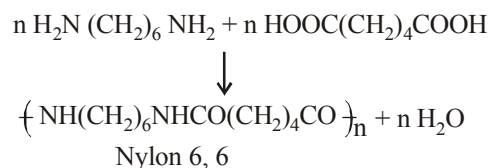
Note: In addition polymerisation a small amount of an organic peroxide is normally used as a free radical initiator.

Condensation polymers

These polymers are formed by repeated condensation reaction between two different bi- functional or tri-functional monomeric units.

In this, elimination of small molecules such as water, alcohol, HCl, etc., takes place.

Ex: Nylon 6, 6, terylene, nylon-6, etc.



Condensation is also known as step growth polymerisation.

Based on Inter Molecular Forces

Elastomers

These polymers are rubber-like solids with elastic properties.

Polymers having weakest inter-molecular forces between polymer chains.

These polymer can be stretched ten times their normal length and they return to original position when force is withdrawn.

For examples : Buna – S, Buna – N, neoprene etc.

Fibres

Polymers in which the intermolecular force of attraction are the strongest are called fibres. These forces are either due to H-bonding or dipole-dipole interaction.

They are thread forming solids possessing high tensile strength, high modulus and least elasticity. In these polymers strong bonding results in close packing of chains and crystalline structure. Example : nylon 6, 6; terylene etc.

Thermoplastics

In these polymers intermolecular forces of attraction are intermediate between elastomers and fibers. They are linear or slightly branched chain molecules.

They can repeatedly soften on heating and gets harden on cooling. Some important examples of this class of polymers are polyvinyl chloride, polythene, polypropylene, polystyrene etc.

Thermosetting

They are semi-fluid substances with low molecular masses which when heated become hard and infusible, because of sufficiently large number of cross links. They acquire a shape of three-dimensional network. Important examples of this class of polymers are bakelite, urea formaldehyde resin, etc.

TYPES OF POLYMERISATION REACTIONS

Addition or Chain Growth Polymerisation

In this, monomers of same or different type add together on a large scale to form polymer. Monomers used are unsaturated compounds, like alkenes, alkadienes, and their derivatives.

For example : polythene, HDPE, Teflon, PAN, etc

Condensation or step growth polymerisation

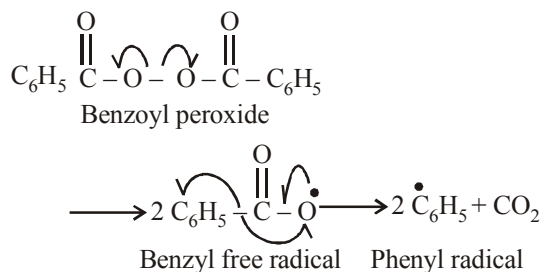
It involves repetitive condensation reaction between two bi-functional monomers. These reactions result in the loss of some simple molecules like water, alcohol, HCl, NH₃, etc.

For example : nylon, polyesters, bakelite, etc.

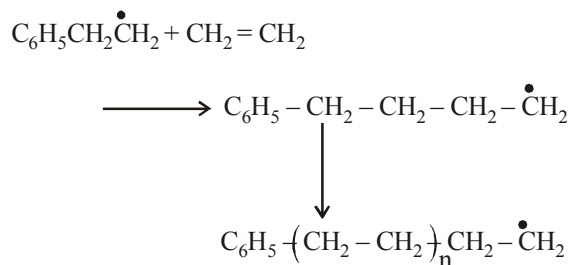
Mechanism for addition polymerization

Addition polymerisation proceeds via free radical addition polymerization. Free radical mechanism of addition polymerization is given as follows :

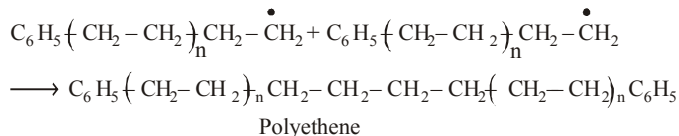
(i) Chain initiation step:



(ii) Chain propagating step:



3. Chain terminating step:

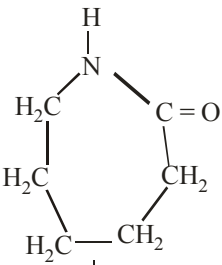
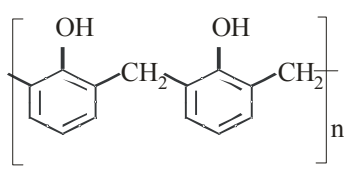
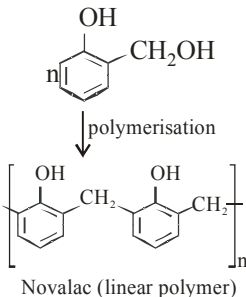
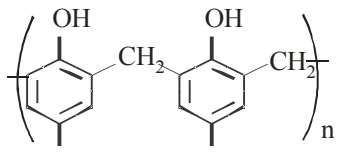
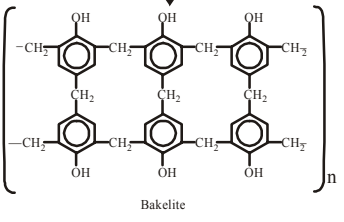


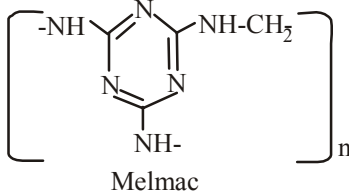
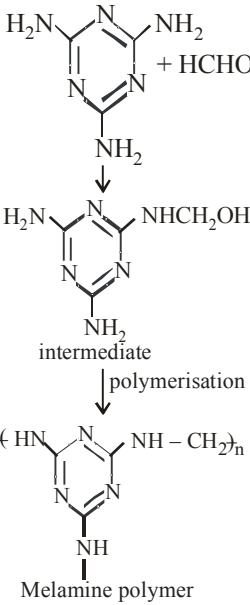
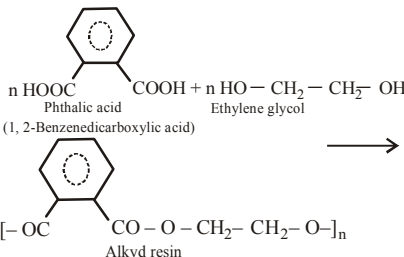
SOME IMPORTANT COMMERCIAL POLYMERS

Name of polymer	Monomer	Structure of repeating unit	Preparation Reaction	Uses
I. Addition polymers				
1. (a) LDPE (Low Density Polyethene)	ethene	$-(\text{CH}_2 - \text{CH}_2)_n$	Polymerisation of ethene under high pressure of 1000 – 2000 atm at a temperature of 350 – 570 K in presence of traces of O ₂ or peroxide initiator. It has highly branched structure.	It is used in insulation of electricity carrying wires and manufacture of squeeze bottles, toys, flexible pipes (it is chemically inert, tough, flexible and poor conductor of electricity)

1. (b) HDPE (High density polyethene)	ethene	$-(\text{CH}_2 - \text{CH}_2)_n$	Polymerisation of ethene in hydrocarbon solvent in presence of zeigler-Natta catalyst at 333–343 K and 6–7 atm. It consists of linear chains which undergoes to close packing. Thus it possesses high density.	It is used for making buckets, dustbins, bottles, pipes, etc. (it is comparatively more chemically inert, tougher and harder)
2. Polytetrafluoro ethene (Teflon)	Tetrafluoro ethene	$-(\text{CF}_2 - \text{CF}_2)_n$	$\begin{array}{c} n\text{CF}_2 = \text{CF}_2 \\ \downarrow \text{catalyst} \\ \text{high pressure} \\ (\text{CF}_2 - \text{CF}_2)_n \end{array}$	It is used in making oil seals and gaskets and also used for non-stick surface coated utensils as it is chemically inert and resistant to attack by corrosive reagents.
3. Polyacrylonitrile (PAN)	Acrylonitrile	$-(\text{CF}_2 - \text{CF} \begin{array}{c} \text{CN} \\ \end{array})_n$	$\begin{array}{c} n\text{CH}_2 = \text{CHCN} \\ \downarrow \text{Peroxide} \\ \text{catalyst} \\ (\text{CH}_2 - \text{CH} \begin{array}{c} \\ \text{CN} \end{array})_n \end{array}$	It is used as a substitute for wool in making commercial fibres as orlon or acrilan.
4. Polypropene	propene	$(\text{CH}_2 - \text{CH} \begin{array}{c} \text{CH}_3 \\ \end{array})_n$	$\begin{array}{c} \text{CH}_3 \\ \\ n\text{CH} = \text{CH}_2 \\ \text{Propylene} \\ \xrightarrow[\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_3]{\text{Ziegler Natta Catalyst}} \\ \left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH} - \text{CH}_2 - \end{array} \right]_n \\ \text{Polypropylene} \end{array}$	It is used in manufacture of ropes, toys, pipes, fibres, etc.
5. Polystyrene	Styrene	$(\text{CH}_2 - \text{CH} \begin{array}{c} \text{C}_6\text{H}_5 \\ \end{array})_n$	$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ n\text{CH} = \text{CH}_2 \\ \text{Styrene} \\ \xrightarrow{\text{Benzoyl Peroxide}} \\ \left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ -\text{CH} - \text{CH}_2 - \end{array} \right]_n \\ \text{Polystyrene} \end{array}$	It is used as an insulator, wrapping material in manufacture of toys, radio and television cabinets.
6. Polyvinyl chloride (PVC)	Vinyl chloride	$-(\text{CH}_2 - \text{CH} \begin{array}{c} \text{Cl} \\ \end{array})_n$	$\begin{array}{c} n\text{CH}_2 = \text{CH} \longrightarrow \\ \\ \text{Cl} \\ \text{Vinyl chloride} \\ [-\text{CH}_2 - \text{CH}-]_n \\ \\ \text{Cl} \\ \text{Polyvinyl chloride} \end{array}$	It is used in manufacture of rain coats, hand bags, vinyl flooring, water pipes, etc.

II. Condensation polymers

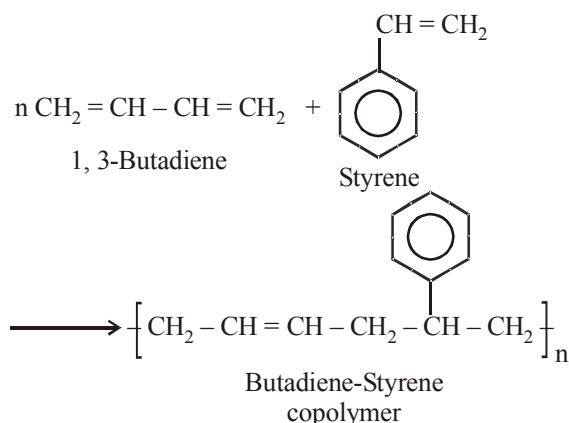
1. Polyamides (a) Nylon 6, 6	hexamethylene diamine and adipic acid	$\text{-(NH(CH}_2\text{)}_6\text{NHCO(CH}_2\text{)}_4\text{CO)}_n\text{-}$	$\text{nHOOC(CH}_2\text{)}_4\text{COOH} + \text{nH}_2\text{N(CH}_2\text{)}_6\text{NH}_2$ $\xrightarrow[553 \text{ K pressure}]{}$ $\text{-(NH(CH}_2\text{)}_6\text{NH-C(=O)-(CH}_2\text{)}_4\text{-C(=O)-)}_n\text{-}$	It is used in making sheets, bristles for brushes and in textile industry
(b) Nylon 6	caprolactum	$\text{-(}\overset{\text{O}}{\parallel}\text{C-(CH}_2\text{)}_5\text{-N-)}_n\text{-}$	 (i) $\text{H}_2\text{O}, \Delta$ (ii) Δ, Polymerisation $\text{-(}\overset{\text{O}}{\parallel}\text{C-(CH}_2\text{)}_5\text{-N-)}_n\text{-}$	It is used in manufacture of tyre cords, fabrics and ropes
2. Polyesters Terylene or Dacron	ethylene glycol and terephthalic acid	$\text{-(O-CH}_2\text{CH}_2\text{-O-C(=O)-C}_6\text{H}_4\text{-C(=O)-)}_n\text{-}$	$\text{nHO-CH}_2\text{-CH}_2\text{-OH} + \text{nHO-CO-C}_6\text{H}_4\text{-CO-OH}$ $\xrightarrow[420-460 \text{ K}]{\text{Zn(OCOCH}_3\text{)}_2, \text{Sb}_2\text{O}_3}$ $\text{-(O-CH}_2\text{-CH}_2\text{-O-C(=O)-C}_6\text{H}_4\text{-C(=O)-)}_n\text{-}$	It is used in manufacture of wear fabrics, tyre cords and seat belts it is used in blending cotton and wool fibres and also used as glass reinforcing materials in safety helmets
3. Phenol formaldehyde polymer (a) Novalac	o-Hydroxy-methylphenol		 Novalac (linear polymer)	It is used in making combs, phonograph records, electrical switches and handles of various utensils, etc.
(b) Bakelite	Novalac + formaldehyde (Phenol and formaldehyde)		 Bakelite	

4. Melamine formaldehyde polymer	Melamine + formaldehyde	 Melmac	 Melamine polymer	It is used in manufacture of unbreakable crockery
5. Urea formaldehyde resin	Urea + formaldehyde	$\left(\text{NH} - \text{CO} - \text{NH} - \text{CH}_2 \right)_n$	—	It is used for making unbreakable cups and laminated sheets
6. Glyptal	Ethylene glycol + phthalic acid	$\left(\text{OCH}_2 - \text{CH}_2\text{OOC} \right)_n$ 	 Alkyd resin	It is used in manufacture of paints and lacquers.

COPOLYMERISATION

It is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer. It can be made by chain as well as step growth polymerisation.

Ex: Buna-S



Properties of copolymers are different from homopolymers. Actually, copolymers have better physical and mechanical

properties. For example : Buna-S is tough and a good substitute for natural rubber.

RUBBER

Natural rubber

It is manufactured from rubber latex which is a colloidal dispersion of rubber in water.

It is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called cis-1, 4 – polyisoprene. Cis-polyisoprene molecule consists of various chains held together by weak Van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

Vulcanization of rubber:

Natural rubber becomes soft at high temperature and brittle at low temperatures and shows high water absorption capacity. It is soluble in non-polar solvents and is non-resistant to attack by oxidising agents. To improve upon these physical properties, vulcanization is carried out. It consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373K to 415K. On vulcanization, sulphur forms cross-links at reactive sites of double bonds and thus rubber gets stiffened.

Note : (i) About 5% sulphur is used for making tyre rubber, 20-25% sulphur for making ebonite and 30% sulphur for making battery case rubber.

(ii) Natural rubber is cis-polyisoprene whereas gutta parcha is trans-polyisoprene.

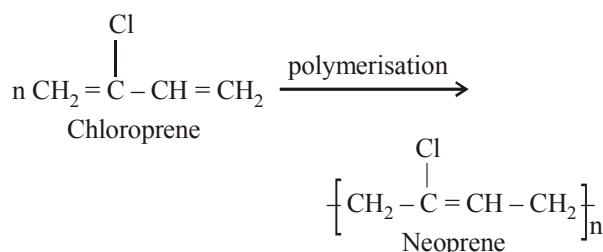
Synthetic rubbers

They are either homopolymers of 1, 3-butadiene derivatives or copolymers of 1, 3-butadiene or its derivatives with another unsaturated monomer.

Preparation:

(i) Neoprene (or polychloroprene)

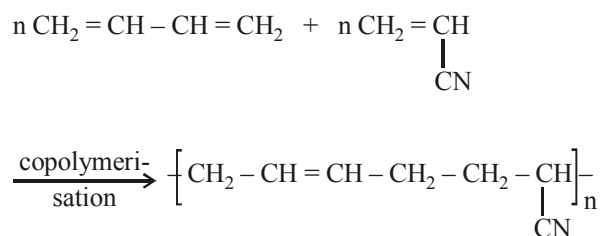
It is prepared by free radical polymerisation of chloroprene.



It is resistant to vegetable and mineral oils. It is used for manufacturing conveyor belts, gaskets and hoses.

(ii) Buna-N

It is obtained by copolymerisation of 1, 3-butadiene and acrylonitrile in presence of peroxide catalyst.



It is resistant to action of petrol, lubricating oil and organic solvents. It is used in making oil seals, tank lining, etc.

MOLECULAR MASS OF POLYMERS

Polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average and can be determined by chemical and physical methods.

Number Average Molecular Weight ($\bar{M}_n$)

$$\bar{M}_n = \frac{\text{Total weight of the molecules}}{\text{Total number of molecules}}$$

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

$\bar{M}_n$ is generally determined by osmotic pressure method.

Weight Average Molecular Weight ($\bar{M}_w$)

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3 + \dots}{w_1 + w_2 + w_3 + \dots} = \sum \frac{w_i M_i}{\sum w_i}$$

$$\text{or } \bar{M}_w = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 + \dots}{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

[weight (w) = no. of molecules (N) × molecular weight (M)]

$\bar{M}_w$ is generally determined by the light scattering method.

PDI (POLY DISPERSITY INDEX)

The ratio of the $\bar{M}_w$ and $\bar{M}_n$ is called PDI

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n}$$

In natural polymers, which are generally mono dispersed, the PDI is unity ($\bar{M}_w = \bar{M}_n$)

In synthetic polymers which are poly dispersed, PDI is greater than unity because $\bar{M}_w$ is always higher than $\bar{M}_n$.

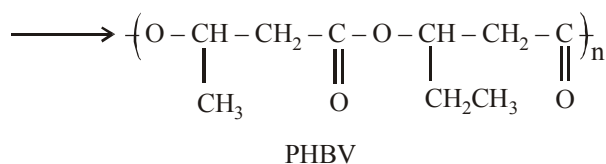
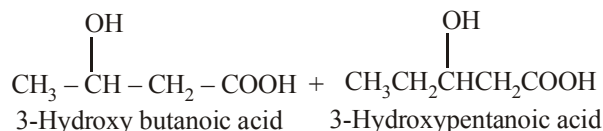
BIODEGRADABLE POLYMERS

A large number of polymers are resistant to environmental degradation processes and are thus responsible for accumulation of polymeric solid waste materials. To overcome this problem, new biodegradable synthetic polymers have been designed and developed.

Aliphatic polyesters are one of the important classes of biodegradable polymers. Some important examples are:

(i) Poly β -hydroxy butyrate-co- β -hydroxy valerate (PHBV)

It is obtained by following reaction:

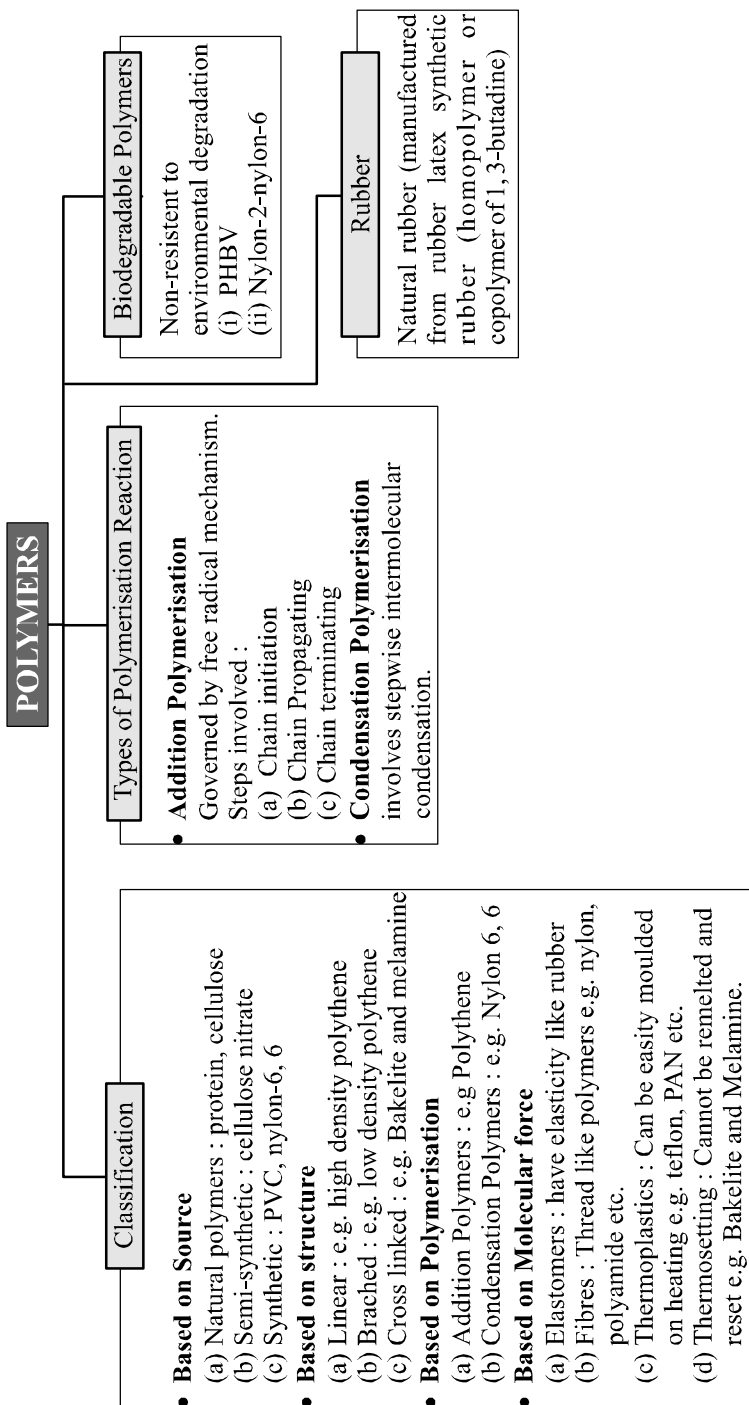


It undergoes bacterial decomposition in environment. It is used in speciality packaging, orthopaedic devices and in controlled release of drugs.

(ii) Nylon-2-nylon-6

It is an alternating copolymer of glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) and amino caproic acid ($\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$) It is biodegradable

CONCEPT MAP



EXERCISE - 1

Conceptual Questions

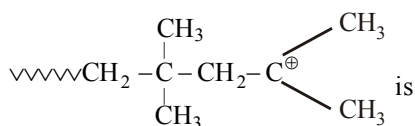
- Which of the following is a polymer containing nitrogen?
(a) Polyvinyl chloride (b) Bakelite
(c) Nylon (d) Terylene
- In elastomer, intermolecular forces are
(a) strong (b) weak (c) zero (d) None of these
- Natural rubber is a polymer of
(a) butadiene (b) isoprene
(c) 2-methylbutadiene (d) hexa-1, 3-diene
- $\sim[\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}]_n\sim$ is a
(a) addition polymer (b) thermosetting polymer
(c) homopolymer (d) copolymer
- Which of the following is an example of thermosetting polymer?
(a) Polythene (b) PVC (c) Neoprene (d) Bakelite
- A condensation polymer among the following is
(a) dacron (b) PVC (c) polystyrene (d) teflon
- Which of the following is not polyamide?
(a) Nylon 6 (b) Glyptal structure
(c) Protein (d) Nylon-66
- Ebonite is
(a) natural rubber (b) synthetic rubber
(c) highly vulcanized rubber (d) polypropene
- Which of the following is not an example of addition polymer?
(a) Polystyrene (b) Nylon
(c) PVC (d) Polypropylene
- Dacron is obtained by the condensation polymerisation of:
(a) Dimethyl terephthalate and ethylene glycol
(b) Terephthalic acid and formaldehyde
(c) Phenol and phthalic acid
(d) Phenol and formaldehyde
- Which of the following is a polyamide?
(a) Bakelite (b) Terylene (c) Nylon-66 (d) Teflon
- PVC is:
(a) thermoplastic polymer (b) compound polymer
(c) thermosetting polymer (d) simple polymer
- The synthetic polymer which resembles natural rubber is
(a) neoprene (b) chloroprene
(c) glyptal (d) nylon
- The condensation of hexamethylenediamine with sebacoyl chloride at 525 K gives
(a) nylon-6,20 (b) nylon-6,01
(c) nylon-6,10 (d) none of these
- Which of the following is not a biopolymer?
(a) Proteins (b) Rubber (c) Cellulose (d) RNA
- Which is not an example of copolymer?
(a) SAN (b) ABS (c) Saran (d) PVC
- For natural polymers PDI is generally
(a) 0 (b) 1 (c) 100 (d) 1000
- Which is used as medicine?
(a) PVC (b) Terylene (c) Glyptal (d) Urotropine
- Nylon 66 is a polyamide obtained by the reaction of
(a) $\text{COOH}(\text{CH}_2)_4\text{COOH} + \text{NH}_2\text{C}_6\text{H}_4\text{NH}_2\text{-(p)}$
(b) $\text{COOH}(\text{CH}_2)_4\text{COOH} + \text{NH}_2(\text{CH}_2)_6\text{NH}_2$
(c) $\text{COOH}(\text{CH}_2)_6\text{COOH} + \text{NH}_2(\text{CH}_2)_4\text{NH}_2$
(d) $\text{COOH}(\text{CH}_2)_4\text{COOH} + \text{NH}_2(\text{CH}_2)_6\text{NH}_2$
- Which of the following is not correctly matched?
(a) Terylene $\left[-\text{OCH}_2\text{CH}_2\text{C}(=\text{O})\text{C}_6\text{H}_4\text{C}(=\text{O})- \right]_n$
(b) Neoprene $\left[-\text{CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2- \right]_n$
(c) Nylon-66 $\left[-\text{NH}(\text{CH}_2)_6\text{NH}-\underset{\text{O}}{\text{C}}(\text{CH}_2)_4\underset{\text{O}}{\text{C}}-\text{O}- \right]_n$
(d) PMMA $\left[\text{CH}_2-\underset{\text{COOCH}_3}{\overset{\text{CH}_3}{\text{C}}} - \right]_n$
- The monomer(s) used to prepare polyvinyl polythene is
(a) vinyl chloride and ethene
(b) ethene
(c) isoprene
(d) 1, 3-butadiene
- Monomer of $\left[\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \right]_n$ is
(a) 2-methylpropene (b) styrene
(c) propylene (d) ethene
- Acrlan is a hard, horny and a high melting material. Which of the following represents its structure?
(a) $\left[-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}- \right]_n$
(b) $\left[-\text{CH}_2-\underset{\text{CN}}{\text{CH}}- \right]_n$
(c) $\left[-\text{CH}_2-\underset{\text{COOCH}_3}{\overset{\text{CH}_3}{\text{C}}} - \right]_n$
(d) $\left[-\text{CH}_2-\underset{\text{COOC}_2\text{H}_5}{\text{CH}}- \right]_n$
- Match List-I (Monomer) with List II (Polymer) and select the correct answer using the codes given below the lists:

List I	List II
I. Hexamethylenediamine	A. Bakelite
II. Phenol	B. Dacron
III. Phthalic acid	C. Glyptal
IV. Terephthalic acid	D. Melamine
	E. Nylon

Codes:

- (a) I-E, II-A, III-B, IV-C (b) I-E, II-A, III-C, IV-B
(c) I-D, II-C, III-A, IV-B (d) I-D, II-C, III-A, IV-B

25. The monomer of the polymer;



- (a) $\text{H}_2\text{C}=\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}$ (b) $\text{CH}_3\text{CH}=\text{CHCH}_3$
(c) $\text{CH}_3\text{CH}=\text{CH}_2$ (d) $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$

26. Orlon is a polymer of

- (a) styrene (b) tetrafluoroethylene
(c) vinyl chloride (d) acrylonitrile

27. P.V.C. is formed by polymerisation of

- (a) ethene (b) 1-chloropropene
(c) propene (d) 1-chloroethene

28. Caprolactam polymerises to give

- (a) terylene (b) teflon (c) glyptal (d) nylon-6

29. The process involving heating of rubber with sulphur is called

- (a) galvanisation (b) vulcanization
(c) bessemerisation (d) sulphonation

30. Which of the following is used in paints?

- (a) Terylene (b) Nylon
(c) Glyptal (d) Chloroprene

31. Which of the following polymers do not involve cross linkages?

- (a) Melmac (b) Bakelite
(c) Polythene (d) Vulcanised rubber

32. Number average molecular mass, $\overline{M}_n$ and weight average molecular mass ($\overline{M}_w$) of synthetic polymers are related as

- (a) $\overline{M}_n = (\overline{M}_w)^{1/2}$ (b) $\overline{M}_n = \overline{M}_w$
(c) $\overline{M}_w > \overline{M}_n$ (d) $\overline{M}_w < \overline{M}_n$

33. Select the correct statement.

- (a) Vinyon is a copolymer of vinyl chloride and vinyl acetate
(b) Saran is a copolymer of vinyl chloride and vinylidene chloride
(c) Butyl rubber is a copolymer of isobutylene and isoprene
(d) All of the above are correct

34. The polymer used in the manufacture of lacquers is

- (a) bakelite (b) glyptal (c) PVC (d) PHBV

35. Low density polythene is prepared by

- (a) Free radical polymerisation
(b) cationic polymerisation
(c) anionic polymerisation
(d) Ziegler-Natta polymerisation

36. Head-to-tail addition takes place in chain-growth polymerisation when monomer is

- (a) $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$ (b) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
(c) $\text{CH}_2=\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{COCH}_3$ (d) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$

37. Polymer used in bullet proof glass is

- (a) lexan (b) PMMA (c) nomex (d) kevlar

38. The monomer(s) used in the preparation of Orlon, a substitute for wool is/are

- (a) caprolactam
(b) tetrafluoroethene
(c) styrene and 1, 3-butadiene
(d) acrylonitrile

39. Glyptals are chiefly employed in

- (a) toy making (b) surface coating
(c) photofilm making (d) electrical insulators

40. The polymer used for making contact lenses for eyes is

- (a) polymethylmethacrylate (b) polyethylene
(c) polyethylacrylate (d) nylon-6

41. Which polymer is used for making magnetic recording tapes?

- (a) Dacron (b) Acrilan (c) Glyptal (d) Bakelite

42. The polymer used in making synthetic hair wigs is made up of

- (a) $\text{CH}_2=\text{CHCl}$ (b) $\text{CH}_2=\text{CHCOOCH}_3$
(c) $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ (d) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

43. The monomer of polystyrene is

- (a) $\text{C}_2\text{H}_5-\text{CH}=\text{CH}_2$
(b) $\text{CH}_2=\text{CHCl}$
(c) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$
(d) $\text{CH}_2=\text{CHCHO}$

44. Which of the following has been used in the manufacture of non-inflammable photographic films?

- (a) Cellulose nitrate (b) Cellulose xanthate
(c) Cellulose perchlorate (d) Cellulose acetate

45. Which of the following is currently used as a tyre cord?

- (a) Terylene (b) Polyethylene
(c) Polypropylene (d) Nylon - 6

46. The plastic household crockery is prepared by using

- (a) melamine and tetrafluoroethane
(b) malonic acid and hexamethylenamine
(c) melamine and vinyl acetate
(d) melamine and formaldehyde

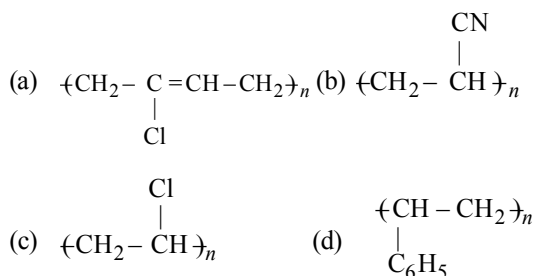
47. The polymer used in orthopaedic devices and in controlled drug release is

- (a) Orlon (b) PTFE (c) SBR (d) PHBV

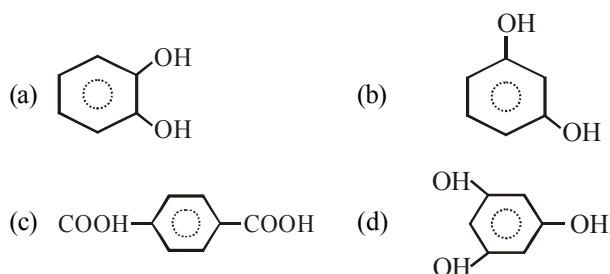
48. Which one of the following polymers is prepared by condensation polymerisation?

- (a) Teflon (b) Natural rubber
(c) Styrene (d) Nylon-66

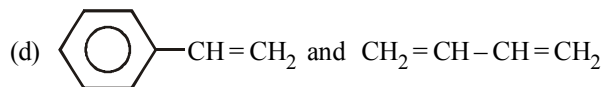
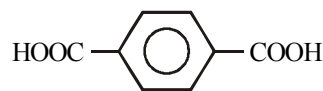
49. Which one of the following statement is *not true*?
- In vulcanization the formation of sulphur bridges between different chains make rubber harder and stronger.
 - Natural rubber has the *trans* -configuration at every double bond
 - Buna-S is a copolymer of butadiene and styrene
 - Natural rubber is a 1, 4 - polymer of isoprene
50. Which of the following structures represents neoprene polymer?



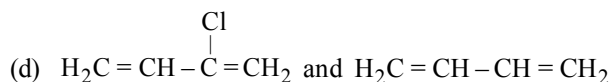
51. Of the following which one is classified as polyester polymer ?
- Terylene
 - Bakelite
 - Melamine
 - Nylon-66
52. Which one of the following is not a condensation polymer ?
- Melamine
 - Glyptal
 - Dacron
 - Neoprene
53. Which of the following statements is false?
- Artificial silk is derived from cellulose.
 - Nylon-66 is an example of elastomer.
 - The repeat unit in natural rubber is isoprene.
 - Both starch and cellulose are polymers of glucose.
54. Bakelite is obtained from phenol by reacting with
- $(\text{CH}_2\text{OH})_2$
 - CH_3CHO
 - CH_3COCH_3
 - HCHO
55. Vinyl chloride can be converted into PVC. In this reaction, the catalyst used is
- peroxides
 - cuprous chloride
 - anhydrous zinc chloride
 - anhydrous AlCl_3
56. The mass average molecular mass & number average molecular mass of a polymer are 40,000 and 30,000 respectively. The polydispersity index of polymer will be
- <1
 - >1
 - 1
 - 0
57. Ethylene-propylene rubber (EPR) is
- unsaturated and stereoregular
 - saturated and stereoregular
 - atactic and unsaturated
 - syndiotactic and unsaturated
58. The monomeric units of terylene are glycol and which of the following



59. The synthetic polymer which resembles natural rubber is
- neoprene
 - chloroprene
 - glyptal
 - nylon
60. Characteristic property of Teflon is
- 2000 poise viscosity
 - high surface tension
 - non-inflammable and resistant to heat
 - highly reactive
61. Which of the following is used in vulcanization of rubber ?
- SF_6
 - CF_4
 - Cl_2F_2
 - C_2F_2
62. What is the percentage of sulphur used in vulcanization of rubber
- 05% to 30%
 - 03% to 25%
 - 10% to 20%
 - 05% to 25%
63. Perlon is
- Rubber
 - Nylon-6
 - Terylene
 - Orlon
64. Plexiglas (PMMA) is a polymer of
- acrylic acid
 - methyl acrylate
 - methyl methacrylate
 - None of these
65. Which one of the following sets forms the biodegradable polymer?
- $\text{CH}_2 = \text{CH} - \text{CN}$ and $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
 - $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$ and $\text{H}_2\text{N} - (\text{CH}_2)_5 - \text{COOH}$
 - $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$ and



66. Buna-N synthetic rubber is a copolymer of :
- $\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2$ and $\text{H}_5\text{C}_6 - \text{CH} = \text{CH}_2$
 - $\text{H}_2\text{C} = \text{CH} - \text{CN}$ and $\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2$
 - $\text{H}_2\text{C} = \text{CH} - \text{CN}$ and $\text{H}_2\text{C} = \underset{\text{CH}_3}{\text{CH}} - \text{C} = \text{CH}_2$

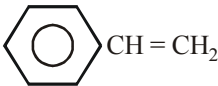
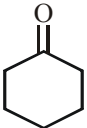


67. The polymer containing strong intermolecular forces e.g. hydrogen bonding, is
- teflon
 - nylon 6, 6
 - polystyrene
 - natural rubber
68. Among cellulose, polyvinyl chloride, nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is
- nylon
 - polyvinyl chloride
 - cellulose
 - natural Rubber
69. The monomer(s) used to prepare polyvinyl polythene is
- vinyl chloride and ethene
 - ethene
 - isoprene
 - 1, 3-butadiene

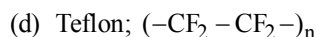
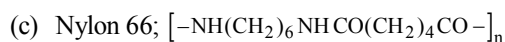
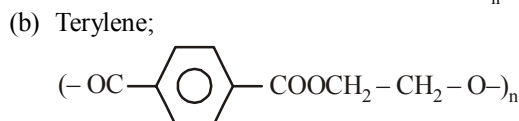
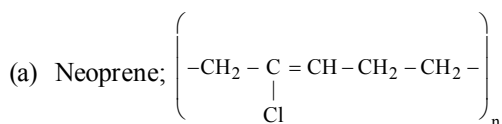
70. The polymer used in orthopaedic devices and in controlled drug release is
 (a) Orlon (b) PTFE
 (c) SBR (d) PHBV
71. The monomer of polystyrene is
 (a) $C_2H_5 - CH = CH_2$
 (b) $CH_2 = CHCl$
 (c) $C_6H_5 - CH = CH_2$
 (d) $CH_2 = CHCHO$
72. A network polymer among the following is
 (a) teflon (b) polythene
 (c) bakelite (d) PVC
73. The monomer(s) used in the preparation of Orlon, a substitute for wool is/are
 (a) caprolactam
 (b) tetrafluoroethene
 (c) styrene and 1, 3-butadiene
 (d) acrylonitrile
74. The polymer used in the manufacture of lacquers is
 (a) bakelite (b) glyptal
 (c) PVC (d) PHBV
75. Teflon, styron and neoprene are all
 (a) Copolymers (b) Condensation polymers
 (c) Homopolymers (d) Monomers

EXERCISE - 2

Applied Questions

1. The monomers used for the preparation of nylon-2-nylon-6 is/are
 (a) caprolactam
 (b) alanine and amino caproic acid
 (c) glycine and amino caproic acid
 (d) hexamethylenediamine and adipic acid
2. Polymer formation from monomers starts by
 (a) condensation or addition reaction between monomers
 (b) coordinate reaction between monomers
 (c) conversion of monomer to monomer ions
 (d) hydrolysis of monomers.
3. Nylon threads are made of
 (a) polyester polymer (b) polyamide polymer
 (c) polyethylene polymer (d) polyvinyl polymer
4. The polymer containing strong intermolecular forces *e.g.* hydrogen bonding, is
 (a) teflon (b) nylon 6, 6
 (c) polystyrene (d) natural rubber
5. $n(CF_2 = CF_2) \xrightarrow[(NH_4)_2S_2O_8]{\text{Benzoyl peroxide or}} X$
 Here, X is :
 (a) RMMA (b) PVC
 (c) PAN (d) None of these
6. Which pair of polymers have similar properties ?
 (a) Nylon, PVC (b) PAN, PTFE
 (c) PCTFE, PTFE (d) Bakelite, alkyl resin
7. Which compound/set of compounds is used in the manufacture of nylon 6?
 (a)  $CH = CH_2$
 (b) $HOOC(CH_2)_4COOH + NH_2(CH_2)_6NH_2$
 (c) $CH_2 = CH - \overset{\overset{CH_3}{|}}{C} = CH_2$ (d) 
8. Among the following, the wrong statement is
 (a) PMMA is plexiglass
 (b) SBR is natural rubber
 (c) PTFE is teflon
 (d) LDPE is low density polythene
9. If a polythene sample contains two monodisperse fractions in the ratio 2 : 3 with degree of polymerization 100 and 200, respectively, then its weight average molecular weight will be :
 (a) 4900 (b) 4600 (c) 4300 (d) 5200
10. When condensation product of hexamethylenediamine and adipic acid is heated to 525K in an atmosphere of nitrogen for about 4-5 hours, the product obtained is
 (a) solid polymer of nylon 66
 (b) liquid polymer of nylon 66
 (c) gaseous polymer of nylon 66
 (d) liquid polymer of nylon 6
11. The polymer used for optical lenses is :
 (a) polypropylene
 (b) polyvinyl chloride
 (c) polythene
 (d) polymethyl methacrylate
12. The compound which cannot be used as a plasticizer, is
 (a) di-*n*-butylphthalate (b) tricresyl phosphate
 (c) di-*n*-octylphthalate (d) diethyl phthalate
13. In which of the following polymers, empirical formula resembles with monomer ?
 (a) Bakelite (b) Teflon
 (c) Nylon-6, 6 (d) Dacron
14. Which is a polymer of three different monomers ?
 (a) ABS (b) SBR
 (c) NBR (d) Nylon-2-Nylon-6
15. Which of the following fibres is made of polyamide ?
 (a) Dacron (b) Orlon (c) Nylon (d) Rayon
16. The polymer which has conducting power is
 (a) polyethylene (b) polybutadiene
 (c) polystyrene (d) polyacetylene

17. Orlon is a –
 (a) homopolymer and addition polymer
 (b) copolymer and addition polymer
 (c) homopolymer and condensation polymer
 (d) copolymer and condensation polymer
18. Dacron is a –
 (a) crease resistant
 (b) polyamide
 (c) addition polymer
 (d) polymer of ethylene glycol and phthalic acid
19. Which of the following is a branched polymer ?
 (a) Low density polymer (b) Polyester
 (c) High density polymer (d) Nylon
20. Given the polymers (i) Nylon-66; (ii) Buna-S; (iii) Polythene, arrange these in increasing order of their inter-molecular forces (lower to higher)
 (a) (i) > (ii) > (iii) (b) (ii) > (iii) > (i)
 (c) (ii) < (iii) < (i) (d) (iii) < (i) < (ii)
21. Structures of some common polymers are given. Which one is **not** correctly presented?



DIRECTIONS for Qs. 22 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

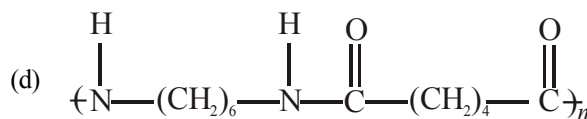
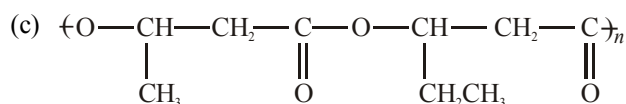
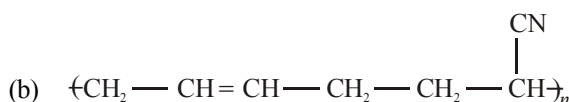
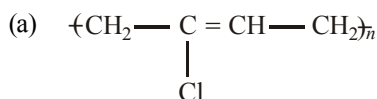
- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement -1
 (b) Statement-1 is true, Statement-2 is true ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is true, Statement-2 is false
 (d) Statement-1 is false, Statement-2 is true
22. **Statement-1** : In vulcanisation of rubber, sulphur cross links are introduced.
Statement-2 : Vulcanisation is a free radical initiated chain reaction.
23. **Statement-1** : Bakelite is a thermosetting polymer.
Statement-2 : Bakelite can be melted again and again without any change.
24. **Statement-1** : The time of vulcanisation and temperature is increased by adding accelerators.
Statement-2 : By vulcanising, a material of high tensile strength can be obtained.
25. **Statement-1** : Teflon has high thermal stability and chemical inertness.
Statement-2 : Teflon is a thermoplastic.

EXERCISE - 3

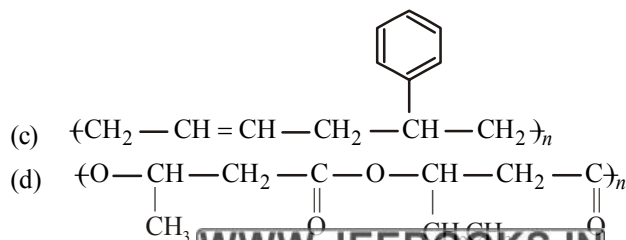
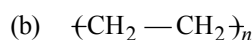
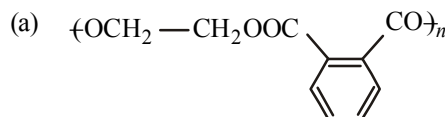
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

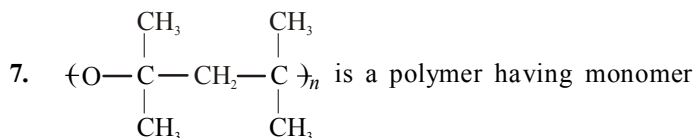
1. Which of the following polymers of glucose is stored by animals?
 (a) Cellulose (b) Amylose
 (c) Amylopectin (d) Glycogen
2. Which of the following is not a semisynthetic polymer?
 (a) cis-polyisoprene (b) Cellulose nitrate
 (c) Cellulose acetate (d) Vulcanised rubber
3. The commercial name of polyacrylonitrile is
 (a) dacron (b) orlon (acrilan)
 (c) PVC (d) bakelite
4. Which of the following polymer is biodegradable?



5. In which of the following polymers ethylene glycol is one of the monomer units?

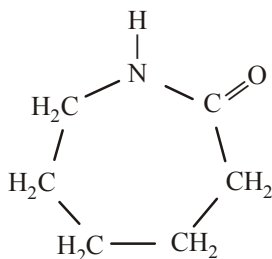


6. Which of the following statements is not true about low density polyethene?
- Tough
 - Hard
 - Poor conductor of electricity
 - Highly branched structure



units

- -
 -
 -
8. Which of the following polymer can be formed by using the following monomer unit?



- Nylon-6, 6
- Nylon-2-nylon-6
- Melamine polymer
- Nylon-6

NEET/AIPMT (2013-2017) Questions

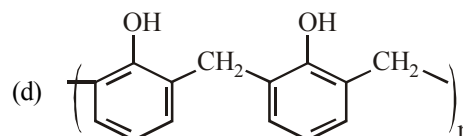
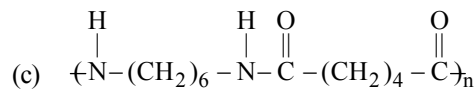
9. Which is the monomer of Neoprene in the following ?

- $\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \text{CH} = \text{CH}_2$
- $\text{CH}_2 = \underset{\text{Cl}}{\text{C}} - \text{CH} = \text{CH}_2$
- $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$
- $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

[2013]

10. Nylon is an example of: [2013]
- Polysaccharide
 - Polyamide
 - Polythene
 - Polyester
11. Which one of the following is an example of a thermosetting polymer? [2014]

- $\left[\text{CH}_2 - \underset{\text{Cl}}{\text{C}} = \text{CH} - \text{CH}_2 \right]_n$
- $\left[\text{CH}_2 - \underset{\text{Cl}}{\text{CH}} \right]_n$



12. Which of the following organic compounds polymerizes to form the polyester Dacron? [2014]

- Propylene and para $\text{HO}-(\text{C}_6\text{H}_4)-\text{OH}$
- Benzoic acid and ethanol
- Terephthalic acid and ethylene glycol
- Benzoic acid and para $\text{HO}-(\text{C}_6\text{H}_4)-\text{OH}$

13. Biodegradable polymer which can be produced from glycine and aminocaproic acid is : [2015]

- PHBV
- Buna - N
- Nylon 6, 6
- Nylon 2- nylon 6

14. Caprolactum is used for the manufacture of : [2015 RS]

- Nylon - 6
- Teflon
- Terylene
- Nylon - 6,6

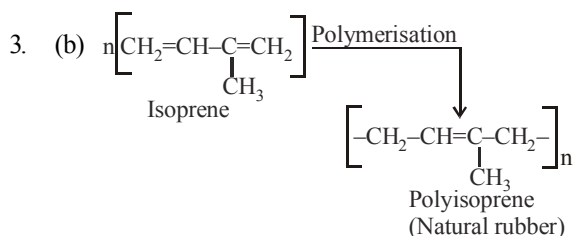
15. Natural rubber has [2016]

- all cis-configuration
- all trans-configuration
- alternate cis-and trans-configuration
- random cis-and trans-configuration

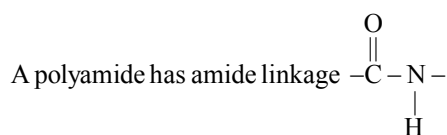
Hints & Solutions

EXERCISE - 1

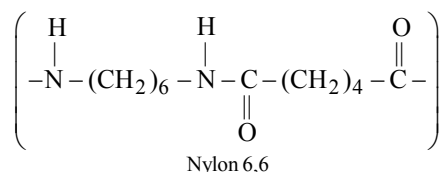
- (c) Nylon is a polymer of adipic acid and hexamethylenediamine thus it contains nitrogen. Polyvinyl chloride is a polymer of vinyl chloride. It does not contain nitrogen. Bakelite is a resin of formaldehyde and phenol. It does not contain nitrogen. Terylene is a polymer of ethylene glycol and terephthalic acid. It does not contain nitrogen. It is also called *dacron*.
- (b) Elastomers are the polymers having very weak intermolecular forces of attraction between the polymeric chains. The weak forces permit the polymer to be stretched.



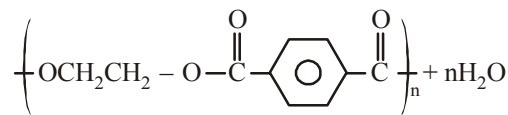
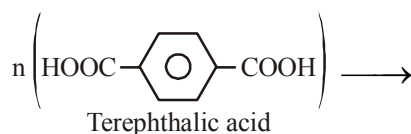
- (d) The given compound is a copolymer of hexamethylene diamine and adipic acid. It is actually Nylon-66.
- (d) Bakelite is a thermosetting polymer. On heating it becomes hard and infusible thus cannot be remoulded.
- (a) Polymers which form from condensation polymerisation are called condensation polymers. Dacron is a condensation polymer of terephthalic acid and ethylene glycol.
- (b) Glyptal is not a polyamide



Example



- (c) Ebonite is a hard highly vulcanized rubber, containing 20-25% sulphur.
 - (b) Nylon is a condensation polymer
 - (a) The polymer of ethylene glycol and terephthalic acid is known as terylene or dacron.
- $n(\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}) +$
Ethylene glycol

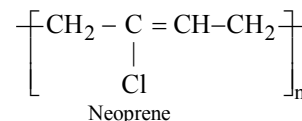
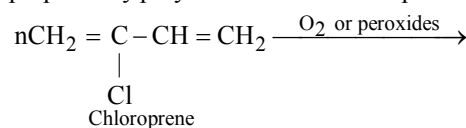


Terylene or Dacron

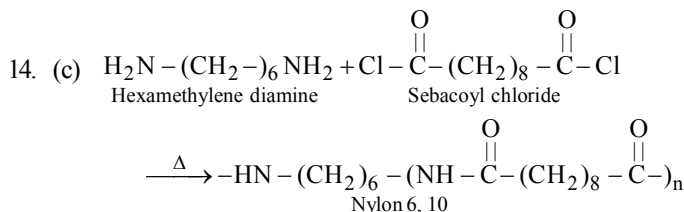
It is a condensation polymer.

[Note: Now a days dimethyl terephthalate is used instead of terephthalic acid. This is due to the fact that terephthalic acid is non-volatile and very slightly soluble in most of the solvents. Dimethyl terephthalate on the other hand, can be purified by distillation very easily]. Thus, option (a) is correct.

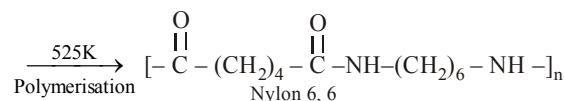
- (c) Nylon is a general name for all synthetic fibres forming polyamides.
- (a) PVC is an example of thermoplastic polymer.
- (a) The synthetic polymer neoprene (polychloroprene) is prepared by polymerisation of chloroprene.



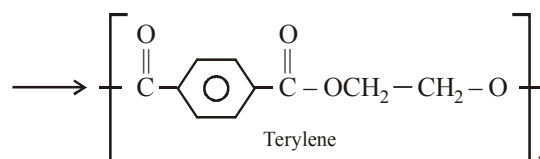
This is inferior to natural rubber but is more resistant to aerial oxidation and to other solvents.



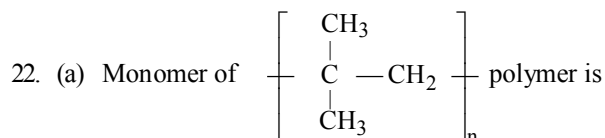
- (b) Since proteins, cellulose and RNA control various activities of plants and animals, they are called biopolymers.
- (d)
- (b)
- (d) Urotropine is used as antibiotic for urinary tract infection.
- (b) $n\text{HOOC}(\text{CH}_2)_4\text{COOH} + n\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$
adipic acid Hexamethylene diamine



- (d) Terylene is prepared by condensing terephthalic acid and ethylene glycol



21. (d)

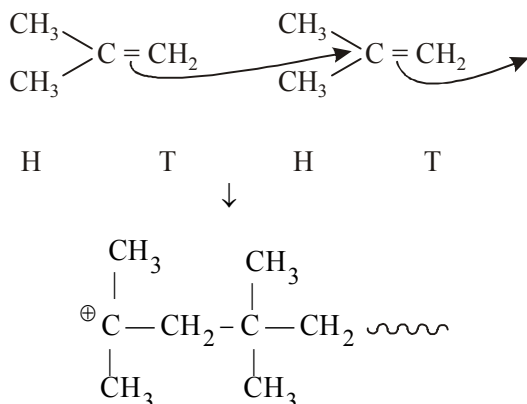


2-methylpropene.

23. (b) Acrilan is a polyacrylonitrile (PAN).

24. (b)

25. (a) Addition of monomers follows isoprene rule



26. (d) Orlon is a trade name of polyacrylonitrile

27. (d) P.V.C. (Polyvinyl chloride) is formed by polymerisation of vinyl chloride, $\text{CH}_2=\text{CHCl}$, whose IUPAC name is 1-chloroethene

28. (d)

29. (b)

30. (c)

31. (c) Polythene is a linear polymer

32. (c) $\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$

For synthetic polymer, $\text{PDI} > 1$

$$\therefore \overline{M}_w > \overline{M}_n$$

33. (d)

34. (b) Glyptal is used in preparation of lacquers.

35. (a) Ethene on free radical polymerisation gives low density polythene.

36. (a)

37. (b) PMMA and polycarbonate is used in bullet proof glass

38. (d) Acrylonitrile is the monomer used in the preparation of orlon.

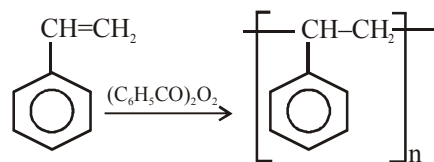
39. (b) Glyptal is an alkyd resin obtained from polyhydric alcohols and polybasic organic acids or their anhydrides. They are used for surface coatings.

40. (a) Also known as PMMA. It is a transparent, excellent light transmitter and its optical clarity is better than glass so it is used in the preparation of lenses for eyes.

41. (d)

42. (a) SARAN, a polymer of vinyl chloride ($\text{CH}_2=\text{CHCl}$) and vinylidene chloride, is used for making synthetic hair wigs.

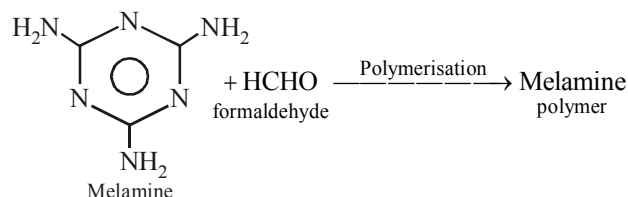
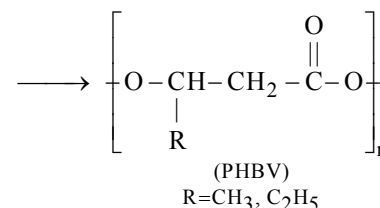
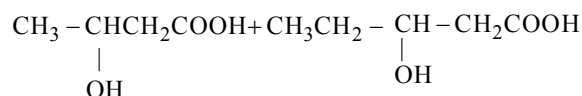
43. (c) Polystyrene is manufactured by polymerization of styrene in presence of benzoyl peroxide.



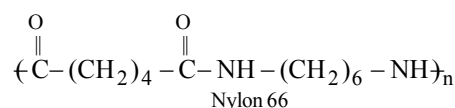
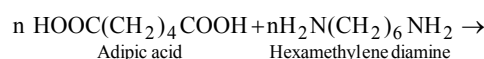
44. (d) Cellulose acetate has been used in the manufacture of non inflammable photographic films.

45. (d) Nylon tyre cord is made from high tenacity continuous filament yarn by twisting and plying.

46. (d) The unbreakable plastic household crockery is made from copolymer of formaldehyde (HCHO) and melamine.

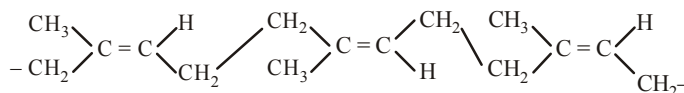
47. (d) Polyhydroxybutyrate-co- β -hydroxyvalerate or PHBV is a biodegradable polymer and thus it can be used as biomaterials in orthopaedic devices and in controlled drug release.

48. (d) Copolymer of adipic acid (6C) and hexamethylene diamine (6C).



It has high tenacity and elasticity. It is resistant to abrasion and not affected by sea water. It is used for reinforcement of rubber tyres, manufacture of parachute, safety belts, carpets and fabrics.

49. (b)

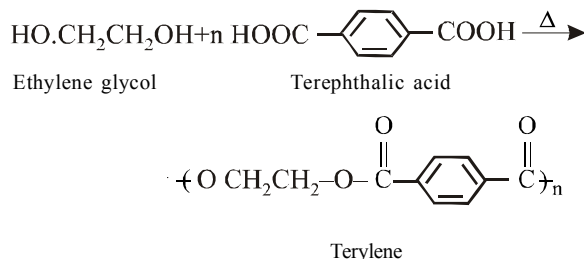


Natural rubber

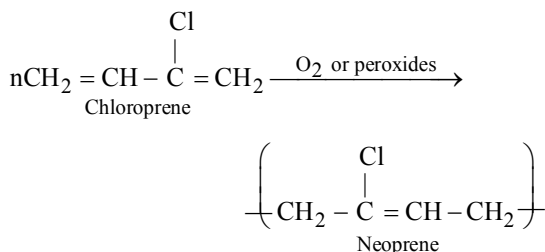
(All cis configuration)

All statements except (b) are correct

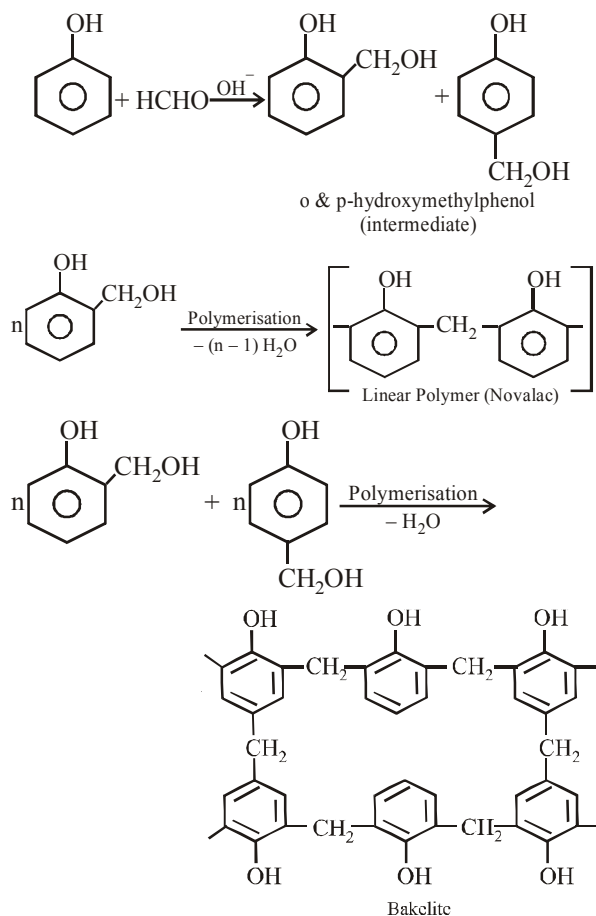
50. (a) Neoprene is a polymer of chloroprene
(2-chloro-1,3-butadiene).
51. (a) Polyesters are condensation polymers of a dibasic acid and a diol. e.g., Terylene



52. (d) Neoprene is an addition polymer of isoprene.



53. (b) Nylon (polyamides) are fibres.
54. (d) Phenol and formaldehyde undergo condensation polymerisation under two different conditions to give a cross linked polymer called bakelite.

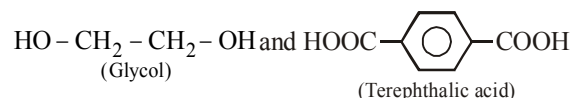


55. (a)

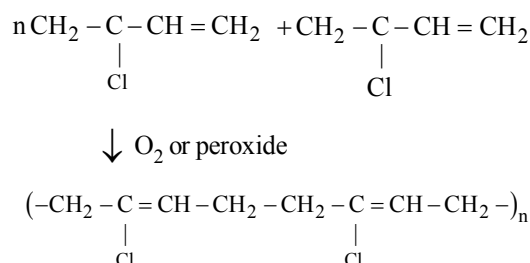
56. (b) Average number molecular weight $\overline{M}_n = 30,000$
Average mass molecular weight $\overline{M}_w = 40,000$
Polydispersity index (PDI) = $\frac{\overline{M}_w}{\overline{M}_n} = \frac{40,000}{30,000} = 1.33$

57. (b)

58. (c) Terylene is made from glycol and Terephthalic acid



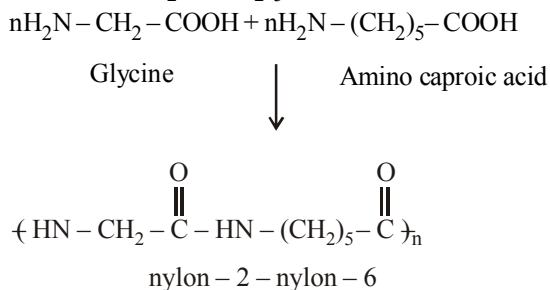
59. (a) The synthetic polymer neoprene is prepared by polymerisation of chloroprene.



Polychloroprene of Neoprene

This is inferior to natural rubber but is more resistant to aerial oxidation and to other solvents.

60. (c) Teflon is non-inflammable and resistant to heat so it is used in coating, particularly in non-sticking frying pans.
61. (a) SF_6 is used in the vulcanisation of rubber. Sulphur is heated with polymer to introduce cross-linking and thus, form tough polymer.
62. (a) Vulcanization is a process in which natural rubber is treated with sulphur and certain organic compounds which accelerate the reaction between the rubber and sulphur. Thus about 5% S is used for making tyre rubber, 20-25% S for making ebonite and 30% S for making battery case rubber.
63. (b) Perlon is Nylon-6. It is prepared from a single monomer having a potential amino group at one end and a potential carbonyl group at other end.
64. (c)
65. (b) Biodegradable polymer is Nylon-2- Nylon-6 which is copolymer of glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) and amino caproic acid ($\text{H}_2\text{N}-(\text{CH}_2)_5-\text{COOH}$).

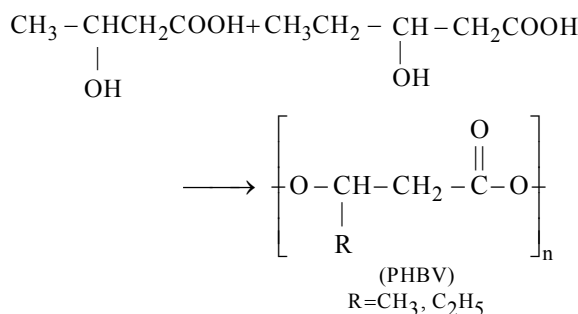


66. (b) Buna-N is a copolymer of butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) and acrylonitrile ($\text{CH}_2=\text{CHCN}$).

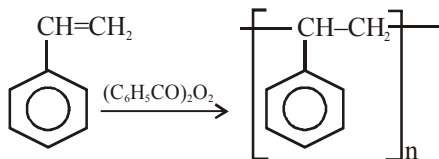
67. (b) Nylon 6, 6 has amide linkage capable of forming hydrogen bonding.
68. (d) Nylon and cellulose, both have intermolecular hydrogen bonding, polyvinyl chloride has dipole-dipole interactions, while natural rubber has van der Waal forces which are weakest.

69. (d)

70. (d) Polyhydroxybutyrate-co- β -hydroxyvalerate or PHBV is a biodegradable polymer and thus it can be used as biomaterials in orthopaedic devices and in controlled drug release.



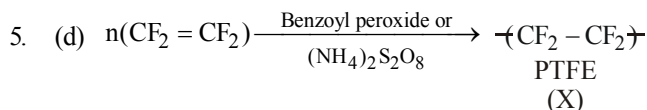
71. (c) Polystyrene is manufactured by polymerization of styrene in presence of benzoyl peroxide.



72. (c) Bakelite is a cross linked polymer.
73. (d) Acrylonitrile is the monomer used in the preparation of orlon.
74. (b) Glyptal is used in preparation of lacquers.
75. (c)

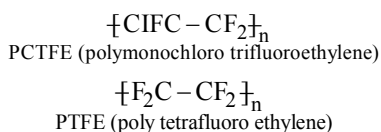
EXERCISE - 2

1. (c) Glycine and amino caproic acid are the monomers used for the preparation of nylon-2-nylon-6.
2. (a) Polymerisation starts either by condensation or addition reactions between monomers
3. (b) Nylon is a polyamide polymer
4. (b) Nylon 6, 6 has amide linkage capable of forming hydrogen bonding.

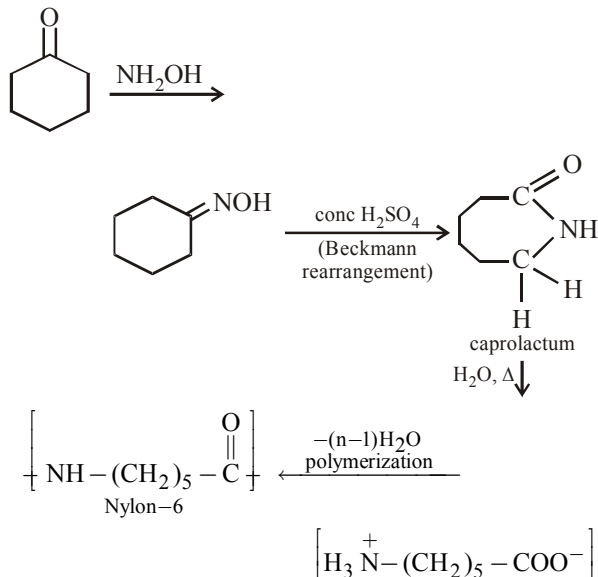


Here X is polytetrafluoroethylene. So, none of these i.e., option (d) is correct choice.

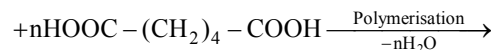
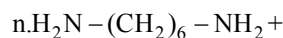
6. (c) PCTFE and PTFE both have same carbon backbone.



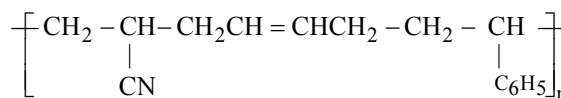
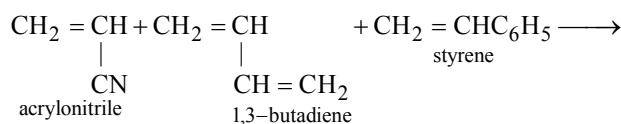
7. (d) Nylon-6 can be manufactured from



8. (b) SBR (styrene-butadiene) is a synthetic rubber.
9. (b)
10. (b) The condensation polymerisation of hexamethylene diamine and adipic acid is done in solution form by interface technique. In this liquid nylon polymer is obtained.



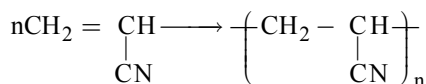
11. (d) Polymethyl methacrylate is hard, fairly rigid. It is used for optical lenses.
12. (d) Generally high boiling esters or haloalkanes act as plasticizer.
13. (b) In addition homopolymers such as teflon, empirical formula resembles with monomer.
14. (a) ABS is acrylonitrile-butadiene-styrene rubber which is obtained by copolymerisation of acrylonitrile, 1, 3-butadiene and styrene.



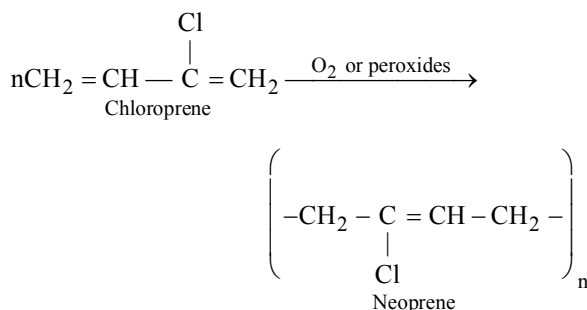
ABS rubber

15. (c) Nylon fibres are made up of polyamides. Dacron and orlon are made up of polyester. Rayon is artificial silk made up of polysaccharides.
16. (d) Polyacetylene, due to presence of double bonds, is a conducting polymer.

17. (a) Orlon is polymer of acrylonitrile $\left(\begin{array}{c} \text{CH}_2 = \text{CH} \\ | \\ \text{CN} \end{array} \right)_n$



18. (a) Dacron is a polyester and is the condensation polymer of ethylene glycol and terephthalic acid. It is crease resistant
19. (a)
20. (c) Nylon 6, 6 is a fibre with hydrogen bonds thus have strongest intermolecular forces. Buna-S is a elastomer whereas polythene is thermoplastic. the intermolecular forces of attraction in thermoplastics is intermediate between elastomer and fibres. Therefore forces in elastomers are weakest.
21. (a) Neoprene is a polymer of chloroprene. Hence, correct representation is

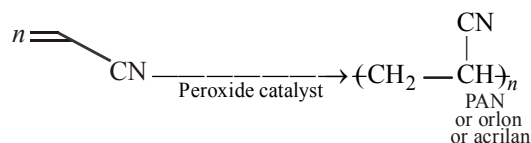


22. (b) Vulcanisation is a process of treating natural rubber with sulphur or some compounds of sulphur under heat so as to modify its properties. This cross-linking give mechanical strength to the rubber.
23. (c) Bakelite can be heated only once.
24. (d) The time of vulcanisation is reduced by adding accelerators and activators.
25. (b) Due to the presence of strong C-F bonds, teflon has high thermal stability and chemical inertness.

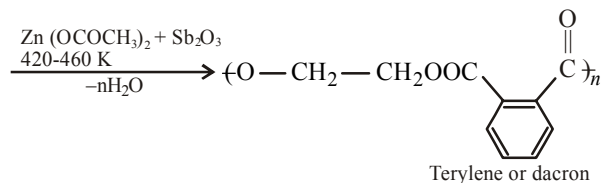
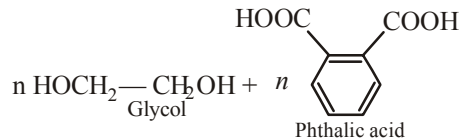
EXERCISE -3

Exemplar Questions

- (d) Glycogen is a polymer of glucose found in liver, brain and muscles of animals.
- (a) cis-polyisoprene is a synthetic polymer.
- (b) The commercial name of polyacrylonitrile is orlon (acrilan).

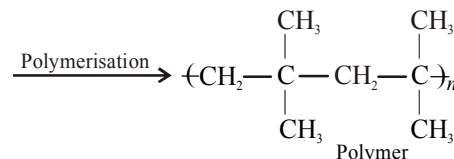


4. (c) PHBV is an example of biodegradable polymer.
5. (a)



6. (d) Low density polythene has slightly branched structure.

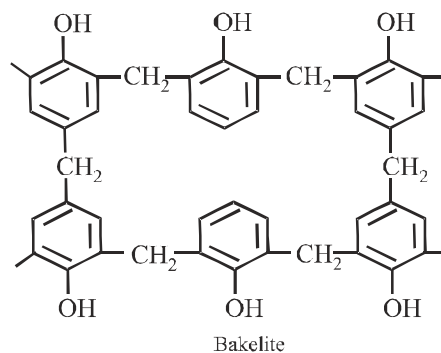
7. (a) $n\text{CH}_2 = \underset{\text{Monomer}}{\text{C}} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$



8. (d) $\begin{array}{c} \text{H} \\ | \\ \text{N} \\ | \\ \text{C} = \text{O} \\ | \\ \text{CH}_2 \end{array} \xrightarrow[\text{-(n-1)H}_2\text{O}]{\Delta, \text{Polymerisation}} \left[\text{NH} - (\text{CH}_2)_5 - \text{C}(=\text{O}) \right]_n$
- Caprolactum Nylon-6

NEET/AIPMT (2013-2017) Questions

9. (b) $\text{CH}_2 = \underset{\text{Cl}}{\text{C}} - \text{CH} = \text{CH}_2$ (chloroprene) is the monomer of neoprene.
10. (b) Nylon is a synthetic polyamide polymer.
11. (d) Thermosetting polymers undergo chemical changes when heated and set to hard mass when cooled e.g. Bakelite.

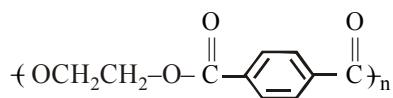


12. (c)



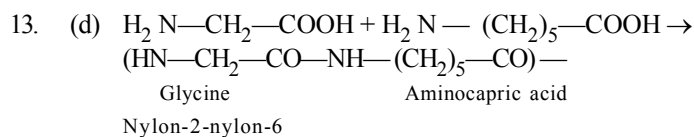
Ethylene glycol

Terephthalic acid

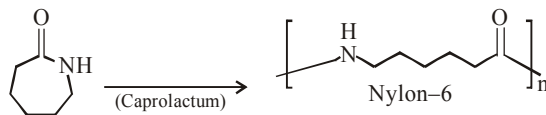


Terylene

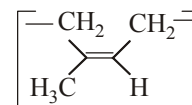
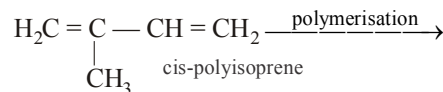
It is resistant to mineral and organic acids. It is used for blending with wool to provide better crease, in safety helmets and aircraft battery boxes.



14. (a)



15. (a) Natural rubber is found to be a polymer of cis-isoprene i.e. it is cis-polyisoprene



Isoprene

Chapter 30

Chemistry in Everyday Life

Drugs are chemicals of low molecular masses ($\sim 100 - 500$ u). They interact with macromolecular targets and produce a biological response. When the biological response is therapeutic and useful, these chemicals are called medicines and are used in diagnosis, prevention and treatment of diseases. If taken in doses higher than those recommended, most of the drugs used as medicines are potential poisons. *Use of chemicals for therapeutic effect is called chemotherapy.*

Note : Medicine is a chemical substance which cures the disease and is safe to use it does not cause any addiction whereas drug is a chemical substance which cures disease but it causes addiction and has serious side effects.

CLASSIFICATION OF DRUGS

- On the basis of pharmacological effect.
For example : analgesics have pain killing effect, antiseptics kill or arrest the growth of microorganisms.
- On the basis of drug action i.e., action of drug on a particular biochemical process. For example : all antihistamines inhibit the action of the compound, histamine.
- On the basis of chemical structure of the drug.
- On the basis of molecular targets. Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids. These are called target molecules or drug targets. Drugs possessing some common structural features may have same mechanism of action on targets.

TYPES OF DRUGS

Antacids

They are used for the treatment of acidity (due to over production of acid in stomach).

For example : NaHCO_3 , a mixture of $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$.

Metal hydroxides are better alternatives because they are insoluble and do not increase the pH above neutrality.

Antihistamines

The drugs which have been used to fight allergy are called **antihistamines**. These are so called because they check the production of histamines. Thus, antihistamines are widely used for treatment to hay fever, conjunctivitis, nasal discharges, irradiation sickness, nausea in pregnancy and post operative vomiting. For example : cimetidine, brompheniramine, terfenadine.

Neurologically Active Drugs

(i) Tranquilizers:

They are used for treatment of stress, and mild or even severe mental diseases. They relieve anxiety, stress, irritability or excitement by inducing a sense of well-being.

They also form an essential component of sleeping pills.

Example:

- Noradrenaline** plays a role in mood changes.
- Chlordiazepoxide** and **meprobamate** are suitable for relieving tension.
- Equanil** is used in controlling depression and hypertension.
- Barbiturates**, i.e., derivatives of barbituric acid like veronal, amytal, nembutal, luminal and seconal. They are hypnotic i.e., sleep producing agents.

(ii) Analgesics : They reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system.

Non-narcotic analgesics

- They relieve skeletal pain, reduce fever (antipyretic).
Ex: aspirin, paracetamol
- Aspirin is used in prevention of heart attacks due to anti blood clotting action.

Narcotic analgesics

- Relieve pain and produce sleep.
- Chiefly used for relief of postoperative pain, cardiac pain and pains of terminal cancer and in child birth.
Ex: morphine, heroin, codeine

Antimicrobials

They tend to destroy / prevent development or inhibit the pathogenic action of microbes such as bacteria, fungi, virus or other parasites selectively. Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

Antibiotics

They are used to treat infections due to their low toxicity for humans and animals. An antibiotic refers to a substance produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys micro-organisms by intervening in their metabolic processes.

For example : sulphanilamide, sulphapyridine, etc.

Types of antibiotics

Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be **broad spectrum antibiotics**. For example : chloramphenicol, vancomycin, Ampicilin, Amoxycilin, etc.

Antibiotics effective few Gram-positive or Gram-negative bacteria are **narrow spectrum antibiotics**. For example : penicillin.

If effective against a single organism or disease, they are referred as **limited spectrum antibiotics**.

Antiseptic and disinfectants

Antiseptics are applied to living tissues such as wounds, cuts, ulcers and diseased skin surfaces.

Examples :

- furacine, soframicine, dettol (mixture of chloroxylenol and terpeniol)
- Bithional is added to soaps to impart antiseptic properties.
- Tincture of iodine (2-3% solution of iodine in alcohol-water mixture) is applied on wounds.
- Iodoform is also used on wounds.
- Boric acid in dilute aqueous solution is weak antiseptic for eyes.

Disinfectants are applied to inanimate objects such as floors, drainage system, instruments etc. For example : Chlorine in concentration of 0.2 to 0.4 ppm in aqueous solution and SO_2 in very low concentrations, are disinfectants. Same substances can act as an antiseptic as well as disinfectant by varying the concentration. For ex: 0.2% solution of phenol is an antiseptic while its 1% solution is disinfectant.

Antifertility Drugs

They are also called birth control pills. They essentially contain a mixture of synthetic estrogen and progesterone. Both of these compounds are hormones.

Example : Norethindrone, ethynylestradiol (novestrol)

Antimalarials

Chemical substances which are used to bring down the body temperature during malaria fever are called *antimalarials*. These are *Chloroquine*, *Paraquine*, *Primaquine* etc.

CHEMICALS IN FOOD

Chemicals are added to food for

- their preservation
- enhancing their appeal
- adding nutritive value in them.

Artificial Sweetening Agents

These are of use to diabetic patients and people who need to control intake of calories.

For example :

- saccharin (ortho-sulphobenzimide)
- aspartame (added to cold foods and soft drinks as it is unstable at cooking temperature)
- alitame
- sucralose (trichloro derivative of sucrose)

Food Preservatives

They prevent spoilage of food due to microbial growth.

For example : table salt, sugar, vegetable oils, salts of sorbic acid and propanoic acid and sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$)

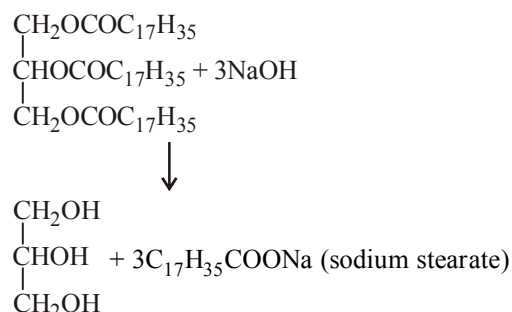
Note : Sodium benzoate is used in limited quantities and is metabolised in the body.

CLEANSING AGENTS

Two types of detergents are used as cleansing agents: soaps and synthetic detergents. They improve cleansing properties of water by helping in removal of fats which bind other materials to the fabric or skin.

Soaps

They are sodium or potassium salts of long chain fatty acids, ex: stearic, oleic and palmitic acids. Only Na and K-soaps are soluble in water and are used for cleaning purposes. K-soaps are comparatively soft to the skin than Na-soaps. Alkaline hydrolysis of oils or fats by NaOH or KOH gives glycerol and sodium or potassium salt of the fatty acid. This reaction is known as **saponification**.



Soaps do not work in hard water. This is because hard water contains calcium and magnesium ions. These ions form insoluble Ca- and Mg soaps when Na or K soaps are dissolved in hard water. These insoluble soaps separate as scum in water and are useless as cleansing agents.

Note : Hair washed with hard water looks dull due to sticky ppt. Dye does not absorb evenly or cloth washed with soap using hard water because of gummy mass.

Synthetic Detergents

They can be used in both soft and hard water as they give foam even in hard water.

They are classified into three categories:

(i) Anionic detergents:

These are sodium salts of sulphonated long chain alcohols or hydrocarbons. The anionic part of the molecule is involved in cleansing action. They are used for household work and also in toothpastes.

For example : sodium laurylsulphate, sodium salts of alkylbenzene-sulphonates.

(ii) Cationic detergents :

These are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cationic part possess a long hydrocarbon chain and a positive charge on N-atom. Hence, the name. They have germicidal properties and are expensive.

For example : cetyltrimethyl ammonium bromide, used in hair conditioners.

(iii) Non-ionic detergents

They do not contain any ion in their composition. Liquid dishwashing detergents are non-ionic type.

ex: $\text{CH}_3(\text{CH}_2)_{16}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$

Note : As the hydrocarbon chain of the detergent becomes branched, degradation becomes difficult which leads to their accumulation and hence pollution.

CONCEPT MAP

CHEMISTRY IN EVERYDAY LIFE

Classification of Drugs

- **Based on pharmacological effect :** It is useful for doctors.
- **Based on drug action :** Drugs which act on a particular biochemical process are kept under one class.
- **Based on Chemical Structure** Drugs having common structural features are grouped together in one class
- **Based on molecular target** useful for medicinal chemists.

Different types of Drugs

- **Antacids :** Control stomach acidity e.g. $\text{Mg}(\text{OH})_2$
- **Antihistamines :** Used to treat allergy e.g. cetirizine
- **Tranquilizers :** Used for treatment of stress and mental diseases e.g. equanil
- **Analgesics :** For relieving pain e.g. aspirin
- **Antibiotics :** (a) Bactericidal destroy microbes e.g. penicillin
(b) Bacteriostatic : Inhibit growth of microbes e.g. Chloramphenicol
- **Antiseptics :** May kill or stop growth of microbes e.g. dettol.
- **Antifertility :** Control menstrual cycle and ovulation of females
- **Artificial Sweeteners :** e.g. Saccharin, Alitame etc.
- **Food Preservatives :** Prevent decaying of food e.g. sodium Benzoate.

Soaps and Detergents

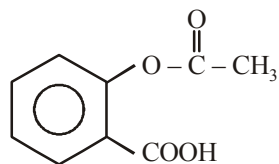
- Soaps**
- Sodium or Potassium salts of long chain fatty acids
 - **Types of Soaps**
 - (a) Toilet soaps
 - (b) Floating soaps
 - (c) Medicated soaps
 - (d) Transparent soaps
 - (e) Shaving soaps
 - (f) Laundry soaps

- Detergents**
- Sodium salts of alkylbenzene sulphonic acids.
 - **Types of detergents**
 - (a) Anionic
 - (b) Cationic
 - (c) Non-ionic

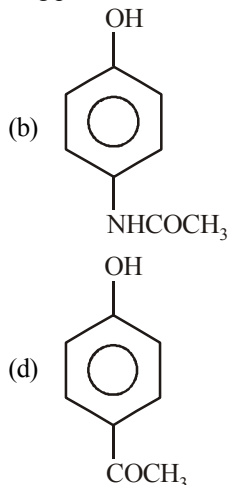
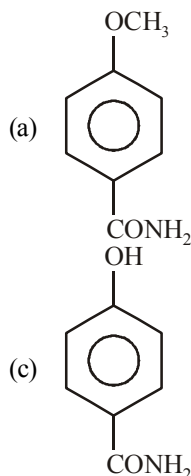
EXERCISE - 1

Conceptual Questions

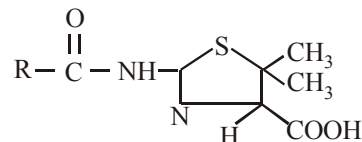
- Synthetic detergents are more effective in hard water than soaps because
 - they are non-ionic
 - their Ca^{++} and Mg^{++} salts are insoluble in water
 - their Ca^{++} and Mg^{++} salts are water soluble
 - they are highly soluble in water
- Aspirin is
 - antibiotic
 - antipyretic
 - sedative
 - psychedelic
- An antipyretic is
 - quinine
 - paracetamol
 - luminal
 - piperazine
- Salol can be used as
 - antiseptic
 - antipyretic
 - analgesic
 - None of these
- Which of the following is used as a 'morning after pill'?
 - Norethindrone
 - Ethynylestradiol
 - Mifepristone
 - Bithional
- Various phenol derivatives, tincture of iodine (2–3%) I_2 in (water / alcohol) and some dyes like methylene blue are
 - antiseptics
 - disinfectants
 - analgesics
 - antipyretics
- The insecticide containing 99% γ – isomer of benzene hexachloride is known as
 - lindane
 - TNT
 - malathion
 - methoxychlor
- The following compound is used as



- an anti-inflammatory compound
 - analgesic
 - hypnotic
 - antiseptic
- The correct structure of the drug paracetamol is

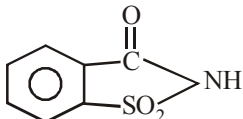
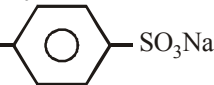


- The general structure of penicillin is



In ampicillin R =

- $\text{CH}_3(\text{CH}_2)_6-$
 - $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$
 -
 -
- Amoxillin is semi-synthetic modification of
 - penicillin
 - streptomycin
 - tetracycline
 - chloroamphenicol
 - Which of these is a hypnotic
 - metalddehyde
 - acetaldehyde
 - paraldehyde
 - None of these
 - Barbituric acid and its derivatives are well known
 - antipyretics
 - analgesics
 - antiseptics
 - traquillizers
 - The drug used for prevention of heart attacks is
 - aspirin
 - valium
 - chloramphenicol
 - cephalosprin
 - Serotonin is usually used as :
 - analgesic
 - tranquilizer
 - antiseptic
 - antioxidant
 - Omeoprazole and lansoprazole are used as –
 - antifertility
 - antiallergic
 - antibiotic
 - antacid
 - Sulpha drugs are used for
 - precipitating bacteria
 - removing bacteria
 - decreasing the size of bacteria
 - stopping the growth of bacteria
 - Which one of the following is an antihistamine?
 - Iproniazid
 - Salvarsan
 - Zantac
 - Chloramphenicol
 - Chloramine-T is a/an
 - disinfectant
 - antiseptic
 - analgesic
 - antipyretic
 - Which of the following is a hypnotic drug?
 - luminal
 - salol
 - catechol
 - chemisol
 - Streptomycin is effective in the treatment of
 - tuberculosis
 - malaria
 - typhoid
 - cholera

22. An antibiotic with a broad spectrum
 (a) kills the antibodies
 (b) acts on a specific antigen
 (c) acts on different antigens
 (d) acts on both the antigens and antibodies
23. Chloramine-T is used as an :
 (a) analgesic (b) antiseptic
 (c) antipyretic (d) anti-inflammatory
24. Which of the following is not an antiseptic drug?
 (a) Iodoform (b) Dettol
 (c) Gammexane (d) Genation violet
25. A medicine which promotes the secretion of urine is called
 (a) uretic (b) monouretric
 (c) diuretic (d) triuretic
26. Veronal, a barbiturate drug is used as
 (a) anaesthetic (b) sedative
 (c) antiseptic (d) None of these
27. A drug effective in the treatment of pneumonia, bronchitis, etc, is
 (a) streptomycin (b) chloramphenicol
 (c) penicillin (d) sulphaguanidine
28. The use of chemicals for treatment of diseases is called as
 (a) isothermotherapy (b) angiotherapy
 (c) physiotherapy (d) chemotherapy
29. Select the incorrect statement.
 (a) Equanil is used to control depression and hypertension.
 (b) Mifepristone is a synthetic steroid used as "morning after pill".
 (c) 0.2 per cent solution of phenol is an antiseptic while its 1.0 per cent solution is a disinfectant.
 (d) A drug which kills the organism in the body is called bacteriostatic.
30. Terfenadine is commonly used as a/an
 (a) tranquilizer (b) antihistamine
 (c) antimicrobial (d) antibiotic
31. Structurally biodegradable detergent should contain
 (a) normal alkyl chain (b) branched alkyl chain
 (c) phenyl side chain (d) cyclohexyl side chain
32. Detergents are prepared by the action of H_2SO_4 on which of the following?
 (a) Cholesterol (b) Lauryl alcohol
 (c) Cyclohexanol (d) *p*-Nitrophenol
33. Arsenic containing medicine used for the treatment of syphilis, is
 (a) erythromycin (b) ofloxacin
 (c) tetracycline (d) salvarsan
34. Sodium alkyl benzene sulphonate is used as
 (a) soap (b) fertilizers
 (c) pesticides (d) detergents
35. Which is correct about vanillin?
 (a) A flavouring agent having vanilla flavour
 (b) *p*-hydroxy-*m*-methoxy benzaldehyde
 (c) A food additive
 (d) All of these
36. Which is correct about saccharin?
 (a) It is 
- (b) It is 600 times sweeter than sugar
 (c) It is used as sweetening agent
 (d) All of these
37. Which of the following acts as an antioxidant in edible oils
 (a) Vitamin B (b) Vitamin C
 (c) Vitamin D (d) Vitamin E
38. Which of the following is used as an antioxidant in food?
 (a) BTX (b) BHT
 (c) BHC (d) All the three
39. End of detergents have
 (a) ester group (b) sodium sulphate
 (c) aldehyde (d) amine group
40. Which one of the following is not a tranquilizer?
 (a) Equanil (b) Veronal
 (c) Salvarsan (d) Serotonin
41. Which of the following represents a synthetic detergent?
 (a) $\text{C}_{15}\text{H}_{31}\text{COOK}$
 (b) $\text{CH}_3[\text{CH}_2]_{16}\text{COONa}$
 (c) $\text{C}_{12}\text{H}_{25}$ 
 (d) None of these
42. Which of the following represents soap
 (a) $\text{C}_{17}\text{H}_{35}\text{COOK}$ (b) $\text{C}_{17}\text{H}_{35}\text{COOH}$
 (c) $\text{C}_{15}\text{H}_{31}\text{COOH}$ (d) $(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}$
43. Benzalkonium chloride is a
 (a) cationic surfactant and antiseptic
 (b) anionic surfactant and soluble in most of organic solvents
 (c) cationic surfactant and insoluble in most of organic solvents
 (d) cationic surfactant and antimalarial
44. Cetyltrimethyl ammonium bromide is a popular
 (a) anionic detergent (b) cationic detergent
 (c) non-ionic detergent (d) sweetener
45. Commonly used antiseptic 'Dettol' is a mixture of
 (a) *o*-chlorophenoxylenol + terpeneol
 (b) *o*-cresol + terpeneol
 (c) phenol + terpeneol
 (d) chloroxylenol + terpeneol
46. Which one of the following is employed as a tranquilizer drug?
 (a) Promethazine (b) Valium
 (c) Naproxen (d) Mifepristone
47. Which one of the following is employed as Antihistamine ?
 (a) Chloramphenicol (b) Diphenylhydramine
 (c) Norothindrone (d) Omeprazole
48. Aspirin is known as :
 (a) acetyl salicylic acid (b) phenyl salicylate
 (c) acetyl salicylate (d) methyl salicylic acid
49. Which one among the following is not an analgesic?
 (a) Ibuprofen (b) Naproxen
 (c) Aspirin (d) Valium
50. Further growth of cancerous cells in the body is arrested by
 (a) physiotherapy (b) chemotherapy
 (c) electrotherapy (d) psychotherapy

EXERCISE - 2

Applied Questions

- Which one of the following is not used as a filler in laundry soaps?
 - Sodium silicate
 - Glycerol
 - Sodium rosinate
 - Borax
- The drug which is effective in curing malaria is
 - quinine
 - aspirin
 - analgin
 - equanil
- Which of the following is a hallucinogenic drug?
 - Methedrine
 - Calmpose
 - LSD
 - Seconal
- Which one of the following is not a neurologically active drug?
 - Veronal
 - Bithionol
 - Equanil
 - Nardil
- Interferon is connected with
 - tonic
 - virus
 - carbohydrate
 - ore of iron
- Which of the following statements about aspirin is **not** true?
 - It is effective in relieving pain.
 - It is a neurologically active drug.
 - It has antiblood clotting action.
 - It belongs to narcotic analgesics.
- Which of the following is an alkaloid?
 - Nicotine
 - Piperine
 - Cocaine
 - All of these
- Phenacetin is used as
 - antipyretic
 - antiseptic
 - antimalarial
 - analgesic
- The artificial sweetener containing chlorine that has the appearance and taste as that of sugar and is stable at cooking temperature is
 - Aspartame
 - Saccharin
 - Sucrolose
 - Alitame
- Morphine is
 - an alkaloid
 - an enzyme
 - a carbohydrate
 - a protein
- A large number of antibiotics have been isolated from
 - Bacteria actinomycetes
 - Acids
 - Alkanals
 - Bacteria rhizobium
- An antibiotic contains nitro group attached to aromatic nucleus. It is
 - penicillin
 - streptomycin
 - tetracycline
 - chloramphenicol
- The cationic detergent that is used in hair conditioners is
 - sodium dodecylbenzene sulphonate
 - sodium lauryl sulphate
 - tetramethyl ammonium chloride
 - cetyltrimethyl ammonium bromide
- Placebo is often given to patients. It is
 - an antidepressant
 - a broad spectrum antibiotic
 - a sugar pill
 - a tonic
- Sulphaguanidine is used for
 - aysentery
 - urinary infections
 - antiseptic
 - antipyretic
- Salts of sorbic acid and propionic acid are used as
 - antioxidants
 - flavouring agents
 - food preservatives
 - nutritional supplements
- The structure given below is known as

 - Penicillin F
 - Penicillin G
 - Penicillin K
 - Ampicillin
- Consider the following antibiotics.
 - Erythromycin
 - Ofloxacin
 - Chloramphenicol
 - Penicillin
 - Tetracycline

The pair of bactericidal antibiotics is

 - i-iii
 - ii-iv
 - iii-v
 - i-iv

19. Match the chemicals in Column I with their uses in Column II.

	Column I		Column II
(A)	Sodium Perborate	(I)	Disinfectant
(B)	Chlorine	(II)	Antiseptic
(C)	Bithional	(III)	Milk bleaching agent
(D)	Potassium stearate	(IV)	Soap

- (a) A - I, B - II, C - III, D - IV
 (b) A - II, B - III, C - IV, D - I
 (c) A - III, B - I, C - II, D - IV
 (d) A - IV, B - I, C - II, D - III
20. Bithional is added to soap as an additive to function as a/an
 (a) softener (b) hardener
 (c) dryer (d) antiseptic

DIRECTIONS for Qs. 21 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

- (a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1

- (b) Statement-1 is true, Statement-2 is true ; Statement-2 is NOT a correct explanation for Statement-1
 (c) Statement-1 is true, Statement-2 is false
 (d) Statement-1 is false, Statement-2 is true
21. **Statement-1 :** The drugs which act on the central nervous system and help in reducing anxiety are called antibiotics.
Statement-2 : Pencillin is an antibiotic.
22. **Statement-1 :** Equanil is a tranquilizer.
Statement-2 : Equanil is used to cure depression and hypertension.
23. **Statement-1 :** Tetracycline is a broad spectrum antibiotic.
Statement-2 : Tetracyclin is effective against a number of types of bacteria, large viruses and typhus fever.
24. **Statement-1 :** Antiseptics are applied to living tissues.
Statement-2 : Iodine is a powerful antiseptic.
25. **Statement-1 :** Sedatives are given to patients who are mentally agitated and violent.
Statement-2 : Sedatives are used to suppress the activities of central nervous system.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

- Which of the following statements is not correct?
 - Some antiseptics can be added to soaps
 - Dilute solutions of some disinfectants can be used as antiseptic
 - Disinfectants are antimicrobial drugs
 - Antiseptic medicines can be ingested
- Which is the correct statement about birth control pills?
 - Contain estrogen only
 - Contain progesterone only
 - Contain a mixture of estrogen and progesterone derivatives
 - Progesterone enhances ovulation
- Which statement about aspirin is not true?
 - Aspirin belong to narcotic analgesics
 - It is effective in relieving pain
 - It has antiblood clotting action
 - It is a neurologically active drug
- The most useful classification of drugs for medicinal chemists is
 - on the basis of chemical structure
 - on the basis of drug action
 - on the basis of molecular targets
 - on the basis of pharmacological effect
- Which of the following statements is correct?
 - Some tranquilizers function by inhibiting the enzymes which catalyse the degradation of noradrenaline
 - Tranquilizers are narcotic drugs
 - Tranquilizers are chemical compounds that do not affect the message transfer from nerve to receptor
 - Tranquilizers are chemical compounds that can relieve pain and fever
- Salvarsan is arsenic containing drug which was first used for the treatment of
 - syphilis
 - typhoid
 - meningitis
 - dysentery
- A narrow spectrum antibiotic is active against
 - gram positive or gram negative bacteria
 - gram negative bacteria only
 - single organism or one disease
 - both gram positive and gram negative bacteria
- The compound that causes general antidepressant action on the central nervous system belong to the class of
 - analgesics
 - tranquilizers
 - narcotic analgesics
 - antihistamines

9. Compound which is added to soap to impart antiseptic properties is
- sodium lauryl sulphate
 - sodium dodecylbenzenesulphonate
 - rosin
 - bithional
10. Equanil is
- artificial sweetener
 - tranquilizer
 - antihistamine
 - antifertility drug
11. Which of the following enhances leathering property of soap?
- Sodium carbonate
 - Sodium rosinate
 - Sodium stearate
 - Trisodium phosphate
12. Glycerol is added to soap. It functions
- as a filler
 - to increase leathering
 - to prevent rapid drying
 - to make soap granules
13. Which of the following is an example of liquid dishwashing detergent?
- $\text{CH}_3(\text{CH}_2)_{10}-\text{CH}_2\text{OSO}_3^- \text{Na}^+$
 - $\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_5-\text{CH}_2\text{CH}_2\text{OH}$
 - $\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3^- \text{Na}^+$
 - $\left[\text{CH}_3(\text{CH}_2)_{15}-\text{N}(\text{CH}_3)_3 \right]^+ \text{Br}^-$
14. Polyethyleneglycols are used in the preparation of which type of detergents?
- Cationic detergents
 - Anionic detergents
 - Non - ionic detergents
 - Soaps
15. Which of the following is not a target molecule for drug function in body?
- Carbohydrates
 - Lipids
 - Vitamins
 - Proteins
16. Which of the following statements is not true about enzyme inhibitors?
- Inhibit the catalytic activity of the enzyme
 - Prevent the binding of substrate
 - Generally a strong covalent bond is formed between an inhibitor and an enzyme
 - Inhibitors can be competitive or non - competitive
17. Which of the following chemicals can be added for sweetening of food items at cooking temperature and does not provides calories?
- Sucrose
 - Glucose
 - Aspartame
 - Sucralose
18. Which of the following will not enhance nutritional value of food?
- Minerals
 - Artificial sweeteners
 - Vitamins
 - Amino acids

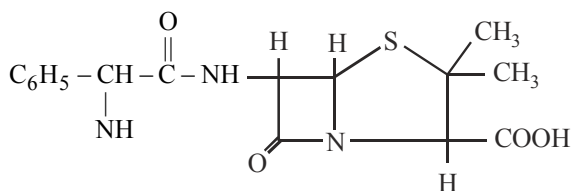
NEET/AIPMT (2013-2017) Questions

19. Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following statements is not true: [2013]
- Chlorine and iodine are used as strong disinfectants.
 - Dilute solutions of boric acid and hydrogen peroxide are strong antiseptics.
 - Disinfectants harm the living tissues.
 - A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant.
20. Dettol is the mixture of [1996, NEET Kar. 2013]
- Terpineol and Bithionol
 - Chloroxylenol and Bithionol
 - Chloroxylenol and Terpineol
 - Phenol and Iodine
21. Artificial sweetner which is stable under cold conditions only is :- [2014]
- Saccharine
 - Sucralose
 - Aspartame
 - Alitame
22. Bithional is generally added to the soaps as an additive to function as a/an : [2015]
- Dryer
 - Buffering agent
 - Antiseptic
 - Softner
23. Which of the following is an analgesic? [2016]
- Novalgin
 - Penicillin
 - Streptomycin
 - Chloromycetin
24. Mixture of chloroxylenol and terpineol acts as: [2017]
- antiseptic
 - antipyretic
 - antibiotic
 - analgesic

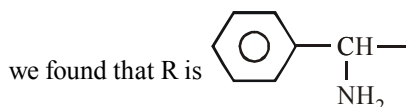
Hints & Solutions

EXERCISE - 1

- (c) Structural features of soaps and detergents are almost same except that the polar end in detergents is $-\text{OSO}_3^- \text{Na}^+$ while in soaps polar end is $-\text{COO}^- \text{Na}^+$. Detergents have an advantage over soaps that its polar end sulphate and sulphonate retain their efficiency in hard water, since the corresponding Ca and Mg salts are soluble. Being salts of strong acids, they yield neutral solution, in contrast, to the soaps, which being salts of weak acids yield slightly alkaline solutions.
- (b) Aspirin is antipyretic i.e., a drug which is responsible for lowering the temperature of feverish organism to normal, other antipyretic drugs are Paracetamol, Phenacetin.
- (b) Paracetamol is an antipyretic
- (a) Salol is Phenyl Salicylate used as antiseptic.
- (c) It is correct answer.
- (a) Antiseptic drugs cause destruction of micro-organism that produce septic disease e.g. Dettol, Savlon, Boric acid, Phenol, Iodoform, KMnO_4 and some dye such as methylene blue, gentian violet.
- (a) Lindane or gammexane is γ isomer of BHC.
- (b) It is acetyl salicylic acid i.e., aspirin analgesic and antipyretic.
- (b) Paracetamol act as analgesic and antipyretic.
- (d) Ampicillin is a semi-synthetic modification of penicillin. Chemical structure of ampicillin is

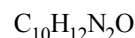
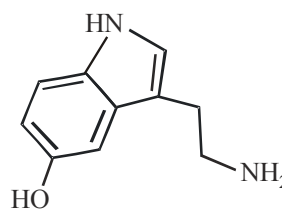


So, on comparing it with general structure of penicillin



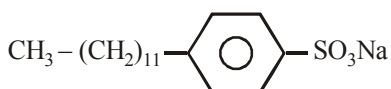
- (a) Amoxicillin is semisynthetic modification of Penicillin
- (c) Paraldehyde is a hypnotic.
- (d)

- (a) Due to anti-blood clotting action of aspirin, it is used to prevent heart attack.
- (a) Serotonin is 5-hydroxytryptamine (or 5-HT) is a monoamine neurotransmitter synthesized in serotonergic neurons in the central nervous system (CNS) and enterochromaffin cells in the gastrointestinal tract of animals including humans. Cerebral serotonin has anti-depressant and analgesic effects and there have been reports that cerebral serotonin can be released by the stimulation of certain acupuncture points



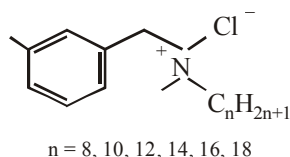
- (d) Antacid decreases acidity in stomach.
- (d) Sulpha drugs (antibacterial and antibiotic) are group of drugs which are derivative of sulphanilamide.
- (c) Iproniazid $\rightarrow$ Tranquilizer
Salvarsan $\rightarrow$ Antimicrobial
Zantac (ranitidine) $\rightarrow$ Antihistamine
Chloramphenicol $\rightarrow$ Antibiotic
- (b) Antiseptic drugs causes destruction of micro-organism that produce septic disease e.g. Dettol, Savlon, acriflavin, Boric acid, Phenol, Iodoform, KMnO_4 and some dyes such as Chloramine T, methylene blue.
- (a) These drugs induce sleep and are habit forming common example of hypnotic drugs are Luminal and Saconal.
- (a) It is the very effective antibiotic for tuberculosis.
- (c) Broad spectrum antibiotics act on different antigens.
- (b) Chloramin - 'T' is used as antiseptic.
- (c) It is an insecticide.
- (c) 26. (b)
- (c) Penicillin is an effective medicine for Pneumonia disease.
- (d)
- (d) Bacteriostatic drugs inhibit the growth of organism while bactericidal drugs kill the microorganisms.

30. (b) Terfenadine is commonly used as antihistamine.
31. (b) Structurally biodegradable detergents should contain branched alkyl chain.
32. (b) 33. (d)
34. (d) It is used as detergent.
35. (d) All are characteristics of Vanillin.
36. (d) All are characteristics of Saccharin.
37. (d) Vitamin E is an antioxidant present in edible oils.
38. (b)
39. (b) A detergent molecule consists of a large hydrocarbon group that is non-ionic and a sulphonate ($\text{SO}_3^- \text{Na}^+$) or a sulphate ($\text{SO}_4^- \text{Na}^+$) group that is ionic. Examples of detergents are sodium-n-dodecyl benzene sulphonate, sodium dodecyl sulphate etc.
40. (c) Salvarsan is an organoarsenic compound, used in the treatment of syphilis. It was the first modern chemotherapeutic agent.
41. (c) The most widely used domestic detergent is the sodium dodecyl benzene sulphonate (SDS).

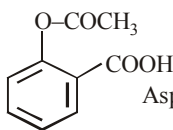


(Sodium dodecyl benzene sulphonate)

42. (a) Soaps are the sodium or potassium salt of higher fatty acids e.g., $\text{C}_{17}\text{H}_{37}\text{COOK}$ (Potassium stearate). These are obtained by alkaline hydrolysis of oils and fats. The reaction is called saponification.
43. (a) Benzalkonium chloride, also known as alkyldimethylbenzylammonium chloride is nitrogenous cationic surface active agent belonging to the quaternary ammonium group. It is used as antiseptic.



44. (b) Cetyltrimethyl ammonium bromide which is a germicide, is a popular cationic detergent.
45. (d) The mixture of chloroxynol and terpenol is dettol which is used as antiseptic.
46. (b)
47. (b) Diphenyl hydramine also known as (Banadry) is an antihistamine.



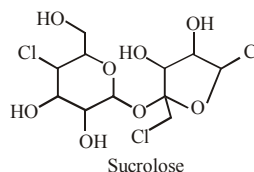
48. (a) Aspirin (Acetyl salicylic acid)

49. (d) Valium is a tranquilizer and not an analgesic. It is used for treatment of stress, fatigue, mild and severe mental diseases.
50. (b) Paul Ehrlich, the father of chemotherapy defined it to injure or destroy infection caused by microorganism by the use of drugs without causing any injury to the host.

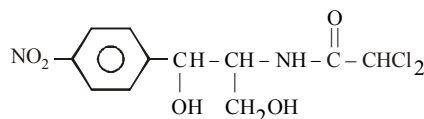
EXERCISE - 2

1. (b) Laundry soaps contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.
2. (a) Substances used for the treatment of malaria are antimalarial e.g. Quinine, chloroquine.
3. (c)
4. (d) Bithional is an antiseptic drug.
5. (b)
6. (d) Aspirin is a non-narcotic analgesic.
7. (d) All these are alkaloids.

8. (a)
9. (c)



10. (a) It is an alkaloid, a class of organic compound which is basic in nature and of plant origin containing at least one nitrogen atom in a ring structure of molecule.
11. (a)
12. (d) Chloramphenicol is



13. (d) Cetyltrimethyl ammonium bromide possesses germicidal properties. Thus it is used as a cationic detergent in hair conditioners.
14. (c) 15. (a)
16. (c) Salts of sorbic acid and propionic acid are used as food preservatives because these chemicals inhibit the growth of yeast bacteria or moulds.
17. (b) It is the known structure of Penicillin G
18. (b)
19. (c) The correct matching is as follows :

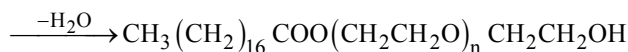
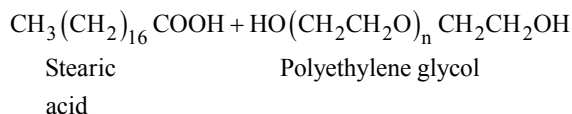
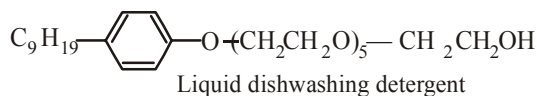
	Column I	Column II
(A)	Sodium Perborate	Milk bleaching agent
(B)	Chlorine	Disinfectant
(C)	Bithional	Antiseptic
(D)	Potassium stearate	Soap

20. (d) Bithional is another well known antiseptic which is added to good quality soaps to reduce the odours produced by bacterial decomposition of organic matter on the skin.
21. (d) The drugs which act on the central nervous system and help in reducing anxiety are called tranquilizers.
22. (a) Tranquilizers are chemicals which are used to cure mental diseases.
23. (a) Broad spectrum antibiotics are those medicines which are effective against several different types of harmful micro organisms.
24. (b) Antiseptics are those chemical which kill or prevent the growth of micro organism. Antiseptics do not harm the living tissues and can be applied on cuts and wounds. They help to reduce odour resulting from the bacterial decomposition in the mouth and on the body.
25. (a) A small quantity of sedative produces a feeling of relaxation, calmness and drowsiness.

EXERCISE - 3

Exemplar Questions

1. (d) Antiseptic is an antimicrobial drug which tends to inhibit the pathogenic action of microbes. They are applied to the living tissues such as wounds, cuts ulcers and diseased skin surface.
So, antiseptic medicines cannot be ingested like antibiotics.
2. (c) Birth control pills contain a mixture of synthetic estrogen and progesterone derivatives. These are sex hormones. Progesterone suppresses ovulation and estrogen control the menstrual cycle.
3. (a) Aspirin inhibits the synthesis of prostaglandins which stimulate inflammation in the tissues and cause pain. So, it is effective in relieving pain as it does not make a person addictive and known to be a non-narcotic drug.
4. (c) Classification on the basis of molecular target: drug usually interact with the biomolecules or biological macromolecules such as proteins, nucleic acids and lipids. These are called drug targets. Drug possessing some common structural features may have the same mechanism of action on a specific drug target. This classification is most useful for the medicinal chemists.
5. (a) Due to the low level of noradrenaline in the body the message transfer process becomes slow and the person suffers from depression. In such cases, tranquilizers are used. These drugs inhibit the enzymes which catalyse the degradation of noradrenaline.
If the enzyme is inhibited, then the neurotransmitter noradrenaline is slowly metabolised and can thus activate the receptor for longer periods thereby counteracting the effect of depression.
6. (a) Paul Ehrlich first synthesised arsenic based structures in order to produce less toxic substances for the treatment of syphilis. Salvarsan also known as arsphenamine was the first effective medicine discovered for syphilis. Salvarsan is toxic to human beings, but its effect on bacteria is much greater than on human being.
7. (a) Broad spectrum antibiotics are effective against a wide range of gram-positive and gram-negative bacteria whereas narrow spectrum antibiotics are effective mainly penicillin- G, against gram-positive or gram-negative bacteria antibiotic is a narrow spectrum antibiotic.
8. (b) Tranquilizers are a class of chemical compounds used for the treatment of stress and mild or even severe mental disease.
9. (d) Bithinol is added to soaps to impart antiseptic properties. Sodium laurylsulphate and sodium dodecyl-benzenesulphonate are anionic detergents.
A gum rosin added to soap to make it leather well.
10. (b) Equanil is a tranquilizer.
11. (b) While preparing soaps, a gum called rosin is added to them. It forms sodium rosinate which leathers well.
12. (c) Glycerol is added to shaving soap to prevent rapid drying.
13. (b) Liquid dishwashing detergents are non-ionic. Mechanism of cleansing action of this type of detergent is same as that of soaps. These also remove grease and oil by micelle formation.
14. (c) Polyethyleneglycols are used in the preparation of non-ionic detergents. Non-ionic detergents do not contain any ion in their constitution.



15. (c) Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acid. These are called drug targets. Vitamins are not a target molecule for drug function in body.
16. (c) Some drugs do not bind to the enzyme's active site but bind to a different site of enzyme which is called allosteric site, which changes the shape of the active site, in such a way that substrate cannot recognize it. If the bond formed between an enzyme and inhibitor is a strong covalent bond and cannot be broken easily the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises the new enzyme.
17. (d) Sucralose is trichloro derivative of sucrose. It is stable at cooking temperature. It does not provide calories.
18. (b) Artificial sweeteners are non-caloric substitutes for sugar. They are often more sweet than sugar but do not enhance nutritional value of food.

NEET/AIPMT (2013-2017) Questions

19. (b) Dilute solutions of boric acid and hydrogen peroxide are weak antiseptics.
20. (c) Dettol is a mixture of chloroxylenol and terpineol.
21. (c) Aspartame is stable under cold conditions.
22. (c) Bithionol is added to soaps to impart antiseptic properties.
23. (a) Novalgin is most widely used as analgesic. Analgesics are pain relieving.
24. (a) Dettol is a mixture of chloroxylenol and terpineol which is a very commonly known antiseptic.