CHAPTER-1

SOLUTIONS

Topic-1	Solution, Different Measures of Concentration of Solids in Liquids, Solubility of Gases in Liquids, Solids Solutions
	Concepts covered: *Solution and their types, Factors affecting solubility, Expression of concentration of solution, Mole fraction, Parts per million, Henry's Law*

💬 Revision Notes

➤ **Solution:** A homogeneous mixture of two or more pure substances is known as a solution.

➤ **Two constituents of the solution are:**

 (i) **Solute:** A substance which is in small quantity dissolved in another substance (a solvent), forming a solution. For example: sugar, salt, etc.

 (ii) **Solvent:** A substance present in large quantity in which another substance is dissolved, forming a solution. For example: water, milk, etc.

➤ **Types of solution:** Any state of matter (solid, liquid, or gas) can act both as a solute or as a solvent during the formation of a solution. Therefore, depending upon the physical states of solute and solvent, we can classify solutions in 9 different types:

S. No.	Types of Solution	Solute	Solvent	Example
1.	Solid–Solid	Solid	Solid	Alloys like brass, bronze, etc.
2.	Solid–Liquid	Solid	Liquid	Solution of sugar, salt, urea, etc., in water.
3.	Solid–Gas	Solid	Gas	Sublimation of substances like iodine, camphor, etc., into air.
4.	Liquid–Solid	Liquid	Solid	Hydrated salts, mercury in amalgamated zinc, etc.
5.	Liquid–Liquid	Liquid	Liquid	Alcohol in water, benzene in toluene.
6.	Liquid–Gas	Liquid	Gas	Aerosol, water vapour in air.
7.	Gas–Solid	Gas	Solid	Hydrogen absorbed in palladium.
8.	Gas–Liquid	Gas	Liquid	Aerated drinks.
9.	Gas–Gas	Gas	Gas	Mixture of gases, etc.

➤ **Solubility:** Solubility is defined as the amount of solute dissolved in 100 g of solvent at a given temperature to form saturated solution.

➤ **Causes of Solubility:**

 (i) **Inter-ionic attraction in the solute molecules:** Molecules are stabilized in the lattice due to electrostatic forces and the energy released is known as **lattice energy.**

 (ii) Inter-molecular attraction between solvent and solute molecules.

 (iii) **Solvation:** It denotes the force of attraction between solute and solvent molecules.

 (iv) Temperature.

➤ **Deciding factors for solubility:**

 (i) **Nature of solute and solvent:** ''Like dissolves like'', i.e., polar solvents like water and ammonia can dissolve polar solute or ionic solute while non-polar solvents can dissolve non-polar organic solutes.

 (ii) **Temperature:** Solubility increase with increases in temperature. It increases for endothermic reaction while it decreases for exothermic reaction.

 (iii) **Pressure:** The solubility of solid in liquid is not affected significantly by pressure because solids and liquids cannot be compressed. Solubility of gas in liquid increases with increase in pressure at a given temperature.

 (iv) **Hydration energy:** It is the amount of energy released when 1 mole of ions gets hydrated. It is an exothermic process.

➤ **Methods of expressing Concentration of Solution:** The concentration of solution is the amount of solute present in the given quantity of solution or solvent. It can be expressed in any of the following types:

(i) Mass percentage (w/W): It is the amount of solute in grams dissolved per 100 g of solution.

$$\text{Mass\% of a solute} = \frac{\text{Mass of solute in the solution}}{\text{Total mass of the solution}} \times 100$$

(ii) Volume percentage (v/V): It is defined as the volume of a solute dissolved per 100 mL of solution.

$$\text{Volume\% of a solute} = \frac{\text{Volume of solute}}{\text{Total volume of the solution}} \times 100$$

(iii) Mass by volume percentage: It is defined as the mass of solute dissolved per 100 mL of solution. It is commonly used in medicine and pharmacy.

$$\text{Mass by volume \% of solute} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

➢ **Mole fraction:** It is the ratio of number of moles of a particular component to the total number of moles of all the components. e.g., mole fraction of component A.

$$\chi_A = \frac{n_A}{n_A + n_B}$$

where n_A is the number of moles of component 'A'.

Similarly,

$$\chi_B = \frac{n_B}{n_A + n_B}$$

where n_B is the number of moles of component B.

Sum of mole fractions of all the components is always one.

$$\chi_A + \chi_B = 1$$

➢ **Molarity:** It is defined as the number of moles of solute dissolve per litre of solution.

$$M = \frac{n_B}{V} \text{ or } M = \frac{W_B \times 1000}{M_B \times V}$$

where n_B is number of moles of solute, W_B is weight of solute, V is volume of solution in mL, M_B is molar mass of solute.

Unit is mol L^{-1} or M (molar).

➢ **Molality:** It is defined as the number of moles of solute dissolve per 1000 g or 1 kg of solvent.

$$m = \frac{n}{W} \text{ or } m = \frac{W_B \times 1000}{M_B \times W_A}$$

where n is number of solute, W_A is weight of solvent, W_B is quantity of solute, M_B is molar mass of solute.

Unit is mol kg^{-1} or molal (m).

Molality and mole fraction do not change with change in temperature.

➢ **Normality:** It is defined as number of gram equivalents of solute dissolved per litre of solution.

$$N = \frac{W_B \times 1000}{E_B \times V}$$

where W_B is mass of solute, E_B is equivalent weight of solute, V is volume of solution in mL.

Unit is N or eq/L.

➢ **Parts per million (ppm):** If a solute is present in trace quantities, the concentration of the solution is expressed in parts per million (ppm).

$$\text{Parts per million of the solute } (ppm) = \frac{\text{Weight of the solute}}{\text{Weight of the solution}} \times 10^6$$

➢ **Parts per million can be expressed in three ways:**

(a) Mass to mass

$$ppm \text{ (mass to mass)} = \frac{\text{Mass of a component}}{\text{Total mass of solution}} \times 10^6$$

(b) Volume to volume

$$ppm \text{ (volume to volume)} = \frac{\text{Volume of a component}}{\text{Total volume of solution}} \times 10^6$$

(c) Mass to volume

$$ppm \text{ (mass to volume)} = \frac{\text{Mass of a component}}{\text{Volume of solution}} \times 10^6$$

➢ **Relationship between Molarity (M) and Molality (m):**

$$\text{Molality } (m) = \frac{1000\,M}{1000\,d - M \times M_B}$$

where m is molality, M is molarity, d is density of the solution and M_B is molar mass of solute.

➤ **Relationship between mole fraction of solute (χ_B) and molality (m):**

$$m = \frac{\chi_B \times 1000}{\chi_A \times M_A}$$

Here, $\chi_A + \chi_B = 1$

where χ_B is mole fraction of solute, m is molality and M_A is molar mass of solvent.

➤ **Relationship between molarity and density:**

$$\text{Molarity } (M) = \frac{\%\text{ Strength } \times \text{Density } \times 10}{M_B}$$

where M_B is molar mass of solute.
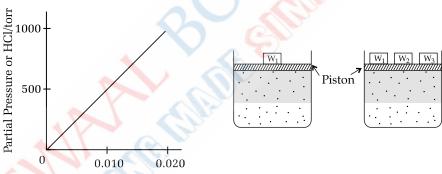
➤ **Relationship between normality and density:**

$$\text{Normality (N) } = \frac{\%\text{ Strength } \times \text{Density } \times 10}{\text{Equivalent mass of solute}}$$

➤ **Henry's Law:** The relationship between pressure and solubility is guided by Henry's Law. According to this law, *"The mass of a gas dissolved in a given volume of the liquid at a constant temperature depends upon the pressure which is applied."*

It can also be stated as the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution.

$$p = K_H \chi$$

where K_H = Henry's constant.

Fig.1 : Experimental results for the solubility of HCl gas in cyclohexane at 239 K. The slope of the line is the Henry's constant, K_H

➤ **Applications of Henry's law:**
  (i) To increase the solubility of CO_2 in soda water and soft drinks, the bottle is sealed under high pressure.
  (ii) To avoid the toxic effects of high concentration of nitrogen in blood, the tanks used by scuba divers are filled with air diluted with He (11.7%), N_2 (56.2%) and O_2 (32.1%).
  (iii) At high altitudes, low blood oxygen causes climber to become weak and make them unable to think clearly, which are symptoms of a condition known as anoxia.

➤ **Limitations of Henry's law:** This law is applicable only when:
  (i) The pressure of gas is not too high and a temperature is not too low.
  (ii) The gas should not undergo any chemical change.
  (iii) The gas should not undergo association or dissociation in the solution.

⌾━ Key Terms

➤ **Mole:** The amount of substance of a system which contains the same number of elementary entities. (e.g., atoms, molecules, ions, electrons, etc.)
➤ **Partial Pressure:** Pressure exerted by the gas if it occupies the same volume in a mixture at the same temperature.
➤ **Concentrated Solution:** Solution in which the amount of solute is relatively large.
➤ **Dilute Solution:** Solution in which the amount of solute is relatively very small.

Topic-2 | Raoult's Law, Ideal and Non-ideal Solutions

Concept covered: *Vapour pressure, Raoult's Law, Ideal and non ideal solution, Positive and negative deviation, Azeotropes*

Revision Notes

➢ Pressure exerted by vapours of a liquid on its liquid layer at equilibrium is called as vapour pressure.

➢ Factors affecting vapour pressure are:
  (i) Nature of liquid: Vapour pressure increases with decreasing intermolecular force.
  (ii) Temperature: Vapour pressure increases with increase in temperature.
  (iii) Pressure of impurities: The pressure of non-volatile impurities lowers the vapour pressure while volatile impurities raises the vapour pressure of the liquid.

➢ **Raoult's law for a solution of volatile liquids:** It states that for a solution of volatile liquids, the partial vapour pressure of each components in the solution is directly proportional to its mole fraction. Mathematically, for component A,

Suppose a solution is prepared by mixing two volatile liquids A and B. Let χ_A and χ_B respectively be their mole fractions, and let P_A and P_B be their partial vapour pressure respectively, in the solution of a particular temperature.

If P_A° and P_B° are respectively, their vapour pressures in the pure state, then according to Raoult's law.

$$P_A = P_A^\circ \chi_A$$

$$P_B = P_B^\circ \chi_B$$

Considering Dalton's law of partial pressure,

$$P_{total} = P_A + P_B$$

Substituting values of P_A & P_B,

$$P_{total} = \chi_A P_A^\circ + \chi_B P_B^\circ$$

$$= (1 - \chi_B) \, P_A^\circ + \chi_B P_B^\circ$$

$$= P_A^\circ + (P_B^\circ - P_A^\circ) \, \chi_B$$

The composition of the vapour phase in equilibrium with the solution can be determined from the partial pressure of the two components. If χ_A and χ_B are the mole fractions of components A and B respectively, in the vapour phase, then

$$P_A = \chi_A P_{Total}$$
$$P_B = \chi_B P_{Total}$$

In general $P_i = \chi_i P_{total}$

➢ **Raoult's law as a special case of Henry's law:** According to Raoult's law, the vapour pressure of volatile component (A) in a given solution is given as:

$$P_A = P\chi_A$$

According to Henry's law,

for solution of a gas in a liquid the gaseous component is normally so volatile that it exists as a gas and solubility depends upon Henry's law to which:

$$P_A = K_H \chi_A$$

$$P_A = K_H$$

On comparing both expressions P_A° is equal to K_H.

> ⚙ **Mnemonics**
>
> **Concept:** ideal and Non ideal solution.
> **Mnemonics: High voltage**
> H- enthalpy of mixing
> V- Volume of mixing

➢ **Raoult's law for non-volatile solute:** For a solution containing non-volatile solute present in a volatile solvent, Raoult's law may be stated as the relative lowering of vapour pressure for a solution is equal to the mole fraction of solute.

$$\chi_B = \frac{P_A^\circ - P_A}{P_A^\circ}$$

where, χ_B = mole fraction of solute,

$P_A - P_A$ = relative lowering of vapour pressure.

➢ **Ideal Solution:** A solution is called as an ideal solution if it obeys Raoult's law over a wide range of concentration at a specific temperature.

   (i) Raoult's law is obeyed, i.e., $P_A = P_A \chi_A$, $P_B = P_A \chi_B$

  (ii) $\Delta_{mix}H = 0$,

  (iii) $\Delta_{mix}V = 0$,

  (iv) The force of attraction between A–A and B–B is nearly equal to A–B.

   Some examples of ideal solutions are:

   (i) *n*-hexane and *n*-heptane,

  (ii) Ethyl bromide and ethyl chloride,

  (iii) Benzene and toluene,

  (iv) Chlorobenzene and bromobenzene.

➢ **Non-ideal solutions:** A solution which does not obey Raoult's law for all the concentrations is called as a non-ideal solution.

   (i) Raoult's law is not obeyed, i.e., $P_A \neq P_A \chi_A$ and $P_B \neq P_A \chi_A$

  (ii) $\Delta_{mix}H \neq 0$,

  (iii) $\Delta_{mix}V \neq 0$,

  (iv) The force of attraction between A–A and B–B is not equal to A–B.

   Some examples of non-ideal solutions are:

   (i) Water and ethanol

  (ii) Chloroform and acetone

  (iii) Ethanol and cyclohexane

   A non-ideal solution can show either positive or negative deviation from Raoult's law.

➢ **Positive deviation from Raoult's law:** In this type of deviation, A–B interactions are weaker than the interaction between A–A or B–B and leads to an increase in vapour pressure.

   Some examples are:

   (i) Water and ethanol

  (ii) Chloroform and water

  (iii) Ethanol and CCl_4

  (iv) Methanol and chloroform

  (v) Benzene and methanol

  (vi) Acetic acid and toluene

➢ **Negative deviation from Raoult's law:** In this type of deviation in non-ideal solutions, the intermolecular attractive forces between A–A and B–B are weaker than those between A–B and leads to decrease in vapour pressure.
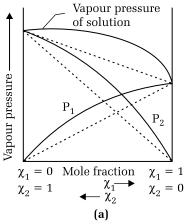
   Some examples are:

   (i) Chloroform and acetone

   A mixture of chloroform and acetone forms a solution with a negative deviation from Raoult's law. This is because chloroform molecule is able to form a hydrogen bond with acetone molecule as shown.

  (ii) Chloroform and methyl acetate

  (iii) H_2O and HCl

  (iv) H_2O and HNO_3

  (v) Acetic acid and pyridine
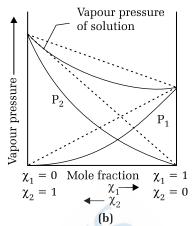
  (vi) Chloroform and benzene

Fig. 2 : The vapour pressures of two component systems as a function of composition :
   (a) A solution that shows positive deviation from Raoult's law, and
   (b) A solution that shows negative deviation from Raoult's law.

➤ **Azeotropes:** The binary mixtures which having the same composition in liquid and vapour phase and boil at a constant temperature are called azeotropes. Components of azeotropic mixture cannot be separated by fractional distillation.

➤ **Minimum boiling azeotropes:** Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes at a specific composition. e.g., water and benzene, chloroform and methanol.

➤ **Maximum boiling azeotropes:** Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which build at temperature higher than the boiling points of its components. e.g., mixture of HNO_3 and H_2O.

⊙━ Key Terms

➤ **Dalton's law of partial pressure:** It states that the total pressure exerted by a mixture of gases is the sum of partial pressure of each individual gas present.

➤ **Raoult's law for a solution of volatile solute in volatile solvent:**

$$P_A = P_A^o \chi_A$$

$$P_B = P_B^o \chi_B$$

➤ **Raoult's law for a solution of non volatile solute in volatile solvent:**

$$\frac{P_A^o - P_A}{P_A^o} = i\chi_B = i\frac{\eta_B}{\eta_A} = i\frac{W_B \times M_A}{W_A \times M_B} \qquad \text{(for dilute solution)}$$

Topic-3 Colligative Properties, Determination of Molecular Mass of Solute, Abnormal Molecular Mass and van't Hoff Factor

Concepts covered: *Colligative properties and types, Reverse osmosis, van't Hoff factor*

💬 Revision Notes

➤ **Colligative properties:** Certain properties of solutions depend only on the number of particles of the solute (molecule or ions) in definite volume of the solvent and do not depend on the nature of solute, such properties are called as colligative properties. These are:

   (i) Relative lowering of vapour pressure   **(iii)** Depression in freezing point
   (ii) Elevation of boiling point   **(iv)** Osmotic pressure

➤ **Relative lowering of vapour pressure:** If the number of particles of solute increases there is decrease in relative vapour pressure.

The relative lowering of vapour pressure is the ratio of lowering of vapour pressure and vapour pressure of pure solvent which is equal to the mole fraction of solute.

Vapour pressure of pure solvent $\rightarrow P_A^\circ$

Lowering of vapour pressure $\rightarrow P_A^\circ - P_A$

Relative lowering of vapour pressure

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \chi_{solute} = \frac{n}{N + n}$$

➢ **Elevation of boiling point:** If the number of particles of solute increases there is increase in boiling point of solution. The difference in boiling point of solution and pure solvent is called as elevation of boiling point.

The boiling point of pure solvent $\rightarrow T_b^\circ$

The boiling point of solution $\rightarrow T_b$

The increase in boiling point $\Delta T_b = T_b - T_b^\circ$ is known as elevation of boiling point for dilute solution.

$$\Delta T_b \propto \frac{\Delta P}{P^\circ} \propto \chi_B$$

$$\Delta T_b = K\chi_B$$

$$\Delta T_b = K \times \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\Delta T_b = K \times \frac{n_B}{W_A} M_A \qquad \left[\therefore \frac{W_B}{M_B} = n_B \right]$$

If W_A = mass of solvent in kg, then $\frac{n_B}{W_A} = m$ (molality)

$$\Delta T_b = K \times M_A \times m$$

Here K and M_A are constants.

$$K \times M_A = K_b$$
$$\Delta T_b = K_b m$$

$K_b \rightarrow$ boiling point elevation constant or molal elevation constant or Ebullioscopic constant.
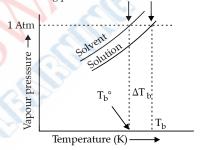

Fig. 3 : The vapour pressure curve for solution lies below the curve for pure water.
The diagram shows that ΔT_b denotes the elevation of boiling of a solvent in solution.

➢ **Depression of Freezing point:** According to Raoult's law, when a non-volatile solid is added to the solvent, its freezing point decreases and becomes equal to that of pure solvent at lower temperature. Thus, the difference in the freezing point of pure solvent and that of the solution is known as depression in freezing point.

The freezing point of pure solvent = T_f°

The freezing point when non-volatile solute is dissolved in it = T_f (Freezing point of solution)

The decrease in freezing point $\Delta T_f = T_f^\circ - T_f$ is known as depression in freezing point.

For dilute solutions,

$$\Delta T_f \propto \frac{\Delta p}{p^\circ} \propto \chi_B$$

$$\Delta T_f = K\chi_B$$

$$\Delta T_f = K \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

We know that

$$\frac{W_B \times 1000}{M_B \times W_A} = \text{Molarity}$$

$$K \times M_A = K_f$$

$$\Delta T_f = K_f m$$

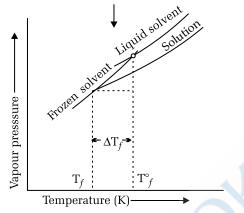where K_f = Freezing point depression constant or molal depression constant or cryoscopic constant.

Fig 4. Diagram showing ΔT_f depression of the freezing point of a solvent in a solution

➢ **Osmosis:** The process in which, there is net flow of solvent from the solution of lower concentration to the higher concentration by a semi-permeable membrane is called as osmosis.

➢ **Osmotic pressure:** The extra pressure that is applied to just stop the flow of solvent to solution across a semi-permeable membrane is called as osmotic pressure of the solution.
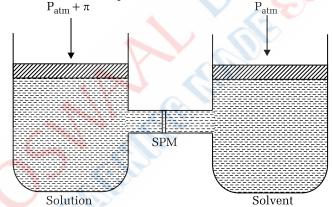

Fig. 5 : The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis

For dilute solutions, osmotic pressure is proportional to the molar concentration (C) of the solution at a given temperature T.

Thus, $\pi = CRT$ where π is the osmotic pressure, R is the gas constant.

➢ **Reverse osmosis:** The direction of osmosis can be reversed, if a pressure larger than the osmotic pressure is applied to the solution side. Now the pure solvent flows out of the solution through the semipermeable membrane. This phenomenon is called as reverse osmosis.
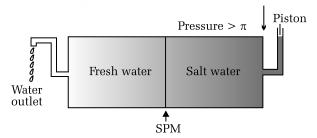

Fig. 6 : Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution

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🧠 Mnemonics

Concept: Reverse osmosis.
Mnemonics: All sea Fishes
Interpretation: Applying pressure on salt solution to desalinate it to fresh water

➢ **Abnormal molecular mass:** When the molecules mass is calculated with the help of colligative property, it is different from theoretical molecular mass, it is called as abnormal molecular mass.

➢ **van't Hoff factor (i):** The ratio of the observed (experimental) value of a colligative property to the normal (calculated) value of the same property is called as van't Hoff factor.

Mathematically,

$$i = \frac{\text{Observed (experimental) value of a colligative property}}{\text{Normal (calculated) value of the same colligative property}}$$

Or,
$$i = \frac{\Delta_{\text{obs}}}{\Delta_{\text{cal}}}$$

where Δ_{obs} and Δ_{cal} respectively represent the observed and calculated value of a colligative property.

Thus,

(i) for lowering of vapour pressure, $\quad i = \dfrac{(\Delta p)_{\text{obs}}}{(\Delta p)_{\text{cal}}}$;

(ii) for elevation of boiling point, $\quad i = \dfrac{(\Delta T_b)_{\text{obs}}}{(\Delta T_b)_{\text{cal}}}$;

(iii) for depression of freezing point, $\quad i = \dfrac{(\Delta T_f)_{\text{obs}}}{(\Delta T_f)_{\text{cal}}}$;

(iv) for osmotic pressure, $\quad i = \dfrac{\pi_{\text{obs}}}{\pi_{\text{cal}}}$;

Since a colligative property is proportional to the number of particle of solute.

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

Normal molecular mass = $i \times$ Calculated molecular mass

$$i = \frac{\text{Total number of moles of particle after association/dissociation}}{\text{Total number of moles of particle before association/dissociation}}$$

🔑 Key Formulae

➢ **Modified equations for colligative properties:**

(i) Relative lowering of vapour pressure of solvent :
$$\frac{P_A{}^\circ - P_A}{P_A{}^\circ} = \frac{n_B}{N_A + n_B}$$

(ii) Elevation of boiling point:
$$\Delta T_b = iK_b m$$

(iii) Depression of freezing point:
$$\Delta T_f = iK_f m$$

(iv) Osmotic pressure of solution:
$$\pi = \frac{inRT}{V}, \text{ Where, } C = n/V$$

or $\quad \pi = i\, CRT$

➢ **Determination of molecular mass using colligative properties:**

(i) Relative lowering of vapour pressure:
$$\frac{P_A{}^\circ - P_A}{P_A{}^\circ} = \chi_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A}$$

$$\frac{P_A{}^\circ - P_A}{P_A{}^\circ} = \frac{W_B \times M_A}{W_A \times M_B}$$

$$M_B = \frac{P_A{}^\circ}{P_A{}^\circ - P_A} \times \frac{W_B \times M_A}{W_A}$$

(ii) Elevation of boiling point:

$$\Delta T_b = K_b \times m$$

$\Rightarrow$

$$\Delta T_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A \text{ in g}}$$

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

(iii) Depression of freezing point:

$$\Delta T_f = K_f \times m$$

$\Rightarrow$

$$\Delta T_f = K_f \times \frac{W_{\text{solute}}}{M_{\text{solute}}} \times \frac{1000}{W_{\text{solvent}}}$$

$$M_B = \frac{1000 \times W_B \times K_f}{\Delta T_f \times W_A}$$

(iv) Osmotic pressure:

$$\pi = CRT,$$

$\Rightarrow$

$$\pi = \frac{\text{No. of moles}}{\text{Volume of solution}} \times R \times T$$

$$\pi = \frac{W_B}{M_B} \times \frac{RT}{V}$$

$$M_B = \frac{W_B \times RT}{\pi \times V}$$

➢ Degree of dissociation (α):

$$\alpha = \frac{i-1}{n-1}$$

$i \to$ van't Hoff factor

$n \to$ No. of ions produced per formula of the compound

➢ Degree of association (α):

$$\alpha = \frac{1-i}{1-\frac{1}{n}}$$

🔑 Key Terms

➢ **Normal boiling point:** Temperature at which the vapour pressure of the liquid equals one atm.
➢ **Molal boiling point:** Boiling point of a 1 molal solution.
➢ **Freezing point:** Temperature at which the vapour pressure of liquid solvent is equal to the vapour pressure of solid solvent.
➢ **Endosmosis:** The inward osmosis of water into the semi-permeable membrane is known as endosmosis.
➢ **Exosmosis:** The outward osmosis of water from the cell membrane is known as exosmosis.
➢ **Desalination:** Sea water can be converted into potable water fit for drinking purposes by reverse osmosis process known as desalination.
➢ **Plasmolysis:** When plant cell is placed in hypertonic solution, the fluid from the plant cell comes out and the cell shrinks. This phenomenon is called plasmolysis and is caused due to osmosis.

❑❑

CHAPTER-2

ELECTRO-CHEMISTRY

Topic-1	Electrochemical Cells, Redox Reactions, Galvanic Cells, Emf of a Cell, Standard Electrode Potential, Nernst Equation, Electrochemical Series and Gibbs Energy
	Concepts covered: *Galvanic cell, Electrode and standard electrode potential, Nernst equation , Gibbs free energy, Electrochemical series*

💬 Revision Notes

➤ **Electrochemistry** is the study of production of electricity from the energy released during a chemical reaction and the use of electrical energy to carry out chemical transformation.

➤ **Electrochemical cell** is a device which converts the chemical energy into electrical energy. It is also called galvanic cell or voltaic cell.

➤ **Redox reaction:** A chemical reaction in which oxidation and reduction both processes take place simultaneously.

➤ Oxidation is a process in which any substance loses one or more electrons.

➤ Reduction is a process in which one or more electrons are gained by a substance.

➤ **Galvanic cell or voltaic cell:** It is a device used to convert chemical energy into electrical energy. It is a combination of two half-cells, containing two electrodes dipped in an electrolytic solution containing its own ions.

Construction: In this cell, a zinc rod is placed in a solution of Zn^{2+} ions (i.e., $ZnSO_4$) in the left container and a bar of copper metal is immersed in a solution of Cu^{2+} ions (i.e., $CuSO_4$) in the right container. The two metals which act as electrodes are connected by a metallic wire through a voltameter. The two solutions are joined by an inverted U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl in gelatin or agar-agar jelly. This arrangement of a U-tube is called **salt bridge**.

(a) At zinc electrode, the metal undergoes oxidation and releases two electrons.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \text{ (Oxidation)}$$

As oxidation takes place, the electrode behaves as anode.

These electrons travel through the wire and reach the copper metal.

(b) $$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \text{ (Reduction)}$$

Electronation takes place which is a reduction process and thus, acts as cathode.

Overall reaction, $$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The deflection in the voltameter shows the flow of current through the external circuit. It flows through the outer circuit from the copper metal to zinc metal, which implies flow of electrons from zinc to copper bar.
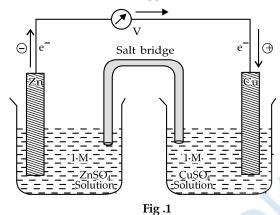
⚙ Mnemonics

Concept: Oxidation reaction	**O** : oxidation
Mnemonics: Loan	**A** : anode
Interpretation:	**N** : negative
L : Left	

Mechanism: Due to the two half-cell reactions, zinc metal dissolves in anode solution to form Zn^{2+} ions, whereas the Cu^{2+} ions are discharged at the cathode by accepting two electrons and are deposited at cathode.

The electrical neutrality is maintained by salt bridge. The anions of the inert electrolyte in the salt bridge migrate to anodic chamber and cations to the cathodic chamber. Copper bar gains weight while zinc rod loses weight. The cell functions till either zinc metal or copper ions in solution are consumed fully.

Fig .1

Case 1 : When $E_{ext} < 1.1$ V

(i) Electrons flow from Zn rod to Cu rod hence, current flows from Cu to Zn.

(ii) Zn dissolves at anode and copper deposits at cathode.

Case 2 : When $E_{ext} = 1.1$ V

(i) No flow of electrons or current.

(ii) No chemical reaction.

Case 3 : When $E_{ext} > 1.1$ V

(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.

(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode

➢ **Salt Bridge and its function:** It is an inverted U-shaped glass tube which contains a suitable salt in the form of a thick paste made up in agar-agar. It performs the following functions:

(i) It completes inner cell circuit.

(ii) It prevents transfer of electrolyte from one half to the other.

(iii) It maintains the electrical neutrality of the electrolytes in the two half cells.

➢ **Daniel cell:** An electrochemical cell of zinc and copper metals is known as Daniel cell.

Cell is represented as,

Zn(s) $|Zn^{2+}$(aq) (C_1) $||$ Cu^{2+}(aq) $(C_2)|$ Cu(s)

➢ **Electrode Potential:** It is the potential difference set up between the metal and solution of its own ions. It shows the tendency of an electrode to either lose or gain electrons.

It is expressed in volts. It is an intensive property, i.e., independent of the amount of species in the reaction.

➢ **Factors affecting the magnitude of electrode potential:**

(i) Nature of metal or electrode

(ii) Concentration of metal ions in solution

(iii) Temperature

➢ **Standard Electrode Potential:** Electrode potential at 25°C, 1 bar pressure and 1 M solution is known as standard electrode potential (E°). The standard electrode potential of any electrode can be measured by connecting it to reference electrode like standard hydrogen electrode (SHE).

SHE has a standard potential at all temperatures, it is also known as Normal Hydrogen Electrode (NHE). It consists of a platinum foil coated with platinum black dipped into an aqueous solution in which the [H⁺] = 1 M at 25°C and 1 bar pressure.

The potential difference between the two electrodes of a galvanic cell is called the **cell potential** (measured in volts). It is also called as the **emf of the cell**, when no current is flowing through the circuit.

➢ **Standard hydrogen electrode.**

Definition: The standard hydrogen electrode (SHE), is a redox electrode having zero standard electrode potential which forms the basis of the thermodynamic scale of oxidation-reduction potentials.
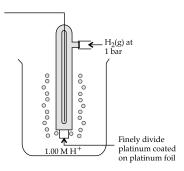
Preparation:

Fig. 2. SHE

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity . This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

Applications:

• SHE is used as a reference to determine the electrode potential of another electrode of half cell connected to SHE.

• It can act as anode half cell and cathode half cell as well.

Limitations:

• It is difficult to construct and maintain.

• It is difficult to maintain the pressure of hydrogen gas and concentration of the acid solution taken such as HCl. It is difficult to get pure hydrogen gas.

• It is difficult to make an ideal platinum electrode. Generally, impurities in hydrogen and HCl spoil ideal platinum electrodes and reduce the life of standard hydrogen electrodes.

➢ **EMF of the cell:** Electromotive force is also called emf (denoted and measured in volts). It is the voltage developed by any source of electrical energy such as battery or dynamo. It is generally defined as the potential for a source in a circuit.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

In terms of standard oxidation electrode potential

$$E°_{cell} = E°_{anode} - E°_{cathode}$$

where $E°_{cathode}$ = Standard electrode potential of cathode

and $E°_{anode}$ = Standard electrode potential of anode

➢ **Standard oxidation potential:** It is the potential difference when given electrode in contact with the ions having 1 molar concentration, undergoes oxidation when coupled with standard hydrogen electrode.

➢ **Standard reduction potential:** It is the potential difference developed when given electrode in contact with its own ions having 1 molar concentration, undergoes reduction when coupled with standard hydrogen electrode. The higher positive value standard oxidation potential E° for a half-cell indicates that reductant in the half cell is stronger reducing agent than hydrogen gas.

➢ The series in which all electrode potentials have been arranged in order of increasing value is known as **electrochemical series**. The characteristics of the electrochemical series are:

(i) The reducing agent with lowest standard reduction potential E° value, considered as the strongest reducing agent, is placed at the last of the electrochemical series. The oxidising agent with highest positive standard reduction potential E° value, considered as the strongest oxidising agent, is placed at the top of electrochemical series. The strongest reducing agent in Electrochemical series is Lithium having electrode potential -3.05V. The strongest oxidizing agent is Fluorine having electrode potential +2.87V.

(ii) Oxidising power increases with increase in E° value.

(iii) Any metal of lower E° value can reduce other metal of higher E° value.

Similarly, any metal of higher E° value can oxidize other metal of lower E° value.

➢ **Applications of electrochemical series:**

(i) In comparison of relative reducing or oxidizing power of the elements.

(ii) In predicting the feasibility of spontaneity of a redox reaction.

(iii) In predicting whether a metal can evolve hydrogen from an acid or not.

(iv) Comparison of reactivities of metals and non-metals.

(v) Determination of standard Gibbs energy change.

(vi) Determination of equilibrium constant.

⚙ Mnemonics

Concept : Electrochemical series
Mnemonics: U. P is Really **OP**
Interpretation: According to the standard reduction potential

Position	Standard reduction potential	Easily	Good
Up	Positive	Reduce	Oxidising agent
Middle	Zero	Reduce or oxidise	Act as both
Down	Negative	oxidise	Reducing agent

➢ **Nernst equation:** The relationship between the concentration of ions and electrode potential is given by Nernst equation. For a general electrode,

$$M^{n+} + ne^- \rightarrow M$$

The Nernst equation can be written as,

$$E^+_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} ln \frac{[M]}{[M^{n+}]}$$

where E° = Standard electrode potential, R = Gas constant and is 8.314 J K^{-1} mol^{-1}, T=Temperature (K), n= Number of moles of electrons and F=Faraday's constant (96500 C)

At equilibrium,

$$E_{cell} = \frac{0.059}{n} log K_c$$

K_c = Equilibrium constant

$$K_c = \frac{[M]}{[M^{n+}]}$$

For the cell with the net reaction,

$$aA + bB \xrightarrow{ne^-} mM + nN$$

the Nernst equation at 298 K can be written as,

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} log \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

where $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

➢ **Gibbs energy:** $\Delta G^\circ = nFE^\circ_{cell}$
For cell reaction to be spontaneous, ΔG must be negative.
Calculations of $\Delta_r G^\circ$ and $\Delta_r G$:

$$\Delta_r G^\circ = -nFE^\circ_{cell}$$
$$\text{and } \Delta_r G = -nFE_{cell}$$

Since, Gibbs energy changes is equal to the useful work done.
For the cell reaction to be spontaneous, ΔG must be negative.

$$\Delta G^\circ = -2.303 \ RT \ log \ K.$$

🔑 Key Formulae

➢ **Nernst equation:**

$$E_{cell} = E^\circ_{cell} - \frac{2.303 \ RT}{nF} log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} log \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ at 298 K}$$

$$E_{cell} = \frac{2.303 \ RT}{nF} log \frac{C_2}{C_1} \text{ where } C_2 > C_1$$

⦿━ Key Terms

➤ **Liquid junction potential:** A potential difference sets up across the junctions of the two solutions of electrolytes when these are in direct contact with each other.

➤ **Over voltage:** It is the difference between the potential required for the solution of a gas and its standard reduction potential. It is also known as bubble over voltage.

➤ **Electrosynthesis:** It is a method of producing substance through non-spontaneous reaction carried by electrolysis. e.g., NaOH and Cl_2 are obtained from Chlor-alkali process.

➤ **Gibbs energy:** Energy associated with a chemical reaction that can be used to do useful work.

➤ **Reference electrode:** The electrode of known potential is called reference electrode. It may be primary reference electrode like hydrogen electrode or secondary reference electrode like calomel electrode.

⚙ Mnemonics

Concept: Electrochemical series
Mnemonics: Priyanka **C**hopra **S**ees **M**ovie
About **Z**ebra **I**n **T**he **L**ibya **H**iring **C**obra
Studying **A**lgebra
Interpretation :
P : Potassium
C : Calcium
S : Sodium
M : Magnesium

A : Aluminium
Z : Zinc
I : Iron
T : Tin
L : Lead
H : Hydrogen
C : Copper
S : Silver
A : Gold (Au)

Topic-2	## Conductance and Kohlrausch's Law
	Concepts covered: *Conductance, Electrolytic conductivity, cell constant, Degree of dissociation, Kohlrausch's Law*

💬 Revision Notes

➤ **Conductance:** The ease with which current flows through a conductor is called its conductance. It is reciprocal of resistance.

➤ **Resistance:** Resistance is a measure of the opposition to current flow through a conductor.

$$C = \frac{1}{R}$$

Unit of conductance is Siemens or 1/ohm or mho.

➤ **Metallic conductance** is the electrical conductance through metal that occurs due to the movement of electrons. It depends upon the:
 (i) Nature and structure of the metal
 (ii) Number of valence electrons per atom
 (iii) Temperature

➤ **Electrolytic or ionic conductance** is the conductance of electricity that occurs due to ions present in the solution. It depends upon the:
 (i) Nature of electrolyte or inter-ionic attractions
 (ii) Solvation of ions
 (iii) Nature of solvent and its viscosity
 (iv) Temperature

➤ **Ohm's law :** According to Ohm's law, "the flow of current in a conductor is directly proportional to the potential difference, provided physical conditions are remain same", i.e.,

$$I = \frac{V}{R}$$

where, R is resistance, V is potential difference and I is current.

➤ **Specific resistivity:** If a solution is placed between two parallel electrodes having cross sectional area 'A' and distance '*l*' apart, then

$$R = \rho \frac{l}{A}, \text{ where } \rho \text{ is specific resistivity.}$$

The unit of specific resistivity is ohm cm or ohm m.

➢ **Specific conductivity (electrolytic conductivity) :** It is reciprocal of the specific resistivity of an electrolytic solution. It is denoted by κ (Kappa).

$$\kappa = C \times \frac{l}{A}$$

where C is conductance of solution, l is the distance and A is the area of cross-section.
Its unit is $ohm^{-1} cm^{-1}$ or in S. I. unit $S m^{-1}$.

➢ **Molar conductivity:** It is defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a solution. It is denoted by Λ_m.

$$\Lambda_m = \frac{\kappa}{C} \times 1000 \, S \, cm^2 \, mol^{-1}$$

where κ = Conductivity and C = Concentration of solution.
Conductivity decreases with dilution while molar conductivity increases with dilution.
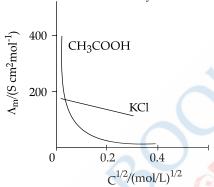

Fig. 3

When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol $\Lambda_m°$.

➢ **Strong electrolytes :** For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \Lambda_m° - AC^{1/2}$$

➢ **Cell constant (G):** It is the ratio of distance between electrodes (l) to the cross-sectional area (A) between electrodes.

$$Cell \; constant = \frac{l}{A} \; cm^{-1} \; or \; m^{-1}$$

➢ A weak electrolyte is not completely dissociated at all the concentrations. With dilution, the degree of dissociation increases resulting in increase in number of ions.

➢ In case of weak electrolytes, the Λ_m value increases steeply with dilution, especially in the low concentration region.

➢ **Degree of dissociation (α):** The ratio of molar conductivity at a specific concentration to the molar conductivity at infinite dilution (limiting molar conductivity) is known as degree of dissociation.

Mathematically:
$$\alpha = \frac{\Lambda_m^c}{\Lambda°_m}$$

where, Λ_m^c = molar conductance of concentration C and $\Lambda°_m$ = molar conductance at infinite dilution.
For weak electrolytes, if K_a is dissociation constant then,

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

➢ **Kohlrausch's law of independent migration of ions :** According to this law, limiting molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of contribution from its individual ions. If the molar conductivity of the cations is denoted by Λ_+^∞ and that of the anions by Λ_-^∞ then, the law of independent migration of ions is:

$$\Lambda_m^\infty = v_+\lambda_+^\infty + v_-\lambda_-^\infty \; or \; \Lambda° = v_+\lambda_+° + v_-\lambda_-°,$$

where, v_+ and v_- are the number of cations and anions per formula of electrolyte respectively (e.g., $v_+ = v_- = 1$ for NaCl but $v_+ = 1$, $v_- = 2$ for $CaCl_2$.

➢ **Applications of Kohlrausch's law:**
 (i) The molar conductivity of a weak electrolyte at infinite dilution can be calculated by using Kohlrausch's law.
 (ii) Degree of dissociation of a weak electrolyte (like acetic acid) at a given concentration can be calculated.
 (iii) Knowing the degree of dissociation, (α), the dissociation constant of the weak electrolyte at a given concentration of the solution can be calculated.

(iv) Determination of solubility of sparingly soluble salts.

🧠 Mnemonics

Concept: Kohlrausch's law

Mnemonic: Cats Cannot have Alcohol

Interpretation: Conductivity is equal to conductivity of cation and anion

🗝 Key Formulae

$$\text{Current (I)} = \frac{\text{Potential difference(V)}}{\text{Resistance(R)}}$$

$$\text{Resistance (R)} = \rho \frac{l}{A}$$

$$\text{Conductance (C)} = \kappa \frac{A}{l}$$

$$\text{Specific conductivity (kappa)} = C \times \frac{l}{A} = \frac{\text{Cell constant}}{R}$$

$$\text{Cell constant (G)} = \frac{l}{A}$$

$$\text{For strong electrolyte, } \Lambda_m = \Lambda^\circ{}_m - A\sqrt{C}$$

$$\Lambda^\circ = v_+\lambda^\circ_+ + v_-\lambda^\circ_-$$

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda^c_m}{\Lambda^\circ_m}$$

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{C\Lambda^\circ_m}{\Lambda^\circ_m(\Lambda^\circ_m - \Lambda_m)}$$

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda^\circ_m}$$

🗝 Key Terms

➢ **Electrolyte:** Substances that give ions when dissolved in water.

➢ **Resistance:** Opposition that a substance offers to the flow of electric current.

➢ **Limiting molar conductivity:** Molar conductivity when concentration approaches zero.

➢ **Conductance (G):** It is inverse of resistance. It is the ease with which current flows through a material. It increases with dilution.

➢ **Specific Conductivity (κ):** Specific conductivity or conductivity of an electrolytic solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with the unit area of cross-section and at a distance of unit length. On dilution, specific conductivity decreases.

Topic-3	## Faraday's Laws of Electrolysis, Batteries and Corrosion
	Concepts covered: *Faraday's Laws of electrolysis, Primary and secondary cell, Corrosion and their prevention.*

💬 Revision Notes

➢ Electrolysis is the process of decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten (fused) state. This process takes place in an **electrolytic cell**.

➢ **Faraday's First Law of Electrolysis:** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.

$$m = Z \times i \times t,$$

where Z = Electrochemical equivalent

➢ **Faraday's Second Law of Electrolysis:** Amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights.

$$\frac{W_1}{E_1} = \frac{W_2}{E_2}$$

➢ Relation between Faraday's constant (F), Avogadro's Number N_0 (or N_A) and charge of an electron:

1 Faraday is an amount of charge flows through 1 mole of electrons.

$$1\ F = 96500\ C; \quad F = N_A e^-$$

➢ **Battery** is an arrangement of two or more galvanic cells connected together in series.

➢ **Commercial cells (Batteries) are of two types:**
   (a) Primary cell : These cells are not chargeable as the electrode reaction occurs only once and after use over a period of time, the cells become dead and cannot be reused. e.g., Dry cell (Leclanche cell), Mercury cell.
   (b) Secondary cell : These cells are rechargeable and can be used again and again. It is recharged by passing current through it from an external source. e.g., Lead storage battery.

➢ **Dry cell (Leclanche cell) :** The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powered MnO_2 and C. The space is filled with a paste of NH_4Cl and $ZnCl_2$.
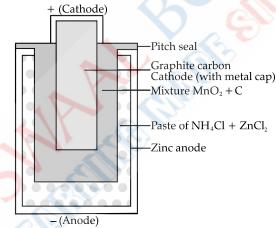

+ (Cathode)

Pitch seal
Graphite carbon
Cathode (with metal cap)
Mixture MnO_2 + C
Paste of NH_4Cl + $ZnCl_2$
Zinc anode

– (Anode)

Fig 5 : A dry cell

At anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At cathode: $MnO_2(s) + NH_4^+(aq) + 2e^- \longrightarrow MnO(OH) + NH_3$

The net reaction: $Zn(s) + NH_4^+(aq) + MnO_2 \longrightarrow Zn^{2+} + MnO(OH) + NH_3$

➢ **Lead storage battery:**
   Anode – Spongy lead
   Cathode – Lead packed with lead dioxide
   Electrolyte – Aqueous solution of H_2SO_4 (38%)

Anode
Cathode
Lead Dioxide (PbO_2)
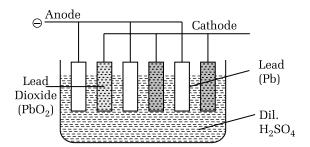Lead (Pb)
Dil. H_2SO_4

Fig. 6 : Lead storage battery

Discharge reaction of cell:

At anode : Following reaction takes place at anode:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^- \text{ (Oxidation)}$$

Reaction at cathode: PbO_2 filled in lead grid gets reduced to Pb^{2+} ions which combines with SO_4^{2-} ions to form $PbSO_4(s)$.

Complete cathode reaction is as follows:

$$PbO_2(s) + 4H^+ + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

Complete cell reaction: Oxidation half reaction takes place at anode and reduction half reaction takes place at cathode, when combined complete cell reaction is obtained.

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

$$PbO_2(s) + 4H^+ + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

Complete cell reaction:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$

Recharge reaction of cell: It changes the direction of electrode reaction $PbSO_4$ accumulated at cathode gets reduced to Pb.

$\therefore$ **At cathode:** $PbSO_4 + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$

At anode, $PbSO_4$ gets oxidised to PbO_2

$$PbSO_4(s) + 2H_2O \longrightarrow PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$$

Complete cell reaction would be as follows:

$$2PbSO_4(s) + 2H_2O(l) \xrightarrow{\text{charge}} Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$$

➤ **Mercury cell:** It consists of zinc-mercury amalgam as anode and a paste of mercuric oxide (HgO) and carbon as cathode. The paste of zinc oxide (ZnO) and potassium hydroxide (KOH) is used as an electrolyte.

Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

Net reaction: $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

➤ **Fuel cells:** Electrical cells that are designated to convert the energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called fuel cells.

In the cells:

Anode: $[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-] \times 2$

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

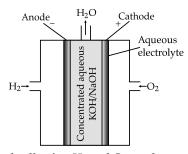**Net reaction:** $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Fig. 7. Fuel cell using H_2 and O_2 produces electricity

➤ **Corrosion:** The process of slow conversion of metals into their undesirable compounds (usually oxide) by reaction with moisture and other gases present in the atmosphere.

Example: Rusting of Iron At anode: $2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 2e^-$

At cathode: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 4H_2O(l)$

Overall reaction: $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

Fe^{2+} oxidises to Fe^{3+} ions and combines with atmospheric oxygen and moisture.

$$4Fe^{2+}(aq) + O_2(g) + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+$$

$$Fe_2O_3(s) + xH_2O(l) \longrightarrow Fe_2O_3.xH_2O$$
$$\text{Rust}$$

➤ **Factors affecting corrosion:** Presence of air, moisture, carbon dioxide, electrolytes in water, temperature, pH value, reactive metal impurities, etc.

➤ **Prevention from corrosion:**
   ♦ **Barrier protection:** Coating the metal surface with paints, oil or grease or by certain chemicals like $FePO_4$.
   ♦ **Sacrificial protection:** Coating the metal surface by some less active metals like zinc.
   ♦ **Cathodic protection:** By use of a more reactive metal as a sacrificial anode along with the less reactive metal to be protected.

⚙ Mnemonics

(1) Concept: Construction of Dry cell

Mnemonics: Dry cell se zindagi aur ghar

Interpretation:

Dry cell : Zinc and graphite

(2) Concept: Construction of Mercury cell and Fuel cell

Mnemonics: Mercury ne bana diya Zn-Hg ka oxide
Fuel ne diya Heat aur Oxygen

Interpretation :
Mercury cell : Zinc mercury amalgam and mercuric oxide.
Fuel cell : H_2 and O_2

⚷ Key Terms

➤ **Faraday constant:** It is the quantity of electricity, 1 F = 96500 C

➤ **Tinning:** Coating of iron with tin.

➤ **Combustion:** An exothermic reaction that involves the fast reaction of a fuel with oxygen.

❑❑

CHAPTER-3

CHEMICAL KINETICS

Topic-1 Rate of Chemical Reaction and Factors Affecting Rate of Reaction

Concepts covered: *Rate of reaction; Factors affecting rate; Rate law; Molecularity Order*

💬 Revision Notes

➤ **Chemical kinetics** is the branch of physical chemistry, which deals with the study of the rate of chemical reaction and mechanism of the reaction.

➤ **Classification of Reactions on the Basis of Rate of Reaction:**
   • **Fast (Instantaneous) reaction:** The reaction proceeds so rapidly, that the determination of rate of reaction is difficult. It occurs within few seconds.
     Example: ionic reactions, organic substitution reactions.
   • **Slow reaction:** The reaction proceeds extremely slow and may take several months for completion.
     Example: Rusting of iron.
   • **Moderate (Molecular) reaction:** The reaction proceeds between very fast and very slow reaction and their rate can be measured conveniently.
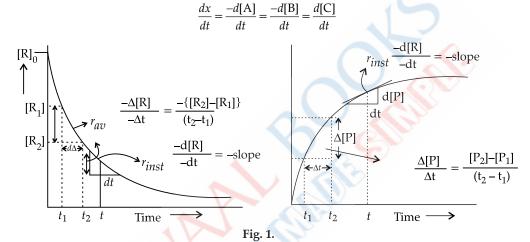   **Example:** Hydrolysis of esters.

- **Elementary reaction:** The reaction in which one or more of the chemical species react directly to form products in a single reaction step and with a single transition step.

➤ **Rate of reaction:** The rate of reaction is the change of concentration of any reactant or product, with time for a reaction.

For reaction, $\qquad$ $A + B \rightarrow C$

Rate of reaction, $A = \dfrac{\text{Decrease in concentration of A}}{\text{Time taken}} = \dfrac{-\Delta A}{\Delta t}$

Similarly for reaction, $B = \dfrac{-\Delta B}{\Delta t}$ and for product $C = \dfrac{\Delta C}{\Delta t}$

Unit : mol L^{-1} s^{-1} or atm s^{-1}.

➤ **Instantaneous Rate of Reaction:** Instantaneous rate is defined as the rate of change in concentration of any one of the reactant or product at a particular time. Instantaneous rate,

$$\frac{dx}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt}$$

Fig. 1.

➤ **Average Rate of Reaction:** The rate of reaction measured over a long time interval is called average rate of a reaction.

Average rate $= \dfrac{\Delta x}{\Delta t}$, where, $\Delta x =$ change in concentration in given time and $\Delta t =$ time taken.

➤ **Factors affecting the rate of a chemical reaction:**

 (i) Effect of concentration: Rate of reaction is directly proportional to the concentration of the reactants. Thus, to increase the rate of a reaction, the concentration of the reactants has to be increased.

 (ii) Temperature of the reaction: The rate of a reaction increases with the increase in temperature. Increase in temperature increases the kinetic energy of the molecules which results in the increase in rate of reaction.

 (iii) Pressure of the reaction: Pressure affects the rate of only gaseous reactions. Increase in pressure decreases volume and increases concentration. Increase in concentration increases the rate of reaction.

 (iv) Presence of catalyst: In the presence of a catalyst, the activation energy of a reaction decreases due to which the reaction proceeds at a faster rate.

 (v) Nature of the reactants: In a chemical reaction, some bonds are broken while some new bonds are formed. Thus, if the molecules are simpler, then less bonds will rupture and the rate of reaction becomes faster while in complex molecules more bonds will rupture and the velocity of the reaction decreases.

 (vi) Surface area of the reactants: In some heterogeneous reactions, the reaction takes place at the surface of the reactant. Thus in such reactions, the reaction rate is greatly affected by the surface area. Marble powder reacts faster than marble chips.

 (vii) Effect of radiations: Those reactions which are initiated by the radiations of particular wavelengths are termed as photochemical reactions. These reactions generally proceed at a faster rate than normal thermal reactions.

 (viii) Effect of physical state: Rate of reaction depends upon physical state of the reactant, e.g., $I_2(g)$ reacts faster than $I_2(s)$, $AgNO_3(aq)$ reacts with NaCl but $AgNO_3(s)$ does not react with NaCl.
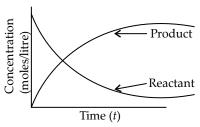
Fig. 2

➤ **Law of Mass Action:** "At constant temperature, the rate of a chemical reaction is directly proportional to the product of active masses of reacting species with each active mass term raised to the power equal to the stoichiometric coefficient of that species in the chemical reaction."

$$a\text{A} + b\text{B} \longrightarrow \text{Products}$$

Here, Rate of reaction $[\text{A}]^a[\text{B}]^b$, where [A] and [B] are active masses of the reactants A and B respectively.

➤ Active mass of a substance in the solution or gas phase is equal to its molar concentration.

➤ **Rate Law:** The rate law states that the rate of reaction is directly proportional to the product of molar concentration of reactants and each concentration is raised to some power which may or may not be equal to stoichiometry coefficients of reacting species

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n$$

➤ **Rate Constant:** Rate constant is also called specific reaction rate. When concentration of both the reactants are unity (one), then the rate of reaction is known as rate constant. It is denoted by 'k'.

➤ **Molecularity:** Total number of atoms, ions or molecules of the reactants Participate in the reaction is termed as molecularity. It is always in whole number. It is never more than three. It cannot be zero.

Example:

$$\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O} \text{ (Unimolecular reaction)}$$
$$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2 \text{ (Bimolecular reaction)}$$
$$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \text{ (Trimolecular reaction)}$$

For a complex reaction, generally, molecularity of the slowest step is same as the order of the overall reaction.

➤ **Rate determining step:** The slowest step in the reaction mechanism is called as the rate determining step.

➤ **Initial rate of reaction:** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called as the initial rate of reaction.

➤ **Order of a reaction:** It is the power to which concentration term of a particular reactant in the rate law is raised.

$$a\text{A} + b\text{B} + c\text{C} \longrightarrow \text{Products}$$
$$\text{Rate} = k[\text{A}]^p[\text{B}]^q[\text{C}]^r$$

where p, q and r represents the order of reaction with respect to A, B and C respectively.

Overall order of reaction $= p + q + r$

➤ **Pseudo first order reaction:** It is the reaction which seems to be of higher order but behave as first order under certain conditions.

➤ This reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substance.

In this reaction , water is taken as excess,

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$$

So, rate = k $[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$

🔑 Key Formulae

➤ Rate of reaction of a reactant $= \dfrac{\text{Decrease in concentration of reactant}}{\text{Time taken}}$

➤ Instantaneous rate of reaction $= \dfrac{dx}{dt} = \dfrac{-d[A]}{dt} = \dfrac{-d[B]}{dt} = \dfrac{-d[C]}{dt}$

➤ Average rate $= \dfrac{\Delta x}{\Delta t}$ where Δx = change in concentration in given time and Δt = time taken

🔑 Key Terms

> **Catalyst:** A substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change at the end of the reaction.

Topic-2	Order of a Reaction, Integrated Rate Equations and Half-Life of a Reaction

Concept covered: *Order of reaction, Half life of reaction*

💬 Revision Notes

> **Order of reaction:** Order is defined as the sum of powers of concentration of the reactants in the rate equation or rate law. Order of reaction is experimentally determined and is not written from the balanced chemical equation. Order of reaction can be whole number, zero or fractional.

> **Zero order reaction:** The rate of reaction does not change with the concentration of the reactants.

i.e., $Rate = k[A]_0$
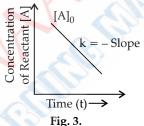
$$k = \frac{[A]_0 - [A]}{t}$$

where, 'k' is rate constant and unit of the rate constant k is mol L^{-1} s^{-1}.

This reaction will be zero order reaction.

Photosynthesis of HCl(g) is an example of zero order reaction.

Graphical representation of a zero order reaction:

Fig. 3.

> **First order reaction:** The rate of reaction is directly proportional to the concentration of reacting substance.

In reaction, $A \rightarrow Products$

$$Rate \propto [A]$$

$$\frac{-d[A]}{dt} = k[A]$$

$\Rightarrow$ $$\frac{-d[A]}{[A]} = kdt$$

On integration, $$\int \frac{-d[A]}{[A]} = \int kdt$$

$-\log_e[A] = kt + C$ [where, C is the constant of integration]   …(1)

At initial, $t = 0$, $[A] = [A]_0$

$$-\log_e[A]_0 = C$$

Therefore, equation (1) becomes,

$$-\log_e[A] = kt - \log_e[A]_0$$
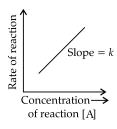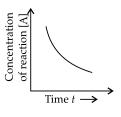
or $$k = -\frac{1}{t}\log_e \frac{[A]}{[A]_0}$$

$$k = \frac{2.303}{t}\log \frac{[A]_0}{[A]}$$

Unit of rate constant is s^{-1}.

Decomposition of NH$_4$NO$_2$ is an example for first order reaction.
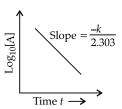
Graphical representation of a first order reaction:

Fig. 4.

➤ **Second order reaction:** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2.

∴
$$\frac{dx}{dt} = k[A]^1[B]^1$$

Unit of rate constant is $mol^{-1} L\ s^{-1}$ or $M^{-1}s^{-1}$, where M is molarity.

Reaction	Order	Unit of rate constant	Example
Zero order	0	$mol\ L^{-1}\ s^{-1}$	$H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$
First order	1	s^{-1}	$2N_2O_5 \rightarrow 4NO_2 + O_2$
Pseudo first order	1	s^{-1}	$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Second order	2	$mol^{-1} L\ s^{-1}$	$H_2 + I_2 \rightleftharpoons 2HI$

➤ **Equation for typical first order gas phase reaction:** $A(g) \rightarrow B(g) + C(g)$

$$k = \frac{2.303}{t} \log \frac{p_i}{p_A}$$

or
$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

where p_i is the initial pressure of A at time, $t = 0$ and p_t is the total pressure at time t.

➤ **Half-life of a reaction:** The time taken for a reaction when half of the starting material has reacted is called **half-life of a reaction**.

For zero order reaction,
$$t_{1/2} = \frac{[A]_0}{2k}$$

Where, $[A]_0$ is the initial and last concentration of reactant it means there is no change in concentration and 'k' is rate constant.

For 1st order reaction,
$$t_{1/2} = \frac{0.693}{k}$$

➤ **n^{th} Order reaction:** In general for n^{th} order reaction of the type

$$A \rightarrow \text{products, where, } \frac{dx}{dt} = k[A]^n$$

$$k_n = \frac{1}{t(n-1)}\left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}\right]$$

Where, $[A]_0$ is initial concentration, $[A]$ is final concentration after time t and n can have all the values except 1.

➤ **Half-life of a reaction of nth order:**

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

$t_{1/2} \propto [A]$ for zero order

$t_{1/2}$ is independent of $[A]$ for 1st order

$$t_{1/2} \propto \frac{1}{[A]} \text{ for 2nd order}$$

$$t_{1/2} \propto \frac{1}{[A]^2} \text{ for 3rd order}$$

Amount of substance left after n half-lives $= \dfrac{[A]_0}{2^n}$

➤ Integrated rate laws for the reactions of zero and first order:

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half life	Units of k
0	$A \rightarrow P$	$\dfrac{d[A]}{dt} = -k$	$kt = [A]_0 - [A]$	$[A]$ Vs. t	$\dfrac{[A]_0}{2k}$	conc. time^{-1}
1	$A \rightarrow P$	$\dfrac{d[A]}{dt} = -k[A]$	$[A] = [A]_0 e^{-kt}$ $kt = \dfrac{\ln[A]_0}{[A]}$	$\ln[A]$ Vs. t	$\ln\dfrac{2}{k}$	time^{-1}

➤ **Lifetime:** The time in which 98% of the reaction is completed is called lifetime.

Mnemonics

Concept: Order of reaction.
Mnemonics: Find Owl that keeps its eye Clean.
Interpretation: First order reaction rate is dependent on concentration of reaction.

Concept: Zero order reaction
Mnemonics: Zebra cannot keep its eye Clean.
Interpretation: Zero order reaction rate is not dependent on concentration of reaction.

Key Formulae

➤ **Zero order reaction:** $k = \dfrac{[A]_0 - [A]}{t}$

$t_{1/2} = \dfrac{[A]_0}{2k}$

➤ **First order reaction:** $k = \dfrac{2.303}{t}\log\dfrac{[A_0]}{A}$

$t_{1/2} = \dfrac{0.693}{k}$

Key Terms

➤ **Photochemical reactions:** The chemical reaction whose rate is influenced by radiations, particularly from ultraviolet and visible light is known as photochemical reactions.

➤ **Intermediate:** Species formed in one step and consumed in another.

Topic-3	Concept of Energy, Collision Theory and Arrhenius Equation
	Concept covered: *Activation energy, Collision theory, Arrhenius equation*

Revision Notes

➤ **Temperature Coefficient:** The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient.

$$\text{Temperature coefficient} = \frac{\text{Rate constant at 308 K}}{\text{Rate constant at 298 K}}$$

➤ It is observed that for a chemical reaction, with rise in temperature by 10°, the rate constant is nearly doubled.

➢ **Activation energy:** It is an extra energy which must be possessed by reactant molecules so that the collision between reactant molecules is effective and leads to the formation of product molecules.

Activation energy (E_a) for a reaction cannot be zero. It is not possible that every collision between molecules will be effective. E_a cannot have negative value.
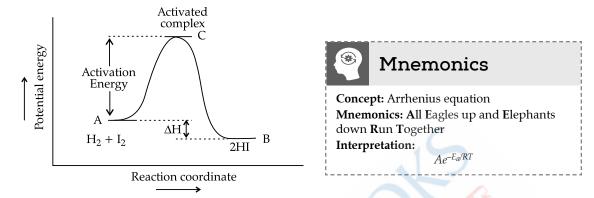

Mnemonics

Concept: Arrhenius equation
Mnemonics: All **E**agles up and **E**lephants down **R**un **T**ogether
Interpretation:
$$Ae^{-E_a/RT}$$

Fig. 5

➢ **Threshold energy:** The minimum energy that the reacting species must possess in order to undergo effective collision to form product molecules is called **threshold energy**.

➢ Those collisions which lead to the formation of product molecules are called effective collisions,

$$\text{Rate of reaction} = f \times Z$$

where 'Z' is collision frequency and 'f' is the fraction of collisions, which are effective.

➢ The number of collisions that take place per second per unit volume of the reaction mixture is called collision frequency. It is represented by 'Z'.

'Z' should be above effective collisions.

➢ Activated complex is defined as an unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product.

➢ **Collision theory:** According to the collision theory, rate of reaction depends on the collision frequency and effective collisions.

$$\text{Rate} = Z_{AB}e^{-E_a/RT}$$

where Z_{AB} represents the collision frequency of reactants A and B. $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a.

➢ According to the Collision theory, another factor P which is called steric factor refers to the orientation of molecules which collide, is important and contributes to effective collision.

$$K = PZ_{AB}e^{-E_a/RT}$$

➢ **Arrhenius equation:** Activated complex is defined as an unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product. Arrhenius equation gives the relation between rate of reaction and temperature.

$$k = Ae^{-E_a/RT}$$

where k = Rate constant
A = Frequency factor (Arrhenius factor)
E_a = Activation energy
R = Gas constant
T = Temperature in Kelvin

$$\ln k = \ln A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

A plot of $\log k$ vs $1/T$ gives a straight line with slope $= \frac{E_a}{2.303R}$

Fig. 6

If k_2 and k_1 are rate constants at temperature T_2 and T_1 respectively, then

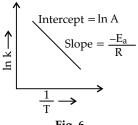$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$$

🔑 Key Formulae

➢ Temperature coefficient $= \dfrac{\text{Rate constant at} (T+10)^0}{\text{Rate constant at } T^0}$

➢ Rate of reaction $= f \times Z$

➢ Arrhenius equation: $k = Ae^{-E_a/RT}$

➢ $k = PZ_{AB}e^{-E_a/RT}$

❏❏

CHAPTER-4

d- AND f-BLOCK ELEMENTS

Topic-1	**d–Block : 3d, 4d and 5d Series** **Concepts covered:** *Transition elements, Electronic configuration, Properties of transition metals, Interstitial compounds.*

💬 Revision Notes

➢ **d-Block elements:** The elements in which last electron enters the *d*-subshell of penultimate shell. The general electronic configuration of these element is $(n–1)d^{1-10}ns^{1-2}$, where n is outermost shell. The *d*-block consisting of groups 3–12 occupies the large middle section of the periodic table.

➢ **Transition elements:** The elements of *d*-block are known as transition elements as they possess properties that are transitional between the *s*-block and *p*-block elements. Transition elements are defined as elements which have incompletely filled *d*-orbitals in its ground state or in any of its oxidation state. Transition elements have four series:

  (i) First transition series: These elements have incomplete 3*d* orbitals and they are from Sc(21) to Zn(30).

  (ii) Second transition series : These elements have incomplete 4*d* orbitals and they are from

    Y(39) to Cd(48).

  (iii) Third transition series: These elements have incomplete 5*d* orbitals and they are from La(57) and Hf(72) to Hg(80).

  (iv) Fourth transition series: These elements have incomplete 6*d* orbitals. The series are starts with Ac (89) followed by Rf (104) to Cn (112).

➢ **General electronic configuration:** $(n – 1)d^{1-10}$, ns^{1-2} where $(n – 1)$ stands for penultimate shell.

➢ **General characteristics:**

  ● **Metallic character:** Almost all the transition elements exhibit typical metallic properties like metallic lustre, malleability, ductility, high tensile strength, etc.

  ● **Atomic radii:** Atomic radii of transition elements first decreases till the middle, become almost constant and then increases towards the end of the period. This decrease in atomic radii in the beginning is due to increase in effective nuclear charge. However, with an increase in the number of electrons in $(n – 1)$ sub-shell, the screening effect of the *d*-electrons on the outermost *ns* electrons increases.
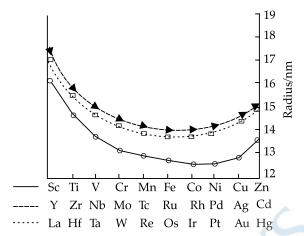
Fig. 1 : Trends in melting points of transition elements

- **Ionic radii:** The ionic radii of the transition elements follow the same order as their atomic radii. It decreases with an increase in oxidation number.
- **Ionisation enthalpy:** The ionisation energies of transition elements are quite high and lies between those of s-block and p-block elements. The first ionisation energy increases with an increase in atomic number across a given transition series, although the increase is not very regular.
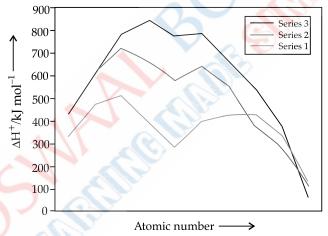
Fig. 2 : Trends in enthalpies of atomisation of transition elements

- **Variable oxidation state:** Since, the energies of ns and $(n - 1)d$ electrons are almost equal, therefore the electrons of both these orbitals take part in the reactions, due to which transition elements show variable oxidation states. Oxidation state is the measure of the electronic state of an atom in a particular compound, equal to the number of electrons it has more than or less than the number of electrons in free atom. Transition metal ions show variable oxidation states.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2	+2	+2	+2	+2	+2	+2	+1	+2
	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+6				
			+6	+6					
				+7					

- **Electrode potential:** The electrode potential developed on a metal electrode when it is in equilibrium with a solution of its ions, leaving electrons from the electrode. Transition metals have lower value of reduction potential. Variation in $E°$, value is irregular due to regular variation in ionisation enthalpies (I.E$_1$ + I.E$_2$), sublimation and hydration enthalpies.
- **Catalytic properties:** Many of the transition metals and their compounds, particularly oxides act as catalysts for a number of chemical reactions. Iron, cobalt, nickel, platinum, chromium, manganese and their compounds are commonly used catalysts.

- **Magnetic properties:** On the basis of the behaviour of substances in magnetic field, they are of two types:
  (i) Diamagnetic,   **(ii)** Paramagnetic
  Diamagnetic substances have paired electrons only. e.g., Zn has only paired electrons.
  In paramagnetic substances, it is necessary to have at least one unpaired electron. Paramagnetism increases with the increase in number of unpaired electrons.
  Paramagnetism may be measured by magnetic moment.

  Magnetic moment $(\mu) = \sqrt{n(n+2)}$ B.M.

  where, n = number of unpaired electrons in an atom or ion and B.M. = Bohr Magneton (unit of magnetic moment). Diamagnetic and paramagnetic substances are repelled and attracted in the magnetic field respectively (Magnetic properties of transition elements).

Ion	Outer electronic configuration	Unpaired electrons	Magnetic moment calculated (B.M.)	Magnetic moment experimental (B.M.)
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.86
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.95
Fe^{2+}	$3d^6$	4	4.90	5.0–5.5
Co^{2+}	$3d^7$	3	3.87	4.4–5.2
Ni^{2+}	$3d^8$	2	2.84	2.9–3.4
Cu^{2+}	$3d^9$	1	1.73	1.4-2.2
Zn^{2+}	$3d^{10}$	0	0	0

- **Formation of coloured compounds:** Transition metals form coloured ions due to the presence of unpaired d-electrons. As a result, light is absorbed in the visible region to cause excitation of unpaired d-electrons (d-d transition) and colour observed corresponds to the complementary colour of the light absorbed. Cu^{2+}, Zn^{2+} and Cd^{2+} are colourless due to the absence of unpaired d-electron (d^{10}).
- **Melting and boiling points:** These elements have high melting and boiling points because of strong interatomic bonding.
- **Formation of alloys:** Alloy formation is due to almost similar size of the metal ions, their high ionic charges and the availability of d-orbitals for bond formation.
- **Coinage metals and currency metals:** Copper (Cu), silver (Ag) and gold (Au) present in group 11 are known as coinage or currency metals.
- **Interstitial compounds:** These are those compounds in which small atoms occupy the interstitial sites in the crystal lattice. Interstitial compounds are well known for transition metals because small sized atoms of H, B, C, N, etc., can easily occupy position in the voids present in the crystal lattice of transition metals.
- **Metal-Metal bonding:** The heavier transition metals show strong tendency to form strong M-M bonds than their light congeners. This is due to their greater enthalpy of atomisation.
- The atomic size or the ionic radii of tri-positive ions decrease steadily from La^{3+} to Lu^{3+} due to increasing nuclear charge and electrons entering inner (n–2) f orbital . This gradual decreases in the size with an increasing atomic number is called Lanthanide Contraction.

🧠 Mnemonics

1. Concept: $3d$ series
Mnemonics: **S**cary **T**iny **v**icious **C**reatures as **M**ean; **F**emales **C**ome to **N**ight **C**lub **Z**en
Interpretation :
Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

2. Concept: $4d$ series
Mnemonics: **Y**es **S**(**Z**)ir, **N**ob **M**ost **T**echnicians **R**ub **R**od's **P**ale **S**ilver **C**adillace
Interpretation :
Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd

3. Concept: $5d$ series
Mnemonics: **L**ate **H**arry **T**ook **W**alk, **R**eached **O**ffice **I**n **P**ajamas **A**fter an **H**our
Interpretation :
La ... Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg

4. Concept: Lanthanides
Mnemonics: **L**adies **C**an't **P**ut **N**eedles **P**roperly is **S**lot-machines. **E**very **G**irl **T**ries **D**aily, **H**owever, **E**very **T**ime **Y**ou'd be **L**ose
Interpretation :
La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Topic-2 f-Block Elements: 4f and 5f Series

Concept covered: *Lanthanoid and their properties, Actinoid and their properties*

💬 Revision Notes

➤ Elements in which last electron enters into *f*-orbital are called *f*-block elements.

➤ The elements in which the differentiating electrons enter into $(n - 2)$ *f*-subshell are called inner-transition elements.

➤ It consists of two series called lanthanoid series and actinoid series.

➤ **Lanthanoids:** The series involving the filling of 4*f*-orbitals following Lanthanum La $(Z = 57)$ is called the lanthanoid series. There are 14 elements in this series starting with Ce $(Z = 58)$ to Lu $(Z = 71)$.

- **Electronic configuration:** $[Xe]\ 4f^{0-14}5d^{0-1}6s^2$
- Highly dense metals.
- High melting points.
- Form alloy easily with other metals.
- Soft, malleable and ductile with low tensile strength.
- **Oxidation state:** The most common oxidation state is +3. It exhibits +2 and +4 oxidation state.
- **Colour:** Some of the trivalent ions are coloured. This is due to the absorption in visible region of the spectrum, resulting in *f-f* transitions as they have partly filled orbitals.
- **Magnetic properties:** La^{3+} and Lu^{3+} have $4f^0$ or $4f^{14}$ electronic configurations which are diamagnetic and all the other trivalent lanthanoid ions are paramagnetic due to presence of unpaired electrons.
- **Reactivity:** Highly electropositive metals have an almost same chemical reactivity.
  - Combines with hydrogen gas on gentle heating to form hydride.
  - On heating with carbon form carbides of formula Ln_3C, LnC_2, Ln_2C_3.
  - With dilute acids, they liberate hydrogen.
    $$2Ln + 6H^+ \longrightarrow 2Ln^{3+} + 3H_2$$
  - With halogens, burn to form halides.
    $$2Ln + 3X_2 \longrightarrow 2LnX_3$$
  - Burn in oxygen to form oxides
    $$2Ln + 3O_2 \longrightarrow Ln_2O_3$$
  - Form oxides and hydroxides of formula M_2O_3 and $M(OH)_3$.
- **Lanthanoid contraction** is a steady decrease in the size of lanthanoids with increase in atomic number. On moving from Ce to Lu, the size of atoms and ions decreases regularly. The 4*f* orbitals are too diffused to screen the nucleus as effectively as the more localised inner shell. So, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number.
- **Uses:**
  - For producing alloy steels for plates and pipes. e.g., Mischmetal, which is an alloy of cerium and various other lanthanoid elements.
  - Steel mixed with La, Ce, Pr and Nd is used in the manufacture of flame throwing tanks.
  - Used as a catalyst for hydrogenation, dehydrogenation and petroleum cracking.
  - Pyrophoric alloys are used for making tracer bullets and shells.

➤ **Actinoids:**
- Elements following actinium, Ac $(Z = 89)$ upto lawrencium $(Z = 103)$ are called as actinoids.
- General electronic configuration: $[Rn]\ 5f^{0-14}6d^{0-2}7s^2$
- Highly dense metals with a high melting point.
- Form alloys with other metals, specially iron.
- Silvery white metals which are highly reactive.
- Gets tarnished when exposed to alkalies.
- **Actinoid contraction:** The atomic and ionic size decrease with an increase in atomic number. Electrons when added to the 5*f*-shell, result in an increase in the nuclear charge causing the shells to shrink inwards.
- **Oxidation state:** All actinoids show +3 oxidation state. The elements in the first actinoid series show higher states also.
- **Colour:** Actinoid ions are coloured.
- **Magnetic properties:** All the actinoids and their compounds are paramagnetic.
- **Reactivity:** Highly electropositive and form salts as well as complexes.
- **Uses:**
  - Thorium is used in the treatment of cancer, incandescent gas mantles and in nuclear chemistry.
  - Uranium is used in the glass industry, textile industry, in medicines and as nuclear fuel.
  - Plutonium is used in nuclear reactors.

Scan to know more about this topic

d- and f-block elements

➢ **Difference between Lanthnoids and Actinoids:**

Lanthanoids	Actinoids
● $4f$ orbitals is filled progressively.	● $5f$ orbital is filled progressively.
● Only Pm is radioactive.	● All are radioactive.
● Less reactive than actinoids.	● More reactive.
● Common oxidation is +3 where other oxidation states are +2, +4. It is due to a large energy gap between $4f$, $5d$ and $6s$ subshell.	● Common oxidation state is +3 where other oxidation states are +2, +4, +5 and +7 due to small energy difference between $5f$, $6d$, and $7s$ orbitals.
● Paramagnetic properties are easily explainable.	● Paramagnetic properties are hard to explain.

🔑 Key Terms

➢ **Transuranic elements:** All the elements beyond uranium are known as transuranic or man-made elements.
➢ **Platinum black:** It is the finely reduced form of platinum in the form of velvety black powder.

🧠 Mnemonics

Mnemonics: Action **T**hor is **p**ro, **U**ranus, **N**eptune, **P**luto Planets sees in **A**merica, **C**urious **B**erks in **C**alifornia, **E**instein **F**ermium, **M**endeleuim, **N**obelium
Interpretation :
A : Actinium
T : Thorium
p : Protactinium
U : Uranium
N : Neptunium

P : Plutonium
A : Americium
C : Curium
B : Berkelium
C : Californium
E : Einsteinium
F : Fermium
M : Mendelevium
N : Nobelium
l : Lawrencium

Topic-3 | Important Compounds of Transition Elements

Concepts covered: *Preparation and Properties of Potassium Permanganate and Potassium Dichromate*

💬 Revision Notes

➢ **Preparation of Potassium permanganate:**
  (i) It is prepared from pyrolusite ore with KOH in the presence of oxidising agent like KNO_3. The dark green potassium manganate undergoes electrolytic oxidation to produce potassium permanganate.
  $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$
  $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^* + MnO_2 + 2H_2O$

  (ii) Commercially, it is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of manganate (VI).

  $$MnO_2 + 2e^- \xrightarrow[\text{Oxidised with air/KNO}_3]{\text{Fused with KOH}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

  $$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} \underset{\text{Permanganate ion}}{MnO_4^-} + 1e^-$$

  (iii) In laboratory, by oxidation of manganese(II) ion salt by peroxodisulphate.

  $$2Mn^{2+} + \underset{\text{Peroxodisulphate}}{5S_2O_8^{2-}} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

➢ **Properties:**
  ● Dark purple crystalline solid.
  ● Sparingly soluble in water.
  ● Decomposes on heating at 513 K.

  $$2KMnO_4 \xrightarrow{513\,K, \Delta} K_2MnO_4 + MnO_2 + O_2$$

- **Oxidising properties:**
➤ Acts as a powerful oxidising agent in acidic, alkaline and neutral medium. For example:

1. In acidic medium oxidises:

(i) Iodide to iodine :

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$\frac{[2I^- \longrightarrow I_2 + 2e^-] \times 5}{2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O}$$

(ii) Ferrous to ferric :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$\frac{[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5}{MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

(iii) Oxalate to carbon dioxide :

$$[MnO_4{-} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$\frac{[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5}{2MnO_4{-} + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

(iv) Hydrogen sulphide to sulphur :

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$\frac{[S^{2-} \longrightarrow S + 2e^-] \times 5}{2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O}$$

(v) Sulphite to sulphate :

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$\frac{[SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5}{5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O}$$

(vi) Nitrite to nitrate :

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$\frac{[NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-] \times 5}{2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O}$$

2. In neutral alkaline medium:

(i) Iodide to iodate :

$$[MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 2$$
$$\frac{I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-}{2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-}$$
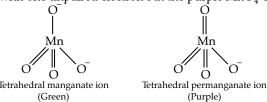
(ii) Manganous to manganese dioxide :

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

➤ **Uses of Potassium permanganate:**
- In analytical chemistry (titration).
- In decolourisation of oils.
- In sterilising wells of drinking water and washing wounds.

➤ **Structure of Potassium permanganate:** Both manganate and permanganate ions are tetrahedral. The green MnO_4^{2-} is paramagnetic with one unpaired electron but the purple MnO_4^- is diamagnetic.

Tetrahedral manganate ion
(Green)

Tetrahedral permanganate ion
(Purple)

➤ **Preparation of Potassium Dichromate (K$_2$Cr$_2$O$_7$):**
- From chromite ore (FeO.Cr$_2$O$_3$ or FeCr$_2$O$_4$)
    (i) Chromite ore is roasted in a reverberatory furnace with sodium carbonate in the presence of air to give sodium chromate.

$$2FeCr_2O_4 + 4Na_2CO_3 + 7/2 O_2 \xrightarrow{\text{Roasted}} 4Na_2CrO_4 + Fe_2O_3 + 4CO_2$$

(ii) Yellow solution of Na_2CrO_4 is filtered and acidified with conc. H_2SO_4 to give $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(iii) Sodium dichromate solution is treated with the calculated amount of KCl and the mixture obtained is cooled when orange crystals of potassium dichromate are obtained.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

➢ **Properties of Potassium dichromate:**
- Orange crystalline solid.
- With alkali dichromate gives chromate:

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$
$$\text{Chromate ion}$$
$$\text{(Yellow)}$$

- With acid chromate gives dichromate:

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$
$$\text{Dichromate ion}$$
$$\text{(Orange Red)}$$

- Oxidising nature:
  (i) It oxidises ferrous to ferric:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$\underline{[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6}$$
$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

  (ii) It oxidises stannous to stannic:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$\underline{[Sn^{2+} \longrightarrow Sn^{4+} + 2e^-] \times 3}$$
$$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$$

  (iii) It oxidises hydrogen sulphide to sulphur:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$\underline{[H_2S \longrightarrow 2H^+ + S + 2e^-] \times 3}$$
$$Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$

  (iv) It oxidises iodides to iodine:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$\underline{[2I^- \longrightarrow I_2 + 2e^-] \times 3}$$
$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

➢ **Structure of chromate and dichromate ions:** Chromate ion has tetrahedral structure with four oxygen atoms around central chromium atom. Dichromate ion contains two tetrahedral sharing corner with Cr — O — Cr bond angle of 126°.

➢ **Uses of Potassium dichromate:**
- Estimation of Fe^{2+} and I^- ions in volumetric analysis.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

- For chrome tanning in leather industry.
- Preparation of azo compounds.

❑❑

CHAPTER-5

COORDINATION COMPOUNDS

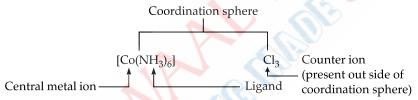| **Topic-1**	Concept of Complexes, Ligands, IUPAC Nomenclature of Mononuclear Coordination Compounds **Concept covered:** *Double salt, Coordination compound, Ligands, Denticity, Coordination number, IUPAC of coordination compounds*

💬 Revision Notes

➢ **Coordination compound:** A coordination compound contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules. It retains their identity in solid as well as in dissolved state. There is a coordinate bond between metal atom and these ions or molecules, e.g., $[Cu(NH_3)_4]^{2+}$.

➢ **Double salt:** When two salts in equimolar ratio are crystallised together from their saturated solution, they are called double salts. These are stable in solid state but dissociate into constituent ions in the solution. e.g., $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt).

➢ **Properties of double salts:**

  (i) They give simple ions in aqueous solution because they are ionic compounds.

  (ii) They do not contain coordinate bonds.

  (iii) They exist only in solid state as double salt.

  (iv) They are soluble in water.

➢ **Coordinate bonds:** A type of covalent bond in which one of the atom donates a pair electrons. It can be considered as a combination of transfer and sharing of electrons. Coordinate bonds are also called semipolar bonds.

➢ **Terms related to coordination compounds**

  1. Complex ion or coordination entity: It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

   (i) Cationic complex entity: It is the complex ion which carries positive charge.

   (ii) Anionic complex entity: It is the complex ion which carries negative charge.

  2. Central atom or ions

  3. Ligand

➢ **Central metal atom or ions:** The atom or ion to which a fixed number of ions or groups are bound to central atom or ion. It is also referred as Lewis acid. It is generally transition or inner transition element. e.g., in $K_4[Fe(CN)_6]$, Fe^{2+} is central metal ion.

➢ **Ligand:** A ligand is an ion or a small molecule having at least one lone pair of electrons and capable of forming a coordinate bond with central atom/ion in the coordination entity. e.g., Cl^-, OH^-, CN^-, CO, NH_3, H_2O, etc. A ligand may be neutral or charged species. It always acts as a Lewis base.

➢ **Types of Ligands:**

  (i) Monodentate ligand: A ligand which forms only one bond with central atom/ion, or have only one donor atom. e.g., CO, NO, NH_3, H_2O, OH^-, etc.

  (ii) Bidentate or didentate ligand: A ligand which forms two bonds with central atom/ion or two donor atoms/ion. e.g., 1, 2-ethane diamine or ethylene diamine (en).

$$CH_2—NH_2$$
$$|$$
$$CH_2—NH_2$$

  (iii) Polydentate ligand: A ligand which forms more than two bonds with central atom/ion or have more than two donor atoms, e.g., Ethylenediamine tetracetate (EDTA). Ligands which have three donor atoms per ligand are called as tridentate ligand, e.g., (dien) diethyl triamine. Tetradentate ligands are ligands that bind with four donor atoms to a central atom to form a coordination complex, e.g., diethylenetetramine. Pentadentate ligands bind with five donor atoms, e.g., triethylenetetramine and hexadentate ligands bind with six donor atoms, e.g., EDTA.

(iv) Chelating ligand: Di or polydentate ligands cause cyclisation around the metal atom which are known as chelate, such ligands uses two or more donor atoms to bind a single metal ion and are known as chelating ligand.

More the number of chelate rings, more is the stability of complex. The stabilisation of coordination compounds due to chelation is known as chelate effect. e.g., $[Pt(en)_2]Cl_2$.

➤ Coordinating of chelating ligand with a metal results in the formation of a closed cyclic ring and the compound is known as chelate. e.g., ethylenediamine complexed with Cu (II) ion forms a chelate:

$$\left[\begin{array}{c} H_2C - H_2N \searrow \quad \nearrow NH_2 - CH_2 \\ | \quad\quad Cu \quad | \\ H_2C - H_2N \nearrow \quad \searrow NH_2 - CH_2 \end{array} \right]^{2+}$$

➤ **Applications of Chelates:**

 (i) In the softening of hard water.

 (ii) In the separation of lanthanoids and actionids.

 (iii) In the detection as well as estimation of some metal ions such as nickel (II) ion.

 (v) Ambidentate ligand: A ligand which can form bond with two different atoms. e.g., NO_2^- or ONO^-, SCN^- or NCS^-.

 (vi) Flexidentate ligand: A ligand which forms different number of bonds with central atom/ion in different complexes. e.g., EDTA.

➤ **Coordination number:** It is defined as the number of coordinate bonds formed by central atom, with the ligands. It may also be defined as total number of chemical bonds formed between central metal ion and donor atom of ligand e.g., in $[Ni(NH_3)_6]^{2+}$, the coordination number of Ni^{2+} is 6.

➤ The central metal ion and the ligands directly attached to it are written inside a square bracket [ ]. It is called **coordination sphere. Werner** called it first sphere of attraction.

<div align="center">Coordination sphere</div>

$$[Co(NH_3)_6] \qquad Cl_3$$

Central metal ion ———————————— Ligand

Counter ion (present out side of coordination sphere)

➤ **Coordination polyhedron:** The spatial arrangement of the ligand atoms which are directly attached to the central atoms or ions define a coordination polyhedron about the central atom e.g., $[PtCl_4]^{2-}$ is square planar.

➤ **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.

➤ **Donor atom:** An atom in the Lewis base that forms the bond with the central atom/ion is called donor atom because it donates the pair of electrons.

➤ **Denticity:** The number of ligating groups in a ligand is called as denticity, e.g., unidentate, didentate, etc.

➤ **Oxidation number of central atom:** It is defined as the charge it would carry, if all the ligands are removed along with the electron pairs that are shared with the central atom. It can be calculated by taking the sum of oxidation state of metal and total ligands equal to charge present on its coordination sphere.

➤ **Types of Complexes:**

 1. Homoleptic

 2. Heteroleptic

1. **Homoleptic and Heteroleptic complexes:** Complexes in which the metal atom or ion is linked to only one type of ligands are called homoleptic complexes., e.g., $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$, etc. The complexes in which the metal atom or ion is linked to more than one kind of ligands are called heteroleptic complexes, e.g., $[Co(NH_3)Cl_2]^+$ and $[Cr(en)_2Cl_2]^+$, etc.

2. **Homonuclear and Polynuclear complexes:** Complexes in which only one metal atom is present are known as homonuclear complexes. e.g., $[Co(NH_3)_6]Cl_3$ and $[Cu(NH_3)_4]SO_4$. Complexes in which more than one metal atom is present are known as polynuclear complexes.

➤ **Counter ions:** The ions which are not included in the primary coordination sphere are known as counter ions. e.g., in $K_4[Fe(CN)_6]$, K^+ ions are counter ions.

➤ **IUPAC rules for naming complex compounds are:**

 (i) Name of compound is written in two parts **(a)** name of cation **(b)** name of anion.

 (ii) The cation whether simple or complex is named first followed by anion.

 (iii) Ligands are named in alphabetical order.

 (iv) For indicating the number of each kind of ligand within the coordination entity, two kinds of numerical prefixes are used (di, tri, tetra, etc.) For ligands containing any of these prefixes in their names, their

numbers are indicated by prefixes bis, tris, tetrakis, etc. Anionic ligands end with -*o*. Neutral ligands retain their names while cationic end with -*ium*.

(v) The coordination sphere is written in square bracket.

(vi) In naming, ligands are named first in alphabetical order followed by metal atom and then the oxidation state of metal by a Roman numeral in parenthesis.

(vii) Name of coordination compounds starts with a small letter and the complex part is written as one word.

(viii) Oxidation number of central atom is indicated in Roman numerals. No space is left between the number and the rest of the name.

Examples:

(a) $[Cr(NH_3)_3(H_2O)_3]Cl_3$ triamminetriquachromium (III) chloride

(b) $K_4[Fe(CN)_6]$ potassium hexacyanoferrate (II)

Type	Charge	Ligand	Formula	Name in Complexes
Monodentate	Neutral	ammonia	NH_3	amine
		water	H_2O	aqua
		carbon monoxide	CO	carbonyl
		pyridine	pyr	pyridine
	Minus one	azide	N_3^-	azido
		bromide	Br^-	bromido
		chloride	Cl^-	chlorido
		cyanide	CN^-	cyanido
		fluoride	F^-	fluorido
		hydroxide	OH^-	hydroxido
		nitrite	NO_2^-	nitrito
		thiocyanate	SCN^- or NCS^-	thiocyanato
Bidentate	Neutral	bipyridine	bipy	bipyridine
		ethylenediamine	en	ethylenediamine
	Minus two	carbonate	CO_3^{2-}	carbonato
		oxide	O_2^-	oxo
		oxalate	$C_2O_4^{2-}$	oxolato
			SO_4^{2-}	sulfato

⚷ Key Terms

➤ **Coordination chemistry:** The study of the coordination compounds is known as coordination chemistry.

➤ **Labile complex:** A complex in which ligand substitution is fast.

➤ **Inert complex:** A complex in which ligand substitution is slow.

➤ **Synergic bonding:** A ligand donates a pair of electrons to the metal atom or ion and then accepts a pair of electrons back in its vacant orbital also from *d*-orbitals of the metal or ion. This is called synergic bonding and the ligands involved are known as π–acid ligands.

➤ **Effective Atomic Number (EAN):** It can be calculated for the metal atom or in the coordination complex by using following reaction:

EAN = Atomic no. (Z) of metal atom – Oxidation number + 2 C.N. where, C.N. is coordination number.

Topic-2 Isomerism, Werner's Theory, VBT, CFT, Stability and Importance of Coordination Compounds

Concept covered: *Structural and stereoisomerism in coordination compounds, Werner's Theory, Valence band theory, Crystal field theory, Application of coordination compounds*
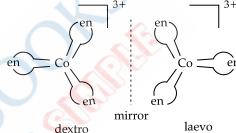
💬 Revision Notes

➤ Compounds having same molecular formula but different properties and structures are known as isomers and this phenomenon is known as **isomerism.**

➤ **Isomerism in coordination compounds is of two types:**

(a) **Structural isomerism:** Complexes having same molecular formula but different structural formula are called as structural isomers and the phenomenon is called as structural isomerism. It is of following types:

(i) Ionisation isomerism: In this type of isomerism, there is an interchange of groups between the coordination sphere of the metal ion and ions outside the coordination sphere, e.g., $[Co(NH_3)_5Cl]^{2+}$ SO_4^{2-} and $[Co(NH_3)_5(SO_4)]^+$ Cl^-.

(ii) Coordination isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex. e.g., $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$.

(iii) Linkage isomerism: In this type of isomerism, the ligand can form linkage with metal through different atoms. It is shown by ambidentate ligands. e.g., nitro (–NO_2) group can link to metal through nitrogen (–NO_2) or through oxygen (—O—N = O) atom i.e.,
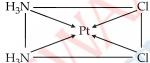
$[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$
Pentaamminenitro–O– Pentaamminenitro–N–
cobalt (III) chloride cobalt (III) chloride

(iv) Solvate isomerism: This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside. e.g., $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

(b) Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. These are of two types:

(i) Optical isomerism: Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro* (*d*) and *laevo* (*l*) depending upon the direction in which they rotate the plane of polarized light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octadehral complexes involving bidentate ligands.

Optical isomers (*d* and *l*) of $[Co(en)_3]^{3+}$

(ii) Geometrical isomerism or *cis-trans* isomerism: In tetra-coordinated square planar complexes, the cis isomer has the same groups on the same side whereas *trans*-isomer has same group on opposite side, e.g.,

cis-diamminedichloroplatinum(II) (*cis*-platinum)   *trans*-diamminedichloroplatinum(II)

➢ **Racemic mixture:** An equimolar mixture of *dextro* and *laevo* form is called racemic mixture. It has zero rotation.

➢ **Werner's theory:**
  ● Werner was able to explain the nature of bonding in complexes. The brief outlines of Werner's theory are as: Metal shows two different kinds of valencies:
  (i) Primary valency
  (ii) Secondary valency
  ● Primary valencies are satisfied by anions while secondary are satisfied either by oppositely charged ions or neutral molecules and sometimes by cationic groups.
  ● Secondary valencies are equivalent of coordination number and they are directed in space in specific number around each central metal atom within the lattice while primary valencies correspond to oxidation number of the metal and are satisfied by anions.

➢ **Limitations of Werner's theory:** This theory does not explain the following queries:
  (i) Why is the complex forming tendency limited to a few elements only?
  (ii) Why do bonds in the coordination complexes are of directional in nature?
  (iii) Why are certain complexes of magnetic nature and show geometrical and optical isomerism?

➢ **Valence Bond theory:** It was developed by Pauling. The brief points are:
  (i) A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bond with the ligands.
  (ii) Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon total number of ligands.
  (iii) The hybridised orbitals are allowed to overlap with those ligands orbitals that can donate an electron pair for bonding.

(iv) The outer orbitals (high spin) or inner orbitals (low spin) complexes are formed depending upon whether outer d-orbitals or inner d-orbitals are used.

➢ **Limitations of Valence bond theory:**
 (i) It cannot explain the detailed magnetic properties of complex compounds.
 (ii) It cannot explain the optical absorption spectra of coordination compounds.
 (iii) It cannot predict property whether a particular 4-coordinate complex is square planar or tetrahedral in nature.
 (iv) It fails to make distinction between strong and weak ligands.

➢ **Crystal field theory (CFT):**
 (i) According to crystal field theory, ligands are point charges.
 (ii) On approaching ligands, d-orbitals of metal ion gets split.
 (iii) Three d-orbitals, i.e., d_{xy}, d_{yz}, d_{zx} are oriented in between the coordinate axes and are called t_{2g} orbitals.
 (iv) The other two d orbitals, i.e., $d_{x^2-y^2}$ and d_{z^2} oriented along xy axis are called e_g orbitals.
   The energy difference between t_{2g} and e_g level is designated by triangle and is called crystal field splitting energy.
 (v) e_g orbitals have higher energy in octahedral and lower energy in tetrahedral complexes.
 (vi) t_{2g} orbitals have high energy in tetrahedral complexes.
   Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak field and consequently result in small splitting of d-orbitals. In general, ligands can be arranged in series in the order of increasing field strength as given below and called as spectrochemical series:
   $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < O_2^- < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO < NO$

🧠 Mnemonics
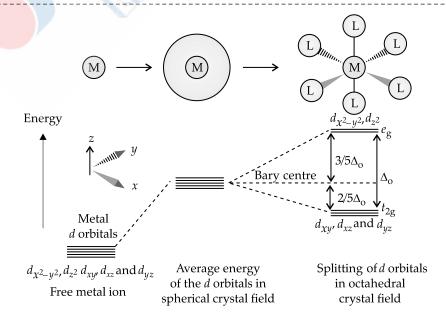
Concept: Spectrochemical series : $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < CN^- < CO$

Mnemonics: I Bought **S**ome **C**opies to **S**tudy **F**undamental **O**f Chemistry **H**e **N**urtured **E**xcellence in **N**ecessary **C**oordination **C**ompounds

Interpretation :

I^- = I	Br^- = Brought	SCN^- = Some
Cl^- = Copies to	S_{2-} = Study	F = Fundamental
OH^- = Of	$C_2O_4^{2-}$ = Chemistry	NCS^- = Nurtured
EDTA = Excellence in	NH_3 = Necessary	CN^- = Coordination
CO = Compounds		

$d_{x^2-y^2}, d_{z^2} \ d_{xy}, d_{xz} \ \text{and} \ d_{yz}$
Free metal ion

Average energy of the d orbitals in spherical crystal field

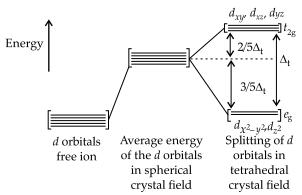Splitting of d orbitals in octahedral crystal field

Fig.2 : *d* orbital splitting in a tetrahedral crystal field

 (vii) Explanation of colour and magnetic behaviour in complexes is possible by crystal field theory.

➤ **Colour in coordination compounds:** Transition metal atom/ion has five degenerate *d*-orbitals in free state. On formation of coordination compounds, *d*-orbitals split into two or more parts as per geometry of complex. When light falls on the complex, it absorbs a portion of light from visible region to promote electrons from lower to higher level and transmits the rest of the light. The colour transmitted is complementary to the absorbed light. This electronic transition is known as *d-d* transition. e.g., $[Ti(H_2O)_6]^{3+}$ appears purple as it absorbs light of blue green colour for the promotion of the only electron from t_{2g} to e_g level and emits purple colour.

 ● Colour of compound with similar metal and ligand in different geometry is dissimilar.
 ● Colour of same metal with different ligand is different.
 ● Colour of complex of same metal in different oxidation states with similar ligand in similar geometry is different.

➤ **Magnetic property in coordination compounds:** Coordination compounds with unpaired electrons are paramagnetic.

➤ Coordination compounds containing all the paired electrons are diamagnetic. Paramagnetic compounds are attracted to applied magnetic field whereas diamagnetic compounds are weakly repelled by magnetic field.

➤ **Shapes of Coordination compounds:**

Coordination number	Type of hybridisation	Geometry of complex
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	dsp^3, sp^3d	Trigonal bipyramidal
6	sp^3d^2, d^2sp^3	Octahedral

➤ **Stability of Coordination compounds:** It depends on the charge present on central atom, nature of metal ion, basic nature of ligand, presence of chelate ring and effect of multidentate cyclic ligand. It is measured as stability constant denoted as K.

In the reaction, $M^{a+} + nL^{x-} \rightleftharpoons [ML_n]^{b+}$

$$K = \frac{[ML_n]^{b+}}{[M^{a+}][L^{x-}]^n}$$

Higher the value of stability constant K, greater will be the stability of the complex.

➤ **Limitations of CFT**
 1. It does not consider the formation of π bonding in complexes.
 2. It does not explain why H_2O is stronger ligand than OH^-.
 3. It gives no account of the partly covalent nature of metal-metal bonds.

➤ **Importance of Coordination compounds:**
 (i) They are used in photography, i.e., AgBr forms coloured complex with sodium thiosulphate in photography.
 (ii) $K[Ag(CN)_2]$ is used as catalyst for electroplating of silver, $K[Au(CN)_2]$ is used for gold plating.
 (iii) Some of ligands oxidize Co^{2+} to Co^{3+} ion.
 (iv) EDTA is used for estimation of Ca^{2+} and Mg^{2+} in hard water.

(v) Silver and gold are extracted by treating Zn with their cyanide complexes.

(vi) Ni^{2+} is tested and estimated by DMG (dimethylglyoxime).

(vii) *Cis*-platin $[Pt(NH_3)_2Cl_2]$ is used as anti-tumor agent in treatment of cancer.

(viii) EDTA is used to remove Pb by forming Pb-EDTA complex which is eliminated in urine.

(ix) Haemoglobin contains Fe, chlorophyll contains Mg and vitamin B_{12} contains Co.

(x) Bauxite is purified by forming complex with NaOH.

🔑 Key Terms

➢ **Facial or fac isomer:** When three ligands with donor atoms are on the same triangular face of the octahedron, the geometrical isomer is known as facial or *fac* isomer.

➢ **Meridional or mer isomer:** When three ligands with donor atoms are on the same equatorial plane of the octahedron or around the meridian of the octahedron, the isomer is called meridional or *mer* isomer.

➢ **Macrocylic effect:** Multidentate ligands happen to be cyclic in nature without causing any steric hindrance, the stability of the complexes is further increased. This is known as macrocyclic effect.

➢ **Stability constants (K):** The relative stabilities of coordination complexes can be compared in terms of stability constant (K) also denoted by β (Beta).

➢ **Polymerisation isomerism:** This is not a true isomerism. It occurs between compounds having the same empirical formula but different molecular masses. e.g., $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_3Cl]_2[PtCl_4]$.

❑❑

CHAPTER-6

HALOALKANES AND HALOARENES

Topic-1	**Haloalkanes**
	Concepts Covered ● *General formula of Haloalkanes,* ● *Classification,* ● *Methods of preparation,* ● *Physical and chemical properties, S_N1, S_N2 reaction,* ● *Polyhalogen compounds.*

💬 Revision Notes

➢ **Haloalkanes**
  ● Halogen derivatives of alkanes are called haloalkanes. On the basis of number of atoms of halogen present, these are called monohalogen, dihalogen, trihalogen and tetrahalogen derivatives. Monohalogen derivatives are called alkyl halides, also on the basis of nature of carbon atom, alkyl halides are called primary (— CH_2X), secondary ($>CHX_2$) and tertiary halide ($->C - X$).

➢ **Classification of Haloalkanes**
  ● If one hydrogen atom of alkane is replaced by a halogen atom, we get monohalogen derivatives having general formula $C_nH_{2n+1}X$.
  ● If two hydrogen atoms of alkane are replaced by two halogen atoms, we get dihalogen derivatives with general formula $C_nH_{2n}X_2$.
  ● If three hydrogen atoms of alkane are replaced by three halogen atoms, we get trihalogen derivatives with general formula $C_nH_{2n-1}X_3$.
  ● If all the four hydrogen atoms of alkane are replaced by four halogen atoms, we get tetrahalogen derivatives with general formula $C_nH_{2n-2}X_4$.
  ● When halogen is attached with primary carbon atom, it is called as primary alkyl halide. e.g., CH_3Br.
  ● When halogen atom is attached with the secondary carbon atom, it is called as secondary alkyl halide. e.g., $CH_3 — CH — CH_3$
    $\qquad\qquad\quad |$
    $\qquad\qquad\quad Cl$

- When halogen atom is attached with tertiary carbon atom, it is called as tertiary alkyl halide. e.g.,

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Cl$$

- If halogen atom is attached with cycloalkyl group, it is called as alicyclic halide. e.g., Cyclohexyl chloride
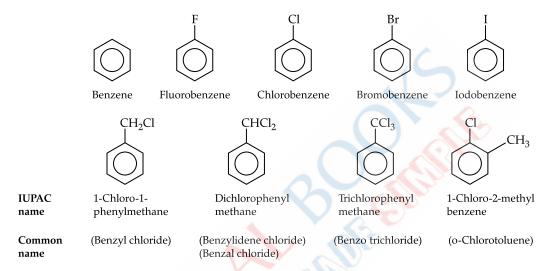

In allylic halides, the halogen is bonded to sp^3 hybridised carbon atom next to a carbon-carbon double bond (i.e., to an allylic carbon). e.g., $CH_2 = CH - CH_2Cl$.

➢ **Nomenclature:** General formula of alkyl halide is $C_nH_{2n+1}X$. Common names of alkyl halides are derived by naming the alkyl group followed by the halide.

Structure	IUPAC Name	Common Name
CH_3Cl	Chloromethane	Methyl chloride
CH_3CH_2Cl	Chloroethane	Ethyl chloride
$CH_3 - CH_2 - CH_2Cl$	1-Chloropropane	n-Propyl chloride
$CH_3 - \underset{\underset{Cl}{\vert}}{CH} - CH_3$	2-Chloropropane	Isopropyl chloride
$CH_3 - CH_2 - CH_2 - CH_2\,Cl$	1-Chlorobutane	n-Butyl chloride
$CH_3 - \underset{\underset{CH_3}{\vert}}{CH} - CH_2\,Cl$	1-Chloro-2-methyl propane	Isobutyl chloride
$CH_3 - CH_2 - \underset{\underset{Cl}{\vert}}{CH} - CH_3$	2-Chlorobutane	*Sec.* butyl chloride
$CH_3 - \underset{\underset{Cl}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - CH_3$	2-Chloro-2-methyl propane	*tert.* butyl chloride
CH_3F	Fluoromethane	Methyl fluoride
CH_3Br	Bromomethane	Methyl bromide
CH_3I	Iodomethane	Methyl iodide
CH_2Cl_2	Dichloromethane	Methylene dichloride
$CHCl_3$	Trichloromethane	Chloroform
CCl_4	Tetrachloromethane	Carbon tetrachloride
$CHBr_3$	Tribromomethane	Bromoform
CHI_3	Triiodomethane	Iodoform
$ClCH_2 - CH_2Cl$	1, 2-Dichloroethane	Ethylene dichloride
CH_3CHCl_2	1, 1-Dichloroethane	Ethylidene chloride
$CH_2 = CHCl$	Chloroethene	Vinyl chloride

$CH_2 = CH - CH_2Br$	3-Bromopropene	Allyl bromide
$(CH_3)_3CCH_2Br$	1-Bromo-2, 2-dimethylpropane	*neo*-pentylbromide
$CF_3CF_2CF_3$	Octafluoropropane	Perfluoropropane
CCl_2F_2	Dichlorodifluoromethane	Freon
$CHCl_2 - CHCl_2$	1, 1, 2, 2-Tetrachloroethane	Acetylene tetrachloride
$CHCl = CCl_2$	1, 1, 2-Trichloroethene	Acetylene trichloride

Benzene   Fluorobenzene   Chlorobenzene   Bromobenzene   Iodobenzene

IUPAC name	1-Chloro-1-phenylmethane	Dichlorophenyl methane	Trichlorophenyl methane	1-Chloro-2-methyl benzene
Common name	(Benzyl chloride)	(Benzylidene chloride) (Benzal chloride)	(Benzo trichloride)	(o-Chlorotoluene)

➢ **Methods of preparation of Haloalkanes:**

(a) From alcohols: Alkyl halides are prepared from alcohols, which are easily accessible.

$$R - OH + HX \xrightarrow[\text{Lucas Reagent}]{\text{HCl+Anhy.ZnCl}_2} R - X + H_2O$$

$$R - OH + NaBr + H_2SO_4 \longrightarrow R - Br + NaHSO_4 + H_2O$$

$$3R - OH + PX_3 \longrightarrow 3R - X + H_3PO_3 (X = Cl, Br)$$

$$R - OH + PCl_5 \longrightarrow R - Cl + POCl_3 + HCl$$

$$R - OH \xrightarrow[X_2 = Br_2, I_2]{\text{Red P/X}_2} R - X$$

$$R - OH + SOCl_2 \longrightarrow R - Cl + SO_2 + HCl$$

The reactions of primary and secondary alcohols with HX requires the presence of the catalyst $ZnCl_2$.

(b) From hydrocarbons: By free radical halogenation

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV Light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

$$\underset{n\text{-Butane}}{} \qquad \underset{n\text{-Butyl chloride}}{} \qquad \underset{Sec.\text{Butyl chloride}}{}$$

neo-Pentane   *neo*-Pentyl chloride

(c) From alkenes:

(i) Addition of hydrogen halide:

$$>C = C< + H - X \longrightarrow >C - C< \qquad (X = Cl, Br, I)$$

（省略）

$$R \overset{\delta+}{-} CH \overset{}{=} CH_2 + \overset{\delta+}{H} - \overset{\delta-}{X} \xrightarrow{\text{Markovnikov' Rule}} R - CH - CH_3$$
$$\underset{X}{|}$$

$$R - CH = CH_2 + H - Br \xrightarrow[\text{(Anti-Markovnikov's addition)}]{\text{Benzoyl peroxide}} R - CH_2 - CH_2 - Br$$

(ii) Addition of Halogens:

$$\overset{H}{\underset{H}{>}} C = C \overset{H}{\underset{H}{<}} + Br_2 \xrightarrow{CCl_4} \underset{\textit{Vic}\text{-Dibromide}}{BrCH_2 - CH_2Br}$$

(d) Halide Exchange:

(i) By Finkelstein Reaction:

$$R - X + NaI \xrightarrow{\text{Dry acetone}} R - I + NaX \ (X = Cl, Br)$$

(ii) By Swarts Reaction:

$$R - X + NaI \xrightarrow{AgF, Hg_2F_2, CoF_2 \text{ or } SbF_3} R - I + NaX$$

$$CH_3 - Br + AgF \longrightarrow CH_3F + AgBr$$
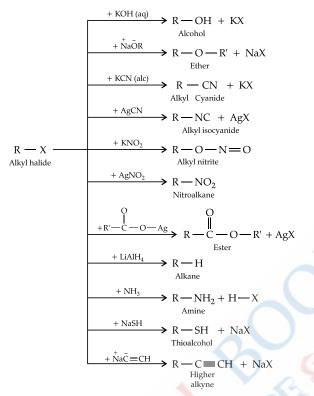
(iii) By Hunsdiecker Reaction:

$$R - \underset{\underset{O}{\|}}{C} - O^- Ag^+ \xrightarrow[CCl_4]{Br_2} R - Br + AgBr + CO_2$$

➤ **Nature of C – X bond in haloalkanes:** The carbon halogen bond is polarised. Carbon atom holds partial positive charge (δ^+) and halogen atom holds partial negative charge (δ^-) . This occurs due to difference in electronegativity. Halogens are more electronegative than carbon. Size of the halogen atoms increases down the group. Fluorine being the smallest and iodine being the largest. Carbon-halogen bond length also increases from C-F to C-I.

➤ **Physical properties of haloalkanes:** Haloalkanes are colourless when pure but compounds of bromine are coloured.

(i) Melting and boiling points: Haloalkanes, due to polar and strong dipole-interactions between their molecules, have high B.P. and M.P. This increase in B.P. and M.P. depends on size and mass of halogens, with weak van Der Waals forces of attraction. The increasing order is , RCl < RBr < RI. With respect to isomeric alkyl halides, B.P. decreases with increase in branching due to less surface area and weak interparticle forces.

(ii) Density: It increases with increase in carbon atoms and halogen atoms.

(iii) Solubility: Haloalkanes are insoluble in water but are soluble in organic solvents.

➤ **Chemical properties of haloalkanes:** Reactivity of haloalkanes depends on the C – X bond cleavage. Higher the bond dissociation energy of C – X bond, lesser will be the reactivity. Dissociation energy of C – X bond decreases with increase in the halogen size, i.e., C – Cl > C – Br > C – I. Reactivity order of haloalkanes would be:

<div align="center">Chlorides < Bromides < Iodides</div>

There are four types of chemical reactions with haloalkanes:

(a) Nucleophilic substitution reactions: When an atom or group of atoms is replaced by a *nucleophile,* the reaction is called as nucleophilic substitution reaction, e.g.,
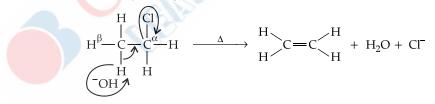
$$\overset{\delta+}{\underset{}{>}}C \overset{\delta-}{-} X + \underset{\text{Nucleophile}}{:\overset{\ominus}{Z}} \longrightarrow \overset{\delta+}{\underset{\text{Product}}{>}}C \overset{\delta-}{-} Z + \underset{\text{Leaving group}}{:\overset{\ominus}{X}}$$

Alkyl halides undergo nucleophilic substitution reactions.

$$CH_3CH_2Br + \overset{..}{\underset{..}{O}}H^- \longrightarrow CH_3CH_2OH + \overset{..}{\underset{..}{Br}}{}^{..}$$

(b) Elimination Reaction: Dehydration is a beta elimination reaction in which halogen from alpha carbon atom and the hydrogen from the beta carbon are eliminated according to Saytzeff rule.

The reaction is called *dehydrohalogenation*.

The following is order of reactivity:

$$RCl < RBr < RI$$

$$RCH_2X < R_2CHX < R_3CX$$

(c) Reaction with metals:

(1) Reaction with magnesium:

$$\underset{\text{Alky halide}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Alkyl magnesium halide} \\ \text{(Grignard reagent)}}}{RMgX}$$

$$\underset{\text{Ethyl bromide}}{CH_3-CH_2-Br} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl magnesium bromide}}{CH_3-CH_2-MgBr}$$

(2) Reduction with sodium (Wurtz reaction):

$$R-X + 2Na + X-R \xrightarrow{\text{Dry ether}} R-R + 2NaX$$

$$CH_3 — CH_2 — Cl + 2Na + Cl — CH_2 — CH_3 \xrightarrow{\text{Dry ether}} CH_3 — CH_2 — CH_2 — CH_3 + 2NaCl$$

(d) Reduction:

$$R — X + 2(H) \xrightarrow[\text{or Zn-Cu/C}_2\text{H}_5\text{OH}]{\text{Zn/HCl (conc.)}} R — H + H — X$$

$$CH_3 — CH_2 — Cl + 2(H) \xrightarrow{\text{Zn/HCl (conc.)}} CH_3 — CH_3 + HCl$$

➢ **Mechanism of Nucleophilic substitution reaction:** Alkyl halide undergoes two types of nucleophilic substitution reactions.

(i) Unimolecular nucleophilic substitution reaction (S_N1): Those substitution reactions in which rate of reaction depends upon the concentration of only one of the reactants, i.e., alkyl halides are called S_N1 reactions, e.g., hydrolysis of tertiary butyl chloride follows S_N1 reaction. This reaction takes place in two steps. The first step involves formation of carbocation.

Step I:

Step II:

The slowest step is rate determining step which involves one species only. Therefore, rate of reaction depends only on the concentration of tertiary butyl chloride. Tertiary halides follow S_N1 mechanism. Polar protic solvents like water, alcohol favour S_N1 mechanism because they stabilise carbocation by solvation. Tertiary halides follow S_N1 mechanism.

(ii) Biomolecular nucleophilic substitution reaction (S_N2): The reaction whose rate depends on the concentration of two species, alkyl halide and nucleophile. They involve one step mechanism. Back side attack of nucleophile and departing of leaving group take place simultaneously.

Non-polar solvents favour S_N2 mechanism. Primary halides follow S_N2 mechanism.

(a) Action of alkali:

$$R — X + KOH \underset{\text{(aq.)}}{\longrightarrow} ROH + KX$$

(b) Action of water:

$$R — X + H_2\ddot{O}: \longrightarrow ROH + HX$$

(c) Action of NaI (Finkelstein Reaction):

$$R — Cl + NaI \xrightarrow{\text{Dry acetone}} RI + NaCl$$

(d) Action of ammonia:

$$R — X \xrightarrow{NH_3} R — NH_2 \xrightarrow{R-X} R_2NH \xrightarrow{R-X} R_3N$$
$$\qquad\quad \textit{pri}\text{-amine} \qquad \textit{sec}\text{-amine} \qquad \textit{tert}\text{-amine}$$

(e) Action of KCN:

$$R — X + KCN \longrightarrow R — CN + KX$$

(f) Action of AgCN:

$$R — X + AgCN \longrightarrow R — NC + AgX$$

(g) Action of KNO_2:

$$R — X + KNO_2 \longrightarrow R — ONO + KX$$

(h) Action of $AgNO_2$:

$$R — X + AgNO_2 \longrightarrow R — NO_2 + AgX$$

(i) Reduction by $LiAlH_4$:

$$4R — X + LiAlH_4 \longrightarrow \underset{\text{Alkane}}{4R — H} + LiX + AlX_3$$

(j) Action of silver salt:

$$R — COOAg + R' — X \longrightarrow 4R — COOR' + AgX$$

Comparing the S_N1 and the S_N2 Reactions		
	S_N1	**S_N2**
Rate Law	Unimolecular (Substrate only)	Bimolecular (substrate and nucleophile)
"Big Barrier"	Carbocation Stability	Steric hindrance
Alkyl halide (electrophile)	3° > 2° >> 1° (worst)	1° > 2° >> 3° (worst)
Nucleophile	Weak (generally neutral)	Strong (generally bearing a negative charge)
Solvent	Polar protic (e.g., alcohols)	Polar aprotic (e.g., DMSO, acetone)
Stereochemistry	Mix of retention and inversion	Inversion only

➤ **Polyhalogen compounds:** The hydrocarbons or any carbon compounds containing more than one halogen atom (group 17 elements of the modern periodic table) are known as polyhalogen compounds.

➤ **Chloroform ($CHCl_3$):** It is the trichloro derivative of methane.

Preparation:

(a) From methane:

$$CH_4 + Cl_2 \xrightarrow[-HCl]{hv/675\,K} CH_3Cl \xrightarrow[-HCl]{+Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{+Cl_2} \underset{\text{Chloroform}}{CHCl_3}$$

(b) By partial reduction of carbon tetrachloride:

$$CCl_4 + 2H \xrightarrow{\text{steam}} CHCl_3 + HCl$$

(c) Laboratory method by action of bleaching powder on ethanol:

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$C_2H_5OH + Cl_2 \longrightarrow CH_3CHO + 2HCl$$

$$\underset{\text{Chloral}}{CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl}$$

(d) From acetone:

$$CaOCl_2 + H_2O \longrightarrow Cl_2 + Ca(OH)_2$$

$$\underset{\text{Acetone}}{CH_3 — \overset{\overset{O}{\|}}{C} — CH_3} + 3Cl_2 \longrightarrow \underset{\text{1,1,1- Trichloro acetone}}{CCl_3 — \overset{\overset{O}{\|}}{C} — CH_3} + 3HCl$$

$$Ca \begin{array}{l} O \\ O \end{array} \boxed{H \quad CCl_3} \overset{O}{\underset{\parallel}{C}} - CH_3 \longrightarrow 2CHCl_3 + \begin{array}{l} CH_3COO \\ CH_3COO \end{array} Ca$$

Chloroform   Calcium acetate

➤ **Properties:**
- Colourless.
- Heavy liquid causing temporary unconsciousness.
- **Oxidation**: Oxidation of $CHCl_3$ gives poisonous gas phosgene (carbonyl chloride). To avoid this oxidation $CHCl_3$ is stored in dark bottles and filled to the brim 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

$$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \xrightarrow[\text{Air}]{\text{Sunlight}} \underset{\substack{\text{Phosgene}\\\text{(Poisonous)}}}{2COCl_2} + 2HCl$$

- **Reduction:**

$$CHCl_3 + 2H \xrightarrow[\text{HCl}]{\text{Zn}} \underset{\substack{\text{Dichloro}\\\text{methane}}}{CH_2Cl_2} + HCl$$

$$CHCl_3 + 6H \xrightarrow[\text{Water}]{\text{Zn dust}} CH_4 + 3HCl$$

- **Hydrolysis:**

$$\underset{\text{(alc)}}{CHI_3} + 3KOH \xrightarrow{3KI} \underset{\text{Unstable}}{[H-C(OH)_3]} \xrightarrow{-H_2O} \underset{\text{Formic acid}}{H-\overset{O}{\underset{\parallel}{C}}-OH} \xrightarrow[-H_2O]{KOH} \underset{\text{Potassium formate}}{H-\overset{O}{\underset{\parallel}{C}}-O^-K^+}$$

- **Nitration:**

$$\underset{}{CHCl_3} + \underset{\text{(conc.)}}{HONO_2} \longrightarrow \underset{\text{(Chloropicrin)}}{CCl_3 \cdot NO_2} + H_2O$$

- **Carbylamine reaction:** With aliphatic or aromatic primary amine, chloroform forms corresponding isocyanide or carbylamine having unpleasant smell.

$$C_6H_5-N\overset{H}{\underset{H}{}} + \underset{Cl}{\overset{Cl}{C}}\overset{H}{\underset{Cl}{}} + \underset{\text{(alc.)}}{3KOH} \xrightarrow{\text{Warm}} \underset{\text{Phenyl isocyanide}}{C_6H_5N^+\equiv C^-} + 3KCl + 3H_2O$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + \underset{\text{Chloroform}}{CHCl_3} + \underset{\substack{\text{Potassium}\\\text{hydroxide}}}{3KOH} \xrightarrow{\text{Warm}} CH_3CH_2-N^+\equiv C^- + 3KCl + 3H_2O$$

- **Reimer-Tiemann reaction:**

➤ **Uses:**
(i) As a solvent for fats, alkaloids, iodine and other substances.

(ii) Production of freon refrigerant.

➤ **Iodoform (CHI_3):**

Preparation:

- **From ethanol:**

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\text{Heat}} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium formate}}{HCOONa} + 5NaI + 5H_2O$$

● **From acetone:**

$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 + 3I_2 + 4NaOH \xrightarrow{Heat} \underset{\underset{(Yellow\ ppt.)}{Iodoform}}{CHI_3 \downarrow} + 3NaI + \underset{Sodium\ acetate}{CH_3 - \overset{\overset{O}{\|}}{C} - ONa} + 3H_2O$$

$$\underset{Propanone}{CH_3COCH_3} + \underset{\underset{hypoiodite}{Sodium}}{3NaOI} \longrightarrow \underset{1,1,1\text{-triiodo-2-propanone}}{CH_3COCI_3} + 3NaOH$$

$$\underset{1,1,1\text{-triiodo-2-propanone}}{CH_3COCI_3} + NaOH \longrightarrow \underset{Sodium\ acetate}{CH_3COONa} + \underset{Iodoform}{CHI_3}$$

➤ **Properties:**

● Yellow crystalline solid and insoluble in water.

● On heating, it decomposes to give iodine vapour.

● Reduction

$$\underset{Iodoform}{CHI_3} + 2H \xrightarrow{P_4 + HI} \underset{(Diiodomethane)}{CH_2I_2} + HI$$

● **Hydrolysis:**

$$\underset{(alc)}{CHI_3} + 3KOH \xrightarrow{3KI} \underset{Unstable}{[H - C(OH)_3]} \xrightarrow{-H_2O} H - \overset{\overset{O}{\|}}{\underset{Formic\ acid}{C}} - OH \xrightarrow[-H_2O]{KOH} H - \overset{\overset{O}{\|}}{\underset{Potassium\ formate}{C}} - O^-K^+$$

● **Carbylamine reaction:**

$$\underset{Aniline}{C_6H_5NH_2} + CHI_3 + \underset{(alc.)}{3KOH} \xrightarrow{Warm} \underset{Phenyl\ isocyanide}{C_6H_5N \equiv C} + 3KI + 3H_2O$$

$$\underset{Methanamine}{CH_3NH_2} + CHI_3 + \underset{(alc.)}{3KOH} \xrightarrow{Warm} \underset{Methyl\ isocyanide}{CH_3 - N \equiv C} + 3KI + 3H_2O$$

● **Dehalogenation:**

$$CHI_3 + 6Ag + CHI_3 \xrightarrow{Heat} \underset{Ethyne}{HC \equiv CH} + 6AgI$$

● **Reaction with silver nitrate:**

$$Iodoform + Silver\ nitrate \xrightarrow[(alc.)]{Heat} Yellow\ ppt\ of\ AgI$$

➤ **Uses:**

  (i) Manufacture of refrigerants and propellants for aerosol cans.

 (ii) As an antiseptic.

(iii) Cleansing agent and spot remover.

(iv) As fire extinguisher in the name of pyrene.

➤ **Freons:** The chlorofluorocarbon compounds of methane and ethane with chlorine and fluorine in combination are known as freons. e.g., CCl_2F_2.
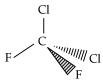
Preparation:

$$\underset{\underset{tetrachloride}{Carbon}}{CCl_4} + 2AgF_2 \longrightarrow \underset{\underset{difluoro\ methane}{Dichloro}}{CCl_2F_2} + 2AgCl$$

Properties:

● Extremely stable.

● Unreactive, non-toxic and non-corrosive.

● Easily liquefiable gas.

Structure:

➤ **Polyhalogen compounds:** Carbon compounds containing more than one halogen atoms are usually referred to as polyhalogen compounds. Many of those compounds are useful in industry and agriculture.

(i) **Dichloromethane (Methylene chloride):** It is prepared industrially by the direct chlorination of methane.

$$CH_4 + 2Cl_2 \xrightarrow{hv} CH_2Cl_2 + 2HCl$$

The mixture so obtained is separated by fractional distillation. It is widely used as solvent in pharmaceuticals and food industry.

(ii) **Chloroform:** It is manufactured by chlorination of methane followed by separation by fractional distillation.

$$CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{hv} CHCl_3 + 3HCl.$$

It is extensively used as solvent for waxes, resins, rubber, fats, etc. It was earlier used as anaesthetic and swallowing agent, but due to formation of phosgene gas (poisonous gas), it is not used at present.

(iii) **Iodoform (Triiodomethane):** It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or Na_2CO_3 and I_2 in water. It is insoluble in water, yellow precipitate of CHI_3 is formed. This reaction is called iodoform reaction.

$$CH_3CH_2OH + 6NaOH + 4I_2 \xrightarrow{heat} CHI_3 + 5NaI + HCOONa + 5H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{heat} CHI_3 + 3NaI + CH_3COONa + 3H_2O$$
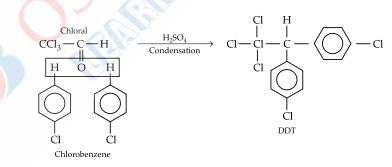
It is used as an antiseptic for dressing wounds.

(iv) **Carbon tetrachloride (Tetrachloromethane):** It is prepared by chlorination of methane or by action of chlorine on CS_2 in the presence of $AlCl_3$ as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + SCl_2 \qquad \text{(Sulphur dichloride)}$$

$$CH_4 + 4Cl_2 \xrightarrow{hv} CCl_4 + 4HCl$$

It is highly used as a solvent for fats, resins, etc. It is used in fire extinguisher.

(v) **DDT:** It is used as an insecticide. It creates pollution due to its extreme stability. It is non biodegradable. It is manufactured by the condensation of chlorobenzene with chloral (trichloroacetaldehyde) in the presence of sulphuric acid. It is also called p, p'-dichlorodiphenyltrichloroethane. It is highly toxic to fish and due to stability, it gets deposited and stored in animal fat tissues. Thus, it was banned in USA and India but still used in other countries of the world.

Key Terms

> **Walden inversion:** S_N2 mechanism in alkyl halides leads to inversion of configuration known as Walden inversion.
> **Synthetic tools:** Alkyl halides are regarded as synthetic tools in the hands of chemistry due to their highly reactive nature.

Topic-2   Haloarenes

Concepts Covered   ● *Methods of preparation of Haloarenes,* ● *Physical and chemical properties.*

💬 Revision Notes

➢ **Haloarenes:** Haloarenes are the compounds formed by replacing one or more hydrogen atoms in an aromatic ring with halogen atoms. For example, monohalogen derivative (X = F, Cl, Br or I).

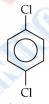➢ When two halogens are at 1, 2-positions of benzene ring, it is called *ortho* disubstituted derivative. e.g.,
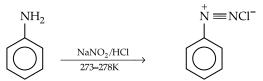
1, 2- dichlorobenzene

➢ When two halogens are at 1, 3-positions of benzene ring, it is called *meta* disubstituted derivative, e.g.,

1, 3- dichlorobenzene

➢ When two halogens are at 1, 4-positions of benzene ring, it is called *para* disubstituted derivative., e.g.,

1, 4- dichlorobenzene

➢ **Methods of preparation of Haloarenes:**

  (i) Reaction of benzene with Halogen (By electrophilic substitution):

$$\text{benzene} + X_2 \xrightarrow[\text{dark}]{\text{Fe or FeX}_3} \text{Halo benzene} - X + H{-}X \quad (X = Cl, Br)$$

$$\text{benzene} + I_2 \xrightarrow[\text{or HNO}_3]{\text{HIO}_3} \text{Iodobenzene} - I + HI$$

  (ii) From diazonium salts:

$$\overset{NH_2}{\text{benzene}} \xrightarrow[\text{273–278K}]{\text{NaNO}_2/\text{HCl}} \overset{\overset{+}{N}{\equiv}NCl^-}{\text{Benzenediazonium chloride}}$$
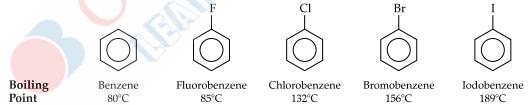
(iii) By Gattermann reaction:

(iv) From silver salt of aromatic acid (Hunsdiecker reaction):

➤ **Physical properties:**
- Colourless with a pleasant smell.
- Insoluble in water.
- Isomeric haloarenes have similar boiling points. But *para* isomers have higher melting point than other two, i.e., *meta* and *ortho* because of the symmetry in *para* isomer which occupies the crystal lattice better than *ortho* and *meta* isomers.

	Benzene	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene
Boiling Point	80°C	85°C	132°C	156°C	189°C

➤ **Chemical properties:**
- **Nature of** C—X **bond in haloarene:** The C—X bond of aryl halide is less reactive than that of haloalkanes. One reason is that in aryl halide, halogen atom is attached to sp^2-hybrid carbon atom whereas in alkyl halides, it is attached to sp^3-hybrid carbon atom. Due to more electronegativity of sp^2-hybrid carbon in comparison to sp^3-carbon atom, there is less charge in separation of C—X bond in haloarene.
- Secondly in aryl halides like chlorobenzene, the lone pair of electrons present on chlorine atom migrate towards the aromatic ring by +R effect due to conjugation of lone pair of electrons with π-electrons of the aromatic ring. As a result of which, the halogen atom is attached with the aromatic ring by partial double bond. The phenyl cation formed is highly unstable. The replacement of such a halogen atom by other nucleophiles becomes difficult.

(i) Nucleophilic substitution reactions are very less possible with haloarenes as C – X bond attains partial double bond character because of resonance effect, difference in hybridization, instability of the formed phenyl cation. Due to these repulsions, it makes difficult for electron rich nucleophile to attack electron rich haloarenes. Under higher temperatures, some of the below mentioned nucleophilic reactions are possible.

(a) Substitution by — OH group (Dow's process):

(b) Substitution by — CN group:

(c) Substitution by — NH₂ group:
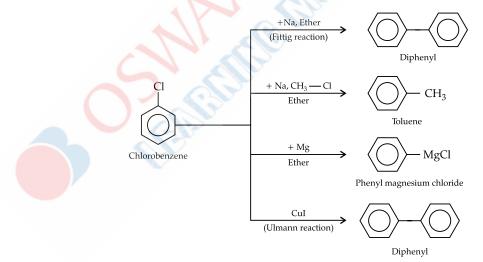
(d) Reaction with metals:

(ii) Electrophilic substitution reactions take place due to – I effect and +M effect of halogen atom. Haloarenes are *o, p*-directing.

(a) Halogenation:

(b) Nitration:

o-nitrochlorobenzene
(Minor)

p-nitrochlorobenzene
(Major)

(c) Sulphonation:

o-chlorobenzene
sulphonic acid
(Minor)

p-chlorobenzene
sulphonic acid
(Major)

(iii) Reduction:

Benzene
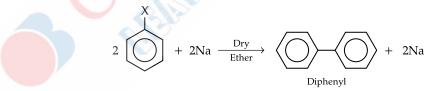
(iv) Wurtz-Fittig reaction: A mixture of an aryl halide and alkyl halide when treated with sodium metal in dry ether gives alkyl arenes.

(v) Fittig reaction: Aryl halides on reaction with sodium in dry ether gives diaryl.

Diphenyl

(vi) Addition reaction with magnesium: Haloarenes react with magnesium in the presence of dry ether (or tetrahydrofuran) to form phenyl magnesium halide.

Phenyl magnesium halide

➢ **Friedel-Craft's reaction:** Aromatic compounds when treated with alkyl halide in presence of Lewis acid catalyst like anhydrous $AlCl_3$, give alkyl arenes.

Toluene

Mnemonics

1. **Concept:** Preparation of Haloalkanes by different methods
   Mnemonics: Alkyl Halide
   Interpretation: Preparation of Haloalkane from Alkane, Alkene, Alcohol, Halogen Transfer
2. **Concept: S_N1 Nucleophilic Substitution**
   Interpretation: Unimolecular reaction with attack of weak nucleophile
   Mnemonics: Weak Nets cannot accomodate Urchins
3. **Concept:** Gatterman Reaction
   Interpretation: Diazonium Chloride with copper powder gives Bromo benzene
   Mnemonics: DC is Current used in Battery for power source.
4. **Concept:** Wurtz-Fitting Reaction
   Interpretation: Reaction of Aryl Halide with Sodium (Na)
   Mnemonics: Walrus found about North pole in Arctic Ocean

Key Terms

➢ **Nucleophilic substitution reaction:** Reaction in which a nucleophile causes the substitution of another weak nucleophile.

➢ **Resonance effect:** The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

❑❑

CHAPTER-7

ALCOHOLS, PHENOLS AND ETHERS

Topic-1	Alcohols and Phenols: Methods of Preparation, Properties and Uses
	Concepts Covered: *Classification of alcohol, General formula, Strucuture and nomenclature, Methods of preparation, Physical and chemical properties, Test for identification, Uses.*

Revision Notes

➢ **Alcohol:** When one hydrogen atom of alkane is replaced by —OH group, the compounds obtained are called alcohols having general formula $C_nH_{2n+1}OH$.

➢ **Classification of alcohols:**

(a) Based on number of hydroxyl(-OH) group

  (i) Monohydric alcohols: the alcohols which contain one –OH group. CH_3OH, C_2H_5OH, etc.

  (ii) Dihydric alcohols: The alcohols which contain two —OH groups , also called diols.

   General formula = $C_nH_{2n}(OH)_2$.

   e.g., $CHOH_2CHOH_2$

      Ethane-1, 2-diol.

  (iii) Trihydric alcohols: The alcohols which contain three hydroxyl (–OH) groups, also called triols. Their general formula is $C_nH_{2n-1}(OH)_3$. e.g.,

$$CH_2OH$$
$$|$$
$$CHOH \quad \text{Propane-1,2,3-triol}$$
$$|$$
$$CH_2OH$$

(b) Based on carbon atom attached to -OH group:

(i) Primary alcohols: The alcohol in which –OH group is attached to primary (1°) carbon atom. e.g., CH_3OH, C_2H_5OH, etc.

(ii) Secondary alcohols: The alcohol in which –OH group is attached to secondary (2°) carbon atom. e.g.,

$$CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \quad \text{(2-propanol)}$$

(iii) Tertiary alcohols: The alcohol in which —OH group is attached to tertiary (3°) carbon atom

$$\text{e.g., } CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH \text{ or } (CH_3)_3C\text{-}OH \text{ (2-methylpropan-2-ol)}$$

Note: Those alcohols which have more than one —OH groups are called polyhydric alcohol. e.g.,

$$\underset{CH_2OH}{\overset{CH_2OH}{|}} \quad \text{Glycol.}$$

(c) Allylic and vinylic alcohols:

(i) Those alcohols in which —OH group is attached to single bonded sp^3- hybridised carbon next to carbon-carbon double bond, that is to allylic carbon are called as allylic alcohols, e.g., $CH_2 = CH - CH_2 - OH$.

(ii) Those alcohols in which —OH group is attached to double bonded sp^2-hybridised carbon atom are called as vinylic alcohols. They are highly unstable and get tautomerised to form aldehydes. e.g.,

$$\underset{\text{(Vinyl alcohol)}}{CH_2 = CHOH} \rightleftharpoons \underset{\text{(Acetaldehyde)}}{CH_3 - \overset{\overset{O}{\|}}{C} - H}$$

(d) Benzyl alcohol: Those in which —OH group is attached to single bonded sp^3-hydridised carbon atom attached to aromatic ring are called as benzylic alcohols. e.g.,

(Benzyl alcohol)
Phenyl methanol

➤ **Isomerism in alcohols:** They show four types of structural isomerism.

(i) Chain isomerism: These isomers differ in the chain of the carbon atoms attached to the hydroxyl group.

$$C_4H_{10}O \qquad \underset{\text{Butan-1-ol}}{CH_3 - CH_2 - CH_2 - CH_2 - OH} \qquad \underset{\text{2-methylpropan-1-ol}}{CH_3 - \underset{\overset{|}{CH} -}{\overset{\overset{CH_3}{|}}{}} CH_2OH}$$
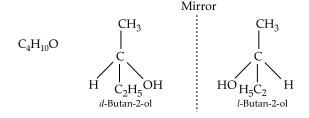
(ii) Position isomerism: These isomers differ in the position of the hydroxyl group.

$$C_3H_8O \qquad \underset{\text{Propan-1-ol}}{CH_3 - CH_2 - CH_2 - OH} \qquad \underset{\underset{\text{Propan-2-ol}}{OH}}{CH_3 - \underset{|}{CH} - CH_3}$$

(iii) Functional isomerism: These isomers differ in the functional group.

$$C_2H_6O \qquad \underset{\text{Ethanol}}{CH_3CH_2 - OH} \qquad \underset{\text{Dimethlyether}}{CH_3 - O - CH_3}$$

(iv) Optical isomerism: Monohydric alcohol containing chiral carbon atom show optical isomerism.

➢ **Common and IUPAC Names of Some Alcohols:**

Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3CHOHCH_3$	*iso*-Propyl alcohol	Propan-2-ol
$(CH_3)_2CH—CH_2OH$	*iso*-Butyl alcohol	2-Methyl propan-1-ol
$CH_3CH_2CHOHCH_3$	*sec*-Butyl alcohol	Butan-2-ol
$(CH_3)_3C—OH$	*tert*–Butyl alcohol	2-Methyl propan-2-ol
$\begin{matrix} CH_2 — CH_2 \\ \mid \quad\ \mid \\ OH \quad OH \end{matrix}$	Ethylene glycol	Ethane-1, 2-diol
$\begin{matrix} CH_2 — CH — CH_2 \\ \mid \quad\ \mid \quad\ \mid \\ OH \quad OH \quad OH \end{matrix}$	Glycerol or Glycerine	Propane-1, 2, 3-triol

➢ **Methods of preparation of Alcohols:**

1. From Haloalkanes: Haloalkanes are hydrolysed to the corresponding alcohols by treatment with aqueous alkali.

$$CH_3 — Cl + KOH\ (aq.) \longrightarrow CH_3—OH + KCl$$

2. From Aldehydes and Ketones:

(i) Reduction: Aldehyde and ketones are reduced to primary and secondary alcohols respectively. The common reducing agents are lithium aluminium hydride ($LiAlH_4$), Sodium borohydride ($NaBH_4$) or hydrogen gas in the presence of nickel or platinum as catalyst.

(a) $\underset{\text{Ethanal}}{CH_3 — \overset{\overset{O}{\|}}{C} — H} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Ethanol}}{CH_3 — CH_2 — OH}$

(b) $\underset{\text{2-Propanone}}{CH_3 — \overset{\overset{O}{\|}}{C} — CH_3} + H_2 \xrightarrow{\text{Ni}} \underset{\text{2-Propanol}}{CH_3 — \overset{\overset{OH}{\mid}}{CH} — CH_3}$

(ii) Using Grignard reagent: This method is used to get all three types of alcohols: Formaldehyde (HCHO) reacts with Grignard reagent to give primary alcohol whereas other aldehydes give secondary alcohols. Ketones give tertiary alcohols. e.g.,

(a) $H — \overset{\overset{\|}{O}}{\underset{}{C}} — H + CH_3MgBr \longrightarrow H — \overset{\overset{OMgBr}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}} — H \xrightarrow{H_2O/H^+} \underset{\text{Ethanol}}{CH_3CH_2OH} + Mg\overset{\diagup OH}{\diagdown Br}$

Hydroxy magnesium bromide

(b) $\underset{\substack{\text{(Acetaldehyde) Methyl magnesium} \\ \text{bromide}}}{CH_3 — \overset{\overset{O}{\|}}{C} — H + CH_3MgBr} \longrightarrow \left[CH_3 — \overset{\overset{OMgBr}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}} — H \right] \xrightarrow{H_2O/H^+} \underset{\substack{\text{2-propanol} \\ \text{(Isopropyl alcohol)}}}{CH_3 — \overset{\overset{OH}{\mid}}{CH} — CH_3} + Mg\overset{\diagup OH}{\diagdown Br}$

Hydroxy magnesium bromide

Acetone	Methyl magnesium bromide	Adduct	2 methyl butane-2-ol

3. From Alkenes:

(i) $CH_2{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H \xrightarrow{H_2O} CH_3CH_2OH + H_2SO_4$
     Ethene   Ethanol

(ii) $CH_3{-}CH{=}CH_2 + H_2SO_4 \longrightarrow CH_3{-}\underset{\underset{OSO_3H}{|}}{CH}{-}CH_3 \xrightarrow{H_2O} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3 + H_2SO_4$
                                                                                                                 Isopropyl alcohol

(iii) $CH_3{-}\underset{\underset{\text{2-methylpropene}}{}}{\overset{\overset{CH_3}{|}}{C}}{=}CH_2 + H_2O \xrightarrow{H^+} CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\text{2-methylpropan-2-ol}}{}}{OH}}{C}}{-}CH_3$

4. Hydroboration oxidation: As per anti-Markovnikov's rule –

$$CH_3{-}CH{=}CH_2 + B_2H_6 \longrightarrow CH_3{-}\underset{\underset{H}{|}}{CH}{-}\underset{\underset{BH_2}{|}}{CH_2} \xrightarrow[NaOH,H_2O]{H_2O_2} CH_3{-}CH_2{-}CH_2OH + H_3BO_3$$
     Propene   Diborane   1-Propanol

5. Reduction of carboxylic acids and esters: With the help of strong reducing agent, lithium aluminium hydride, carboxylic acids are reduced to primary alcohols.

$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$

Carboxylic acids   1° alcohol

Commercially, acids are reduced to alcohols by converting them to esters, followed by catalytic hydrogenation.

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[Catalyst]{H_2} RCH_2OH + R'OH$$

6. From amines:

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$$
     Ethanamine   Ethanol

7. By alcoholic Fermentation:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$
                                                    (Glucose)   (Fructose)

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

- **Physical properties:**
  - Lower alcohols are colourless liquid members, from $C_5 - C_{11}$ are oily liquids and higher members are waxy solids.
  - Characteristic alcoholic odour and burning taste.
  - Polar in nature.
  - Forms intermolecular hydrogen bonding .
  - Soluble in water which decreases with increase in molecular mass.
  - Boiling point is considerably higher than those of corresponding hydrocarbons, haloalkanes, ethers etc. 1° > 2° > 3°.
  - Toxic in nature.
- **Chemical properties:** Alcohols act both as nucleophiles and electrophiles. The bond between O—H is broken when alcohols act as *nucleophiles*.

$$R{-}\overset{..}{\underset{..}{O}}{-}H + \overset{+}{C} \longrightarrow R{-}\overset{+}{O}{-}\underset{\underset{H}{|}}{\overset{|}{C}}{-} \longrightarrow R{-}O{-}\overset{|}{\underset{|}{C}}{-} + H^+$$

The bond between C—O is broken when they act as *electrophiles*.

$$R{-}CH_2{-}OH + \overset{+}{H} \longrightarrow R{-}CH_2{-}\overset{+}{O}H_2$$

$$\overset{-}{Br} + CH_2{-}\overset{+}{O}H_2 \longrightarrow Br{-}CH_2 + H_2O$$
        $\underset{R}{|}$ $\underset{R}{|}$

➤ **Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of O—H bond. An electron-releasing group ($-CH_3, - C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O—H bond. This decreases the acid strength. For this reason, the acid strength of alcohol decreases in the order.

$$R \rightarrow CH_2OH > \underset{R}{\overset{R}{\diagdown}} CHOH > > R \rightarrow \underset{R}{\overset{R}{\diagdown}} C - OH$$

Primary   Secondary   Tertiary

Alcohols can act as Bronsted acids as well as bases due to donation of proton and presence of unshared pair of electrons on oxygen respectively.

➢ **Reaction with active metals:**

$$2R-OH+2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2RONa} + H_2 \uparrow$$

➢ **With metal hydrides:**

$$2CH_3OH+2NaH \longrightarrow 2CH_3ONa+H_2\uparrow$$

➢ **With Grignard's reagent:**

$$ROH+\underset{\substack{\text{Grignard's} \\ \text{reagent}}}{R'-Mg-X} \longrightarrow \underset{\text{Alkane}}{R'-H}+ \underset{\substack{\text{Alkoxy} \\ \text{magnesium halide}}}{Mg \diagup^{OR}_{\diagdown X}}$$

➢ **Esterification:**

$$\underset{\substack{\text{Carboxylic} \\ \text{acid}}}{R-\overset{\overset{O}{\|}}{C}-OH}+ \underset{\text{Alcohol}}{HOR} \underset{\overleftarrow{}}{\overset{\text{Conc}}{\underset{H_2SO_4}{\longrightarrow}}} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'}+H_2O$$

➢ **Acylation:**

$$\underset{\text{Acid chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl}+H-O-R' \overset{\text{Pyridine}}{\longrightarrow} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'}+HCl$$

$$\underset{\text{Acid anhydride}}{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R}+H-O-R' \overset{\text{Pyridine}}{\longrightarrow} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-O-R'}+\underset{\text{Acid}}{R-\overset{\overset{O}{\|}}{C}-OH}$$

➢ **With hydrogen halides:**

$$R-OH+HX \longrightarrow \underset{\text{Haloalkane}}{R-X}+H_2O$$

➢ **With phosphorus halides:**

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+PCl_5 \longrightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl}+ \underset{\substack{\text{Phosphorus} \\ \text{oxychloride}}}{POCl_3}+HCl\uparrow$$

$$\underset{\text{Ethyl alcohol}}{3CH_3CH_2OH}+PCl_3 \longrightarrow \underset{\text{Chloroethane}}{3CH_3CH_2Cl}+ \underset{\substack{\text{Phosphorus} \\ \text{acid}}}{H_3PO_3}$$

➢ **With thionyl chloride:**

$$R-OH+ \underset{\substack{\text{Thionyl} \\ \text{chloride}}}{SOCl_2} \overset{\text{Pyridine}}{\longrightarrow} \underset{\text{Chloroalkane}}{R-Cl}+SO_2\uparrow+HCl\uparrow \triangleleft$$

➢ **With NH_3:**

$$CH_3-OH+HNH_2 \xrightarrow[633K]{Al_2O_3} \underset{(1°\text{amine})}{CH_3NH_2}+H_2O$$

$$\underset{\text{Methyl alcohol}}{2CH_3OH}+HNH_2 \xrightarrow[633K]{Al_2O_3} \underset{(2°\text{amine})}{CH_3-\underset{\underset{H}{|}}{N}-CH_3}+H_2O$$

$$\underset{\text{Methyl alcohol}}{3CH_3OH}+HNH_2 \xrightarrow[633K]{Al_2O_3} \underset{(3°\text{amine})}{H_3C-\underset{\underset{CH_3}{|}}{N}-CH_3}+3H_2O$$

➢ **Dehydration:**

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow[\text{at 443K}]{\text{conc.}H_2SO_4} \underset{\text{Ethene}}{CH_2\!=\!CH_2}+H_2O$$

$$2CH_3CH_2OH \xrightarrow[\text{at 413 K}]{\text{conc. } H_2SO_4} CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$$

Ethyl alcohol   Diethyl ether

Ease of dehydration of alcohols $3° > 2° > 1°$.

Mechanism of dehydration:

● **Protonation of alcohol:**

● **Loss of water molecule (Carbocation formation):**

It is a slowest step and rate determining step.

● **Loss of proton**

➤ **Oxidation by $Na_2Cr_2O_7/K_2Cr_2O_7$/acidified $KMnO_4$:**

➤ **Dehydrogenation:**

$$CH_3 - CH_2OH \xrightarrow[573K]{Cu} CH_3 - CHO + H_2 \uparrow$$

1° Alcohol   Aldehyde

➤ **Reaction with halogens:**

$$CH_3-\underset{\underset{2°\,Alcohol}{|}}{\overset{\overset{CH_3}{|}}{CH}}-OH \xrightarrow[-2HBr]{Br_2(Oxidation)} H_3C-\overset{\overset{CH_3}{|}}{C}=O \xrightarrow[-3HBr\,(Bromination)]{3Br_2} \underset{Tribromoacetone}{CBr_3-\overset{\overset{CH_3}{|}}{C}=O}$$

3° alcohols are not oxidised by halogens.

- **Preparation of methanol by Bosch process:** Firstly water gas $(CO+H_2)$ will be prepared from coal at 1270 K.

$$\underset{Coal}{C}+H_2O \longrightarrow CO+H_2$$

Methanol (CH_3OH) is prepared from water gas by adding ZnO/Cr_2O_3 catalyst.

$$CO+2H_2 \longrightarrow CH_3OH$$

➤ Preparation of ethanol by fermentation of sugar present in molasses, sugarcane or fruits like grapes. Sugar on fermentation in presence of invertase is converted to glucose and fructose which on further fermentation in presence of zymase enzyme gives ethanol.

$$\underset{Sucrose}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow{Invertase} \underset{Glucose}{C_6H_{12}O_6}+\underset{Fructose}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH+2CO_2$$

➤ **Uses of alcohol:**
- Methanol and ethanol are used as solvents for paints, varnishes, etc.
- Methanol is used for making formaldehyde.
- Ethanol is used in preparation of large number of compounds.

➤ **Distinction between primary, secondary and tertiary alcohols by Lucas Test:** Alcohols on treatment with Lucas reagent (conc. $HCl+ZnCl_2$) form corresponding halides which are insoluble and produce turbidity. Tertiary alcohol gives turbidity immediately, secondary alcohol within five minutes and primary alcohols do not give turbidity at room temperature.

➤ **Conversion of lower alcohol to a higher alcohol:**

$$R-OH \xrightarrow[-H_2O]{HI} RI \xrightarrow[-KI]{KCN} RCN \xrightarrow[Reduction]{4[H]} RCH_2NH_2 \xrightarrow{HNO_2} RCH_2OH$$

➤ **Conversion of higher alcohol to a lower alcohol:**

$$RCH_2OH \xrightarrow[K_2Cr_2O_7]{[O]} RCHO \xrightarrow{[O]} RCOOH \xrightarrow{NaOH} RCOONa \xrightarrow[Heat]{NaOH+CaO} RH \xrightarrow{Cl_2} R-Cl$$
$$R-OH \xleftarrow{aq.\,KOH}$$

➤ **Conversion of primary alcohol to a secondary alcohol:**

$$R-CH_2-CH_2-OH \xrightarrow{SOCl_2} RCH_2CH_2Cl \xrightarrow{KOH(alc.)} RCH=CH_2 \xrightarrow{HBr} R-\overset{\overset{Br}{|}}{CH}-CH_3$$
$$R-\underset{\underset{}{|}}{\overset{\overset{OH}{|}}{CH}}-CH_3 \xleftarrow{aq.\,KOH}$$
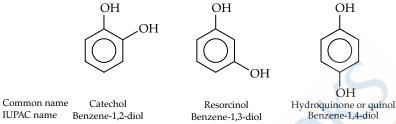
➤ **Conversion of secondary alcohol to a tertiary alcohol:**

$$R_1-\underset{\underset{R_2}{|}}{\overset{\overset{H}{|}}{C}}-OH \xrightarrow[K_2Cr_2O_7]{[O]} R_1-\underset{\underset{R_2}{|}}{\overset{}{C}}=O \xrightarrow{R_3MgBr} R_1-\underset{\underset{R_2}{|}}{\overset{\overset{R_3}{|}}{C}}-OMgBr \xrightarrow[-MgBr(OH)]{H_2O} R_1-\underset{\underset{R_2}{|}}{\overset{\overset{R_3}{|}}{C}}-OH$$

➤ **Conversion of primary alcohol to a tertiary alcohol:**

$$R-CH_2-CH_2OH \xrightarrow[443K]{conc.\,H_2SO_4} R-CH_2=CH_2 \xrightarrow{HBr} R-\overset{\overset{Br}{|}}{CH}-CH_3 \xrightarrow[-KBr]{KOH} R-\overset{\overset{OH}{|}}{CH}-CH_3$$

$$R-\underset{\underset{R'}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xleftarrow[-MgBr(OH)]{H_2O} R-\underset{\underset{R'}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_3 \xleftarrow{R'MgBr} R-\overset{\overset{O}{||}}{C}-CH_3 \xleftarrow{K_2Cr_2O_7}$$

➤ **Nomenclature of phenols:** Phenol is the monohydroxy derivative of benzene. Substituents in phenol compounds are identified by the position, in which they are attached to the hydroxyl group in the benzene ring called as *ortho*-(1,2-disubstituted), *meta*-(1,3-disubstituted) and *para*-(1, 4-disubstituted).

Common name	Phenol	o-Cresol	m-Cresol	p-Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

➤ Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- or 1, 4-benzenediol.

Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

➤ **Preparation of phenols:**
  ● **Dow's process:** Phenol is prepared by heating chlorobenzene with 10% NaOH solution at 623 K under 300 atm followed by hydrolysis.

  ● **From salts of benzene sulphonic acid:**

  ● **From diazonium salts:**

  ● **From cumene (for commercial preparation):**

➤ **Physical Properties:**
  ● Colourless liquids or crystalline solids with low melting point.
  ● Phenol and few di and trihydric phenols are fairly soluble in water due to their ability to form intermolecular hydrogen bonding with water.

Solubility of phenol in water is much lower than that of alcohols due to presence of large hydrophobic benzene ring.
- Boiling points of phenols are higher than the arenes, aryl halides and aryl ethers of comparable molecular masses. It is due to the presence of intermolecular hydrogen bonding which results in molecular association.

----O—H----O—H----O—H----

➢ **Chemical Properties:**
- **Phenol acts as weak acid.**

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$
$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

- **Reaction with Zn dust:**

- **Friedel-Crafts reaction:**

- **Fries rearrangement:**

- **With PCl$_5$:**

- **Electrophilic substitution reaction:**
  (i) Bromination:

2, 4, 6- tribromophenol
(White ppt.)

(ii) Nitration: In presence of HNO$_3$ (dil.), it gives *ortho* and *para* product but with HNO$_3$ (conc.) it forms picric acid.

2,4,6- Trinitrophenol
(Picric acid)

(iii) Sulphonation:

4- Phenol sulphonic acid
(Major)

2- Phenol sulphonic acid
(Major)

- **Kolbe's reaction:**

Sodium
phenoxide

Sodium
salicylate

2-hydroxybenzoic
acid (Salicylic acid)

- **Reimer-Tiemann reaction:**

o-Hydroxybenzaldehyde
(Salicylaldehyde)

- **Oxidation:**

p-Benzoquinone

- **Coupling reaction:**

Diazonium
salt

Phenol

4-hydroxyazobenzene
(Azo dye)

➢ **Uses of phenol:**
  - In perfume.
  - In the production of dyes, plastics, etc.
➢ **Test for phenol:**
  - **FeCl$_3$ test:** Unlike alcohols, phenols react with neutral FeCl$_3$ to give violet coloured water soluble complex.

$$6C_6H_5OH + FeCl_3 \rightarrow [Fe(OC_6H_5)_6]^{3-} + 3HCl + 3H^+$$
  Violet complex

  - **Azo dye test:** Phenol reacts with benzene diazonium chloride in presence of an alkaline medium to give an orange coloured compound azo dye.

4-hydroxyazobenzene
(Azo dye)

⚷ Key Terms

➢ **Wood spirit:** Methanol is known as wood spirit as it is prepared by destructive distillation of wood.

➢ **Methylated spirit:** Denatured ethyl alcohol which is unfit for drinking purpose is called methylated spirit.

➢ **Fusel oil:** In the fermentation of starch, ethyl alcohol is prepared but in small amount. Some higher alcohol also forms like isopentyl alcohol or isoamyl alcohol. This mixture is quite often called fusel oil.

➢ **Power alcohol:** It is the mixture of 20% alcohol and 80% petrol with ether, benzene or tetralin. It is used as a substitute for petrol for running internal combustion engines in cars, scooters, etc.

➢ **Lederer-Manasse reaction:** Phenol condenses with formaldehyde in presence of acid or base to give bakelite (polymer). The reaction is known as Lederer-Manasse reaction.

➢ **Rectified Spirit:** It contains about 95.5 percent alcohol.

➢ **Electrophile:** Positively charged or neutral species which is electron deficient e.g., H^+, H_3O^+, Cl^+, etc.

➢ **Nucleophile:** Negatively charged or neutral species with lone pair of electrons e.g., Br^-, CN^-, etc.

➢ **Substitution reaction:** Reaction in which an atom or group of atoms is replaced by some other atom or group of atoms without any change in the structure of the remaining part of the molecule. e.g.,

$$CH_3 — CH_2—OH + HBr \rightarrow CH_3—CH_2—Br + H_2O$$

➢ **Addition reaction:** When a molecule is added across a double or triple bond to form single product is called addition product, such reactions are called addition reactions. e.g.,

$$CH_2 = CH_2 + HCl \rightarrow CH_3 — CH_2 — Cl$$

➢ **Oxonium ion:** The ion which is formed by reaction of alcohol or ether with H^+. The oxygen atom in this ion has positive charge.

➢ **Absolute alcohol:** It is 100% ethanol. It is obtained by fractional distillation of 95% ethanol and little amount of benzene.

🧠 Mnemonics

Formation of Alcohols

1. **Mnemonics:** **F**ourth **GR**ade **H**igh income **P**er **A**nnuaam
   Interpretation.
   Formaldehyde reacts with **GR**ignard reagent followed by **H**ydrolysis to form **P**rimary **A**lcohol.

2. **Mnemonics: AGRa Hai B**harat ki **ShAn**
   Interpretation.
   Acetaldehyde reacts with **GR**ignard reagent followed by hydrolysis to form **S**econdary **A**lcohol.

   Reaction of Alcohols with Lucas reagent

1. **Mnemonics: TA**ta namak vs **L**aho**RI** namak
   Interpretation.
   Tertiary **A**lcohols react with Lucas reagent to form turbidity immediately.

2. **Mnemonics: SA**Le main **5**% off hain
   Interpretation.
   Secondary **A**lcohols react with Lucas reagent to form turbidity within 5 minutes.

3. **Mnemonics: PAL RuNneR Tha**
   Interpretation.
   Primary **AL**cohols do not **R**eact with Lucas reagent at **R**oom temperature.

   Test for phenols
   Mnemonic : Feel cool and drink **violet** cool

   FeCl$_3$ ↓
        violet coloured complex

   Alkji ne liyo **golanamak** our banaya **dye**
   ↓   ↓   ↓
   Alkaline   diazonium   azodye
   medium   salt

Topic-2

Ethers: Methods of Preparation, Properties and Uses

Concepts Covered: *Nomenclature of ether, General formula, Methods of preparation, Physical and chemical properties, Uses.*

💬 Revision Notes

➢ **Ethers:** Ethers are organic compounds in which alkyl or aryl groups are attached to a divalent oxygen known as etheral oxygen. Compounds with general formula $C_nH_{2n+2}O$. They are represented by general structure, R–O–R′.

➢ **Nomenclature of Ethers:** Ethers are named from names of alkyl/aryl group written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix '*di*' is added before the alkyl group. For example, $C_2H_5OC_2H_5$ is diethyl ether. These types of ethers are called symmetrical ethers. If both the alkyl groups are the different, for example, $CH_3OC_2H_5$ is ethylmethyl ether.

These types of ethers are called unsymmetrical ethers. During naming ethers, the larger alkyl group is chosen as the parent hydrocarbon.

Common and IUPAC names of some Ethers are:

Compound	Common Name	IUPAC Name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl *n*-propyl ether	1-Methoxy propane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6—CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O—\underset{\underset{CH_3}{\vert}}{CH}—CH_3$	Methyl isopropyl ether	2-Methoxypropane
$C_6H_5—O—CH_2—CH_2—\underset{\underset{CH_3}{\vert}}{CH}—CH_3$	Phenyl isopentyl ether	1-phenoxy 3-methyl butane
$CH_3—O—CH_2—CH_2—OCH_3$	—	1, 2-Dimethoxyethane
$\begin{array}{c} H_3C \quad CH_3 \\ OC_2H_5 \end{array}$ (cyclohexane)	—	2-Ethoxy-1, 1-dimethylcyclohexane

➢ **Methods of Preparation of Ethers:**

(a) Williamson's synthesis: Only primary alkyl halide reacts with sodium alkoxide, ethers are formed while tertiary alkyl halides give alkene due to steric hindrance. e.g.,

$$C_2H_5Br + CH_3—\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—ONa \longrightarrow CH_3—\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—OC_2H_5 + NaBr$$
2-ethoxy-2-methylpropane

(b) Dehydration of alcohols: Alcohols are dehydrated to ethers in presence of concentrated sulphuric acid at 413 K. The reaction involves the removal of one molecule of water from two moles of alcohols.

$$C_2H_5\boxed{OH + H}OC_2H_5 \xrightarrow[413\ K]{conc.\ H_2SO_4} C_2H_5OC_2H_5 + H_2O$$
Ethyl alcohol   Diethyl ether (Ethoxy ethane)

Alcohol can also be dehydrated by heating with alumina at 523 K and high pressure. This method is not suitable for preparation of unsymmetrical ethers.

(c) Heating alkyl halides with dry silver oxide: Ethers can be prepared by heating alkyl halides with dry silver oxide (Ag_2O).

$$2C_2H_5Cl + Ag_2O \xrightarrow{heat} C_2H_5—O—C_2H_5 + 2AgCl$$

$$CH_3Cl + Ag_2O + C_2H_5Cl \longrightarrow CH_3—O—C_2H_5 + 2AgCl$$

Mixed ether or unsymmetrical ether can be prepared by this method.

(d) Reaction of lower halogenated ethers with Grignard reagent: Higher homologues ethers can be prepared by action of Grignard reagent on lower halogenated ethers.

$$\underset{\text{Chlorodimethyl ether}}{CH_3OCH_2Cl} + BrMgC_2H_5 \longrightarrow \underset{\text{Methyl propyl ether}}{CH_3—O—CH_2—C_2H_5} + Mg\begin{matrix}Br\\Cl\end{matrix}$$

(e) Action of diazomethane on alcohols: Ethyl methyl ether can be prepared by action of diazomethane on alcohols in the presence of catalysts like BF_3.

$$C_2H_5OH + CH_2N_2 \xrightarrow{BF_3} \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + N_2$$

➢ **Physical properties of ethers:**
● **Boiling points:** Ethers are weakly polar molecules due to weak dipole-dipole attraction. Thus, their boiling points are comparable to the alkenes of similar molecular mass. Boiling points of ethers are much lower than the corresponding alcohols due to the presence of H-bonding in alcohols.
● **Miscibility:** Lower ethers (upto three carbon atoms) are soluble in water and their miscibility with water is similar to alcohols of the same molecular masses. This is due to the formation of H-bonds with water molecule.

➢ **Chemical properties of ethers:**
● **With chlorine:**

$$\underset{\text{Ether}}{R'CH_2—O—R} + Cl_2 \xrightarrow{\text{Dark}} \underset{\text{Chloroalkylether}}{R'CHCl—O—R} + HCl$$

$$\underset{\text{Diethyl ether}}{CH_3—CH_2—O—CH_2—CH_3} + \underset{\text{Excess}}{10Cl_2} \xrightarrow[\text{-10HCl}]{\text{Light}} \underset{\text{Perchlorodiethyl ether}}{CCl_3—CCl_2—O—CCl_2—CCl_3} + 10HCl$$

● **Combustion:**

$$\underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

● **Oxidation:**

$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{Light}]{O_2(\text{air})} \begin{matrix} CH_3—CH—O—CH_2CH_3 \\ | \\ \underset{\text{1-ethoxyethyl-hydroperoxide}}{H—O—O} \end{matrix}$$

● **With cold conc. H_2SO_4 or HCl:**

$$\underset{\text{Ether}}{R—\overset{..}{\underset{..}{O}}—R} + \underset{\text{(Conc.)}}{HCl} \longrightarrow \left[\underset{\text{Dialkyloxomium chloride}}{R—\overset{\overset{H}{|}}{\underset{..}{O}}—R} \right]^+ Cl^-$$

● **With halogen acids (HX):**

$$\underset{\text{Ether}}{R—O—R} + \underset{(X=I\text{ or Br})}{HX} \xrightarrow{\text{cold}} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX}$$

$$\underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + 2HI \xrightarrow{\text{cold}} \underset{\text{Iodoethane}}{C_2H_5I} + \underset{\text{Ethanol}}{C_2H_5OH}$$

$$R—O—R + \underset{\text{Excess}}{2HX} \xrightarrow{\Delta} 2RX + H_2O$$

$$C_2H_5—O—C_2H_5 + \underset{\text{Excess}}{2HI} \xrightarrow{\Delta} 2C_2H_5I + H_2O$$

● **Hydrolysis:**

$$R—O—R + HOH \xrightarrow{\text{Boil}} \underset{\text{Alcohol}}{2R—OH}$$

● **With PCl_5:**

$$R—O—R + PCl_5 \xrightarrow{\Delta} \underset{\text{Alkyl chloride}}{2R—Cl} + POCl_3$$

Mnemonics

Concept : Preparation of Ethers
1. **Mnemonics: WRE**stling
   Interpretation.
   Williamson Reaction is used to prepare Ethers.
2. **Mnemonics: DAESA**ng award
   Interpretation.
   Dehydration of Alcohols gives Ethers in the presence of conc. Sulphuric acid.

➢ **Preparation of Aryl Ether:**

➢ **Physical properties of aryl ether:**
   Ethers are weakly polar, thus have comparably less boiling points than alcohols due to lack of hydrogen bonding. Similar to alcohols, ethers are miscible with water as they also form hydrogen bonds with water.
   (a) Nitration: Aromatic ethers react with conc. HNO_3 and conc. H_2SO_4 to form nitro compounds.

(b) Sulphonation: Aromatic ethers, on reaction with conc. H_2SO_4 form sulphonic acids.

(c) Halogenation: Aromatic ethers, on halogenation forms chloro substituted ethers.

(d) Friedel-Crafts reaction: Aromatic ethers undergo alkylation, when reacted with alkyl halide in presence of anhydrous $AlCl_3$.

➢ **Uses of ethers:**
   ● Diethyl ether is used as inhalation anaesthetic.
   ● As industrial solvent for oils, resins, gums, etc.
   ● Diphenyl ether acts as a heat strangler medium.

🔑 Key Term

➢ **Grignard reagent:** An organometallic chemical compound formed from reaction of an alkyl or aryl halide with elemental magnesium.

❑❑

CHAPTER-8

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

	Aldehydes and Ketones: Methods of Preparation, Properties and Uses
Topic-1	**Concepts Covered:** *Classification of aldehydes and ketones, Nomenclature, Meth-ods of preparation, Physical and chemical properties uses*

💬 Revision Notes

➤ **Aldehydes and Ketones:**
  (i) Aldehydes are those compounds in which carbonyl group is attached to either two hydrogen atoms or one hydrogen atom and one carbon containing group such as alkyl or aryl group with hydrogen atom. RCHO, e.g., HCHO, CH_3CHO, C_2H_5CHO, C_6H_5CHO, etc.

  (ii) Ketones are those compounds in which carbonyl group is attached with two alkyl or two aryl or one alkyl and one aryl group. e.g., RCOR' CH_3COCH_3, $CH_3COC_6H_5$, $C_6H_5COC_6H_5$, etc.

➤ **Classification of aldehydes:**
  ● **Aliphatic aldehyde:** An alkyl group or a H-atom is attached to an aldehydic (—CHO) group. e.g., formaldehyde (HCHO), acetaldehyde (CH_3CHO).
  ● **Aromatic aldehdye:** An aryl group is attached to an aldehydic (—CHO) group. e.g., benzaldehdye (C_6H_5CHO).

➤ **Classification of ketones:**
  ● **Simple or symmetrical:** Both the attached alkyl or aryl groups are similar. e.g.,

Propanone

Diphenylmethanone

  ● **Mixed or unsymmetrical:** Both the attached alkyl or aryl groups are different. e.g.,

Butan-2-one

Phenylethanone

➤ **Nomenclature of Aldehydes and Ketones:**
  ● Common names of aldehydes are derived from the common names of carboxylic acids by replacing the 'ic' with aldehyde. Greek letter α, β, γ and δ, etc. denote the location of the substitution in the carbon chain.

Benzaldehyde

β-bromobutyraldehyde

  ● Common names of the ketones are derived by writing the names of alkyl groups attached to the $>C=O$ group in alphabetical order, followed by the word ketone.

$CH_3 — \overset{\overset{O}{\|}}{C} — C_2H_5$ (Ethyl methyl ketone)

  ● IUPAC names are written by replacing the word 'e' of corresponding alkanes by 'al' and 'one' of the open chain aliphatic aldehydes and ketones respectively.

Aldehyde	General formula: $R - \overset{\overset{\displaystyle O}{\|}}{C} - H$ where $R = C_nH_{2n+1}$		
Structural formula	**Condensed structural formula**	**Common name**	**IUPAC name**
$H - \overset{\overset{\displaystyle O}{\|}}{C} - H$	HCHO	Formaldehyde	Methanal
$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - H$	CH_3CHO	Acetaldehyde	Ethanal
$CH_3 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - H$	CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - H$	$CH_3CH_2CH_2CHO$	Butyraldehyde	Butanal
$CH_3 - \underset{\underset{\displaystyle CH_3}{\|}}{CH} - \overset{\overset{\displaystyle O}{\|}}{C} - H$	$CH_3 - \underset{\underset{\displaystyle CH_3}{\|}}{CH} - CHO$	Isobutyraldehyde	2-Methylpropanal
$CH_3CH_2CH_2CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - H$	$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_3 - \underset{\underset{\displaystyle CH_3}{\|}}{CH} - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - H$	$CH_3 - \underset{\underset{\displaystyle CH_3}{\|}}{CH} - CH_2CHO$	Isovaleraldehyde	3-Methylbutanal
$CH_3 - CH_2 - \underset{\underset{\displaystyle CH_3}{\|}}{CH} - \overset{\overset{\displaystyle O}{\|}}{C} - H$	$CH_3 - CH_2 - \underset{\underset{\displaystyle CH_3}{\|}}{CH} - CHO$	α-Methylbutyraldehyde	2-Methylbutanal

C_6H_5CHO or Benzaldehyde (with CHO on benzene ring)	Phenylacetaldehyde (2-Phenylethanal) (CH₂—CHO on benzene ring)	$\overset{4}{CH_3} - \underset{\underset{\displaystyle Br}{\|}}{\overset{3}{CH}} - \overset{2}{CH_2} - \overset{\overset{\displaystyle O}{1\|}}{C} - H$ β-Bromobutyraldehyde (3-Bromobutanal)
$CH_2 = CH - CHO$ Acrolein (Prop-2-en-1-al) (Cyclohexanecarbaldehyde) (CHO on cyclohexane ring)	$CH_3 - CH = CH - CHO$ Crotonaldehyde (But-2-en-1-al) (CHO on cyclohexane ring with NO₂) 4-Nitrobenzaldehyde (4-Nitrophenylcarbaldehyde)	$CH_3 - CH_2 - CH = CH - \overset{\overset{\displaystyle O}{\|}}{C} - H$ Pent-2-enal $C_6H_5 - CH = CH - \overset{\overset{\displaystyle O}{\|}}{C} - H$ Cinnamaldehyde (3-Phenylprop-2-en-1-al) $\underset{\underset{\displaystyle CHO}{\|}}{CHO}$ Glyoxal (Ethane-1,2-dial)

		$CH_3 - CH_2 - CH_2 - CH - CH - CH_2 - C - H$ with Br, CH_3, O substituents 4-Bromo-3-methylheptanal

Ketone	**General formula: R — C — R′ and R′ = $C_nH_{2n'+1}$ ($n = n'$, $n \neq 0$)** (with C=O)		
Structural formula	**Condensed formula**	**Common name**	**IUPAC name**
$CH_3 - \overset{O}{\overset{\|}{C}} - CH_3$	CH_3COCH_3	Acetone	Propanone
$CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - CH_3$	$CH_3COCH_2CH_3$	Ethyl methyl ketone	Butan-2-one
$CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - CH_2 - CH_3$	$CH_3COCH_2CH_2CH_3$	Methyl n-Propyl ketone	Pentan-2-one
$CH_3 - \underset{CH_3}{CH} - \overset{O}{\overset{\|}{C}} - \underset{CH_3}{CH} - CH_3$	$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethyl pentan-3-one
$CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - CH_2 - CH_3$	$CH_3CH_2COCH_2CH_3$	Diethyl ketone	Pentan-3-one
$CH_3 - \underset{CH_3}{CH} - \overset{O}{\overset{\|}{C}} - CH_3$	$(CH_3)_2CHCOCH_3$	Isopropyl methyl ketone	3-Methylbutan-2-one
$CH_3 - \underset{CH_3}{C} = CH - \overset{O}{\overset{\|}{C}} - CH_3$	$(CH_3)_2C = CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one
β-Methylcyclopentanone (3-Methylcyclopentanone)	$CH_3 - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - OH$ Pyruvic acid (2-Oxopropanoic acid) Cyclohexan-1, 4-dione	$CH_3 - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - CH_3$ Diacetyl (Butane-2-3-dione)	p-Benzoquinone (Cyclohexa-2, 5-diene-1, 4-dione)
$\overset{O}{\overset{\|}{C}} - CH_3$ Acetophenone (Phenylethanone)	$\overset{O}{\overset{\|}{C}} - CH_2 - CH_3$ (Phenyl Propanone)	$COCH_3$ ... Br m-Bromoacetophenone 1-(3-Bromophenyl) ethanone	COC_6H_5 ... Br m-Bromobenzophenone (Bromediphenyl methanone)

➢ **Structure of Carbonyl group:** The carbon atom of the carbonyl group is sp^2 hybridised. All the three atoms attached to carbonyl carbon lie in the same plane.

It is polar in nature. Carbonyl compounds may be regarded as resonance hybrid of the two given structure.

➢ **Methods of preparation of Aldehydes and Ketones:**

(A) Preparation of Aldehydes:

(i) By oxidation of primary alcohols: Aldehydes can be prepared by the oxidation of primary alcohols.

$$\underset{\text{1° alcohol}}{RCH_2OH} + [O] \xrightarrow{KMnO_4} \underset{\text{Aldehyde}}{R-CHO} + H_2O$$

$$\underset{\text{1° alcohol}}{R-CH_2-OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{Aldehyde}}{R-CHO}$$

(ii) By catalytic dehydrogenation of alcohols: In this method alcohol vapours are passed over heavy metal catalyst (Ag/Cu).

$$\underset{\text{1° alcohol}}{RCH_2OH} \xrightarrow{Cu/573\,K} \underset{\text{Aldehyde}}{R-CHO} + H_2$$

(iii) From hydrocarbons:

(a) By ozonolysis of alkenes:

$$\xrightarrow[-ZnO]{H_2O, Zn} \underset{\text{Aldehyde}}{R-CHO + R'-CHO}$$

(b) By hydration of alkynes:

(iv) From acid chloride (Rosenmund's reduction):

Formaldehyde cannot be prepared by this method as HOCl is highly unstable.

(v) From nitriles and esters:

$$R-C\equiv N + HCl + SnCl_2 \longrightarrow \underset{\text{Imine}}{R-CH=NH} \xrightarrow{H_3O^+} R-CHO + NH_3$$

$$R-CN \xrightarrow[\text{2. } H_2O]{\text{1. } AlH(iBu)_2} \underset{\text{Aldehyde}}{R-CHO}$$

(B) Preparation of Benzaldehyde:

(i) By oxidation of toluene:

This reaction is called **Etard reaction**.

(ii) By side chain chlorination followed by hydrolysis:

(iii) By Gatterman – Koch reaction:

(C) Preparation of Ketones:

(i) By oxidation of secondary alcohols:

$$\underset{\substack{\text{2° Alcohol}}}{\underset{R'}{\overset{R}{\diagdown}}CH{-}OH + [O]} \xrightarrow[\text{or } CrO_3]{K_2Cr_2O_7/H_2SO_4} \underset{\substack{\text{Ketone}}}{\underset{R'}{\overset{R}{\diagdown}}C{=}O + H_2O}$$

(ii) By catalytic dehydrogenation of secondary alcohols:

$$\underset{\substack{\text{2° Alcohol}}}{\underset{R'}{\overset{R}{\diagdown}}CH{-}OH} \xrightarrow[573\,K]{Cu} \underset{\substack{\text{Ketone}}}{\underset{R'}{\overset{R}{\diagdown}}C{=}O + H_2}$$

(iii) From Hydrocarbons:

(1) By catalytic ozonolysis of alkenes:

(2) By hydration of alkynes:

(iv) From acyl chlorides and Grignard's reagent:

$$2R - MgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$$

(v) From nitriles:

(vi) Oppenauer oxidation:

$$R_2CHOH + (CH_3)_2 C = O \xrightarrow{[(CH_3)_3CO]_3 Al} R_2C = O + (CH_3)_2 CHOH$$

2° Alcohol   Ketone   Isopropyl alcohol

(D) Preparation of Aromatic ketones:

(i) By Friedel-Crafts acylation:

Benzene   acyl chloride   Acetophenone

Benzene   Benzoyl chloride   Benzophenone

(ii) From nitriles:

$$CH_3 - CH_2 - C \equiv N + C_6H_5MgBr \xrightarrow{Ether} CH_3 - CH_2 - \overset{\overset{\displaystyle NMgBr}{||}}{C} - C_6H_5$$

Ethylcyanide

$$\xrightarrow{H_3O^+} CH_3 - CH_2 - \overset{\overset{\displaystyle O}{||}}{C} - C_6H_5 + Mg \overset{NH_2}{\underset{Br}{<}}$$

Propiophenone

➤ **Physical properties of Aldehydes and Ketones:**

(i) Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have a pleasant smell.

(ii) Both of these have relatively high boiling point as compared to hydrocarbons of comparable molecular masses. But they have lower boiling point than alcohols of comparable molecular masses due to absence of intermolecular hydrogen bonding.

(iii) The lower members of aldehydes and ketones (upto four carbon atoms) are soluble in water in all proportions due to hydrogen bonding capacity. In water, their solubility decreases with increase in the size of alkyl group.

(iv) Aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc.

(v) Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.

➤ **Chemical properties of Aldehydes and Ketones:** Aldehydes and ketones are highly reactive compounds. Both undergo nucleophilic addition reaction.

Some important nucleophilic addition reactions: Reactivity order is:

$$HCHO > CH_3CHO > C_2H_5CHO > CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - CH_3$$

It is due to +I effect of alkyl groups which decrease the positive charge on carbonyl carbon and steric hindrance.

(i) Addition of hydrogen cyanide (HCN):

$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$

$$\text{>}C=O + :\bar{C}N \rightleftharpoons \left[\text{>}C\text{<}^{O^-}_{CN} \right] \xrightarrow{H^+} \text{>}C\text{<}^{CN}_{OH}$$

Cyanohydrin

(ii) Addition to sodium hydrogen sulphite:

$$\text{>}C=O + NaHSO_3 \rightleftharpoons \text{>}C\text{<}^{OSO_2Na}_{OH}$$

Bisulphite
(additon compound)—White crystalline solid

This reaction is used for the separation and purification of aldehydes and ketones.

(iii) Addition of Grignard reagent:

$$\text{>}C=O + RMgX \longrightarrow \text{>}C\text{<}^{OMgX}_{R} \xrightarrow{H_2O/H^+} \text{>}C\text{<}^{OH}_{R} + Mg\text{<}^{OH}_{X}$$

Carbonyl   Grignard   Alcohol
compound   reagent

(iv) Addition of alcohol:

$$^R_H\text{>}C=O \xrightarrow[\text{HCl gas}]{R' OH} {}^R_H C\text{<}^{OH}_{OR'} \xrightarrow[\text{HCl gas}]{R' OH} {}^R_H C\text{<}^{OR'}_{OR'} + H_2O$$

Aldehyde   Hemiacetal   Acetal

Ketones do not react with monohydric alcohols but react with dihydric alcohols to give ketals.

$$^R_{R'}\text{>}C=O + \left| ^{CH_2-OH}_{CH_2-OH} \xrightarrow[\text{dil HCl}]{\text{HCl gas}} {}^R_{R'}C\text{<}^{O-CH_2}_{O-CH_2} | + H_2O$$

Ketone   Ethylene glycol   Ethylene glycol ketal

$$RCHO + RHN_2 \rightarrow RCH = NHR$$

(Schiff's Base)

(v) Addition of ammonia and its derivatives:

$$\text{>}C=O + H_2N-Z \rightleftharpoons \left[\text{>}C\text{<}^{OH}_{NHZ} \right] \longrightarrow \text{>}C=N-Z + H_2O$$

Ethylene glycol ketal

$$RCHO + RHN_2 \rightarrow RCH = NHR$$

(Schiff's Base)

where Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

$$6HCHO + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$$

(Urotropine)

Urotropine on controlled nitration gives the well known explosive RDX (Research and Development explosive).

➢ **Reduction:** Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$.

(i) Reduction to alcohols:

$$R-CHO + 2[H] \xrightarrow[\text{or NaBH}_4]{\text{LiAlH}_4} R-CH_2-OH$$

Aldehyde   1° Alcohol

$$^R_R\text{>}C=O + H_2 \xrightarrow{\text{Ni or Pt}} {}^R_R\text{>}CH-OH$$

Ketone   2° Alcohol

(ii) Reduction to hydrocarbons:

$$\text{>}C=O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} \text{>}CH_2 + H_2O \text{ (Clemmensen reduction)}$$

$$\text{>}C=O \xrightarrow[-H_2O]{NH_2NH_2} \text{>}C=NNH_2 \xrightarrow[\text{glycol, }\Delta]{\text{KOH/Ethylene}} \text{>}CH_2 + N_2 \text{ (Wolff-Kishner reduction)}$$

➢ **Oxidation:** Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents or mild oxidising agent like Tollen's reagent or Fehling's solution.

$$R \underset{\text{Aldehyde}}{-\!\!-\! CHO} + [O] \xrightarrow[\substack{\text{or} \\ KMnO_4/H_2SO_4}]{K_2Cr_2O_7/H_2SO_4} R \underset{\text{Carboxylic acid}}{-\!\!-\! COOH}$$

Ketones undergo oxidation under vigorous conditions with cleavage of carbon bond.

$$CH_3 \overset{\overset{\displaystyle O}{\|}}{-\! C} -\! CH_3 + 3[O] \xrightarrow{\text{Conc. } HNO_3} HCOOH + CH_3 -\! COOH$$

$$\overset{1}{CH_3} -\! \overset{\overset{\displaystyle O}{\|}}{\underset{2}{C}} -\! \overset{3}{CH_2} -\! \overset{4}{CH_2} -\! CH_3 \xrightarrow{K_2Cr_2O_7/H_2SO_4}$$

$C_1\text{-}C_2 \text{ bond Cleavage} \rightarrow$ HCOOH + CH$_3$CH$_2$CH$_2$COOH
(Minor product)

$C_1\text{-}C_2 \text{ bond Cleavage} \rightarrow$ CH$_3$—COOH + CH$_3$—CH$_2$—COOH
(Major product)

(a) Tollen's test – Aldehydes give bright silver mirror with tollen's reagent:

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + 2\underset{\substack{\text{silver} \\ \text{mirror}}}{Ag\downarrow} + 2H_2O + 4NH_3$$

(b) Fehling's test – Fehling solution gives a reddish brown precipitate with aldehydes except benzaldehyde.

$$R\text{–}CHO + 2Cu^{2+} + 5OH^- \rightarrow RCOO^- + \underset{\text{red ppt}}{Cu_2O\downarrow} + 3H_2O$$

➤ **Iodoform reaction:** When the reaction takes place with sodium hypoiodite, NaOI (NaOH + I$_2$), the iodoform formed is a bright yellow precipitate.

$$CH_3 -\! \overset{\overset{\displaystyle O}{\|}}{C} -\! CH_3 + 3NaOI \longrightarrow CH_3COCI_3 + 3NaOH$$

$$CH_3COCI_3 + NaOH \longrightarrow CH_3COONa + \underset{\substack{\text{Iodoform} \\ \text{(Yellow ppt.)}}}{CHI_3 \downarrow}$$

Among aldehydes, this test is given by only acetaldehyde as other aldehydes do not possess $CH_3 -\! \overset{\overset{\displaystyle O}{\|}}{C} -\!$ group. Among ketones, all methyl ketones give this test.

➤ **Reaction due to α-hydrogen.**

α-hydrogen in aldehydes and ketones is acidic in nature due to strong electron withdrawing effect of carbonyl group. As a result, aldehydes and ketones undergo a number of reactions.

$$\underset{H\,):B}{-\! \overset{\overset{\displaystyle O}{\|}}{C} -\! \overset{|}{\underset{|}{C}} -\!} \longrightarrow -\! \overset{\overset{\displaystyle O}{\|}}{C} -\! \underset{\ominus}{C} -\! \longleftrightarrow -\! \overset{\overset{\displaystyle \bar{O}}{|}}{C} =\! \overset{|}{C} -\!$$

(i) Aldol condensation: Aldehydes and ketones having at least one α-hydrogen react in the presence of dilute alkali to form β-hydroxy aldehdyes (aldol) or β-hydroxy ketones (Ketol).

$$\underset{\text{Ethanal}}{2CH_3\!-\!CHO} \underset{\text{dil.NaOH}}{\overset{\text{dil.NaOH}}{\rightleftharpoons}} \underset{\substack{OH \\ \text{3-Hydroxybutanal} \\ \text{(Aldol)}}}{CH -\! \overset{|}{CH} -\! CH_2 -\! CHO} \xrightarrow[-H_2O]{\Delta}$$

$$\underset{\text{But-2-enal}}{CH_3 -\! CH = CH -\! CHO}$$

$$2\,CH_3 -\! CO -\! CH_3 \underset{}{\overset{Ba(OH)_2}{\rightleftharpoons}} CH_3 -\! \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\text{Ketol}}{OH}}{C}} -\! CH_2CO -\! CH_3 \xrightarrow[-H_2O]{\Delta}$$

$$\underset{\text{4-Methyl pent -3-en-2-one}}{CH_3 -\! \overset{\overset{\displaystyle CH_3}{|}}{C} = CH -\! CO -\! CH_3}$$

(ii) Cross aldol condensation: When two different aldehydes and/or ketones undergo aldol condensation, it is called cross aldol condensation.

Base catalysed cross aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen reaction** or **Claisen–Schmidt condensation**.

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta]{1.\ NaOH}$$

$$CH_3 - CH = CH - CHO$$
But-2-enal

$$+$$

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{CH_3 - C = CH - CO - CH_3}}$$
4-methyl pent-3-en-2-one
Simple or aldol products

$$\overset{\displaystyle CH_3 - CH = C - CHO}{\underset{\displaystyle |}{CH_3}}$$

$$CH_3CH_2 - CH = CHCHO$$
Cross aldol products

(iii) Cannizzaro Reaction: Aldehydes undergo self oxidation and reduction on heating with conc. alkali. The aldehydes which do not have α-hydrogen undergo this reaction.

$$\underset{H}{\overset{H}{>}}C=O + \underset{H}{\overset{H}{>}}C=O + conc.\ KOH \xrightarrow{\Delta} H - \overset{H}{\underset{H}{\overset{|}{C}}} - OH + H - C\underset{O^- K^+}{\overset{O}{\diagdown}}$$

Carbonyl compound   Methanol   Potassium formate

$$2\ \langle\text{ring}\rangle - CHO + conc.\ NaOH \xrightarrow{\Delta} \langle\text{ring}\rangle - CH_2OH + \langle\text{ring}\rangle - COONa$$

Benzaldehyde   Benzyl alcohol   Sodium benzoate

➤ **Electrophilic substitution reaction:** Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group shows +R effect, therefore acts as a deactivating and *meta* directing group.

CHO
$$\langle\text{ring}\rangle + HNO_3 \xrightarrow[273-283K]{conc.\ H_2SO_4} \langle\text{ring}\rangle NO_2 + H_2O$$
      (conc.)
Benzaldehyde   *m*-nitrobenzaldehyde

O‖C—CH₃
$$\langle\text{ring}\rangle + HNO_3 \xrightarrow{conc.\ H_2SO_4} \langle\text{ring}\rangle NO_2 + H_2O$$
      (conc.)
Acetophenone   *m*-nitroacetophenone

O‖C—CH₃
$$\langle\text{ring}\rangle \xrightarrow[Halogenation]{Br_2/Anhy.\ AlCl_3\ (excess)} \langle\text{ring}\rangle Br$$
      COCH₃
Acetophenone   *m*-bromoacetophenone

➤ **Test to distinguish between formaldehyde and acetaldehyde by Iodoform test:**
Acetaldehyde gives a yellow precipitate of iodoform on heating with iodine in the presence of an alkali.

$$CH_3CHO + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 \downarrow + HCOONa + 3NaI + 3H_2O$$

Acetaldehyde   Iodoform
                                      (yellow ppt.)

Formaldehyde does not give this test.

➤ **Test to distinguish between aldehydes and ketones:**

Test	Aldehydes	Ketones
Tollen's reagent	Gives silver mirror	No reaction
Fehling's solution	Gives reddish brown precipitate	No reaction
Schiff's reagent	Restores pink colour	No reaction
Reaction with LiAlH$_4$	Forms primary alcohol	Forms secondary alcohol

➤ **Uses of Aldehydes and Ketones:**
- Formaldehdye is used as disinfectant and germicide.
- Formaldehdye is used in the manufacture of Bakelite, resin and other polymers.
- Formaldehyde is used to manufacture medicine for urine infection.
- Acetaldehyde is used as a starting material for synthesis of acetic acid, drugs and polymers.
- Acetone is a constituent of liquid nail polish.
- Paraldehyde is used as a hypnotic in medicine.

➤ **Physical properties of benzaldehyde:**
- Colourless liquid with a characteristic almond like odour:
- Highly reactive.
- Boiling point of 452 K.

➤ **Chemical properties of benzaldehyde:**
- **Oxidation:**

Benzoic acid

Reduction:

Benzyl alcohol

- **Nucleophilic Addition Reaction:**

 (i) With HCN:

Benzaldehyde
cyanohydrin

 (ii) With NaHSO$_3$:

Benzaldehyde
bisulphite compound

(iii) With Grignard's reagent:

Addition product

Diphenyl carbinol (2° alcohol)

(iv) With ammonia:

Hydrobenzamide

(v) With hydroxyl amine:

Benzaldoxime

(vi) With hydrazine:

Benzaldehyde hydrazone

Benzaldehyde dihydrazone

(vii) With phenyl hydrazine:

Benzaldehyde phenylhydrazone

(viii) With PCl$_5$:

$$C_6H_5CHO + PCl_5 \longrightarrow C_6H_5CHCl_2 + POCl_3$$
Benzal chloride

(ix) Benzoin condensation:

Acetaldehyde

Benzoin

(x) Perkin's reaction:

Aceticanhydride

$C_6H_5-CH=CH-COOH + CH_3COOH$

Cinnamic acid   Acetic acid

(xi) Wittig reaction:

$$>C=O+PPh_3=CH_2$$

$$\downarrow$$

$$>C=CH_2+Ph_3P=O$$

● **Electrophilic Substitution Reaction:**
   (i) Halogenation:

m-bromobenzaldehyde

(ii) Nitration:

m-nitrobenzaldehyde

(iii) Sulphonation:

m-benzaldehyde
sulphonic acid

➤ Test to distinguish between benzaldehyde and acetaldehyde by Iodoform test:

Acetaldehyde gives a yellow precipitate of iodoform when heated with iodine, in the presence of alkali.

$$CH_3CHO + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 \downarrow + HCOONa + 3NaI + 3H_2O$$

Iodoform
(yellow ppt.)

Benzaldehyde does not give iodoform test.

➤ **Uses of benzaldehyde:**
   ● Manufacturing of dyes.
   ● As a flavouring essence in perfumery.
   ● Synthesis of cinnamic acid, cinnamaldehyde, etc.

⊙━ᴍ **Key Terms**

➤ **Hydroformylation:** In this process, alkenes give aldehydes by the reaction of hydrogen and CO.

➤ **Collin's reagent:** This reagent can be prepared by mixing pyridine (C_5H_5N), CrO_3 and HCl in the presence of dichloromethane. This reagent is used to prepare aldehydes, by controlled oxidation process.

➤ **Baeyer-Villiger oxidation:** In this process, when ketones are treated with peroxy acids (per acetic acid), e.g., in the presence of an acid catalyst give carboxylic esters by insertion of esters.

➤ **MPV-reduction:** It is Meerwein Ponndorf Verley reduction. In this process, ketones are reduced to secondary alcohols with isopropyl alcohol in the presence of aluminium isopropoxide.

➤ **Oppenauer oxidation:** It is the reverse process of MPV-reduction.

➤ **Urotropine:** It is hexamethylenetetramine and used as a urinary antiseptic.

➤ **Formalin:** 40% aqueous solution of formaldehyde.

⚙ **Mnemonics**

Concept: Detection Test

Mnemonics: TASte FAAR IMLy

Interpretation:

TASte → Tollen's test, Aldehyde group, Silver Morror

FAAR → Fehling's Aliphatic Aldehyde, Red-Brown ppt.

IMLy → Iodoform test, Methyl group

$$
\overset{\quad O}{\underset{\text{linked to}}{}}\!\!-\!\overset{\parallel}{C}\!-\,,\ \text{Yellow ppt}
$$

Topic-2 | Carboxylic Acids: Methods of Preparation, Properties and Uses

Concepts Covered: *Classification of carboxylic acid, Methods of preparation, Physical and chemical properties, Test to identify carboxylic acid uses*
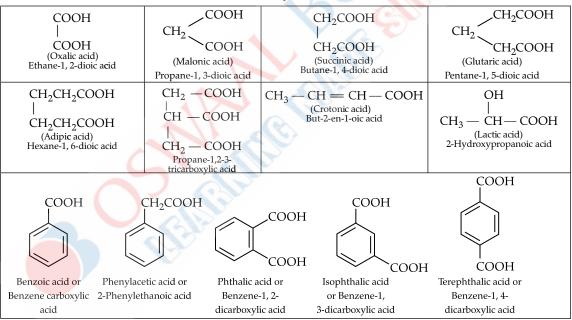

💬 **Revision Notes**

➤ Carboxylic acids are the organic compounds which contain the carboxyl group $\left[-\overset{\displaystyle O}{\overset{\parallel}{C}}-OH\right]$.

➤ **Classification of carboxylic acid:**

(i) **Based on nature of group attached to the carboxyl group:**

● **Aliphatic carboxylic acids:** Alkyl group or hydrogen atom is attached to carboxylic group. e.g., acetic acid (CH_3COOH), formic acid (HCOOH).

● **Aromatic carboxylic acids:** Aryl group is attached to carboxylic group. e.g., benzoic acid (C_6H_5COOH).

(ii) **Based on number of carboxyl group:**

● **Monocarboxylic acid:** If carboxylic acid contains one —COOH group, it is termed as monocarboxylic acid. e.g., acetic acid (CH_3COOH).

● **Dicarboxylic acid:** If carboxylic acid contains two —COOH groups, it is termed as dicarboxylic acid. e.g., oxalic acid $\begin{pmatrix} COOH \\ | \\ COOH \end{pmatrix}$.

● **Tricarboxylic acid:** If carboxylic acid contains three —COOH groups, it is termed as tricarboxylic acid. e.g., citric acid.

$$
\begin{array}{c}
COOH \\
| \\
HOOC-C-COOH \\
CH_2\ |\ CH_2 \\
OH
\end{array}
$$

➤ **Nomenclature of carboxylic acid:** Monocarboxylic acids are named as alkanoic acids, i.e., name of parent alkane + oic acid. Dicarboxylic acids are termed as alkanedioic acids.

Carboxylic acid	General Formula: $R - \overset{\overset{\displaystyle O}{\|}}{C} - OH$, where $R = C_nH_{2n+1}$		
Structural formula	**Condensed formula**	**Common name**	**IUPAC name**
$H - \overset{\overset{\displaystyle O}{\|}}{C} - OH$	HCOOH	Formic acid	Methanoic acid
$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - OH$	CH_3COOH	Acetic acid	Ethanoic acid
$CH_3CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - OH$	CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - OH$	$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$CH_3 - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{\|}}{CH}} - \overset{\overset{\displaystyle O}{\|}}{C} - OH$	$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid

Dicarboxylic Acids

COOH | COOH (Oxalic acid) Ethane-1, 2-dioic acid	CH₂⟨COOH, COOH⟩ (Malonic acid) Propane-1, 3-dioic acid	CH₂COOH | CH₂COOH (Succinic acid) Butane-1, 4-dioic acid	CH₂⟨CH₂COOH, CH₂COOH⟩ (Glutaric acid) Pentane-1, 5-dioic acid
CH₂CH₂COOH | CH₂CH₂COOH (Adipic acid) Hexane-1, 6-dioic acid	CH₂ — COOH | CH — COOH | CH₂ — COOH Propane-1,2-3-tricarboxylic acid	$CH_3 - CH = CH - COOH$ (Crotonic acid) But-2-en-1-oic acid	OH | CH₃ — CH — COOH (Lactic acid) 2-Hydroxypropanoic acid

Benzoic acid or Benzene carboxylic acid	Phenylacetic acid or 2-Phenylethanoic acid	Phthalic acid or Benzene-1, 2-dicarboxylic acid	Isophthalic acid or Benzene-1, 3-dicarboxylic acid	Terephthalic acid or Benzene-1, 4-dicarboxylic acid

➢ **Structure of —COOH group:** In the carboxyl group, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. It exhibits resonance due to the presence of lone pair of electrons present on the O-atoms.

$$-\overset{\overset{\displaystyle \ddot{O}}{\|}}{C}\overset{}{\underset{\displaystyle :\ddot{O}-H}{}} \longleftrightarrow -\overset{+}{C}\overset{\ddot{O}^-}{\underset{\displaystyle :\ddot{O}-H}{}} \longleftrightarrow -\overset{\overset{\displaystyle :\ddot{O}^-}{}}{C}=\overset{+}{\underset{\displaystyle \ddot{O}-H}{}}$$

➢ **Methods of preparation of Carboxylic acids:**

 (i) By oxidation of primary alcohols and aldehydes:

$$R - CH_2 - OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Alk. KMnO}_4} R - COOH$$

$$R - CHO + [O] \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} R - COOH$$

 (ii) From alkyl cyanides and amides:

$$R - C \equiv N \xrightarrow[\text{H}_2\text{O}]{\text{H}_3\text{O}^+} R - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2 \xrightarrow[\text{H}_2\text{O}]{\text{H}_3\text{O}^+} R - \overset{\overset{\displaystyle O}{\|}}{C} - OH$$
Acid amide

(iii) From Grignard reagent:

$$R-Mg-X+ \overset{\overset{\displaystyle O}{\|}}{C}=O \xrightarrow[\text{Ether}]{\text{Dry}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OMgX \xrightarrow{H_3O^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

➤ **Physical properties of Carboxylic acids:**

(i) Lower members are colourless liquid with pungent smell, while higher members are odourless waxy solid. Benzoic acid is a crystalline solid.

(ii) First four members are water miscible due to tendency to form hydrogen bond. Higher acids are insoluble.

(iii) Carboxylic acid have higher boiling point due to their ability to form intermolecular hydrogen bonding.

➤ **Chemical Properties:** Chemical properties of carboxylic acids are classified as follows:

(i) **Reduction involving H atom:**

(a) **Acidic nature:**

$$\underset{\text{Carboxylic acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH}+H_2O \rightleftharpoons \underset{\text{Carboxylate ion}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-}+\underset{\substack{\text{Hydronium}\\\text{ion}}}{H_3O^+}$$

Greater the extent of ionisation, greater is the strength of the acid. The presence of an electron releasing group decreases the acidic strength of the carboxylic acid while the presence of electron withdrawing group increases the acidic strength of the carboxylic acid.

(b) **Reactions showing acidic character:**

$$2RCOOH+2Na \longrightarrow 2RCOONa+H_2$$

$$R-COOH+NaOH \longrightarrow R-COONa+H_2O$$

$$R-COOH+NaHCO_3 \longrightarrow R-COONa+H_2O+CO_2\uparrow$$

$$2R-COOH+Na_2CO_3 \longrightarrow 2RCOONa+CO_2\uparrow+H_2O$$

(ii) **Reaction involving —OH group:**

(a) **Formation of acid anhydride:**

$$\underset{\text{Carboxylic acid}}{2R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[\text{or } P_2O_5, \, \Delta]{H^+, \Delta} \underset{\text{Acid anhydride}}{\begin{matrix}R-\overset{\overset{\displaystyle O}{\|}}{C}\\ \qquad\quad O\\ R-\underset{\underset{\displaystyle O}{\|}}{C}\end{matrix}} + H_2O$$

(b) **Esterification:**

$$\underset{\substack{\text{carboxylic acid} \quad \text{alcohol}}}{R-COOH+R'-OH} \rightleftharpoons \underset{\text{esters}}{R-COOR'+H_2O} \quad \xrightarrow{H^+}$$

(c) **Reaction with PCl$_5$, PCl$_3$ and SOCl$_2$**

$$\underset{\substack{\text{Carboxylic} \quad \text{Phosphorous} \quad \text{Acylchloride}\\ \text{acid} \qquad \text{pentachloride}}}{R-COOH+PCl_5} \longrightarrow RCOCl+POCl_3+HCl$$

$$\underset{\substack{\text{Carboxylic} \quad \text{Phosphorous}\\ \text{acid} \qquad \text{trichloride}}}{3R-COOH+PCl_3} \longrightarrow \underset{\substack{\text{Acid chloride} \quad \text{Phosphorous}\\ \text{acid}}}{3R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+H_3PO_3}$$

$$\underset{\substack{\text{Carboxylic} \qquad \text{Thionyl} \qquad \text{Acylchloride}\\ \text{acid} \qquad \text{chloride}}}{R-COOH+SOCl_2} \longrightarrow RCOCl+SO_2\uparrow+HCl\uparrow$$

(d) **Reaction with ammonia:**

$$\underset{\text{Carboxylic acid}}{R-COOH+NH_3} \rightleftharpoons R-COO-NH_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Acid amide}}{R-CONH_2}$$

(iii) **Reaction involving carboxyl group:**

Decarboxylation (Removal of —CO$_2$)

$$\Rightarrow \quad \underset{\substack{\text{Sodium salt of}\\\text{carboxylic acid}}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa} + NaOH \xrightarrow[\text{Heat}]{CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

➤ **Electrolysis of aqueous solution of sodium or potassium salt:**

$$2RCOONa \longrightarrow \underset{\text{Carboxylate ion}}{2RCOO^-} + 2Na^+$$

At anode: $\underset{\text{Carboxylate ion}}{2RCOO^-} \longrightarrow \underset{\text{Alkane}}{R-R} + 2CO_2 + 2e^-$

At cathode: $2H_2O \rightleftharpoons 2H^+ + 2OH^- (2H^+ + 2e^- \longrightarrow H_2)$

This process is known as **Kolbe's electrolysis**.

$$\Rightarrow \quad \underset{\text{Calcium methanoate}}{\overset{HCOO}{\underset{HCOO}{>}}Ca} \xrightarrow{\text{Distillation}} HCHO + CaCO_3$$
$$\underset{\text{Methanal}}{}$$

$$\Rightarrow \quad \underset{\text{Silver ethanoate}}{CH_3COOAg} + Br_2 \xrightarrow{CCl_4, \text{Reflux}} \underset{\text{Bromomethane}}{CH_3Br} + CO_2 + AgBr$$

This is called as **Hunsdiecker reaction**.

(b) Reduction:

⇒ **Partial reduction to alcohols:**

$$RCOOH + 2H_2 \xrightarrow[\text{(or LiAlH}_4)]{\text{Copper chromite}} \underset{\text{Alcohol}}{RCH_2OH} + H_2O$$

⇒ **Complete reduction to alkanes:**

$$RCOOH + 6HI \xrightarrow[\text{Heat}]{\text{Red P}} \underset{\text{Alkane}}{RCH_3} + 3I_2 + 2H_2O$$
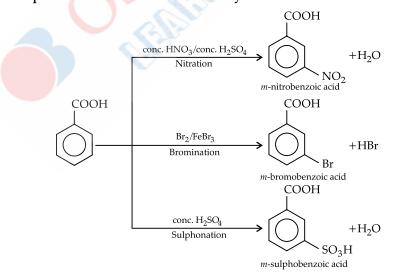
(iv) Reaction involving alkyl group

● **Halogenation**

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[(-HCl)]{Cl_2, \text{Red P}} \underset{\substack{\text{Monochloro}\\\text{acetic acid}}}{CH_2ClCOOH} \xrightarrow[(-HCl)]{Cl_2, \text{Red P}} \underset{\substack{\text{Dichloro}\\\text{acetic acid}}}{CHCl_2COOH} \xrightarrow[(-HCl)]{Cl_2, \text{Red P}} \underset{\substack{\text{Trichloro}\\\text{acetic acid}}}{CCl_3COOH}$$

This is called as **Hell-Volhard-Zelinsky (HVZ) reaction**.

(v) Electrophilic substitution in aromatic carboxylic acids:

➤ **Test for carboxylic acid:**

● **Test**   **Formic acid**

Tollen's reagent   Gives silver mirror or black precipitate.

Fehling's solution   Gives red precipitate.

With acidified $KMnO_4$ Decolourises pink colour.

- **Test**   **Acetic acid**
  With bicarbonates and carbonates   Liberates CO_2 gas.
  With ferric chloride   Forms wine red colour.
  On warming with ethyl alcohol and   Pleasant fruity odour of ethyl acetate is formed.
  conc. H_2SO_4

- **Test**   **Benzoic acid**
  On boiling   Dissolves in water.
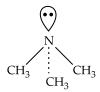 On cooling   Separates out in the form of white shining leaflets.
  With ferric chloride   Gives buff coloured precipitate.
  On warming with a little alcohol and   A fragrant odour of ethyl benzoate is formed.
  conc. H_2SO_4

➢ **Uses of Formic acid:**
  - As an antiseptic.
  - As coagulating agent in rubber industry.
  - For dye baths in textiles.

➢ **Uses of acetic acid:**
  - As vinegar.
  - Solvent for resins, cellulose, etc.
  - Production of esters, perfumes, acetone, etc.
  - Manufacture of cellulose acetate.

➢ **Uses of benzoic acid:**
  - Food preservative.
  - As urinary antiseptic in medicine.
  - Manufacture of antiseptics and dyes.
  - Esters of benzoic acid are used in perfume.

Key Terms

➢ **Electron withdrawing group:** An atom or functional group that withdraws electron density from neighbouring atoms towards itself by resonance or indicative effects.

➢ **Electron donating group:** An atom or functional group that releases electron density to neighbouring atoms from itself by resonance or inductive effects.

❑❑

CHAPTER-9

ORGANIC COMPOUNDS CONTAINING NITROGEN

Revision Notes

➢ **Amines:** Derivatives of ammonia obtained by the replacement of hydrogen atoms of alkyl or aryl groups. Aliphatic amino compounds are called as **amino alkanes.** e.g., CH_3NH_2, $C_2H_5NH_2$. Aromatic amino compounds are called as **amino arenes.** e.g., $C_6H_5NH_2$.

➢ **Classification:**
  - **Primary amines:** Amines containing — NH_2 group. e.g.,
    $CH_3—NH_2$, $C_6H_5—NH_2$
    Methanamine   Aniline
  - **Secondary amines:** Amines containing — NH group. e.g.,
    |
    $CH_3 — NH— CH_3$, $C_6H_5—NHCH_3$
    N–Methyl   N–Methylaniline
    methanamine

● **Tertiary amines:** Amines containing $— \overset{|}{\underset{|}{N}}$ group. e.g.,

$$CH_3—\overset{|}{\underset{\underset{\text{CH}_3}{|}}{N}}—CH_3, \qquad\qquad C_6H_5—\overset{|}{\underset{\underset{\text{CH}_3}{|}}{N}}—CH_3$$

N,N–Dimethyl methanamine　　　N, N– Dimethylaniline

➢ **Nomenclature:** In common system, aliphatic amines are named as alkylamines or aminoalkanes. In the IUPAC system they are named as alkanamines.

➢ **Nomenclature of some Alkylamines and Arylamines:**

Amines	Common name	IUPAC name
$CH_3—CH_2—NH_2$	Ethylamine	Ethanamine
$CH_3—CH_2—CH_2—NH_2$	n-Propylamine	Propan-1-amine
$CH_3—\overset{|}{\underset{\underset{\text{NH}_2}{|}}{CH}}—CH_3$	Isopropylamine	Propan-2-amine
$CH_3—\overset{|}{\underset{\underset{\text{H}}{|}}{N}}—CH_2—CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3—\overset{|}{\underset{\underset{\text{CH}_3}{|}}{N}}—CH_3$	Trimethylamine	N, N-Dimethylmethanamine
$C_2H_5—\overset{1\quad2\quad3\quad4}{\underset{\underset{\text{C}_2\text{H}_5}{|}}{N}}—CH_2—CH_2—CH_2—CH_3$	N, N-Diethylbutylamine	N,N-Diethylbutan-1-amine
$\underset{NH_2—CH_2—CH=CH_2}{1\quad\quad2\quad\;3}$	Allylamine	Prop-2-en-1-amine
$NH_2—(CH_2)_6—NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	o-Toluidine	2-Aminotoluene
	p-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N, N–Dimethylaniline	N,N–Dimethylbenzenamine

➢ **Structure:** Nitrogen in amines is sp^3 hybridized and geometry is pyramidal. Nitrogen atom has one orbital containing an unshared pair of electrons.

$$
\begin{array}{c}
\overset{\displaystyle \cdot\cdot}{N} \\
CH_3 \quad \vdots \quad CH_3 \\
CH_3
\end{array}
$$

➢ **Methods of preparation of amines:**

(i) By reduction of nitro compounds:

(a) $\underset{}{C_6H_5{-}NO_2} \xrightarrow[\text{Ethanol}]{H_2/Pd} C_6H_5{-}NH_2$

(b) $\underset{}{C_6H_5{-}NO_2} \xrightarrow[\text{or Fe+HCl}]{Sn+HCl} C_6H_5{-}NH_2$

(c) $R-NO_2 + 6[H] \xrightarrow[\text{or } LiAlH_4 \text{ (or } H_2/Ni)]{\text{Sn / HCl or Fe / HCl}} \underset{\text{Alkylamine}}{RNH_2} + 2H_2O$

(ii) By ammonolysis of alkyl halides: (Hoffmann's ammonolysis method)

$$\underset{\text{Haloalkane}}{RX + NH_3} \xrightarrow[-HX]{373K} \underset{(1° \text{ amine})}{RNH_2} \xrightarrow[-HX]{RX} \underset{(2° \text{ amine})}{R_2NH} \xrightarrow[-HX]{RX} \underset{(3° \text{ amine})}{R_3N} \xrightarrow[-HX]{RX} \underset{\substack{\text{Quaternary}\\\text{ammonium salt}}}{R_4\overset{+}{N}\overset{-}{X}}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base:

$$R\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R{-}NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

(a) Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

(b) Order of reactivity of halides with amines is RI > RBr > RCl.

(c) Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

(iii) From cyanide:

$$R{-}C \equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} \underset{\text{Primary amine}}{R{-}CH_2{-}NH_2}$$

(iv) By reduction of amides:

$$\overset{\displaystyle O}{\underset{}{R{-}\overset{\|}{C}{-}NH_2}} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} \underset{\text{Primary amine}}{R{-}CH_2{-}NH_2}$$

By Hoffmann bromamide reaction:

$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2 + Br_2 + 4NaOH \longrightarrow R{-}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(v) By the ammonolysis of alcohols:

$$CH_3OH + NH_3 \xrightarrow[(350°C)]{Al_2O_3} \underset{1° \text{amine}}{CH_3NH_2} + H_2O$$

$$CH_3NH_2 + CH_3OH \longrightarrow \underset{2° \text{ amine}}{(CH_3)_2NH} + H_2O$$

$$(CH_3)_2 NH + CH_3OH \longrightarrow \underset{3° \text{ amine}}{(CH_3)_3N} + H_2O$$

(vi) Gabriel's Phthalimide Synthesis:

Phthalimide $\qquad$ Potassium phtalimide

Sodium salt of phthalic acid $\qquad$ N-alkylphthalimide

(vii) Schmidt reaction

$$RCOOH + \underset{\substack{\text{Hydrazoic} \\ \text{acid}}}{N_3H} \xrightarrow{\text{Conc.}H_2SO_4} \underset{\text{Alkylamine}}{R\text{-}NH_2} + N_2\uparrow + CO_2$$

➢ **Physical properties of amines:**

● Lower aliphatic amines are gases, primary amines with more than two carbon atoms are liquids and higher amines are solids.

● **Solubility:** Lower members are readily soluble in water which decreases in water and increases in organic solvents with an increase in molecular weight. Amines are soluble in organic solvents like alcohol, ether and benzene. Alcohols are more polar than amines and forms stronger intermolecular hydrogen bonds than amines.

● Boiling point of 1°amine is higher than 3° amine because of the presence of two H-atoms attached directly with N resulting in H-bonding in 1°amines. Boiling points of amines are lower than that of alcohols of almost similar molar mass. The relative order of boiling point among amines is:

1° amine > 2° amine > 3° amine

➢ **Basic character of amines:** Aliphatic amines are stronger whereas aromatic amines are less basic than ammonia. Basic strength of amines depends on inductive effect of substituent attached to nitrogen as well as solvation effect and steric hindrance.

In small alkyl groups, the order of basicity is secondary amine > primary amine > tertiary amine. In case of bigger alkyl groups, the order of basicity is secondary amine > tertiary amine > primary amine.

Aromatic amines are weaker bases than ammonia, due to lone pair of electrons present on nitrogen atom is delocalised over benzene ring due to resonance and less available for protonation.

In aromatic amines, basic strength increases in the order tertiary > secondary > primary. Electron releasing groups like —OCH_3 , —CH_3 increase basic nature while electron withdrawing groups like – NO_2, —SO_3H, – X decrease basic character.

➢ **Chemical properties of amines:**

(i) Basic nature:

• **With water:**

$$RNH_2 + H_2O \rightleftharpoons RNH_3.OH \rightleftharpoons [RNH_3]^+ + OH^-$$
$$\text{1° amine}$$

$$R_2NH + H_2O \rightleftharpoons R_2NH_2.OH \rightleftharpoons [R_2NH_2]^+ + OH^-$$
$$\text{2° amine}$$

$$R_3N + H_2O \rightleftharpoons R_3NH.OH \rightleftharpoons [R_3NH]^+ + OH^-$$
$$\text{3° amine}$$

• **With acids:** They form salts with acids.

(ii) Alkylation:

$$\underset{\text{1° amine}}{RNH_2} \xrightarrow[-HX]{RX} \underset{\text{2° amine}}{R_2NH} \xrightarrow[-HX]{RX} \underset{\text{3° amine}}{R_3N} \xrightarrow[-HX]{RX} \underset{\text{Quaternary salt}}{[R_4N]^+X^-}$$

(iii) Acylation:

$$R-NH_2 + R'COCl \longrightarrow R-NH-COR' + HCl$$

$$\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \longrightarrow \underset{\text{N-ethylethanamide}}{CH_3-\overset{\overset{\textstyle O}{\|}}{C}-NHCH_2CH_3} + CH_3COOH$$

$$R_2NH + R'COCl \longrightarrow R_2N.COR' + HCl$$

In aromatic amines, acylation occurs in the presence of base such as pyridine as catalyst.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{\text{Base}} \underset{\substack{\text{N-Phenylethanamide} \\ \text{(Acetanilide)}}}{C_6H_5NHCOCH_3} + HCl$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Ethanoic anhydride}}{(CH_3CO)_2O} \xrightarrow{\text{Base}} \underset{\text{N-Phenylethanamide}}{C_6H_5NHCOCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Mechanism:

(iv) Benzoylation: Primary and secondary amines react with benzoyl chloride (C_6H_5COCl) in the presence of base to give substituted amide.

$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} + \underset{}{C_6H_5COCl} \xrightarrow{\text{Base}} \underset{\text{N–Ethylbenzamide}}{CH_3CH_2NH-\overset{\overset{\textstyle O}{\|}}{C}-C_6H_5} + HCl$$

(v) With carboxylic acid:

$$\underset{\text{Alkylamine}}{R-NH_2} + RCOOH \longrightarrow \underset{\substack{\text{N–Alkylammonium} \\ \text{alkanoate}}}{RCOO\overset{-}{N}H_2\overset{+}{R}}$$

(vi) Carbylamine reaction (Isocyanide test): Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides (or carbylamines) having unpleasant smell.

$$\underset{\text{Alkylamine}}{R-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{\text{Heat}} \underset{\substack{\text{Alkyl} \\ \text{isocyanide}}}{R-NC} + 3KCl + 3H_2O$$

Secondary and tertiary amines do not show this reaction.

(vii) With nitrous acid:

$$R-NH_2 + O=N-OH \xrightarrow{NaNO_2+HCl} [R-\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} R-OH + N_2 + HCl$$

$$R_2NH + HO-N=O \xrightarrow[-H_2O]{} \underset{\text{Nitrosoamine}}{R_2N-N=O}$$

$$R_3N \xrightarrow{NaNO_2+HCl} \underset{\text{Tertiary ammonium nitrite}}{[R_3NH]^+NO_2^-}$$

➢ **Identification of primary, secondary and tertiary amines:**

S. No.	Test	Primary amine	Secondary amine	Tertiary amine
1.	Action with HNO_2	Alcohol is formed and nitrogen is evolved.	Nistrosoamine is formed which reacts with phenol and conc. H_2SO_4 gives green odour **(Liebermann Test)**.	In cold, nitrite salt is formed which on heating gives nitrosoamine. This nitrosoamine gives **Liebermann test**.
2.	Action with $CHCl_3$ and alc. KOH	Isocyanide with offensive odour is formed.	No reaction.	No reaction.
3.	Action with CS_2 and $HgCl_2$ (Mustard oil reaction)	Formed compound has smell like that of mustard oil.	No reaction.	No reaction.
4.	Action with acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No reaction.
5.	Action with **Hinsberg's** $(C_6H_5SO_2Cl)$ **reagent**	Mono alkyl sulphonamide derivative is formed which is soluble in KOH.	Dialkyl sulphonamide derivative is formed which is insoluble in KOH.	No reaction.

➢ **Preparation of aniline:**

(i) Reduction of nitrobenzene:

(ii) Hoffmann bromamide reaction:

➢ **Physical properties of aniline:**
- Steam volatile.
- Toxic in nature.
- Aniline and other aromatic amines are colourless liquids but get coloured on storage due to atmospheric oxidation.

➢ **Chemical properties of aniline:**
- **With HCl and H_2SO_4 (Basic nature):**

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_2 \cdot HCl$$

Benzenamine   Anilinium hydrogen chloride

$$C_6H_5NH_2 + H_2SO_4 \longrightarrow C_6H_5.NH_2.HSO_3$$

Benzenamine   Benzenesulphanilic acid

- **Alkylation:**

- **Acetylation:**

- **Benzoylation:**

- Benzoylation of aniline is known as *Schotten Baumann reaction.*

- **Carbylamine reaction:**

- **Diazotisation:** Step I. $NaNO_2 + HCl \longrightarrow NaCl + HNO_2$

Step II:

- **Electrophilic Substitution Reaction:**

  – **Bromination:**

  – **Nitration:**

- **Sulphonation:**

- **Friedel-Crafts Reaction:** Aniline **does not** undergo Friedel-Crafts reaction.

$$\underset{\text{Aniline}}{\bigcirc\!\!\!\!\ddot{N}H_2} \xrightarrow[\text{Anhyd. AlCl}_3]{\text{R—Cl}} \underset{\text{Salt}}{\bigcirc\!\!\!\!\overset{+}{N}H_2 AlCl_3^-}$$

- Aniline does not undergo Friedel-Craft reaction due to salt formation with ammonium chloride, the lewis acid, which is used as a catalyst.

➢ **Test for aniline:** Aniline gives carbylamine test and azodye test.

➢ **Uses of aniline:**
  - Preparation of benzenediazonium chloride.
  - Preparation of Schiff's bases, sulpha drugs.
  - As a solvent in rubber industry.

➢ **Preparation of cyanides:**

  (i) From alkyl halides: On heating alkyl halide with an alcoholic solution of sodium or potassium cyanide, alkyl cyanides are formed.

$$RX + \overset{+}{K}\overset{-}{CN} \longrightarrow R—C \equiv N + \overset{+}{K}\overset{-}{X}$$
$$\text{(alc.)}$$

  (ii) From acid amides: On heating an acid amide with P_2O_5 or $SOCl_2$, the amide undergoes dehydration to form corresponding cyanide.

$$R—\underset{\substack{|| \\ O}}{C}—N H_2 \xrightarrow[\Delta]{P_2O_5 \text{ or } SOCl_2} R—C \equiv N + H_2O$$

➢ **Preparation of isocyanide:**

  (i) From alkyl halides: When an alkyl halide is treated with an alcoholic solution of silver cyanide, alkyl isocyanide is formed.

$$RX + AgCN \text{ (alc.)} \longrightarrow R—N \equiv C + AgX$$

  (ii) From primary amines: On heating suitable primary amine with chloroform and alcoholic KOH solution, alkyl isocyanide is formed. This reaction is known as carbylamine reaction.

$$\underset{\substack{\text{Primary} \\ \text{amine}}}{RNH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R—N \equiv C} + 3KCl + 3H_2O$$
$$\qquad\qquad\qquad \text{(alc.)}$$

➢ **Nitro compounds:** Compounds that contain nitro group $\left((—NO_2)—N\!\!\!\overset{O}{\underset{O}{\diagdown}} \text{ or } \overset{+}{N}\!\!\!\overset{O}{\underset{O^-}{\diagdown}} \right)$ as the functional group.

  Methods of preparation of nitro compounds:

  (i) From alkyl halides:

$$RX + AgNO_2 \text{ (alc.)} \xrightarrow{\Delta} R—NO_2 + AgX$$
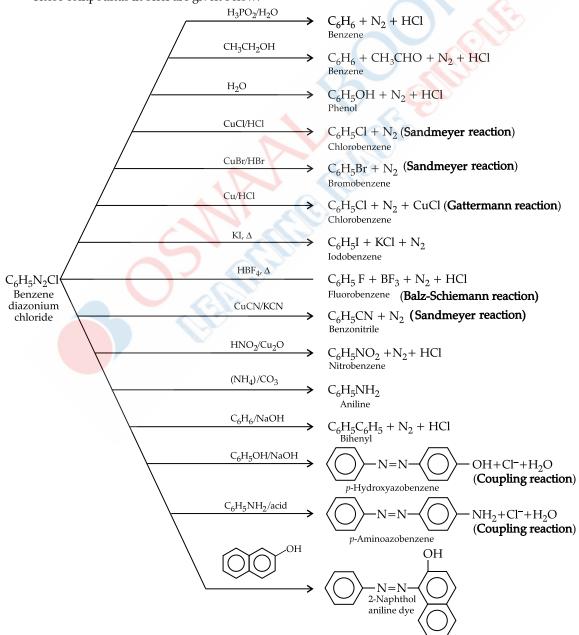
  (ii) From hydrocarbons:

$$\underset{\text{Alkane}}{R–H} + \underset{\text{(fuming)}}{HONO_2} \longrightarrow \underset{\text{Nitroalkane}}{RNO_2} + H_2O$$

➢ **Diazonium salts** are the compounds containing $N_2^+ X^-$ as functional group. Their general formula is $ArN_2^+X^-$, where X^- ion may be Cl^-, Br^-, HSO_4^-, NO_3.

  Preparation of diazonium salts: Aniline is treated with sodium nitrite and hydrochloric acid at 273-278 K resulting in the formation of benzenediazonium chloride. This reaction is called diazotisation.

$$\underset{\text{Aniline}}{\overset{\overset{\displaystyle \cdot\cdot}{\text{NH}_2}}{\text{C}_6\text{H}_5}} \xrightarrow[\text{273-278 K}]{\text{NaNO}_2+\text{HCl}} \underset{\substack{\text{Benzene diazonium} \\ \text{chloride}}}{\overset{\overset{+}{\text{N}_2}\overset{-}{\text{Cl}}}{\text{C}_6\text{H}_5}} + \text{NaCl} + 2\text{H}_2\text{O}$$

➢ **Physical properties of diazonium salts:**

● Colourless crystalline solid.

● Readily soluble in water.

● Stable for short time in solution at low temperature thus cannot be stored.

● Alkyl diazonium salts are highly unstable.

● Arene diazonium salts are relatively more stable.

➢ **Importance of Diazonium Salts in Organic Synthesis:** All chemical reactions of diazonium salts are very important in organic synthesis. Synthesis of all types of organic compounds is possible by these reactions. These compounds in brief are given below:

Mnemonics

1. **Concept: Carbylamine test**
    Mnemonics: Pafsi (Say **P**epsi**)**
    Interpretation: Primary **a**mine gives **F**oul **s**mell of **I**socyanicle with $CHCl_3$ + KOH Amine Smell
    $RNH_2 + CHCl_3 + KOH \rightarrow RNC + KCl + H_2O$
2. **Concept: Coupling Reaction**
    Mnemonics: DSPO DAY (Say, **D**e**SPO D**ay**)**
    Interpretation: Diazonium **S**alt + **P**henol → **O**range **d**ye
    Diazonium **S**alt + **A**niline → **Y**ellow **d**ye

(Orange dye)

(Yellow dye)

Key Terms

➢ **Gomberg-Bachmann reaction:** In the alkaline medium of sodium hydroxide, benzene diazonium chloride reacts with aromatic compound like benzene. When the diazo group is replaced by phenyl or aryl group, the reaction is called Gomberg-Bachmann reaction.

➢ **Baker-Mulliken test:** The hydroxyl amines when warmed with Tollens' reagent convert it to metallic silver. This reaction is used as a test for nitro compound and known as Baker-Mulliken test.

➢ **Schotten-Baumann reaction:** Benzoylation of amines with benzoyl chloride is known as Schotten-Baumann reaction.

➢ **Cope Elimination:** It is quite useful to determine the structure of tertiary amines. It involves the treatment of a tertiary amine in which one of the alkyl group contains at least one β-hydrogen atom with hydrogen peroxide to get an amine oxide, which later upon heating forms an alkane and a dialkyl hydroxyl amine.

❑❑

CHAPTER-10

BIOMOLECULES

Topic-1

Carbohydrates

Concepts Covered : *Classification of carbohydrates, Glucose and fructose preparation and properties, Oligo and polysaccharides, Importance of carbohydrates.*

Revision Notes

➢ **Biomolecules:** Biomolecules are the naturally occurring organic compounds present as essential constituents of living organism in different cells. e.g., proteins, carbohydrates, etc.

➢ **Carbohydrates:** Carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or compound which produce such units on hydrolysis. e.g., cellulose, glycogen, starch, etc.

➢ **Classification of carbohydrates:** On the basis of molecular size, carbohydrates have been classified into following four types:

   (i) Monosaccharides: Monosaccharides include non-hydrolysable carbohydrates. They are soluble in water. Those containing aldehydic group are called aldoses while other containing a ketonic group are called ketoses. Some monosaccharides with examples are given in the table as shown below:

Class	Molecular Formula	Structural formula	Example
Aldoses			
Aldotriose	$C_3H_6O_3$	$CH_2OH.CHOH.CHO$	Glyceraldehyde
Aldotetrose	$C_4H_8O_4$	$CH_2OH.(CHOH)_2.CHO$	Erythrose, Threose
Aldopentose	$C_5H_{10}O_5$	$CH_2OH.(CHOH)_3CHO$	Arabinose, Ribose, Xylose, Lyxose
Aldohexose	$C_6H_{12}O_6$	$CH_2OH.(CHOH)_4CHO$	Glucose, Mannose, Galactose, Talose, Iodose, Allose, Altrose
Ketoses			
Ketotriose	$C_3H_6O_3$	$CH_2OH.CO.CH_2OH$	Dihydroxyacetone
Ketotetrose	$C_4H_8O_4$	$CH_2OHCOCHOHCH_2OH$	Erythrulose
Ketopentose	$C_5H_{10}O_5$	$CH_2OH.CO(CHOH)_2CH_2OH$	Ribulose, Xylulose
Ketohexose	$C_6H_{12}O_6$	$CH_2OHCO(CHOH)_3.CH_2OH$	Fructose, Sorbose, Tagatose, etc.
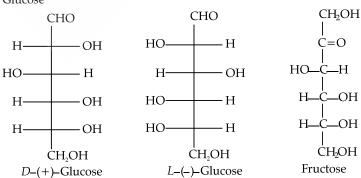
   (ii) Disaccharides: Those carbohydrates which on hydrolysis yield two molecules of monosaccharides are called disaccharides. They are crystalline, soluble in water and sweet in taste. e.g., Cane sugar, maltose, etc.
   (iii) Oligosaccharides: Those carbohydrates which yield 2 to 10 monosaccharides molecules on hydrolysis are called oligosaccharides. e.g., Raffinose on hydrolysis gives glucose, fructose and galactose.
   (iv) Polysaccharides: Those carbohydrates which produce large number of monosaccharide units on hydrolysis are called polysaccharides. They are formed by linking together a large number of monosaccharide units through glycosidic linkage. e.g., starch, amylase and cellulose.
➢ **Classification of carbohydrates based on reducing property:**
   (i) Reducing sugars: Carbohydrates which reduce Fehling's solution and Tollens' reagent are known as reducing sugar. e.g., All the monosaccharides.
   (ii) Non-reducing sugars: Carbohydrates which do not reduce Tollens' reagent and Fehling's solution are known as non-reducing sugars. e.g., sucrose.

> ⊛ **Mnemonics**
>
> **Concept:** Classification of carbohydrates.
> **1. Mnemonics: M**ona **G**lues **F**ruit to her **G**lasses
> **Interpretation:** Monosaccharide Glucose, Fructose, Galactose
> **2. Mnemonics: D**iana **W**ears **S**mall **M**edium and **L**arge
> **Interpretation:** Disaccharides Sucrose, maltose, lactose
> **3. Mnemonics: P**oly eats fibres, **starch** and **G**lides
> **Interpretation:** Polysaccharides Glycogen

➢ **Structure of Glucose and Fructose:**
   ● **Open chain structure:**
   Glucose

D–(+)–Glucose L–(–)–Glucose   Fructose

   ● **Cyclic structure:** All the pentoses and hexoses exists in cyclic hemiacetal or hemiketal structures. In the free state, they form six-member cyclic structures called pyranose form while in combined state, some of these form five-member cyclic structures called furanose form.

α-*D*(+)-glucose

β-*D*(+)-glucose

α-*D*–(–)–Fructofuranose

β-*D*–(–)–Fructofuranose

➢ **Glucose:** Glucose occurs in nature in free as well as in combined form. It is present in sweet fruits and honey.

➢ **Methods of preparation of Glucose:**

(i) **From sucrose:**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose   Glucose   Fructose
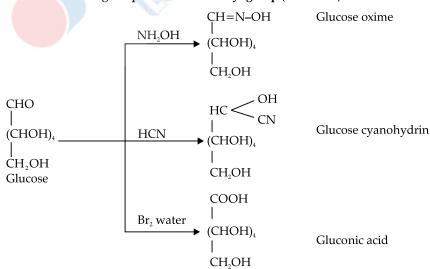
(ii) **From starch:** Commercially, glucose is obtained by hydrolysis of starch by boiling it with dil. H_2SO_4 at 393K.

$$(C_6H_{10}O_5)_n + n H_2O \xrightarrow[393K,\ 2\text{-}3\ bar]{H^+} n C_6H_{12}O_6$$

Glucose

➢ **Reactions of Glucose:**

(i) **With HI:**

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{Glucose} \end{array} \xrightarrow[\Delta]{HI} CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

(ii) **Reactions showing the presence of carbonyl group (C = O):**

$$\begin{array}{c} CH=N-OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$ Glucose oxime

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{Glucose} \end{array}$$

$$\begin{array}{c} HC{<}^{OH}_{CN} \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$ Glucose cyanohydrin

$$\begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$ Gluconic acid

Arrows: NH₂OH, HCN, Br₂ water
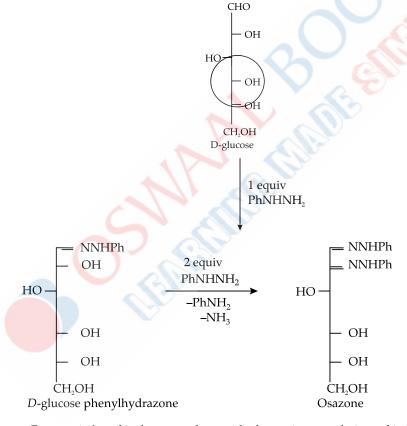
(iii) Acetylation of glucose:

$$
\begin{array}{c}
CHO \\
| \\
(CHOH)_4 \\
| \\
CH_2OH \\
Glucose
\end{array}
\xrightarrow{\text{Acetic Anhydride}}
\begin{array}{c}
CHO \quad O \\
| \qquad \parallel \\
(CH{-}O{-}C{-}CH_3)_4 \\
\qquad \qquad O \\
| \qquad \quad \parallel \\
CH_2 {-} O {-} C {-} CH_3 \\
\text{Glucose pentaacetate}
\end{array}
$$

(iv) Reaction showing the presence of alcoholic (-OH) group:

$$
\begin{array}{c}
CHO \\
| \\
(CHOH)_4 \\
| \\
CH_2OH \\
Glucose
\end{array}
\xrightarrow[\text{HNO}_3]{\text{Oxidation}}
\begin{array}{c}
COOH \\
| \\
(CHOH)_4 \\
| \\
COOH \\
\text{Saccharic acid}
\end{array}
\xleftarrow{\text{Oxidation}}
\begin{array}{c}
COOH \\
| \\
(CHOH)_4 \\
| \\
CH_2OH \\
\text{Gluconic acid}
\end{array}
$$

(v) Reaction with phenyl hydrazine:

D-glucose

1 equiv
PhNHNH$_2$

D-glucose phenylhydrazone

2 equiv
PhNHNH$_2$
$-$PhNH$_2$
$-$NH$_3$

Osazone

➢ **Fructose:** Fructose is found in free state along with glucose in many fruits and in honey (50%).

➢ **Methods of preparation of fructose:**

  (i) From hydrolysis of cane sugar:

$$
\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Dil.H}_2\text{SO}_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}
$$

  (ii) From insulin:

$$
\underset{\text{Insulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Dil.H}_2\text{SO}_4} \underset{\text{Fructose}}{nC_6H_{12}O_6}
$$

➢ **Reactions of Fructose:**

● **With HI:**

Fructose $+ HI \xrightarrow{\Delta} CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$
n-Hexane

● **With hydroxylamine:**
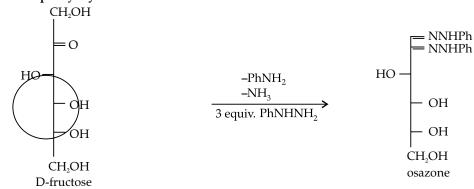
$$
\begin{array}{c}
CH_2OH \\
| \\
C=O \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
CH_2OH \\
\text{D-Fructose}
\end{array}
\xrightarrow{NH_2OH}
\begin{array}{c}
CH_2OH \\
| \\
C=NOH \\
| \\
HC-OH \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
CH_2OH \\
\text{Fructose oxime}
\end{array}
$$

● **With Br$_2$ water: No reaction**

● **With HCN:**

$$
\begin{array}{c}
CH_2OH \\
| \\
C=O \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
CH_2OH \\
\textit{D}\text{-Fructose}
\end{array}
\xrightarrow{HCN}
\begin{array}{c}
CH_2OH \\
| \\
NC-C-OH \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
CH_2OH \\
\text{Fructose cyanohydrin}
\end{array}
$$

● **With HNO$_3$:**

$$
\begin{array}{c}
CH_2OH \\
| \\
C=O \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
H-C-OH \\
| \\
CH_2OH \\
\text{D-Fructose}
\end{array}
\xrightarrow{HNO_3}
\begin{array}{c}
CH_2OH \\
| \\
COOH \\
\text{Glycolic acid}
\end{array}
\; + \;
\begin{array}{c}
COOH \\
| \\
(CHOH)_2 \\
| \\
COOH \\
\text{Tartaric acid}
\end{array}
$$

● **With phenyl hydrazine:**

$$
\begin{array}{c}
CH_2OH \\
=O \\
HO- \\
-OH \\
-OH \\
CH_2OH \\
\text{D-fructose}
\end{array}
\xrightarrow[\text{3 equiv. PhNHNH}_2]{\begin{array}{c}-PhNH_2 \\ -NH_3\end{array}}
\begin{array}{c}
=NNHPh \\
=NNHPh \\
HO- \\
-OH \\
-OH \\
CH_2OH \\
\text{osazone}
\end{array}
$$

➢ **Test for Glucose and Fructose:** Bromine water test - When glucose is treated with bromine water, red colour of bromine water disappears as —CHO group changes to —COOH group whereas fructose does not decolourise the red colour of bromine water.

$$
\underset{\text{Glucose}}{\overset{\displaystyle CHO}{\underset{\displaystyle CH_2OH}{\mid}}{(CHOH)_4}} \quad + \quad [O] \quad \xrightarrow[\text{Water}]{Br_2} \quad \underset{\text{Gluconic acid}}{\overset{\displaystyle COOH}{\underset{\displaystyle CH_2OH}{\mid}}{(CHOH)_4}}
$$

➢ **Sucrose:** Sucrose on hydrolysis with enzyme invertase gives equimolar mixture of α-D(+)–glucose and β-D(–) fructose. It is a non-reducing sugar.

α-D(+)-Glucose   β-D(–)-Fructose

➢ **Maltose:** On hydrolysis, maltose produces only α-D-glucose. It is a reducing sugar. In maltose, C-1 of one glucose is linked to C-4 of other glucose by glycosidic linkage.

α-D-Glucose   α-D-Glucose

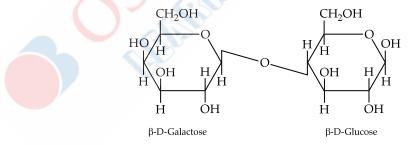➢ **Lactose:** On hydrolysis, it produces equimolar mixture of β-D-glucose and β-D-galactose. In lactose, C-1 of galactose is linked with C-4 of glucose by glycosidic linkage. It is found in milk. It is a reducing sugar.

β-D-Galactose   β-D-Glucose

➢ **Polysaccharides:** They act as food storage or structural materials.

● **Starch:** It is one of the main storage polysaccharide of plants. It is the most important dietary source for human beings. It has two components:

(a) **Amylose:** It constitutes around 15-20% of starch. It has a straight chain polymer of α-D (+)- glucose units held by $C_1 – C_4$ glycosidic linkage with about 200-1000 units. It is water soluble.

(b) Amylopectin: It constitutes around 80-85% of starch. It is a branched chain polymer of α-D-glucose. A chain is made by $C_1 - C_4$ glycosidic linkage and the chains are joined to each other by $C_1 - C_6$ glycosidic linkage.

- **Cellulose:** It is the most abundant organic substance in plant kingdom and is the main constituent of cell walls of plant cells. It is composed of straight chain polymer of β-D-glucose joined by $C_1 - C_4$ glycosidic linkage.

- **Glycogen:** It is present in animal body as stored carbohydrate. It is highly branched polymer of α–D–glucose. It is found in liver, muscles and brain. It is also present in yeast and fungi.

➢ **Importance of carbohydrates:**
- It acts as food reserve in animals and plants.
- It is the major source of energy for human beings and animals.
- Cell wall of bacteria and plants is made up of cellulose.
- Wines are made by fermentation of carbohydrates.
- Nucleic acids contain D-ribose and α-deoxy-D-ribose.
- Manufacturing of dyes.
- As a flavouring essence in perfumery.
- Synthesis of cinnamic acid, cinnamaldehyde, etc.

🔑 Key Terms

➢ **Triose:** Monosaccharide which has three carbon atoms.
➢ **Invert Sugar:** An equimolar mixture of glucose and fructose which is formed as a result of hydrolysis of sucrose is known as invert sugar.
➢ **Mutarotation:** When either of the two forms of glucose is dissolved in water, there is a spontaneous change in specific rotation till the equilibrium value of +52.5 degree. This is known as mutarotation.
➢ **Epimers:** Monosaccharides differing in configuration at a carbon other than anomeric carbon are called epimers, e.g., glucose and galactose differ in configuration at C_4 hence called epimers.

Topic-2	**Proteins, Hormones, Vitamins and Nucleic Acids**
	Concepts Covered: *Amino and types, Structure of proteins, Classification of proteins, Enyzmes, Hormones and their function, Vitamins and their types, Nucleic acids include RNA and DNA*

💬 Revision Notes

➢ **Proteins:** Proteins are complex polyamides formed from amino acids. They are essential for proper growth and maintenance of body. They have many peptide $(-\overset{\overset{\textstyle O}{\|}}{C}-NH-)$ bonds.
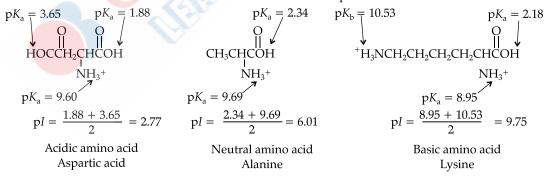
➢ **Amino acids:** The compounds, which contain carboxylic acid group and amino group, are called amino acids. Amino acids form proteins.

➢ **Types of Amino Acids:**
  Acidic, Basic and Neutral Amino Acids: Amino acids are acidic, basic or neutral depending upon the relative number of amino and carboxyl group in their molecule. If equal number of amino and carboxyl group is present, it is **neutral**. More number of amino groups than carbonyl group makes it **basic** and more carboxyl group as compared to amino group makes it **acidic**.
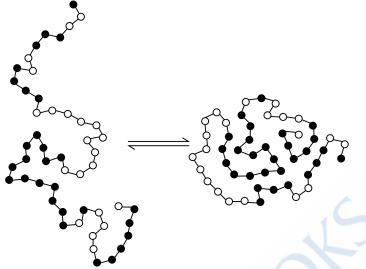 **Essential and Non-essential Amino Acids:** The amino acids which can be synthesized in the body are known as **non-essential amino acids.** e.g., glycine, alanine, glutamine, etc. On the other hand, those which cannot be synthesized in the body and must be obtained by diet are known as **essential amino acids.**

➢ **Zwitter ion:** 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. This is neutral but contains both positive and negative charges.
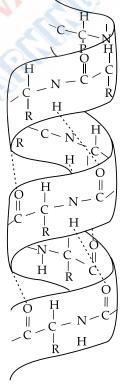
➢ **Isoelectric point:** The hydrogen ion concentration of the solution (or pH) in which the concentration of cation and anion is equal and does not migrate under the influence of electric field is known as isoelectric point of that amino acid. Each amino acid has a characteristic isoelectric point.

$$pI = \frac{1.88 + 3.65}{2} = 2.77$$

Acidic amino acid
Aspartic acid

$$pI = \frac{2.34 + 9.69}{2} = 6.01$$

Neutral amino acid
Alanine

$$pI = \frac{8.95 + 10.53}{2} = 9.75$$

Basic amino acid
Lysine

➢ **Classification of Proteins:** Proteins are classified into two types on the basis of their properties:
  (i) **Fibrous Proteins:** They have thread like molecules which tend to lie side by side to form fibers. e.g., keratin, collagen, etc.
  (ii) **Globular Proteins:** They have molecules which are folded into compact units that often approach spheroidal shape. e.g., insulin, albumins, haemoglobin, etc.

➢ **Classification of proteins on the basis of hydrolysis products:**
  (i) Simple: These yield only alpha amino acids upon hydrolysis. e.g., albumin.
  (ii) Conjugated proteins: These yield alpha amino acids and non protein part called prosthetic group. e.g., glycoprotein.
  (iii) Derived protein: These are obtained by partial hydrolysis of simple or conjugated proteins. e.g. Protease
➢ **Structure of Proteins:** There are four levels at which the structure of proteins are studied. These are primary, secondary, tertiary and quaternary level.
  (i) Primary structure: The sequence of amino acids present in a polypeptide chain held by peptide linkage is known as primary structure. e.g., Val, Ala, Gly, Ala, Val, Gly ....
  (ii) Secondary structure: It refers to the shape and arrangement of polypeptide chains due to H-bonding. These are of two types:
    (a) α-helix structure: Polypeptide chains are coiled like a helix with two adjacent turns held by forming hydrogen bond between $C = O$ of one turn and NH of next turn. e.g., keratin in hair, nails.

    (b) β-pleated sheet structure: Polypeptide chains run parallel to each other and are held together by forming H-bond between $C = O$ and NH of adjacent chain. e.g., silk.

(iii) **Tertiary structure:** It represents overall folding of polypeptide chains by H-bonds, disulphide linkages, van der Waal's and electrostatic force of attraction. e.g., fibrous and globular proteins.

(iv) **Quaternary structure:** Conformation of tertiary structure in three dimensional space is called quaternary structure.

➢ **Peptide bond:** Proteins are the polymers of α-amino acids and they are connected to each other by peptide bond or peptide linkage. When two α-amino acids combine —COOH of one condense with —NH$_2$ of second

amino acid with the elimination of water forms $-\overset{\overset{\displaystyle O}{\|}}{C}-NH$ or peptide linkage.

➢ **Different Proteins and their functions:**

S.No.	Type of Protein	Example	Function
1.	Enzyme	Trypsin, Pepsin	As a catalyst in biochemical reactions.
2.	Structural	Collagen, Keratin	Structural and protective action in teeth, nails and hair.
3.	Transport	Haemoglobin	Transport of oxygen from lungs by blood stream to different tissues.
4.	Movement	Myosin, Actin	For movement of muscles.
5.	Hormone	Insulin	Regulate body metabolism.
6.	Storage	Ferritin, Casein	Store nutrients.

➢ **Haemoglobin** is a globular protein. Its prosthetic group is heme. It contains 574 amino acid units distributed in 4 polypeptide chains. 2 chains containing 141 amino acid residues each are called alpha chains and 2 chains containing 146 amino acid residues are called beta chains.

➢ Sickel cell anaemia is caused by defective haemoglobin obtained by replacing only one amino acid, i.e., glutamic acid by valine.

➢ **Denaturation of Protein:** When a protein in its native form is subjected to change, like change in temperature or pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. It is called denaturation of protein. e.g., coagulation of egg white on boiling, curding of milk, etc.

➢ **Enzyme:** Enzymes are essential biological catalysts which are needed to catalyse biochemical reaction, e.g., maltase, lactase, invertase, etc. Almost all enzymes are globular proteins.

➢ **Some specific Enzymes and the reactions catalysed by them:**

Enzyme	Reaction Catalysed
Maltase	Maltose $\longrightarrow$ Glucose
Lactase	Lactose $\longrightarrow$ Glucose + Galactose
Amylase or Ptyalin	Starch $\longrightarrow$ Glucose
Invertase	Sucrose $\longrightarrow$ Glucose + Fructose
Urease	Urea $\longrightarrow$ NH_3 + CO_2
Trypsin, Pepsin	Protein $\longrightarrow$ Amino acid

➢ **Hormones:** Hormones are the chemical substances produced by ductless glands called endocrine glands such as thyroid, adrenal, etc. They are released into the blood stream and influence and regulate the functions of the other organs of the body. Hormonal deficiency leads to specific biological disorder which can be cured by the administration of the specific hormones.

➢ **Steroid hormones:** Those hormones which have structure similar to steroids, e.g., Cortisone, testosterone, estrogen and progesterone.

➢ **Various Hormones, Glands of secretion and their functions:**

S.No.	Hormones	Gland	Function
1.	**Steroid hormones:** (a) Testosterone (androgens) (b) Estrogen and progesterone (c) Cortisone	Testes Ovary Adrenal cortex	Responsible for development of male sex organs. Influences development of female sex organs, maintains pregnancy. Regulates metabolism of water, mineral salts.
2.	**Amine hormones:** (a) Adrenaline (b) Thyroxine	Adrenal medulla Thyroid	Increases blood pressure and pulse rate. It also release glucose from glycogen and fatty acids from fats. Stimulates rate of oxidative metabolism and regulates general growth and development.
3.	**Peptide hormone:** (a) Oxytocin (b) Vasopressin (c) Insulin (d) Glucagon	Posterior pituitary Posterior pituitary Pancreas Pancreas	Causes constriction of some smooth muscles. It causes contraction of uterus during child birth. Controls the reabsorption of water in kidneys. (ADH-Antidiuretic hormone). Controls blood glucose level. Increases blood glucose level.

➢ **Vitamins:** Vitamins are group of organic compounds which are required in very small amount for the healthy growth and functioning of living organisms. They cannot be made by organism and so have to be part of our diet.

➢ **Types of Vitamins:**
   (i) Fat soluble vitamins: Vitamins A, D, E and K are fat soluble but insoluble in water.
   (ii) Water soluble vitamins: Vitamins belonging to group B (B_1, B_2, B_6, B_{12}, etc.) and vitamin C are soluble in water.

➢ **Different Types of Vitamins:**

| Vitamin	Sources	Function	Deficiency Diseases
Vitamin A	Milk, butter, egg, fish, spinach, green vegetable, carrot, etc.	Essential for vision and growth. Develops resistance against diseases.	Night blindness, xerophthalmia, retarded growth and decrease the immunity of body towards various diseases.
Vitamin B_1	Egg, fish, meat, rice, wheat, yeast, etc.	For proper functioning of nervous system.	Beri-Beri, anaemia, weakness of muscles, etc.
Vitamin B_2	Milk, cheese, egg, meat, green vegetables, liver, etc.	Essential for growth of body.	Cracking skin particularly at the corners of mouth, glossitis, and dermatitis.
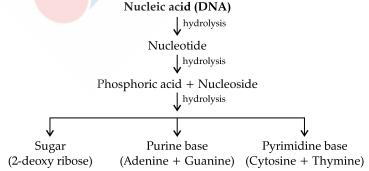
Vitamin B_6	Wheat, maize, husk of rice, meat, fish, egg, etc.	In blood formation.	Anaemia, paralysis.
Vitamin B_{12}	Liver, egg, fish, meat, milk, etc.	In blood formation.	Macroytic anaemia or pernicious anaemia.
Vitamin C	Citrus fruits such as lemon, orange, tomatoes, amla, green vegetables, etc.	For bones, teeth and healing of wounds, healthy skin.	Scurvy, pyria, pain in joints, loosening of teeth, mental depression, anaemia, bleeding of gums.
Vitamin D	Egg, meat fish, liver oil, butter, etc.	Control of metabolism of calcium and phosphorus in the formation of bones.	Rickets, osteomalacia.
Vitamin E	Milk, egg, meat, pulses, green vegetables, seeds, beans, etc.	Antisterility or reproduction.	Loss of reproductive ability or sterility.
Vitamin K (Vitamin K_1 or K_2)	Cabbage, spinach, green vegetables, egg, fish, etc.	Help in clotting of blood.	Delay in blood clotting, haemorrhage.

➢ **Nucleic acid:** The polymers of nucleotides help in synthesis of protein and transfer genetic traits.
Nucleic acids are of two types:
(i) Deoxyribonucleic acid (DNA)
(ii) Ribonucleic acid (RNA)
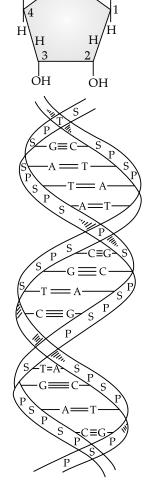**Constituents of nucleic acids:** Pentose sugar, phosphoric acid and nitrogenous bases.

➢ **Nitrogen containing bases:**
● **Pyrimidines:** These are three bases derived from, pyrimidines. These are cytosine (C), thymine (T) and uracil (U). In DNA, T is present but in RNA, U is present.
● **Purines:** There are two bases derived from purine. These are adenine (A) and guanine (G).
● **Nucleoside:** A unit formed by the attachment of a base to 1'-position of sugar is known as nucleoside.
● **Nucleotide:** When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, the unit obtained is called nucleotide.

➢ **Simple structure of nucleic acid chain:**

$$\text{Base} \qquad \text{Base} \qquad \text{Base}$$
$$| \qquad\qquad | \qquad\qquad |$$
$$-\text{Sugar- Phosphate -} [-\text{Sugar- Phosphate-}]_n \ \text{Sugar-}$$

➢ **DNA:** DNA consists of two polynucleotide chains, each chain form a right handed helical spiral with ten bases in one turn of the spiral. The two chains coil to double helix and run in opposite direction. These are held together by hydrogen bonding.

Nucleic acid (DNA)
⬇ hydrolysis
Nucleotide
⬇ hydrolysis
Phosphoric acid + Nucleoside
⬇ hydrolysis

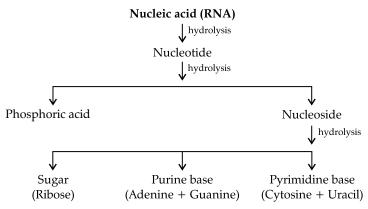| Sugar (2-deoxy ribose)	Purine base (Adenine + Guanine)	Pyrimidine base (Cytosine + Thymine)

➢ **RNA:**
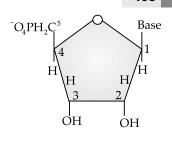(i) *m*-RNA (Messenger RNA)
(ii) *r*-RNA (Ribosomal RNA)
(iii) *t*-RNA (Transfer RNA)

Double helix structure of DNA molecule

Nucleic acid (RNA)

↓ hydrolysis

Nucleotide

↓ hydrolysis

Phosphoric acid   Nucleoside

↓ hydrolysis

Sugar   Purine base   Pyrimidine base
(Ribose)   (Adenine + Guanine)   (Cytosine + Uracil)

➤ **Differences between DNA and RNA:**

S.No.	DNA	RNA
(i)	It is the genetic material.	It is not the genetic material except in certain viruses. e.g., TMV (Tobacco Mosaic Virus), Retrovirus.
(ii)	It is double stranded with α-helix structure with two strands coiled spirally.	RNA is single stranded with some viruses as exception.
(iii)	It contains deoxyribose sugar.	It contains ribose sugar.
(iv)	Bases present are thymine, adenine, cytosine and guanine.	Bases present are uracil, adenine, cytosine and guanine.
(v)	DNA transcribes genetic information to RNA.	RNA translates the transcribed message for forming polypeptides.

Key Terms

➤ **N-Terminal end:** There is a free amino group at one end of molecule of amino acid which is known as N-Terminal end.

➤ **C-Terminal end:** There is a free carboxyl at the end of amino acid molecule which is known as C-Terminal end.

➤ **Enzyme inhibitors:** These are the chemical substances which tend to reduce the activity of a particular enzyme instead of increase it.

Mnemonics

Concept: Fat soluble vitamins
Mnemonics: KEDA
Interpretation
Interpretation:
Vitamin K—Haemorrhage
Vitamin E—Sterility
Vitamin D—Ricket
Vitamin A—Night blindness

Mnemonics

Concept: Vitamin deficiency disease
Mnemonics: Beri Cracke the theor **Playing** with **Papan**
Interpretation
B_1—Beri Beri
B_2—Cracks in lips
B_3—Pellagra
B_5—Parsthesia/Acne
B_6—Anaemia (Microcytic)
B_9—Anaemia (Macrocytic)

❑❑