

CHAPTER-1

SOLUTIONS

Topic- 1

Types of Solutions, Expression of Concentration of Solutions and Solubility

Concepts Covered • Types of solution, • Molarity, • Normality, • ppm, • Mass by volume%, • Mole Fraction, • Volume by volume%, • Henry's Law

Revision Notes

- **Solution:** A homogeneous mixture of two or more pure substances is known as solution.
- If the constituents of the solution are two, it is called binary, if three then ternary, if four then quaternary and so on.
- **Two constituents of the solution are:**
 - (i) **Solute:** A substance that is dissolved in another substance in lesser amount, forming a solution. For example: Sugar, salt, etc.
 - (ii) **Solvent:** A substance in which another substance is dissolved in larger amount, forming a solution. For example: Water, milk, etc.
- **Note:** Solvent determines the physical state of the solution.
- **Types of Solutions:** Any state of matter (solid, liquid or gas) can act both as a solvent and as a solute during the formation of a solution. Therefore, depending upon the physical states of solute and solvent, we can have following nine different types of solutions:

S. No.	Types of Solution	Solute	Solvent	Examples
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, dust or smoke particles in 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 adsorbed in palladium.
8.	Gas – Liquid	Gas	Liquid	Aerated drinks.
9.	Gas – Gas	Gas	Gas	Mixture of gases, etc.



Key Word

Aerosol: It is suspension of fine solid or liquid particles in air , e.g.: Fog.

- **Aqueous solution:** A solution containing water as solvent is known as aqueous solution. For example, sugar solution.
- **Non- aqueous solution:** A solution containing solvent other than water is known as non- aqueous solution. For example, iodine dissolved in alcohol.
- **Saturated solution:** A solution in which no more solute can be dissolved at the same temperature is known as saturated solution.
- **Unsaturated solution:** A solution in which more amount of solute can be dissolved at the same temperature is known as unsaturated solution.
- **Method of expressing concentration of solution:** The concentration of solution is the amount of solute present in the given quantity of solute or solvent. It can be expressed in any of the following types:

- (i) **Mass percentage** $\frac{w}{W}$: 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** $\frac{v}{V}$: It is defined as 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** $\frac{w}{V}$: It is defined as mass of solute dissolved per 100 mL of solution. It is commonly used in medicine and pharmacy.

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

- (iv) **Parts per million (ppm)**: It can be defined as the parts of a component per million (10^6) parts of the solution. It is used to express the concentration of a solute present in trace quantities.

$$\text{ppm (A)} = \frac{\text{Number of the parts of the component (A)}}{\text{Total number of parts of all the components of the solution}} \times 10^6$$

Parts per million can be expressed in three ways:

- (a) Mass to mass

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

- (b) Volume to volume

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

- (c) Mass to volume

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

- (v) **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' and n_B is the number of moles of component 'B'.

$$\text{Similarly, } \chi_B = \frac{n_B}{n_A + n_B}$$

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

$$\chi_A + \chi_B = 1$$

- (vi) **Molarity (M)**: It is defined as the number of moles of solute per litre of solution.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in Litres)}}$$

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

where, W_B = Weight of solute, V = Volume of solution in mL, M_B = Molar mass of solute.
Unit is mol L⁻¹ or M (molar).

And $\frac{\text{Weight of solute (W}_B\text{)}}{\text{Molar mass of solute (M}_B\text{)}} = \text{Moles of solute}$

- (vii) **Molality (m):** It is defined as the number of moles of solute per 1000 g or 1 kg of solvent.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$m = \frac{W_B \times 1000}{M_B \times W}$$

where, W_B = Weight of the solute, M_B = Molar mass of solute, W = Mass of solvent in g

Unit is mol kg⁻¹ or molal (m). Molality and mole fraction do not change with change in temperature.



Key Formulae

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2} \quad (x_1 + x_2 = 1)$$

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in Litre}}$$

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$\text{Normality (N)} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in Litre}}$$

$$\text{Mass percentage } \left(\frac{w}{W} \right) = \frac{\text{Mass of solute in the solution}}{\text{Total mass of the solution}} \times 100$$

$$\text{Volume percentage } \left(\frac{v}{V} \right) = \frac{\text{Volume of solute}}{\text{Total volume of the solution}} \times 100$$

$$\text{Mass by volume percentage } \left(\frac{w}{V} \right) = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

$$\text{ppm of component A} = \frac{\text{Mass of component A}}{\text{Total mass of solution}} \times 10^6$$

- (viii) **Normality (N):** It is defined as number of gram equivalents of solute dissolved per litre of solution.

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in Litre}}$$

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

where, W_B = Mass of solute, E_B = Equivalent weight of solute, V = Volume of solution in mL

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

$$\frac{1}{m} = \frac{d}{M} - \frac{M_B}{1000}$$

where, m = Molality of solution, M = Molarity of solution,

M_B = Molar mass of solute, d = Density of solution in g ml⁻¹

- **Relationship between Mole fraction of solute (χ_B) and Molality (m):**

$$m = \frac{\chi_B \times 1000}{(1 - \chi_B) \times M_A}$$

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

- **Solubility:** Solubility can be defined as the maximum amount of solute that can be dissolved in 100 g of solvent to form a saturated solution at a given temperature.

- **Factors affecting Solubility:**

- 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.
- Temperature:** Solubility increases with increase in temperature. It increases for endothermic reaction while it decreases for exothermic reaction.
- Pressure:** The solubility of solid in liquid is not affected significantly by pressure because solids and liquids cannot be compressed.

► **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 given volume of the liquid at a constant temperature depends upon the pressure applied."

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

$$p = K_H \chi,$$

where K_H = Henry's constant.

- **Applications of Henry's law:**

- To increase the solubility of CO_2 in soda water and soft drinks, the bottle is sealed under high pressure.



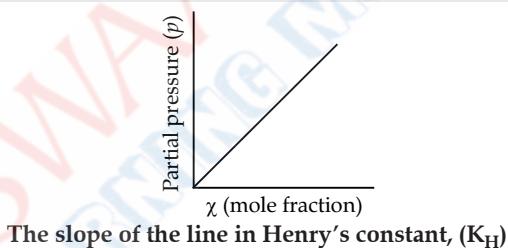
Key Formulae

- $m = \frac{\chi_B \times 1000}{(1 - \chi_B) \times M_A}$

- **Henry's Law:** $p = K_H \chi$



Key Diagram



- To avoid the toxic effects of high concentration of nitrogen in blood, the tanks used by scuba divers are filled with air diluted with helium (11.7%), nitrogen (56.2%) and oxygen (32.1%).

- 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:

- The pressure of gas is not too high and temperature is not too low.
- The gas should not undergo any chemical change.
- The gas should not undergo association or dissociation in the solution.

Topic-2

Raoult's Law, Ideal and Non-ideal Solutions

Concepts Covered • Raoult's law, Ideal solutions, Non - Ideal Solutions, Azeotropes - Maximum boiling and Minimum Boiling

Revision Notes

- Vapour pressure is the pressure exerted by vapours over a liquid at equilibrium state at constant temperature.
► Vapour pressure depends on the following factors:

- (i) **Nature of the liquid:** Liquids having intermolecular forces are volatile and possess higher vapour pressure.
(ii) **Temperature:** Vapour pressure of a liquid increases with increase in temperature.
- **Raoult's law for a solution of volatile liquids:** It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction in solution. 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^0 and p_B^0 be their partial vapour pressures respectively in the solution at a particular temperature. If p_A^0 and p_B^0 are their vapour pressures in the pure state respectively, then according to Raoult's law:

$$p_A = p_A^0 \chi_A$$

$$p_B = p_B^0 \chi_B$$

Considering Dalton's law of partial pressure,

$$p_{\text{total}} = p_A + p_B$$

Substituting values of p_A and p_B ,

$$\begin{aligned} p_{\text{total}} &= \chi_A p_A^0 + \chi_B p_B^0 \\ &= (1 - \chi_B) p_A^0 + \chi_B p_B^0 \\ &= p_A^0 + (p_B^0 - p_A^0) \chi_B \end{aligned}$$

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

$$\begin{aligned} p_A &= \chi_A p_{\text{total}} \\ \text{and } p_B &= \chi_B p_{\text{total}} \end{aligned}$$

In general $p_i = \chi_i p_{\text{total}}$

- **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:

$$p_A = p_A^0 \chi_A$$

According to Henry's law, in the 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:

$$p_A = K_H \chi_A$$

On comparing both expressions p_A^0 is equal to K_H .

- **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.

$$\chi_B = \frac{p_A^0 - p_A}{p_A^0},$$

where, χ_B = Mole fraction of solute,

$$p_A^0 - p_A = \text{Lowering of vapour pressure.}$$

Key formula

Raoult's law for volatile liquids: Raoult's law for volatile liquids:

$$P_{\text{solute}} = X_{\text{solute}} \cdot P_{\text{solute}}^0$$

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P_{\text{solvent}}^0$$

where, P^0 is the vapour pressure of pure component

Raoult's law for non volatile solute:

$$X_B = (P_A^0 - P_A)/P_A^0$$

where, $P_A^0 - P_A$ = lowering of vapour pressure

X_B = mole fraction of solute

- **Ideal solution:** A solution which obeys Raoult's law over a wide range of concentration at specific temperature is called ideal solution.



Mnemonics

Concept: Raoult's law for Non-volatile Solute

Mnemonics: R.L. is Very Poor Student = Most Failure Student

Interpretations:

Relative Lowering Of Vapour Pressure For A Solution Is Equal To The Mole Fraction Of Solute.

- (i) Raoult's law is obeyed. $p_A = p_A^0 \chi_A$, $p_B = p_B^0 \chi_B$
 - (ii) $\Delta_{\text{mix}}H = 0$,
 - (iii) $\Delta_{\text{mix}}V = 0$,
 - (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 solution:** A solution which does not obey Raoult's law for all the concentrations is called a non-ideal solution.
- (i) Raoult's law is not obeyed, i.e., $p_A \neq p_A^0 \chi_A$ and $p_B \neq p_B^0 \chi_B$
 - (ii) $\Delta_{\text{mix}}H \neq 0$,
 - (iii) $\Delta_{\text{mix}}V \neq 0$,
 - (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



Mnemonics

Concept: Ideal solution

Mnemonics: ISRaE_L

Interpretations:

Ideal Solution Obeys Raoult's Law

Concept: Non-Ideal solution

Mnemonics: Nano Scale Device Research Laboratory

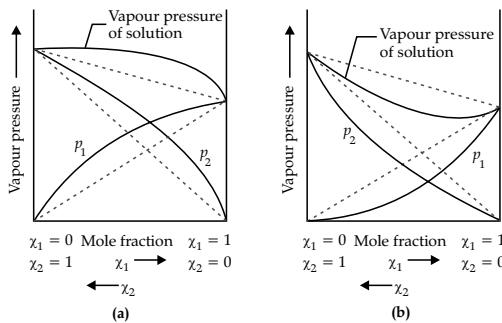
Interpretations:

Non-Ideal Solution Does Not Obey Raoult's Law

- 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 increase in vapour pressure.
- Some examples are:**
- (i) Water and ethanol,
 - (ii) Chloroform and water,
 - (iii) Ethanol and CCl₄,
 - (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,
 - (ii) Chloroform and methyl acetate,
 - (iii) H₂O and HCl,
 - (iv) H₂O and HNO₃,
 - (v) Acetic acid and pyridine,
 - (vi) Chloroform and benzene.



Key Diagram



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:** Liquid mixtures which distil over without change in composition are called constant boiling mixtures or azeotropes or azeotropic mixtures.
- **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 boil at temperature higher than the boiling points of its components. e.g., mixture of HNO_3 and H_2O .

Topic- 3

Colligative Properties, Determination of Molecular Mass, abnormal Molecular Mass, van't Hoff Factor

Concepts Covered • Colligative properties, calculation of abnormal molecular mass and Van't Hoff Factor



Revision Notes

- **Colligative properties:** Certain properties of solutions depend only on the number of particles of the solute (molecules or ions) and do not depend on the nature of solute, such properties are called colligative properties. These are:
 - (i) Relative lowering of vapour pressure,
 - (ii) Depression of freezing point,
 - (iii) Elevation of boiling point,
 - (iv) Osmotic pressure of the solution.
- **Relative lowering of 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.

$$\text{Vapour pressure of pure solvent} = p_A^0$$

$$\text{Lowering of vapour pressure} = p_A^0 - p_A$$

$$\text{Relative lowering of vapour pressure}$$

$$\frac{p_A^0 - p_A}{p_A^0} = \chi_{\text{solute}} = \frac{n}{N+n}$$

where n and N are the number of moles of solute and solvent respectively.

- **Elevation of the boiling point:** The difference in boiling point of solution and pure solvent is called elevation of the boiling point.

$$\text{Boiling point of pure solvent} = T_b^{\circ}$$

$$\text{Boiling point of solution} = T_b$$

Increase in boiling point $\Delta T_b = T_b - T_b^0$ is known as elevation of boiling point for dilute solution.

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

Where,

w_2 = weight of solute in g

M_2 = Molar mass of solute

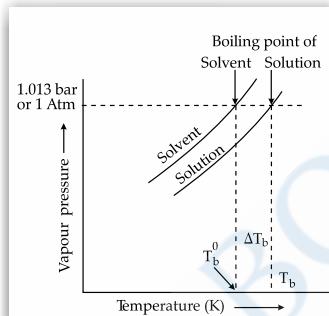
w_1 = weight of solvent in g

$$\Delta T_b = K_b m$$

K_b = Boiling point elevation constant or molal elevation constant or **Ebullioscopic constant**.



Key Diagram



Elevation of boiling point

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

The freezing point of pure solvent = T_f^0

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

The decrease in freezing point $\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point.

For dilute solution,

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

We know,

$$(i) \quad \frac{W_B \times 1000}{M_B \times W_A} = \text{molality}$$

$$(ii) \quad \Delta T_f = \frac{K_f \times 1000 \times W_2}{M_2 \times W_1}$$

K_f = Freezing point depression constant or molal depression constant or **Cryoscopic constant**.



Key Diagram

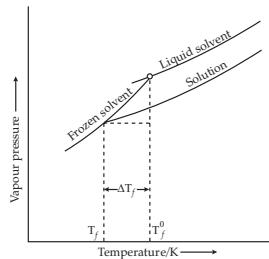


Diagram showing ΔT_f , depression of the freezing point of a solvent in a solution.

Key Formulae

► **Modified equations for colligative properties :**

(i) Relative lowering of vapour pressure of solvent

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{n}{N+n}$$

(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

$$\pi = \frac{imRT}{V}$$

or

$$\pi = iCRT \quad \left[\because \frac{m}{V} = C \right]$$

► **Osmosis:** The process in which there is net flow of solvent to the solution by a semipermeable membrane is called osmosis.

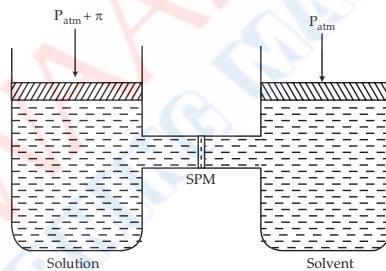
► **Osmotic pressure:** The extra pressure that is applied to stop the flow of solvent to solution across a semipermeable membrane is called osmotic pressure of the solution.

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

Thus $\pi = CRT$ as π is the osmotic pressure and R is the gas constant.

$$\pi = \frac{n}{VRT} \quad (n \text{ is the number of moles, } V \text{ is the volume of solution})$$

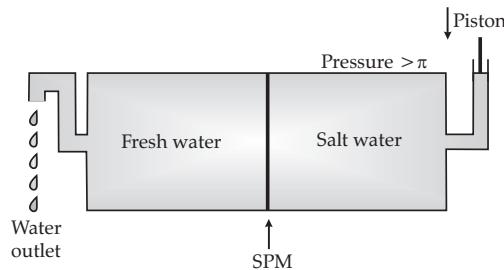
Key Diagram



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

► **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 reverse osmosis.

Key Diagram



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

► **Abnormal molecular mass:** When the molecular mass calculated with the help of colligative property is different from theoretical molecular mass, it is called 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,

Observed (experimental)

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

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,

$$i = \frac{(\Delta p)_{\text{obs}}}{(\Delta p)_{\text{cal}}}$$

(i) For lowering of vapour pressure,

$$i = \frac{(\Delta T_b)_{\text{obs}}}{(\Delta T_b)_{\text{cal}}};$$

(ii) For elevation of boiling point,

$$i = \frac{(\Delta T_f)_{\text{obs}}}{(\Delta T_f)_{\text{cal}}};$$

(iii) For depression of freezing point,

$$i = \frac{\pi_{\text{obs}}}{\pi_{\text{cal}}};$$

(iv) For osmotic pressure,

Since a colligative property is proportional to number of particles of solute.

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

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

Total number of moles of particle

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

- **Hypertonic solution:** A solution is called hypertonic, if its concentration is higher than that of the solution separating it by a semipermeable membrane.
- **Hypotonic solution:** A solution is called hypotonic, if its concentration is lower than that of the solution separating it by a semipermeable membrane.
- **Isotonic solution:** Two solutions are called isotonic, if they exert the same osmotic pressure at a given temperature. Isotonic solutions have same molar concentration. When such solutions are separated by semipermeable membrane no osmosis occurs between them.



Mnemonics

Concept: Different Colligative properties

Mnemonics: RLVP_DFP_EBP_OP

Interpretations:

Relative Lowering Of Vapour Pressure

Depression OF Freezing Point

Elevation Of Boiling Point

Osmotic Pressure

CHAPTER-2

ELECTRO-CHEMISTRY

Topic- 1

Electrolytic Conductivity, Electrolytes and Kohlrausch's Law

Concepts Covered • *Conductivity, Resistivity, Kohlrausch's Law, cell constant*



Revision Notes

- **Electrochemistry** is the branch of chemistry which deals with the study of the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to result in non-spontaneous chemical transformations.
- **Electrolytic conduction:** The flow of electric current through an electrolytic solution is called electrolytic conduction.
- **Electrolyte:** A substance that dissociates in solution to produce ions and hence conducts electricity in dissolved state or molten state.
Weak electrolyte – H_2CO_3 , CH_3COOH , HCN.
Strong electrolyte – NaCl, HCl, NaOH.
- **Degree of ionisation:** It is the ratio of number of ions produced to the total number of molecules in electrolyte.
- **Resistance** is defined as the property of given substance to obstruct the flow of charge. It is directly proportional to the length (l) and inversely proportional to its area of cross-section (A).

$$R \propto \frac{l}{A} \quad \text{or; } R = \rho \frac{l}{A}$$

ρ = Resistivity or specific resistance.



Key Facts

Fascinating Facts on electrolysis:

- (1) Electrolysis is even used at the beauty parlour. To prevent hair from growing, professional use electric current to damage the hair follicles.
- (2) Magnesium is produced by the electrolysis of seawater.
- (3) Electrolysis is used for rust removal and cleaning of metal objects including old coins.



Mnemonics

Concept: Electrolyte

Mnemonics: SEDC

Interpretations: Strong Electrolytes Dissociate Completely.

Mnemonics: WED Prime

Interpretations: Weak Electrolytes Dissociate Partially.

- **Resistivity:** If a solution is placed in between two parallel electrodes having cross sectional area 'A' and distance ' l ' apart, then

$$R = \rho \frac{l}{A},$$

where ρ = **resistivity** and its SI unit is Ohm-m or Ohm-cm.

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

i.e.,
$$C = \frac{1}{R} = \frac{A}{\rho l}$$

The SI unit of conductance is **Siemens (S)**.

- **Conductivity:** It is the reciprocal of resistivity and is denoted by κ (Greek Kappa).

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

where C = Conductance of the solution

l = Distance/ length

A = Area of cross section

Its SI unit is $S\ m^{-1}$ and it is also expressed as $S\ cm^{-1}$.

It depends upon the:

(i) Nature of the material

(ii) Temperature

(iii) The number of valence electrons per atom or size of the ions produced and their solvation (electrolytes).

Key Equation

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

- Metallic conductance is the electrical conductance in metals 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

Key Word

Conductance: The ability of electric charge to flow.

Resistivity: The property of a material to stop the flow of electric current.

- **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 interionic attractions
 - (ii) Solvation of ions
 - (iii) Nature of solvent and its viscosity
 - (iv) Temperature
- **Cell constant (G):** It is the ratio of distance between electrodes to the cross-sectional area between electrodes.

$$\text{Cell constant (G)} = \frac{l}{A} \text{ in } cm^{-1} \text{ or } m^{-1}$$

It depends on the:

- (i) Distance between the electrodes
- (ii) Area of cross section.

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

$$\Lambda_m = \frac{\kappa}{C} \times 1000$$

where, κ = Conductivity

C = Concentration of solution.

SI unit of molar conductivity is $S\ m^2\ mol^{-1}$.

- **Debye Huckel Onsager equation:** It is applicable for strong electrolyte:

$$\Lambda_m = \Lambda_m^\circ - A \sqrt{C}$$

where, Λ_m° = Limiting molar conductivity, Λ_m = Molar conductivity, A = Constant and C = Concentration of solution.

- **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 contributions of 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

$$\Lambda_m^\infty = v^+ \lambda_+^\infty + v^- \lambda_-^\infty$$

where, v^+ and v^- are the number of cations and anions per formula of electrolyte.

Applications of Kohlrausch's law

- (i) Calculation of molar conductivities of weak electrolyte at infinite dilution.

- (ii) Calculation of degree of dissociation (α) of weak electrolytes:

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

- (iii) Determination of dissociation constant (K) of weak electrolytes:

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{C\Lambda_m^2}{\Lambda_m^0(\Lambda_m^0 - \Lambda_m)}$$

- (iv) Determination of solubility of sparingly soluble salts:

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

Key Equations

(i) For strong electrolyte, $\Lambda_m = \Lambda_m^\circ - A \sqrt{C}$

$$\Lambda_m^\infty = v^+ \lambda_+^\infty + v^- \lambda_-^\infty$$

(ii) Degree of dissociation (α) = $\frac{\Lambda_m^c}{\Lambda_m^\circ}$

Example 1

Q. Calculate the molar conductivity and degree of dissociation. Conductivity of 2.5×10^{-4} M methanoic acid is 5.25×10^{-5} S cm⁻¹.

(Given : $\Lambda_{(H^+)}^\circ = 349.5$ S cm² mol⁻¹ and $\Lambda_{(HCOO^-)}^\circ = 50.5$ S cm² mol⁻¹.)

Solution:

Step 1:

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

Step 2:

$$\begin{aligned} \Lambda_m &= \frac{1000 \times 5.25 \times 10^{-5}}{2.5 \times 10^{-4}} \text{ S cm}^2 \text{ mol}^{-1} \\ &= 210 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

Step 3:

$$\begin{aligned} \Lambda_m^\circ \text{ HCOOH} &= \Lambda_{(HCOO^-)}^\circ + \Lambda_{(H^+)}^\circ \\ &= (50.5 + 349.5) \text{ S cm}^2 \text{ mol}^{-1} \\ &= 400 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\alpha = 210 / 400 = 0.525$$

Topic-2

Redox Reactions and Electrochemical Cells, Electrode Potential and Nernst Equation

Concepts Covered • Galvanic cell, redox reaction, SHE, Nernst equation, Gibbs energy.

Revision Notes

- **Redox reaction:** A chemical reaction in which oxidation and reduction both processes takes place simultaneously is known as redox reaction. Oxidation is a process in which any substance loses one or more electrons while

- reduction is the process in which one or more electrons are gained by another substance.
- **Galvanic cell:** A device in which the redox reaction is carried indirectly and chemical energy is converted to electrical energy. It is also called galvanic cell or voltaic cell.
 - **Redox couple:** It is defined as having together the oxidised and reduced form of a substance taking part in an oxidation or reduction half reaction.



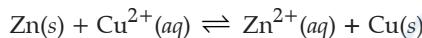
Mnemonics

Concept: Redox reaction

Mnemonics: eRROR

Interpretations: Redox reaction involves both oxidation and reduction

- **Galvanic cell or Voltaic cell:** It consists of two metallic electrodes dipped in electrolytic solutions. Electrical energy is produced as a result of chemical reaction which takes place in this cell.
- **Daniell cell:** It is a type of galvanic cell which consist of two electrodes (Zn & Cu) in contact with the solution of its own ion, i.e., ZnSO_4 & CuSO_4 respectively.



Cell is represented as,



- **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 in agar-agar. It performs following functions:
 - (i) It completes inner cell circuit.
 - (ii) It prevents transference of electrolyte from one half-cell to the other.
 - (iii) It maintains the electrical neutrality of the electrolytes in the two half-cells.
- **Electrode Potential:** It is the potential developed by the electrode with respect to the standard reference electrode. By convention, the reference electrode is standard hydrogen electrode which have a potential of zero volt.
- **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 Standard Hydrogen Electrode (SHE). SHE has a standard potential at all temperatures. It consists of a platinum foil coated with platinum black dipped into an aqueous solution in which the $[\text{H}^+] = 1 \text{ M}$ 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 the emf of the cell when no current is flowing through the circuit.
- **EMF of the cell:** It is the sum of electric potential differences produced by separation of charges that occur at each phase boundary in the cell.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

In terms of standard oxidation electrode potential :

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

where E_{cathode}° = standard electrode potential of cathode

and E_{anode}° = standard electrode potential of anode

Example 2

- Q. A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $\text{Zn(NO}_3)_2$ solution and metallic plate of lead in 0.02 M $\text{Pb(NO}_3)_2$ solution. Calculate the emf of the cell. Write the chemical equation for the electrode reactions and represent the cell.

(Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$; $E^\circ_{\text{Pb}^{2+}/\text{Pb}} = -0.13 \text{ V}$)

Solution:

Here, Zn is taken as anode and Pb as cathode.

Write the reactions taking place at anode and cathode.

Anode reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-$

Cathode reaction: $\text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb(s)}$

Cell representation:



According to Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]}$$

$$\begin{aligned} E_{\text{cell}} &= [-0.13 - (-0.76)] - \frac{0.0591}{2} \log \frac{0.1}{0.02} \\ &= 0.63 - 0.02955 \times \log 5 \\ &= 0.63 - 0.02955 \times 0.6990 \\ &= 0.63 - 0.0206 = 0.6094 \text{ V} \end{aligned}$$

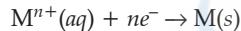
- **Standard oxidation potential:** The potential difference when given electrode is in contact with its ions having 1 molar concentration, undergoes oxidation when coupled with standard hydrogen electrode is known as Standard Oxidation Potential.
- **Electrochemical series:** It is the arrangement of the element in order of their increasing electrode potential values. The series has been established by measuring the potential of various electrodes versus SHE.



Key Word

Standard oxidation Potential: It is the tendency of a chemical species to be oxidised.

- **Nernst equation:** If the concentration of species in the electrode reaction is not equal to 1 M, then we use Nernst equation. For a general electrode,



the Nernst equation can be written as

$$E_{(\text{M}^{n+}/\text{M})} = E_{(\text{M}^{n+}/\text{M})}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{M}_{(\text{s})}]}{[\text{M}^{n+}(\text{aq})]}$$

where E° = Standard electrode potential,

R = Gas constant ($8.31 \text{ JK}^{-1} \text{ mol}^{-1}$), T = Temperature (K), n = Number of moles of electrons and F = Faraday (96500 C).

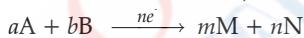
At equilibrium,

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

K_c = Equilibrium constant

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

For the cell with the net reaction,



the Nernst equation at 298 K can be written as

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

where $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$



Mnemonics

Concept: Nernst equation

Mnemonics: OPIIEc

Interpretations: Oxidising Power Increases With Increase In E° Value.

- **Gibbs energy:**

For cell reaction to be spontaneous, ΔG must be negative.

Calculations of $\Delta_r G^{\circ}$ and $\Delta_r G$:

$$\Delta_r G^{\circ} = -nF E_{\text{cell}}^{\circ}$$

$$\text{and } \Delta_r G = -nF E_{\text{cell}}$$

We also know that, Gibbs energy change is equal to the useful work done.

For cell reaction to be spontaneous, ΔG must be negative.

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



Key Equations

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

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

$$(iii) \Delta_r G^\circ = -2.303 RT \log K_C$$

Topic-3

Electrolysis, Law of Electrolysis, Batteries, Fuel Cells and Corrosion

Concepts Covered • *Electrolysis, Faraday's Law, Batteries*



Revision Notes

- Electrolysis is the process of decomposition of an electrolyte when an electric current is passed through either its aqueous solution or molten (fused) state. This process takes place in electrolytic cell.
- **Faraday's first law of electrolysis:** The amount of chemical reaction which occurs at any electrode during electrolysis 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.

$$\frac{w_1}{E_1} = \frac{w_2}{E_2}$$



Key Equation

$$m = Z \times I \times t$$

- **Products of electrolysis depend on**
 - (i) Physical state of material.
 - (ii) Types of electrode being used.
- **Battery** is a combination of galvanic cells in series and used as a source of electrical energy.
- **Types of batteries:**
 - (i) Primary batteries are nonchargeable batteries such as Lechlanche cell and Dry cell.
 - (ii) Secondary batteries are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.
- **Dry cell (Lechlanche cell):** The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powdered MnO_2 and C. The space is filled with paste of NH_4Cl and $ZnCl_2$.

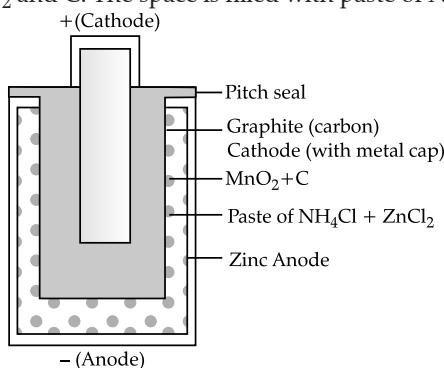


Fig 1 : Dry Cell

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

At cathode: $\text{MnO}_2(\text{s}) + \text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$

The net reaction: $\text{Zn} + \text{NH}_4^+(\text{aq}) + \text{MnO}_2 \rightarrow \text{Zn}^{2+} + \text{MnO(OH)} + \text{NH}_3$

► **Lead storage battery:**

Anode - Spongy lead

Cathode - Lead packed with lead dioxide

Electrolyte - Aqueous solution of H_2SO_4 (38%).

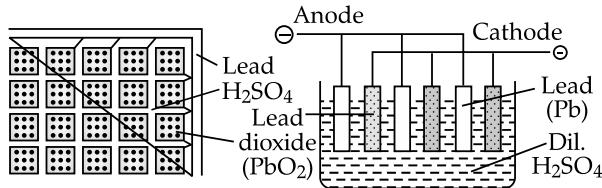
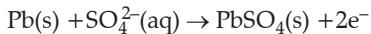


Fig 2 : Lead storage battery

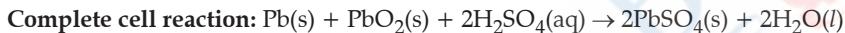
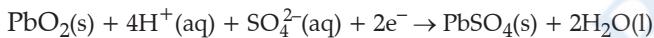
Discharge reaction of cell:

At anode: Following reaction takes place at anode:

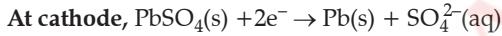


Reaction at cathode: PbO_2 filled in lead grid gets reduced to Pb^{2+} ions which combines with SO_4^{2-} ions to form $\text{PbSO}_4(\text{s})$.

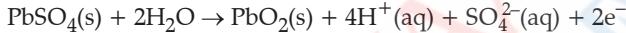
Complete cathode reaction is as follows:



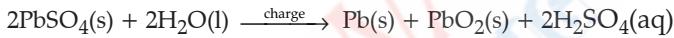
Recharge reaction of cell: It changes the direction of electrode reaction. PbSO_4 accumulated at cathode gets reduced to Pb.



At anode, PbSO_4 gets oxidised to PbO_2 .



Complete cell reaction would be as follows:



► **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 cell:

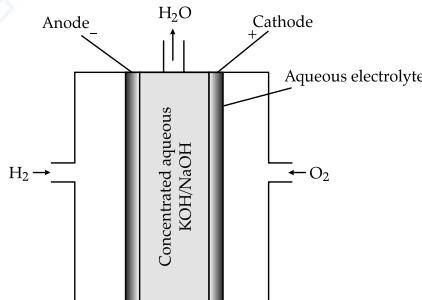
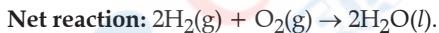


Fig 3 : Fuel cell using H_2 and O_2 produces electricity



Mnemonics

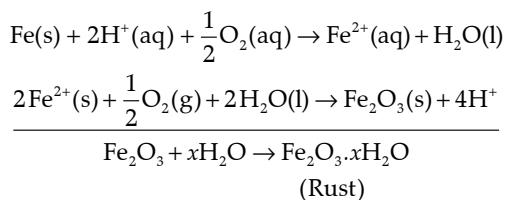
Concept: Fuel Cell

Mnemonics: FCCEE

Interpretations: Fuel Cell Converts Chemical Energy of Fuel Into Electrical Energy

- **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.

Rusting of iron:



Prevention of Corrosion:

- (i) **Barrier protection:** By covering the surface with paint or a thin film of grease or by electroplating.
- (ii) **Sacrificial protection:** By galvanization.
- (iii) **Alloying.**

CHAPTER-3

CHEMICAL KINETICS

Topic- 1

Rate of a Chemical Reaction and Factors Affecting Rate of Reactions

Concepts Covered • Rate of chemical reaction, factors affecting it, rate constant and molecularity



Revision Notes

- **Chemical Kinetics:** It is the branch of physical chemistry which deals with study of the rate of chemical reaction and the mechanism by which the reaction occurs.
- **Rate of Reaction:** The rate of reaction is the change of concentration of any reactant or product with time, for a reaction.



Rate of reaction,

$$\text{A} = \frac{\text{Decrease in concentration of A}}{\text{Time taken}}$$

$$= \frac{-\Delta[\text{A}]}{\Delta t}$$

Similarly,

$$\text{B} = \frac{-\Delta[\text{B}]}{\Delta t}$$

and for product

$$\text{C} = \frac{\Delta[\text{C}]}{\Delta t}$$

where, [A], [B] and [C] are molar concentrations of the reactants and the product respectively.



Key Fact

Peter Waage and Cato Guldberg are credited with pioneering the field of chemical kinetics by describing the law of mass action. The law of mass action states the speed of a reaction is proportional to the amount of reactants.

- Unit of rate of reaction: $\text{mol L}^{-1} \text{ s}^{-1}$ or $\text{mol L}^{-1} \text{ min}^{-1}$ (in liquid), atm s^{-1} or atm min^{-1} (in gaseous form).
- **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.

$$\text{Instantaneous rate} = \frac{dx}{dt}$$

$$\begin{aligned}
 &= \frac{-d[A]}{dt} = \frac{-d[B]}{dt} \\
 &= \frac{+d[C]}{dt}
 \end{aligned}$$

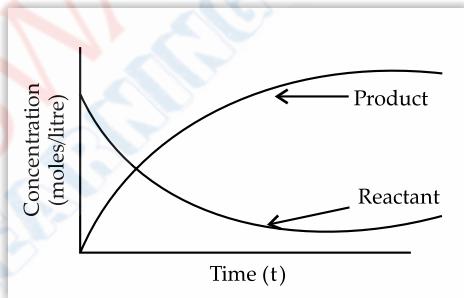
- **Average rate of reaction:** The rate of reaction measured over a long time interval is called average rate of a reaction. Average rate = $\frac{\Delta x}{\Delta t}$, where, Δx = change in concentration in given time and Δt = time taken.
- **Factors affecting the rate of a chemical reaction:**
 - (i) **Concentration of reactants:** 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:** 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:** 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:** The rate of many reactions is greatly affected by the presence of a **catalyst**. In the presence of a catalyst, the activation energy of a reaction decreases due to which the reaction proceeds at a faster rate.



Key Word

Catalyst: A substance that increases the rate of reaction without participating in it.

- (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 fast while in complex molecules, more bonds will rupture and consequently the rate of 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:** The 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.

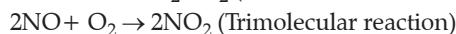


- (viii) **Effect of physical state:** Rate of reaction depends upon physical state of the reactant, e.g., $I_2(g)$ reacts faster than $I_2(s)$. $AgNO_3(aq)$ reacts with $NaCl$ but $AgNO_3(s)$ does not react with $NaCl$.
- **Rate Law:** Rate law or rate equation is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant. The rate law states that the rate of reaction is directly proportional to the product of molar concentration of reactants and each concentration term is raised to some power which may or may not be equal to stoichiometric coefficients of reacting species.

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

- **Rate Constant:** Rate constant is also called specific reaction rate. When concentration of both 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 involved in the reaction is termed as molecularity. It is always a whole number. It is never more than three. It cannot be zero.

Example:



- **Elementary Reaction:** An elementary reaction is a chemical 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 state.
- For a complex reaction, generally, molecularity of the slowest step is same as the order of the overall reaction.
- **Initial rate of reaction:** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called initial rate of reaction.
- **Rate Determining Step:** The slowest step in the reaction mechanism is called rate determining step.

Topic-2

Order of a Reaction, Integrated Rate Equations and Half-life of a Reaction

Concepts Covered • Order of reaction, zero order, first -order, pseudo first order, second order, half life, integrated rate laws.



Revision Notes

- **Order of reaction:** Order is defined as the sum of powers of concentration of the reactants in the experimentally derived rate equation or rate law expression. 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 = $k [A]_o$,

$$k = \frac{[A]_o - [A]}{t}, \text{ where 'k' is rate constant, } [A]_o \text{ is initial concentration of reactant.}$$



Mnemonics

Concept: Zero order

Mnemonics: ZOR don't CCR

Interpretations: In zero order reaction, the rate of reaction does not change with concentration of the reactants.

Unit of the rate constant k is mol L⁻¹ s⁻¹. This reaction will be zero order reaction. Decomposition of gaseous ammonia on hot platinum, **thermal decomposition** of HI on gold surface and photochemical reaction between hydrogen and chlorine are examples of zero order reaction.



Key Word

Thermal decomposition: Breaking of compound on heating.

- **First order reaction:** The rate of reaction is directly proportional to the first power of the concentration of reacting substance. Rate constant of the first order reaction is

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\Rightarrow k = \frac{2.303}{t} \log \frac{[A]_o}{[A]},$$

where ' a ' is initial concentration and $(a - x)$ is the concentration after time ' t '.

Unit of ' k ' is s⁻¹ or min⁻¹.

Decomposition of N₂O₅ and N₂O are examples.



Key Formula

Integrated Rate Equations:

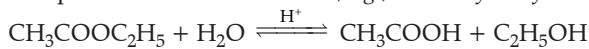
- (i) For a zero order reaction:

$$t = \frac{[R]_o - [R]}{k} \text{ and } t_{\frac{1}{2}} = \frac{[R]_o}{2k}$$

- (ii) For a first order reaction:

$$t = \frac{2.303}{k} \log \frac{[R]_o}{[R]} \text{ and } t_{\frac{1}{2}} = \frac{0.693}{k}$$

- **Pseudo first order reaction:** If a reaction is not truly of the first order but under certain conditions becomes reaction of first order is called pseudo first order reaction, e.g., acidic hydrolysis of ester (ethyl acetate).



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

$$\therefore \frac{dx}{dt} = k[\text{A}][\text{B}]$$

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

Reaction	Order	Unit of rate constant	Example
Zero order	0	$\text{mol}^{-1} \text{L}^{-1} \text{s}^{-1}$	$\text{H}_2 + \text{Cl}_2 \xrightarrow{\text{Sunlight}} 2\text{HCl}$
First order	1	s^{-1}	$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$
Pseudo first order	1	s^{-1}	$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
Second order	2	$\text{mol}^{-1} \text{L s}^{-1}$	$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$

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

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

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

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 initial value has reacted is called **half-life of a reaction**.

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

where $[\text{A}]_0$ is initial and last concentration of reaction it means there is no change in concentration and 'k' is rate constant.

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

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

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

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

where, $[\text{A}]_0$ is initial concentration, $[\text{A}]$ is final concentration after time t and n can have all the values except 1.



Key Fact

In radioactivity, half-life is the time interval required for one-half of the atomic nuclei of a radioactive sample to decay.

- **Half-life of a reaction of n^{th} order:**

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

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

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

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

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

$$\text{Amount of substances left after } n \text{ half-lives} = \frac{[\text{A}]_0}{2^n}$$



Key Fact

The radioactive isotope cobalt- 60, which is used for radiotherapy, has, for example, a half-life of 5.26 years. Thus after that interval, a sample originally containing 8 g of cobalt- 60 would contain only 4 g of cobalt- 60 and would emit only half as much radiation. After another interval of 5.26 years, the sample would contain only 2 g of cobalt- 60. Neither the volume nor the mass of the original sample visibly decreases, however, because the unstable cobalt- 60 nuclei decay into stable nickel-60 nuclei, which remain with the still-undecayed cobalt

► 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	$A \rightarrow P$	$\frac{d[A]}{dt} = -k$	$kt = [A]_o - [A]$	$[A]$ vs. t	$\frac{[A]_o}{2k}$	conc. time $^{-1}$
1	$A \rightarrow P$	$\frac{d[A]}{dt} = -k[A]$	$[A] = [A]_o e^{-kt}$ $kt = \frac{\ln[A]_o}{[A]}$	$\ln[A]$ vs. t	$\ln \frac{2}{k}$	time $^{-1}$

► **Life time :** The time in which 98% of the reaction is completed is called life time.

Topic- 3

Concept of Collision Theory, Activation Energy and Arrhenius Equation

Concepts Covered • Collision theory, Activation energy, Threshold energy, Arrhenius equation, catalyst.



Revision Notes

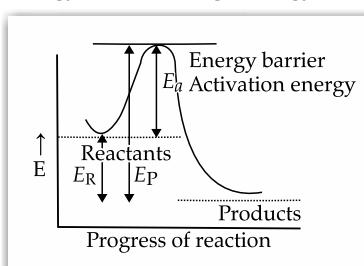
► The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient.

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

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

- **Activation energy:** It is an extra energy which must be possessed by reactant molecules so that 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.
- **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.

Activation theory (E_a) = Threshold energy (E_T) – Average energy of the reactions (E_R)



► **Arrhenius equation:** **Activated complex** is defined as 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.



Key Word

Activated complex: The high energy state in which a reaction goes through for the conversion of reactants to products.

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

where, k = Rate constant

A = Frequency factor (Arrhenius factor)

R = Gas constant

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

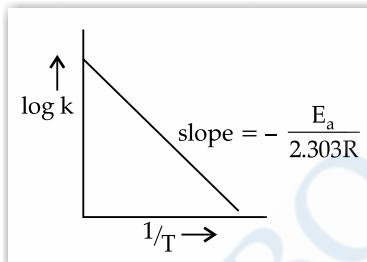
$$\log k = \log A - \frac{E_a}{2.303 RT}$$

E_a = Activation Energy.

T = Temperature in Kelvin

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

If k_2 and k_1 are rate constants at temperature T_2 and T_1 respectively, then $\log \frac{k_2}{k_1} = -\frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 - T_2} \right]$



- 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 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'.
- Activated complex is defined as unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product.
- 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 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,

$$k = P Z_{AB} e^{-E_a/RT}$$



Mnemonics

Concept: Effect of Collision

Mnemonics: ECFPM

Interpretations:

Effective collisions lead to formation of product molecules.

Concept: Catalyst

Mnemonics: CAR

Interpretations: A catalyst alters the reaction

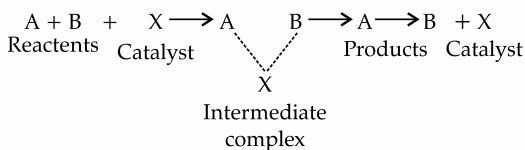


Key Equation

$$\text{Arrhenius equation : } k = A e^{-E_a/RT}$$

- **Catalyst:** A catalyst is a substance that alters the rate of reaction without itself undergoing any chemical change at the end of reaction.

Intermediate complex theory:



Intermediate complex

Characteristics of catalyst:

- (i) Catalyzes only the spontaneous reaction.
- (ii) Does not change the equilibrium constant.
- (iii) Catalyzes both the forward and backward reactions.
- (iv) Does not alter the free energy change (ΔG) of a reaction.
- (v) A small amount of the catalyst can catalyse large amount of reactions.



Key Fact

Through the use of chemical kinetics and thermodynamics, engineers can control how the fuel burns to reduce the release of certain pollutants.

Example

- Q. 1.(i)** For the reaction $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction?
- (ii)** The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and it lowers to $50.14 \text{ kJ mol}^{-1}$ with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25°C ?

Answer:

$$\text{STEP I: (i)} \quad r = k[R]^n$$

When concentration is increased three times,

$$[R] = 3a$$

$$27r = k(3a)^n$$

$$\frac{27}{r} = \frac{k(3a)^n}{ka^n} \text{ or } 27$$

$$= 3^n \text{ or } 3^3 \Rightarrow n = 3$$

- (ii) STEP I:** According to Arrhenius equation,

$$\log k_1 = \log A - \frac{E_a}{2.303 RT}$$

[1]

For uncatalysed reaction,

$$\log k_1 = \log A - \frac{E_{a(1)}}{2.303 RT} \quad \dots(\text{i}) [1/2]$$

STEP II: For catalysed reaction

$$\log k_2 = \log A - \frac{E_{a(2)}}{2.303 RT} \quad \dots(\text{ii}) [1/2]$$

STEP III: A is equal for both the reactions.

Subtracting equation (i) from equation (ii)

$$\log \frac{k_2}{k_1} = \frac{E_{a(1)} - E_{a(2)}}{2.303 RT}$$

$$\log \frac{k_2}{k_1} = \frac{(75.2 - 50.14) \text{ kJ mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$\log \frac{k_2}{k_1} = 4.39$$

$$\frac{k_2}{k_1} = \text{antilog}(4.39)$$

$$= 2.45 \times 10^4$$

$$k_2 = (2.45 \times 10^4)k_1$$

Rate of reaction increases by 2.45×10^4 times. [1]

CHAPTER-4

d- AND f- BLOCK ELEMENTS

Topic-1

d-Block Elements, their Properties and Compounds

Concepts Covered • d -block elements, different transition series, • general characteristics of transition elements • oxides of transition metals and their uses.



Revision Notes

- **d-block elements:** The elements in which last electron enters in the *d* - sub-shell i.e. penultimate shell and lies in the middle of the periodic table belonging to groups 3-12.
- **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 the elements which have incompletely filled *d*-orbitals in their ground states or in its most common oxidation state. Transition elements have four series:
 - (i) **First transition series:** These elements have incomplete $3d$ -orbitals and they are from Sc (21) to Zn (30).
 - (ii) **Second transition series:** These elements have incomplete $4d$ -orbitals and they are from Y (39) to Cd (48).
 - (iii) **Third transition series:** These elements have incomplete $5d$ - orbitals and they are La (57) and then from Hf (72) to Hg (80).
 - (iv) **Fourth transition series:** This series is yet incomplete and these elements have incomplete $6d$ - orbitals. Known elements of this series are—actinium (89) and then from Rf (104) and other elements.
- 3. **General electronic configuration of transition elements:** Valence shell electronic configuration is $(n-1)d^{1-10}, ns^{1-2}$, where n is the outermost shell.

Electronic configuration of *d*-block elements

Series	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12
3d series	Sc (21) $3d^1 4s^2$	Ti (22) $3d^2 4s^2$	V (23) $3d^3 4s^2$	Cr (24) $3d^5 4s^1$	Mn (25) $3d^5 4s^2$	Fe (26) $3d^6 4s^2$	Co (27) $3d^7 4s^2$	Ni (28) $3d^8 4s^2$	Cu (29) $3d^{10} 4s^1$	Zn (30) $3d^{10} 4s^2$
4d series	Y (39) $4d^1 5s^2$	Zr (40) $4d^2 5s^2$	Nb (41) $4d^4 5s^1$	Mo (42) $4d^5 5s^1$	Tc (43) $4d^5 5s^2$	Ru (44) $4d^7 5s^1$	Rh (45) $4d^8 5s^1$	Pd (46) $4d^{10} 5s^0$	Ag (47) $4d^{10} 5s^1$	Cd (48) $4d^{10} 5s^2$
5d series	La (57) $4f^0 5d^6 s^2$	Hf (72) $4f^{14} 5d^2 6s^2$	Ta (73) $4f^{14} 5d^3 6s^2$	W (74) $4f^{14} 5d^4 6s^2$	Re (75) $6s^2 5d^5 4f^{14}$	Os (76) $4f^{14} 5d^6 6s^2$	Ir (77) $4f^{14} 5d^7 6s^2$	Pt (78) $4f^{14} 5d^9 6s^1$	Au (79) $4f^{14} 5d^{10} 6s^1$	Hg (80) $4f^{14} 5d^{10} 6s^2$
6d series	Ac (89) $5f^0 6d^1 7s^2$	Rf (104) $5f^{14} 6d^2 7s^2$	Db (105) $5d^{14} 6d^3 7s^2$	Sg (106) $5f^{14} 6d^4 7s^2$	Bh (107) $5f^{14} 6d^5 7s^2$	Hs (108) $5f^{14} 6d^6 7s^2$	Mt (109) $5f^{14} 6d^7 7s^2$	Ds (110) $5f^{14} 6d^8 7s^2$	Rg (111) $5f^{14} 6d^{10} 7s^1$	Cn (112) $5f^{14} 6d^{10} 7s^2$



Mnemonics

3-d series

Concept: First Row Transition Elements-3-d series

Mnemonics: Scary Tiny Vicious Creatures Mingle (with) Fellow Cow Nilgai Cougar Zebra.

Interpretations: Scandium(Sc), Titanium(Ti), Vanadium(V), Chromium(Cr), Manganese(Mn), Iron(Fe), Cobalt(Co), Nickel(Ni), Copper(Cu), Zinc(Zn)

4-d series

Concept: Second Row Transition Elements-4-d series

Mnemonics: Yesterday Zora Nabbed a Monkey TRicking her Rheumatic Padosan Agnes Cadillac.

Interpretations: Y, Zr, Nb > Mo, Tc, Ru, Rh, Pd, Ag, Cd

5-d series

Concept: Third Row Transition Elements-5-d series

Mnemonics: Late Harry Took Walk, Reached Office In Pajamas After an Hour.

Interpretations: La....., Hf, Ta, W, Re, OS, Ir, Pt, Au, Hg

► **General characteristics of Transition Elements:**

Physical Properties:

- All are metals.
- All are malleable and ductile except mercury (liquid).
- High thermal and electrical conductivity.
- Metallic lustre and sonorous.
- Atomic radii:** Smaller than atomic size of s-block elements, larger than atomic size of p-block elements in a period. In a transition series, as the atomic number increases, the atomic radii first decreases till the middle, becomes constant and then increases towards end of the period.
It usually increase down the group. The size of 4d elements is almost of the same size as of the 5d series elements. The filling of 4d before 5d orbitals results in regular decrease in atomic radii which is called as lanthanoid contraction.
- Ionic radii:** The ionic radii decrease with increase in oxidation state.
- Density:** From left to right in a period, density increases.
- Ionisation enthalpy:** Along the series from left to right, there is an increase in ionisation enthalpy. Irregular trend in the first ionisation enthalpy of 3d metals is due to irregularity in electronic configuration of 4s and 3d orbitals. In a group, IE decreases from 3d to 4d-series but increases from 4d to 5d series due to lanthanoid contraction.
- Metallic bonding:** In metallic bonding, regular **lattice** of positive ions are held together by a cloud of free electrons, which can move freely through the lattice. Transition metal atoms are held together by strong metallic bonds.



Key Word

Lattice: A set of points that when joined together form the geometric shape of crystal.

- Enthalpy of atomisation:** Enthalpy of atomisation is the heat required to convert 1 mole of crystal lattice into free atoms. Transition elements have high enthalpy of atomisation. It first increases, becomes maximum in the middle of the series and then decreases regularly.
 - 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. Transition metal ions show variable oxidation states except the first and last member of the series.
 - Electrode potential:** The electrode potential develops 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 the regular variation in ionisation enthalpies (I.E¹ + I.E²), 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 the commonly used catalysts.
- All transitional metals show multiple oxidation states and have large surface area so, all metals work as a catalyst.
- 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 no (zero) 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.

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

where n = number of unpaired electrons in 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).



Key Fact

d-block elements are called so because they have their valence electrons in one or more d-orbitals.

(xv) **Melting and boiling points:** Except zinc, cadmium and mercury, all other transition elements have high melting and boiling points. This is due to strong metallic bonds and presence of partially filled *d*-orbitals in the shell of the atom of element.

(xvi) **Complex formation:** They have tendency to form complex ions due to high charge on the transition metal ions and the availability of *d*-orbitals for accommodating electrons donated by the ligand atoms.

(xvii) **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^+ , Zn^{2+} and Cd^{2+} are colourless due to the absence of unpaired *d*-electron (d^{10}).

(xviii) **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. Therefore, these metals can mutually substitute their position in their crystal lattice to form alloys. e.g., steel, brass.

(xix) **Formation of interstitial compounds:** Interstitial compounds are known for transition metals as small-sized atoms of H, B, C, N, etc. can easily occupy positions in the voids present in the crystal lattices of transition metals. Characteristics of interstitial compounds:

- High melting points
- Hard
- Chemically inert
- Retain metallic conductivity
- Non-stoichiometric

► **Oxides of Transition metals:** They form oxides of the general composition MO , M_2O_3 , MO_2 , M_2O_5 and MO_6 . Oxides in the lower oxidation states are generally basic while those in the higher oxidation states are amphoteric or acidic. For example,

MnO Basic	Mn_2O_3 Amphoteric	Mn_3O_4 Amphoteric	MnO_2 Amphoteric	Mn_2O_7 Acidic
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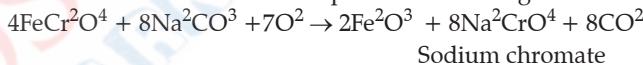
Key Fact

Potassium is a necessary nutrient for life; as an electrolyte, it conducts electric signals in the body; along with sodium, it's crucial for proper muscle contraction. The drug potassium chloride is commonly used to treat potassium deficiency, but the dose makes the poison: Potassium chloride has also been used in lethal injections. In large enough quantities, the drug stops the heart by disrupting the electrical signals that force the muscle to contract and relax.

► **Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)**

Preparation: It is prepared from chromite ore in the following steps:

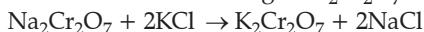
(i) Chromite ore is fused with sodium carbonate in the presence of air to give sodium chromate.



(ii) Na_2CrO_4 is filtered and acidified with conc. H_2SO_4 to give $\text{Na}_2\text{Cr}_2\text{O}_7$.



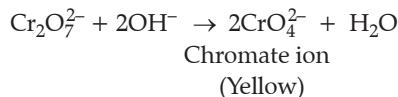
(iii) Sodium dichromate solution is treated with KCl to give $\text{K}_2\text{Cr}_2\text{O}_7$.



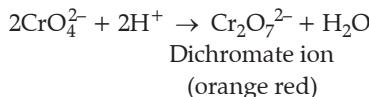
Properties:

(a) It is an orange, crystalline solid.

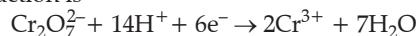
(b) **With alkali:**



(c) **With acid:**

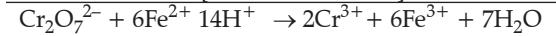
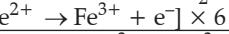
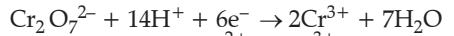


In acidic solutions, oxidising action is

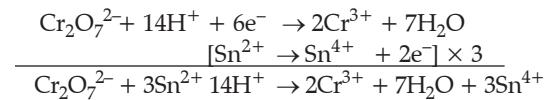


(d) It is a powerful oxidising agent. For example,

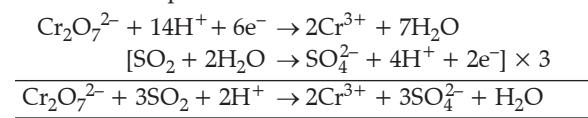
(i) It oxidises ferrous to ferric.



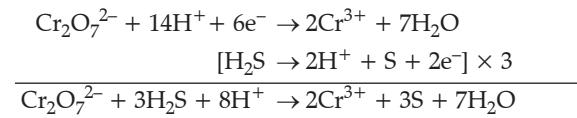
(ii) It oxidises stannous to stannic.



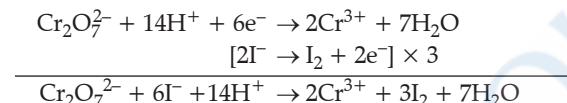
(iii) It oxidises sulphur dioxide to sulphate.



(iv) It oxidises hydrogen sulphide to sulphur.



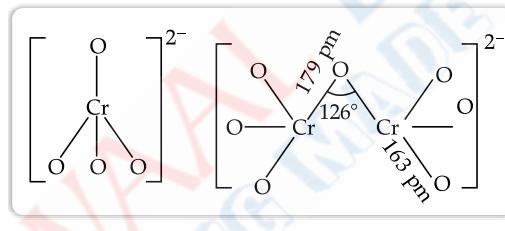
(v) It oxidises iodides to iodine.



Uses:

- (i) In leather industry for chrome tanning.
- (ii) Preparation of azo compounds.
- (iii) As a primary standard in volumetric analysis for the estimation of reducing agent.

Structure:



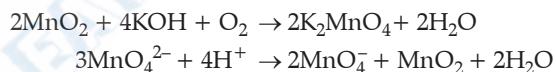
Chromate ion

Dichromate ion

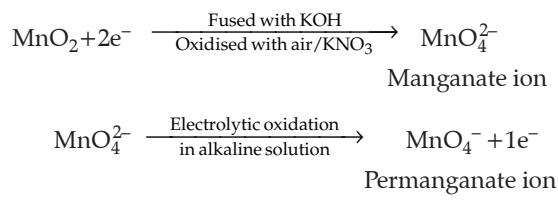
► Potassium permanganate (KMnO_4)

Preparation:

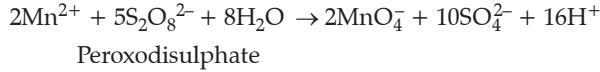
(i) It is prepared from pyrolusite ore with KOH in the presence of oxidising agent like KNO_3 . The dark green potassium manganate undergoes electrolytic oxidation to produce potassium permanganate.



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



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



Properties:

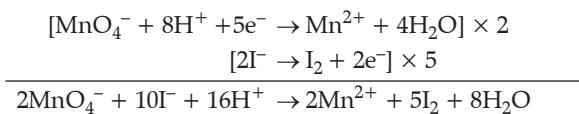
- (i) Dark purple crystalline solid.
- (ii) Sparingly soluble in water.
- (iii) Decomposes on heating at 513 K.



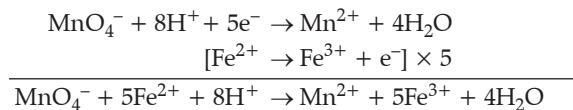
(iv) Acts as a powerful oxidising agent in acidic, alkaline and neutral medium. For example:

1. In acidic medium oxidises:

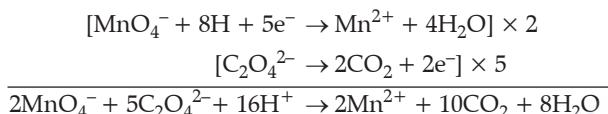
(i) Iodide to iodine



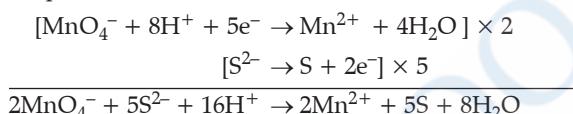
(ii) Ferrous to ferric



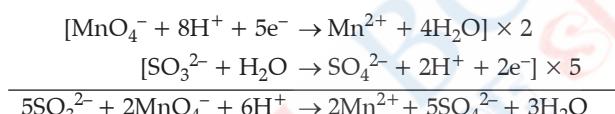
(iii) Oxalate to carbon dioxide :



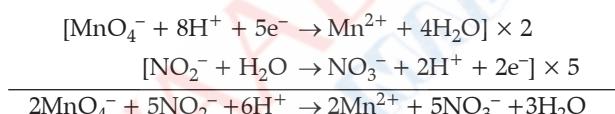
(iv) Hydrogen sulphide to sulphur



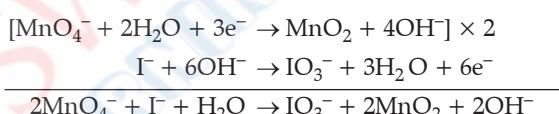
(v) Sulphite to sulphate



(vi) Nitrite to nitrate

**2. In neutral alkaline medium:**

(i) Iodide to iodate



(ii) Manganous to manganese dioxide



(iii) Thiosulphate to sulphate

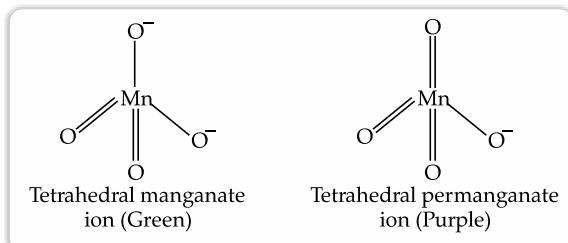
**Uses:**

(i) Bleaching of wool, silk, cotton and other textile fibres, etc.

(ii) Decolourisation of oils.

(iii) In analytical chemistry (titration).

(iv) In organic synthesis.

Structure:

Example 1

Q. (i) For M^{2+}/M and M^{3+}/M^{2+} systems, E° values for some metals are as follows :

$Cr^{2+}/Cr = -0.9\text{ V}$	$Cr^{3+}/Cr^{2+} = -0.4\text{ V}$
$Mn^{2+}/Mn = -1.2\text{ V}$	$Mn^{3+}/Mn^{2+} = +1.5\text{ V}$
$Fe^{2+}/Fe = -0.4\text{ V}$	$Fe^{3+}/Fe^{2+} = +0.8\text{ V}$

Use this data to comment upon

(a) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+} .

(b) the ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

(ii) What can be inferred from the magnetic moment of the complex $K_4[Mn(CN)_6]$? (Magnetic moment : 2.2 BM)

Solution:

(i) (a) Cr^{3+}/Cr^{2+} has a negative reduction potential. Hence, Cr^{3+} cannot be reduced to Cr^{2+} . Cr^{3+} is most stable. Mn^{3+}/Mn^{2+} have large positive E° values. Hence, Mn^{3+} can be easily reduced to Mn^{2+} . Thus Mn^{3+} is least stable. Fe^{3+}/Fe^{2+} couple has a positive E° value but is small. Thus, the stability of Fe^{3+} is more than Mn^{3+} but less stable than Cr^{3+} .

(b) If we compare the reduction potential values, Mn^{2+}/Mn has the most negative value i.e., its oxidation potential value is most positive. Thus, it is most easily oxidised. Therefore, the decreasing order for their ease of oxidation is $Mn > Cr > Fe$.

(ii) $K_4[Mn(CN)_6]Mn$ is in +2 oxidation state. Magnetic moment 2.2 indicates that it has one unpaired electron and hence forms inner orbital or low spin complex. In presence of CN^- which is a strong ligand, hybridization involved is d^2sp^3 (octahedral complex).

Topic- 2

f-Block Elements : Lanthanoids and Actinoids

Concepts Covered • General introduction of f block elements • Properties and uses of Lanthanoids • Properties and uses of Actinoids

Revision Notes

► **f-block elements:** The elements in which filling of electrons takes place in $(n-2)f$ -subshell which belongs to anti-penultimate (third to the outermost) energy shell. This block consists of two series of elements known as **Lanthanoids and Actinoids**. These elements are also known as inner transition elements. The general electronic configuration of the f - block elements is:

$$(n-2)f^{1-14} (n-1)d^{0-1} ns^2$$

For lanthanoids, n is 6 while its value is 7, for actinoids. There are many exceptions in the electronic configuration.

► **Lanthanoids:** The series involves the filling of $4f$ -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 ($Z = 71$).



Mnemonics

Lanthanides

Concept: Lanthanides Series

Mnemonics: Late CEO Promoted Nadia Palmer Smart to Europe so she said Goodbye to Toby a Day before Hoarding Eroding Timber in Yard of Lu.

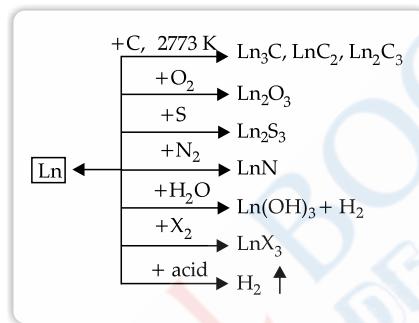
Interpretations: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

- **Electronic configuration:** $[Xe] 4^{1-14} 5d^{0-1} 6s^2$

- **Physical properties:**

- Highly dense metals, soft, malleable and ductile.
- High melting point.

- (iii) Forms alloys easily with other metals.
 - (iv) **Magnetic properties:** Among lanthanoids, La^{3+} and Lu^{3+} which have $4f^0$ or $4f^{14}$ electronic configurations are diamagnetic and all other trivalent lanthanoid ions are paramagnetic due to the presence of unpaired electrons.
 - (v) **Atomic and ionic sizes:** With increasing atomic number, the atomic and ionic radii decreases from one element to the other but the decrease is very small.
A steady decrease in the size of lanthanoids with increase in atomic number is known as **lanthanoid contraction**.
 - **Consequences of Lanthanoid contraction:**
 - It leads to similar physical and chemical properties among lanthanoids.
 - Zr and Hf have same properties, due to similar atomic radii.
 - Chemical separation of lanthanoids become difficult.
 - (vi) **Oxidation state:** They mainly give +3 oxidation state. Some elements show +2 and +4 oxidation states.
 - (vii) **Colour:** Some of the trivalent ions are coloured. This happens due to the absorption in visible region of the spectrum resulting in *f-f* transitions.
- Chemical properties:** All lanthanoids are highly electropositive metals and have almost similar chemical reactivity.



Uses:

- (i) Misch metal is the alloy of cerium (about 55%) and various other Lanthanoid elements (40-43%). It also contains iron upto 5% and traces of sulphur, carbon, silicon calcium and aluminium. It is a pyrophoric material, hence it is used in lighter flints.
- (ii) Lanthanoid oxides are used for polishing glass.
- (iii) Cerium salts are used in dyeing cotton and also as catalysts.
- (iv) Lanthanoid compounds are used as catalyst for hydrogenated dehydrogenation and petroleum cracking.
- (v) Pyrophoric alloys are used for making tracer bullets and shells.

► **Actinoids:** The series involving the filling of 5f orbitals from actinium, Ac ($Z = 89$) upto lawrencium, Lr ($Z = 103$) comprises of actinoids.

All the elements beyond uranium are known as transuranic or man-made elements. These elements do not occur in nature because their half-life periods are so short.

- **Electronic configuration:** [Rn] $5f^{1-14} 6d^{0-1} 7s^2$
- **Physical properties:**
 - Highly dense metals and form alloys with other metals.
 - Silvery white metals.
 - Highly electropositive.
 - High melting point.
 - Ionic and atomic radii:** The atomic and ionic size decreases with an increase in atomic number due to actinoid contraction. The electrons are added to 5f shell resulting in an increase in the nuclear charge causing the shell to shrink inwards. This is known as actinoid contraction.
 - Colour:** Many actinoid ions are coloured.
 - Magnetic properties:** Many actinoid ions are paramagnetic.
 - Oxidation State:** The common oxidation state exhibited is +3. They also exhibit oxidation state of +4, +5, +6 and +7.
 - Many elements are radioactive.
- **Chemical reactivity:** Less reactive towards acids.
- **Uses:**
 - Thorium is used in the treatment of cancer and in incandescent gas mantles.
 - Uranium is used in the glass industry, in medicines and as nuclear fuel.
 - Plutonium is used in atomic reactors and in atomic bombs.



Mnemonics

Actinides

Concept: Actinide Series

Mnemonics: Active Thor Paid Ur Nephew for Pumpkins.

- Amy Came Back from California.
- Einstein and Fermi Made No. of Laws.

Interpretations: Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr

► Difference between Lanthanoids and Actinoids:

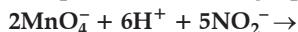
S. No.	Lanthanoids	Actinoids
(i)	4f orbital is progressively filled.	5f orbital is progressively filled.
(ii)	+3 oxidation state is most common along with +2 and +4.	+3 oxidation state is most common, but exhibit higher oxidation state of +4, +5, +6, +7.
(iii)	Except promethium, all are non-radioactive.	All are radioactive.
(iv)	Less tendency of complex formation.	Strong tendency of complex formation.
(v)	Chemically less reactive than actinoids.	More reactive than lanthanoids.

Example 2

Q. (i) How would you account for the following:

- Actinoid contraction is greater than lanthanoid contraction.
- Transition metals form coloured compounds.

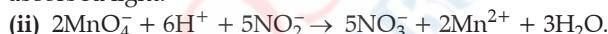
(ii) Complete the following equation:



Solution:

(i) (a) Actinoid contraction is greater than lanthanoid contraction due to more effective shielding by intervening 5f-electrons.

(b) Transition elements generally forms coloured compounds on account of *d-d* transition. When the visible light falls on the compounds, they absorb certain radiations and reflect others. The colour observed corresponds to absorbed light.



CHAPTER-5

COORDINATION COMPOUNDS

Topic- 1

Coordination Compounds : Properties and IUPAC Name

Concepts Covered • Coordination Compound, Coordinate bond, Ligand, Types of ligand, Coordination number, Isomers (Structural, Stereo Isomerism)

Revision Notes

- **Coordination Compound:** A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. There is a coordinate bond between metal atom and these ions or molecules, e.g., $[\text{Cu}(\text{NH}_3)_4]^{2+}$.
- **Double Salt:** When two or more salts are added to form a stable solid together and break into constituent ions when dissolved in water or any solvent, e.g., $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (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 atoms supplies both the electrons. It can be considered as a combination of transfer and sharing of electrons. Coordinate bonds are also called semi-polar bonds.

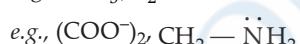
► **Central metal atom or ion:** The metal atom or ion surrounded by fixed number of ions or molecules is called central metal atom or ion, e.g., in $\text{K}_4[\text{Fe}(\text{CN})_6]$, Fe^{2+} is central metal ion.

► **Ligand:** The neutral molecules or ions (usually anions) which are attached with the central metal atom or ion in complex compound. e.g., Cl^- , OH^- , CN^- , CO , NH_3 , H_2O , etc. A **ligand** may be neutral or charged species. It always act as a Lewis base.

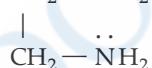
● **Types of ligands:**

(a) **On the basis of number of donor sites:**

- (i) **Unidentate ligands:** Contain one donor atom. e.g., NH_3 , $\text{H}_2\ddot{\text{O}}$:



- (ii) **Bidentate ligands:** Contain two donor atoms.



- (iii) **Polydentate ligands:** Contain several donor atoms. e.g., EDTA.

(b) **On the basis of charge:**

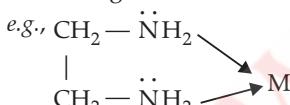
- (i) **Cationic ligands:** Carry positive charge. e.g., NO_2^+ , N_2H_5^+ .

- (ii) **Anionic ligands:** Carry negative charge. e.g., X^- (halo), CN^- (cyano).

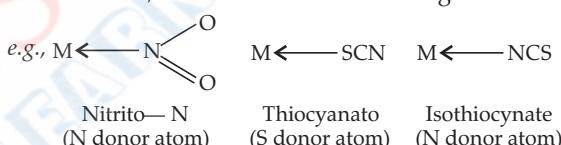
- (iii) **Neutral ligands:** Do not carry any charge. e.g., NH_3 (ammine), $\text{H}_2\ddot{\text{O}}$ (aqua).

(c) **On the basis of nature of ligand:**

- (i) **Chelate ligands:** A bidentate or polydentate uses its two or more donor atoms to bind a single metal ion, then a ring like structure is obtained. It is called **chelate** and the ligand is known as chelate ligand.



- (ii) **Ambidentate ligand:** A ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal/ion is called ambidentate ligand.



Key Words

Ligand: An ion or molecule that binds to a central metal to form a coordination complex.

Chelate: An organic compound formed when a polydentate ligand bonds to a central metal atom.

- **Coordination number:** Number of monodentate ligands attached to central metal ion in a complex is called coordination number. It may also be defined as total number of chemical bonds formed between central metal ion and donor atom of ligand e.g., in $[\text{Ni}(\text{NH}_3)_6]^{2+}$, the coordination number of Ni is 6.
- **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., $[\text{Pt Cl}_4]^{2-}$ 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 or coordinating atoms in a ligand is called denticity e.g., unidentate, bidentate, etc.

► **Applications of chelates:**

- In the softening of hard water.
- In the separation of lanthanoids and actinoids.
- In the detection as well as estimation of some metal ions such as nickel (II) ion.



Key Fact

Interesting Facts: Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures.

- **Coordination sphere:** The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as coordination sphere e.g., in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$.
- **Flexidentate character of ligands:** Certain polydentate ligands have flexible character and are called flexidentates. e.g., EDTA is hexadentate in nature but in some cases, it may act as pentadentate or tetradeятate ligand.
- **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 is represented by Roman numerical.
- **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 $[Fe(CN)_6]^{4-}$. The complexes in which the metal atom or ion is linked to more than one kind of ligands are called heteroleptic complexes. e.g., $[Co(NH_3)_4Cl_2]^+$ and $[Cr(en)_2Cl_2]^+$.
- **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.
- **Coordination ions:** The coordination entity with charge is called as coordination ion.
- **Nomenclature of Coordination compounds:**
 - The cation whether simple or complex is named first followed by anion.
 - Ligands are named in alphabetical order.
 - 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 in -o. Neutral retain their names while cationic end in -ium.
 - The coordination sphere is written in square bracket.
 - 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.
 - Name of coordination compounds starts with a small letter and the complex part is written as one word.
 - Oxidation number of central atom is indicated in Roman numerals. No space is left between the number and the rest of the name.
- **Isomers:** Two or more coordination compounds which have the same molecular formula but differ in the arrangement of ligands around the central metal atom or ion are called isomers. This phenomenon is called isomerism.
- **Types of isomerism:** Two types of isomerism are observed in coordination compounds.
 - **Structural Isomerism is of the following types:**
 - Ionization isomerism:** In this type of isomerism, isomers have same molecular formula but gives different ions in solution. e.g., $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$.
 - Coordination isomerism:** This type of isomerism is shown by those complexes in which both the cation and the anion are complex ions and they differ in the coordination of ligands. e.g., $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$.
 - Solvate isomerism:** Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. e.g., $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, $[Cr(H_2O)_6]Cl_3$.
 - Linkage isomerism:** Isomers having the same molecular formula but different linking atom, this is due to the presence of **ambident ligand**. e.g., $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$.

Key Word

Ambidentate Ligand: A type of ligand which have the ability to bind to the central atom via the atoms of two different elements.

Example 1

Q. (i) What type of isomerism is shown by the pair $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$?

- (A) Ionisation isomerism (B) Coordination isomerism
 (C) Solvate isomerism (D) Linkage isomerism

[CBSE OD Set-3 2020]

Solution:

Option (C) is correct.

Solvate / Hydrate isomerism

Solvate or hydrate isomers have the same composition but differ with respect to the number of solvent ligand molecules as well as the counter ion in the crystal lattice.

Step I: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ have same composition.

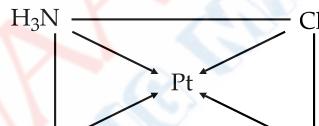
Step II: In $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, the number of water molecules inside the co-ordination sphere is six and the number of water molecules outside the co-ordination sphere is 0.

Step III: In $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ the number of water molecules inside the co-ordination sphere is five and the number of water molecules outside the co-ordination sphere is one.

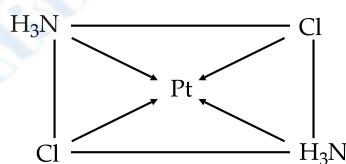
Step IV: Thus, it is a solvate isomerism.

- Stereo isomerism is of following types:

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

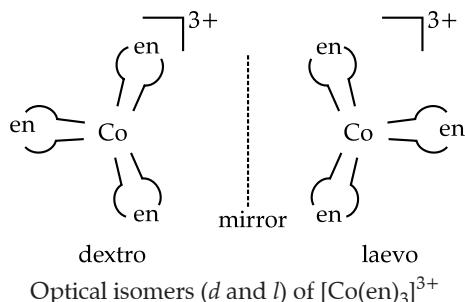


cis-diamminedichloroplatinum (II)



trans-diamminedichloroplatinum (II)

(ii) **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*) or 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 octahedral complexes involving bidentate ligands.



Topic- 2**Werner's Theory, Bonding, VBT, CFT**

Concepts Covered • Werner's Theory, Valence Bond Theory, Crystal Field Theory, metal carbonyls.

Revision Notes► **Werner's Theory of Coordination compounds:**

Different postulates of Werner's coordination theory are given below:

- Metal ions possess two types of valency (a) primary or ionisable valency and (b) Secondary or non-ionisable valency.
- Every metal ion has a fixed number of secondary valency and this is known as coordination number.
- Primary valencies are satisfied by anions while secondary valencies are satisfied by negative group or neutral molecules with lone pair of electrons.
- Secondary valencies are directed in space towards internal positions.

► **Limitations of Werner's theory:** This theory does not explain the following queries—

- Why is the complex forming tendency limited to a few elements only?
- Why bonds in the coordination complexes are of directional nature?
- 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:

- 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.
- Central metal ion can use appropriate number of s , p or d -orbitals for hybridisation depending upon total number of ligands.
- The hybridised orbitals are allowed to overlap with those ligand orbitals that can donate an electron pair for bonding.
- 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.

► **Limitation of Valence bond theory:**

- It cannot explain the detailed magnetic properties of complex compounds.
- It cannot explain the optical absorption spectra of coordination compounds.
- It cannot predict property whether a particular four coordinate complex is square planar or tetrahedral in nature.
- It fails to make distinction between strong and weak ligands.
- It does not explain thermodynamic or kinetic stabilities of coordination compounds.

► **Crystal field theory (CFT):**

- The ligand is considered as point charge or point dipole.
- Interaction between metal ion and ligand is considered as electrostatic in nature.
- Metal ion is supposed to be present at the origin of the axis. Ligands approach to metal ion along the axis of octahedral complex between the axis of tetrahedral complex and in the case of square planar complex four ligand approach to metal ion along x , y plane.
- Due to the approach of the ligand hence due to the electrostatic interaction between ligands electrons and metal d -orbital electron, degeneracy of d -orbital is lost and splitting of d -orbitals occurs.
- Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d -orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below and is called as spectrochemical series:

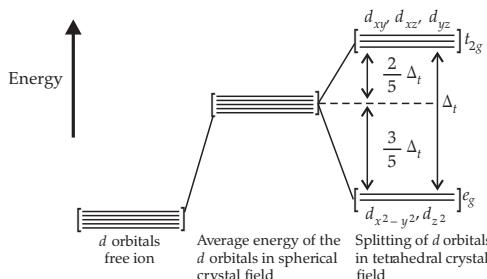
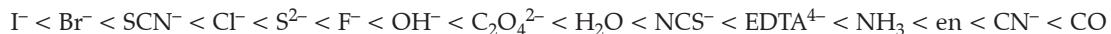
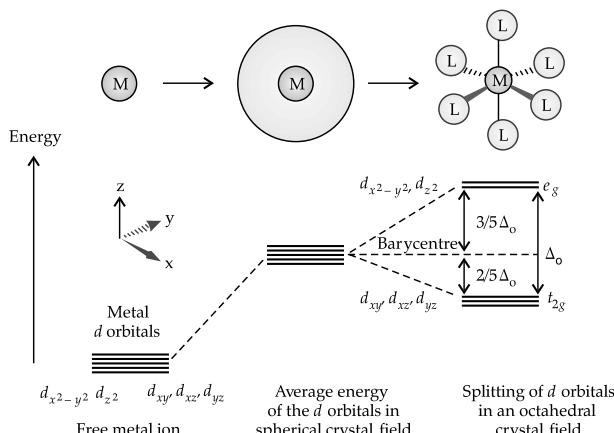


Fig. 2 : d orbital splitting in a tetrahedral crystal field

d -orbital splitting in a tetrahedral crystal field



d-orbital splitting in an octahedral crystal field

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



Mnemonics

Concept: Ligands causing Crystal Field Splitting are arranged in order of increasing field strength-Spectrochemical Series

Mnemonics: I Brought SCaNned Classnotes to Study Fundamentals of Chemistry.
He Nurtured Excellence in NHew (New) CoordinatioN COnpounds chapter.

Interpretations: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < CN^- < CO$

I^- = I

Br^- = Brought

SCN^- = SCaNned

Cl^- = Classnotes

S^- = Study

F^- = Fundamentals

OH^- = Of

$C_2O_4^{2-}$ = Chemistry

(Chromate ion)

H_2O = He

NCS^- = Nurtured

$EDTA^{4-}$ = Excellence

NH_3 = NHew

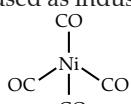
CN^- = Coordination

CO = Compounds (Carbonyl group)

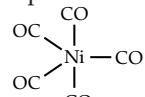
► **Metal carbonyls:** Homoleptic carbonyls are formed by d-block elements and contain carbonyl ligands only. e.g., $V(CO)_6$, $Cr(CO)_6$, $[Mo(CO)_6]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Ni(CO)_4]$, etc. Metal carbonyls of outside the central part of d-block are unstable.

Properties of metal carbonyls:

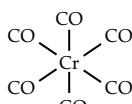
- Metal carbonyls are mostly solids at room temperature and pressure. Exceptions being iron and nickel carbonyls which are liquids.
- The mononuclear carbonyls are volatile and toxic.
- Most of metal carbonyls are soluble in hydrocarbon solvents except $[Fe_2(CO)_9]$.
- Mononuclear carbonyls are either colourless or light coloured.
- They are highly reactive due to metal centre and the CO ligands.
- Metal carbonyls are used as industrial catalyst and as precursor in organic synthesis.



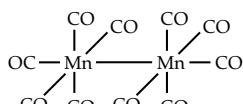
$Ni(CO)_4$
Tetrahedral



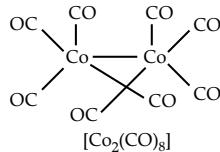
$Fe(CO)_5$
Trigonal bipyramidal



$Cr(CO)_6$
Octahedral



$[Mn_2(CO)_{10}]$



► **Bonding in metal carbonyls:** It also involves both σ - and π -bond. σ -bond is formed by overlapping of lone pair on CO to the vacant d -orbitals of metal whereas π -bond is formed by back donation of pair of d -electrons to vacant antibonding orbital of carbonyl.

► **Factors affecting the stability of 'coordination' complexes:**

- Nature of the central ion: Greater the charge density on the central metal ion, greater is the stability of the complex.
- Nature of the ligand: More basic ligands have a tendency to donate the electron pairs to central metal ion more easily resulting in a stable complex.
- Chelate effect: Entropy increases when chelation occurs and so the formation of the complex becomes more favourable.

► **Applications of Complex compounds:**

- They are used in photography, i.e., AgBr forms soluble complex with sodium thiosulphate in photography.
- $\text{K}[\text{Ag}(\text{CN})_2]$ is used for electroplating of silver, $\text{K}[\text{Au}(\text{CN})_2]$ is used for gold plating.
- Some of ligands oxidise Co^{2+} to Co^{3+} ion.
- EDTA is used for estimation of Ca^{2+} and Mg^{2+} in hard water.
- Silver and gold are extracted by treating Zn with their cyanide complexes.
- Ni^{2+} is tested and estimated by DMG (dimethyl glyoxime).
- cis*-platin $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is used as anti-tumor agent in the treatment of cancer.
- EDTA is used to remove Pb by forming Pb-EDTA complex which is eliminated in urine.
- Haemoglobin contains Fe, chlorophyll contains (Mg) and vitamin B12 contain Co^{2+} 'which are all coordination compounds'.
- Bauxite is purified by forming complex with NaOH.
- Coordination compounds are used as catalysts for many industrial processes.

Example 2

Q. Describe the type of hybridization for the complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

Solution:

Fe exists as Fe^{2+} . Fe (II) in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} = 3d^6 4s^0 4p^0 4d^0$

As water is a weak ligand, pairing does not occur and the 6 lone pairs available from each water molecule moves to one 4s, three 4p and two 4d orbitals.

Thus, the hybridization involved is sp^3d^2 .

CHAPTER-6

HALOALKANES AND HALOARENES

Topic-1

Haloalkanes and their Properties

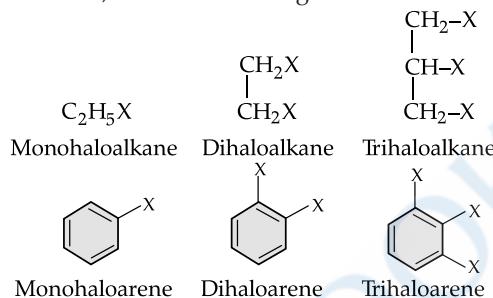
Concepts Covered • Haloalkanes and their classifications, Nomenclature, Methods of preparation, Physical and chemical properties, S_N1 and S_N2 reactions and their mechanisms, Nature of C-X bond, Optical Rotation



Revision Notes

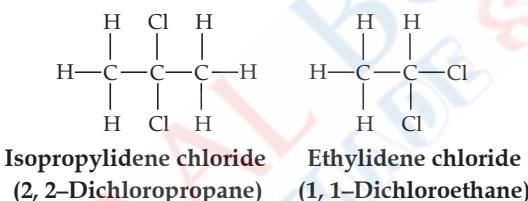
- Haloalkanes are aliphatic hydrocarbons where a hydrogen atom is replaced by halogen, while haloarenes are aromatic hydrocarbons where hydrogen in the benzene ring is replaced with halogen atom.
- Halogen atom is attached to sp^3 hybridised carbon atom in haloalkanes while in haloarenes it is attached to sp^2 hybridised carbon atom of the aryl group.
- **Classification:**

- **On the basis of the number of halogen atom:** These may be classified as mono, di or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,



Dihalogen compounds may be further classified as:

- (i) **Geminal dihalides:** Two halogen atoms are attached to the same carbon atom. For example,

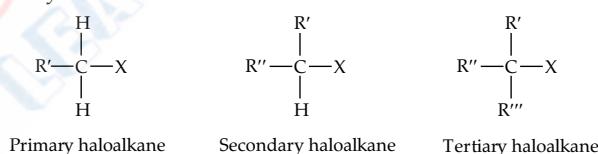


- (ii) **Vicinal dihalides:** Two halogen atoms are attached to the adjacent carbon atoms. For example,

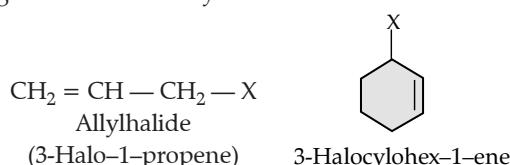


- **On the basis of sp^3 hybridisation:**

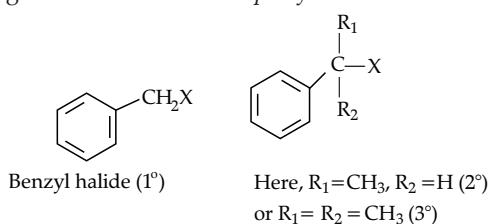
- (i) Haloalkanes or alkyl halides ($R-X$): General formula is $C_nH_{2n+1}X$. They are further classified as primary, secondary and tertiary haloalkanes.



- (ii) **Allylic halides:** Halogen is bonded to allylic carbon.

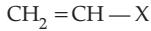


- (iii) **Benzyllic halides:** Halogen atom is bonded to sp^3 hybridised carbon atom next to an aromatic ring.



● On the basis of sp^2 hybridisation:

(i) **Vinylic halides:** Halogen is bonded to one of the carbon atoms of a vinylic carbon.



Vinyl halide



1-Halocylohex-1-ene

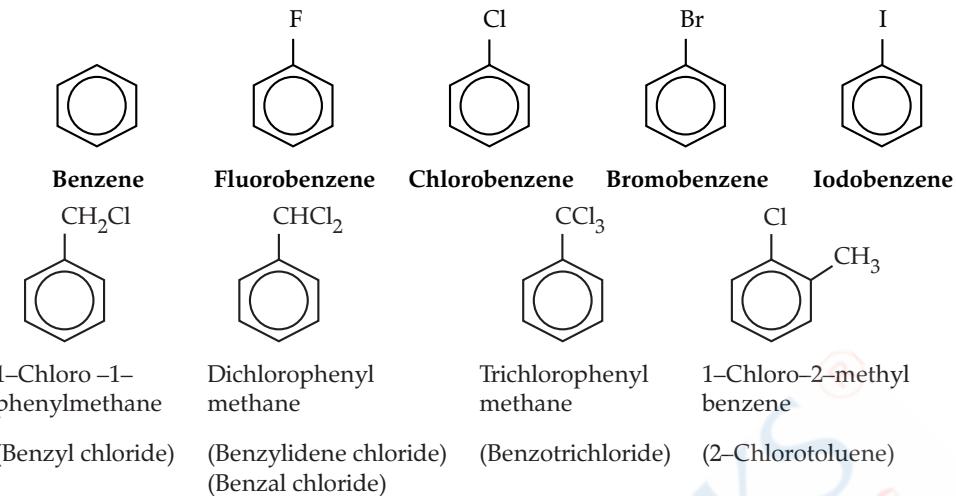
(ii) **Aryl halides:** Halogen atom is directly bonded to sp^2 hybridised carbon atom of an aromatic ring.



Halobenzene

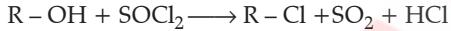
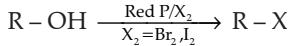
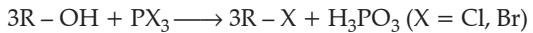
► Common and IUPAC name of some halides:

Structure	IUPAC Name	Common names
CH_3Cl	Chloromethane	Methyl chloride
$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane	Ethyl chloride
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Cl}$	1-Chloropropane	<i>n</i> -Propyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chloropropane	Isopropyl chloride
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{Cl}$	1-Chlorobutane	<i>n</i> -Butyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	1-Chloro-2-methyl propane	Isobutyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chlorobutane	<i>Sec.</i> butyl chloride
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chloro-2-methyl propane	<i>Tert.</i> 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
$\text{ClCH}_2 - \text{CH}_2\text{Cl}$	1, 2-Dichloroethane	Ethylene dichloride
CH_3CHCl_2	1, 1-Dichloroethane	Ethylidene chloride
$\text{CH}_2 = \text{CHCl}$	Chloroethene	Vinyl chloride
$\text{CH}_2 = \text{CH} - \text{CH}_2\text{Br}$	3-Bromopropene	Allyl bromide
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	1-Bromo-2, 2-dimethylpropane	neo-pentylbromide
$\text{CF}_3\text{CF}_2\text{CF}_3$	Octafluoropropane	Perfluoropropane
CCl_2F_2	Dichlorodifluoromethane	Freon
$\text{CHCl}_2 - \text{CHCl}_2$	1, 1, 2, 2-Tetrachloroethane	Acetylene tetrachloride
$\text{CHCl} = \text{CCl}_2$	1, 1, 2-Trichloroethene	Acetylene trichloride



► **Methods of preparation of Haloalkanes:**

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



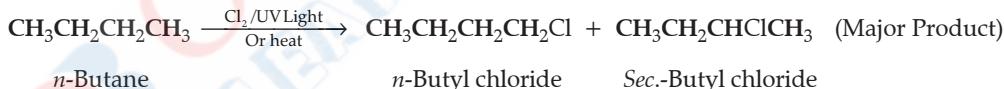
The reactions of primary and secondary alcohols with HX require the presence of the anhydrous $ZnCl_2$.



Key Word

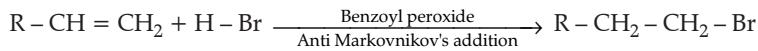
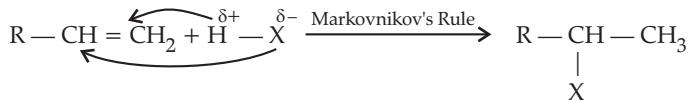
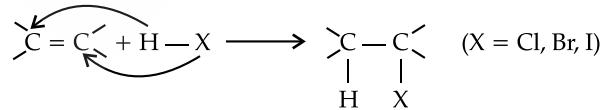
Halogenation: It is the process of adding halogen atom/s to a compound.

(b) From hydrocarbons: By free radical **halogenation**.

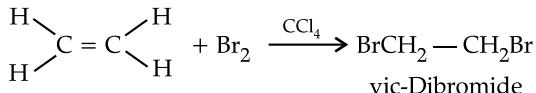


(c) From alkenes:

(i) Addition of hydrogen halide:

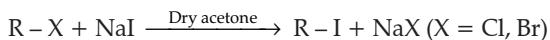


(ii) Addition of Halogens:



(d) Halide Exchange:

(i) By Finkelstein Reaction:



(ii) By Swarts Reaction:



► **Nature of C-X bond in haloalkanes:** The carbon-halogen bond is polarized. Carbon atom holds partial positive charge and halogen atom holds partial negative charge. This occurs due to difference in electronegativity. Halogens are more electronegative than carbon. Size of the halogen atoms increases down the group from Fluorine to Iodine. Hence, 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.

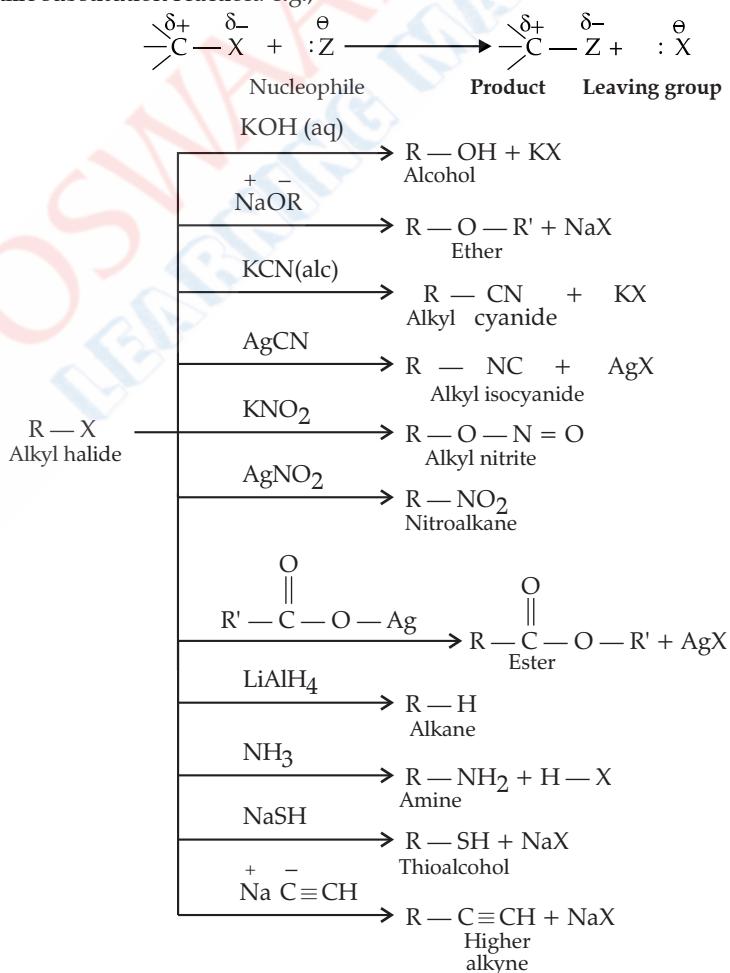
- (i) **Melting and boiling points:** Due to polar and strong dipole-dipole interactions between the molecules of halogen derivatives, have high B.P. and M.P. than their parent hydrocarbons. This increase in B.P. and M.P. depends on increasing size, mass of halogens and magnitude of van der Waals forces of attractions. The increasing order of boiling point of alkyl halides is $\text{RF} < \text{RCI} < \text{RBr} < \text{RI}$. With respect to isomeric alkyl halides, B.P. decreases with increase in branching due to less surface area and weak intermolecular forces.
 - (ii) **Density:** It increases with increase in carbon atoms, halogen atoms and atomic mass of the 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., $\text{C}-\text{Cl} > \text{C}-\text{Br} > \text{C}-\text{I}$. Reactivity order of haloalkanes would be:



There are four types of chemical reactions with haloalkanes:

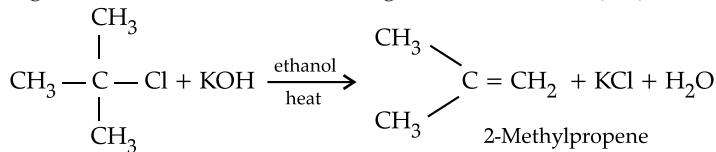
(a) Nucleophilic substitution reactions: When an atom or group of atoms is replaced by a *nucleophile*, the reaction is called nucleophilic substitution reaction. e.g.,



Alkyl halides undergo nucleophilic substitution reactions.

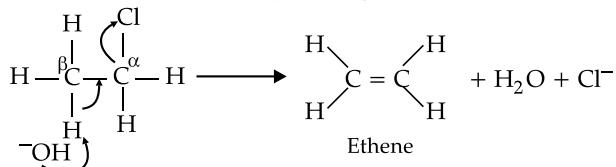


(b) Elimination reaction: Alkyl halides undergo β -elimination of hydrogen atom from β -carbon atom and halogen atom to form alkenes on being heated with KOH (alc.) or KNH₂, e.g.,



2-Chloro-2-methylpropane

The reaction is called *dehydrohalogenation*.

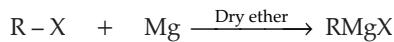


The following is order of reactivity:



(c) Reaction with metals:

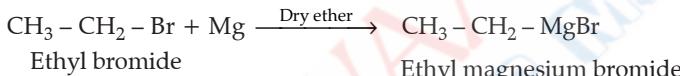
(1) Reaction with magnesium:



Alkyl halide

Alkyl magnesium halide

(Grignard reagent)

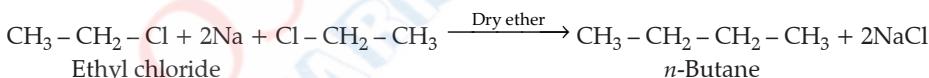


(2) Reaction with sodium (Wurtz reaction):

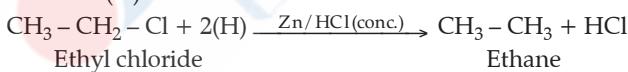


Alkyl halide

Alkane



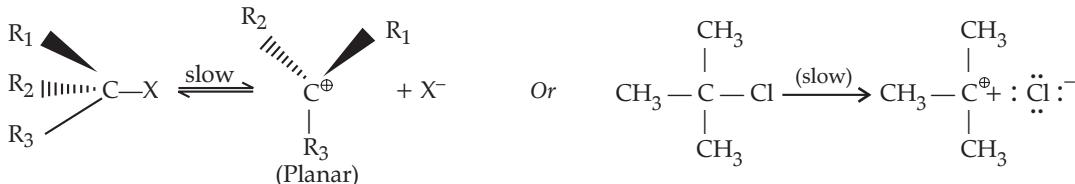
(d) Reduction:

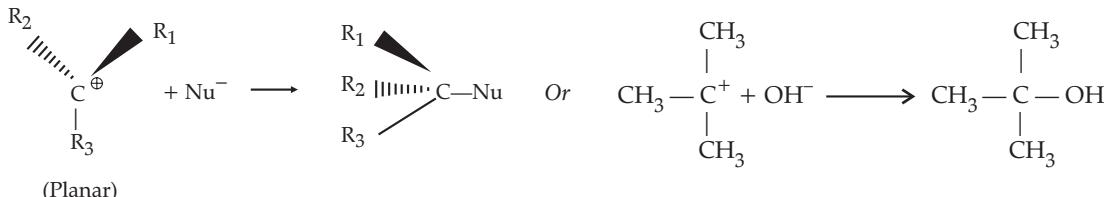


- **Mechanism of Nucleophilic substitution reaction:** Alkyl halides undergo two types of nucleophilic substitution reactions.

(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:

STEP I:

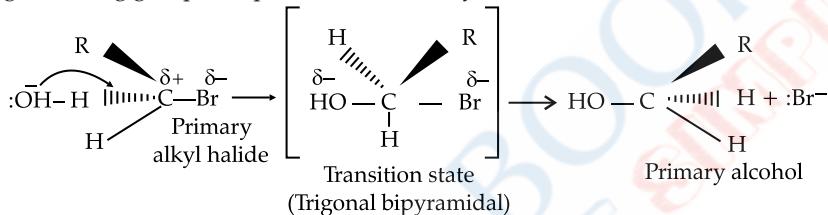


STEP II:**Key Word**

Polar protic solvents: These are the solvents that are polar and lacks acidic proton.

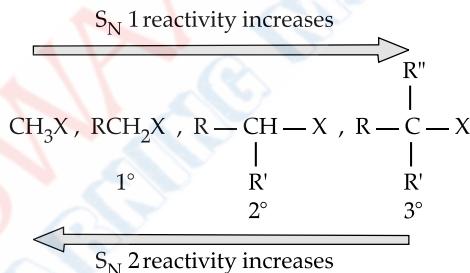
The slowest step is rate determining step which involves one species only. Therefore, rate of reaction depends only on the concentration of tertiary butyl chloride. **Polar protic solvents** like water, alcohol favour S_N1 because they stabilise carbocation by solvation. Tertiary alkyl halides follow 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 alkyl halides follow S_N2 mechanism.

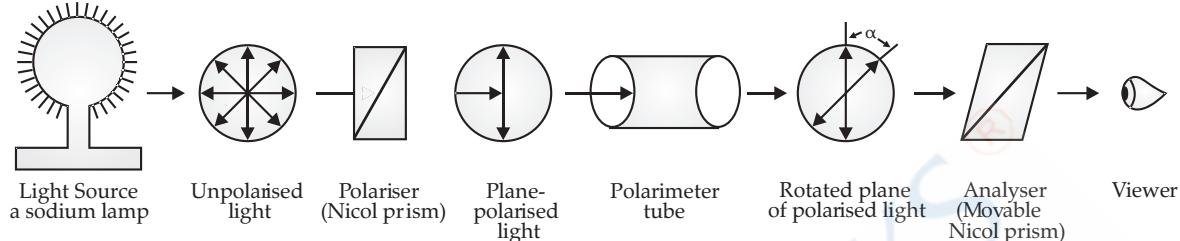
► **Reactivity of S_N1 and S_N2 mechanisms:** S = Substitution, N = Nucleophilic, 2 = Bimolecular, 1 = Unimolecular. Nucleophilic substitution seldom occurs exclusively by one mechanism only. With a given halogen, primary, secondary and tertiary halides show opposite order of reactivity in the two mechanisms.



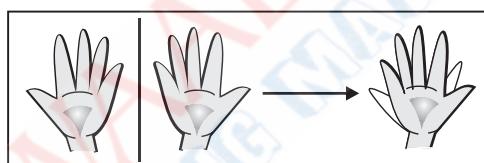
- **Stereoisomerism:** Isomerism exhibited by two or more compounds with the same molecular and structural formula, but different spatial arrangements of atoms or groups in space is called stereoisomerism.
- **Plane-polarized light:** The beam of light whose oscillations or vibrations are confined to one plane only is called plane-polarized light. It is obtained by passing a monochromatic light (light of single wavelength) through a Nicol prism.
- **Nicol prism:** A Nicol prism is a special type of prism made from calcite, a special crystalline form of calcium carbonate. It is a device for producing plane polarized light.
- **Optical rotation:** Property of rotating the plane of polarization either towards left or right.
- **Dextrorotatory:** Those substances which rotate the plane of polarization of light towards right, i.e., in clockwise direction are called dextrorotatory. It is conventionally given a positive sign. It is denoted by '*d*' and a positive (+) sign is placed before the degree of rotation.
- **Laevorotatory:** Those substances which rotate the plane of polarization of light towards the left, i.e., in anticlockwise direction are called laevorotatory. It is denoted by '*l*' and a negative (-) sign is placed before the degree of rotation.
- **Specific rotation:** The extent of experimentally observed angle of rotation (optical rotation, represented by α_{obs}) of a substance depends upon the following factors:
 - (i) nature of substance,
 - (ii) wavelength of the light used,
 - (iii) the number of optically active molecules in the path of light beam (which depends upon concentration of sample),
 - (iv) length of polarimeter tube,
 - (v) solvent used.

$$\text{Mathematically, Specific rotation } [\alpha]_D^{^{\circ}\text{C}} = \frac{\text{observed rotation } (\alpha_{\text{obs}})}{\text{length of tube } (d_m) \times \text{concentration of solution } (\text{g mol}^{-1})}$$

- **Optically active substances:** Those substances which rotate the plane of polarization of plane-polarized light when it is passed through their solutions are called optically active substances. This phenomenon is called optical activity.
- **Polarimeter:** The angle of rotation by which the plane-polarized light is rotated, can be measured by using an instrument called polarimeter. A schematic diagram of a polarimeter is shown in the figure below:

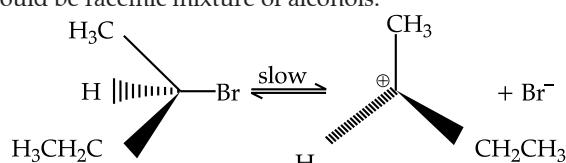


- **Enantiomers:** Those stereoisomers which are mirror images of each other but non-superimposable are called enantiomers, e.g., *d*(+)-glucose and *l*(-)-glucose are enantiomers.
- **Asymmetric molecule:** If all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.
- **Symmetrical objects:** Those objects whose projections are superimposable on their mirror images are symmetrical objects, e.g., a sphere, a cube, a cone, a tetrahedron are all identical to their mirror images and can thus be superimposed.
- **Chiral:** An object which is non-superimposable on its mirror image is said to be chiral. The property of being chiral is known as chirality. A chiral object is also called dissymmetric. e.g.,

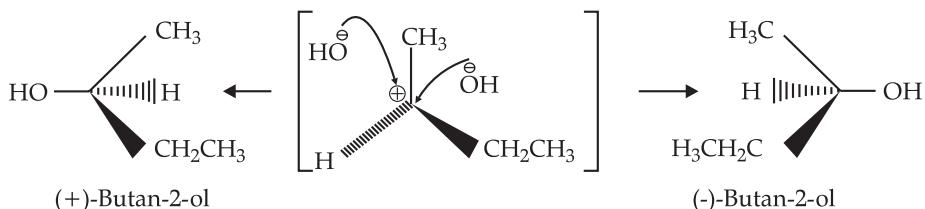


Non-superimposable hands

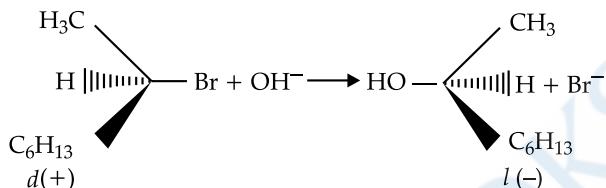
- **Achiral:** Achiral objects are those objects which are superimposable on their mirror images.
- **Asymmetric carbon (Chiral carbon):** The carbon atom which is attached with four different groups of atoms is called asymmetric or chiral carbon atom.
- **Racemic mixture:** A mixture containing equal amounts of enantiomers which does not show any optical activity. It is optically inactive due to external compensation.
- **Racemization:** The process of conversion of an enantiomer into racemic mixture is known as racemization.
- **Absolute configuration:** The three dimensional structure of a molecule that has one or more centres of chirality is referred to its absolute configuration.
- **Diastereoisomers:** Those pairs of stereoisomers which are not mirror images of each other and are non-superimposable.
 - (i) Diastereoisomers have different physical properties.
 - (ii) Diastereoisomers differ in magnitude of specific rotation.
 - (iii) A compound with two chiral centres does not always have four stereoisomers.
- **Example of racemization in S_N1 mechanism:** When optically active alkyl halide undergoes S_N1 mechanism, it is accompanied by racemization because intermediate carbocation formed is *sp*²-hybridised and polar. Nucleophile (OH⁻) has equal probability of attacking it from either side leading to formation of equal amount of dextro and laevo-rotatory alcohols. As the products of S_N1 mechanism has both inversion as well as rotation, the products formed by this reaction would be racemic mixture of alcohols.



(-)-2-Bromobutane



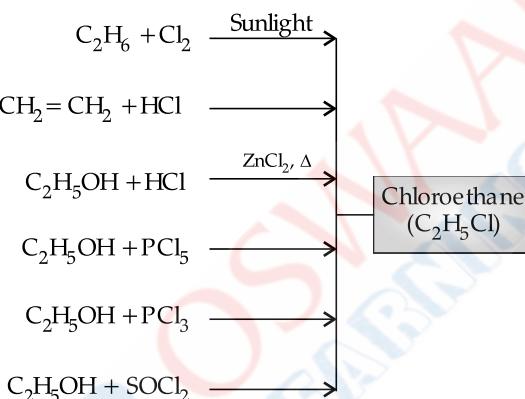
- **Meso compounds:** Those compounds which have two or more (even number) chiral carbon atoms and have an internal plane of symmetry are called meso compounds. They are optically inactive due to internal compensation.
 - **Example of inversion in S_N2 mechanism:** When optically active *d* (+) alkyl halide is treated with OH^- , we get optically active *l* (-) alcohol due to back side attack of nucleophile.



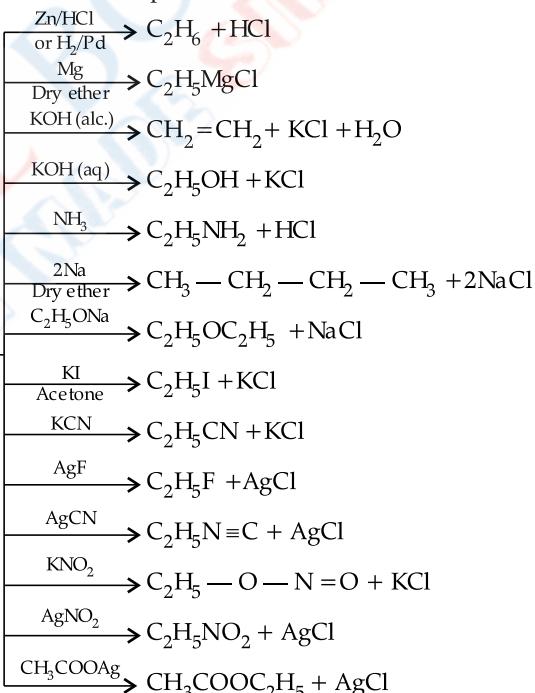
When *d*(+)-2-bromoocetane is reacted with NaOH, *l*(-)-2-octanol is formed. Thus, S_N2 mechanism leads to inversion of configuration. This inversion is called Walden's inversion.

- Important reactions of chloroethane:

Preparation



Chemical Properties



Topic-2

Haloarenes and Polyhalogen Compounds

Concepts Covered

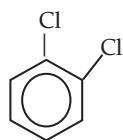
Concepts Covered • Haloarenes, Methods of preparation of Haloarenes, Physical properties, Chemical properties, Nature of C-X bonds, Uses of Polyhalogen Compounds



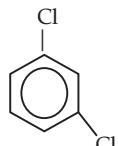
Revision Notes

- **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).

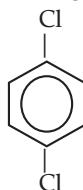
- When two halogens are at 1, 2- positions of benzene ring, it is called *ortho* substituted derivative. e.g.,



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

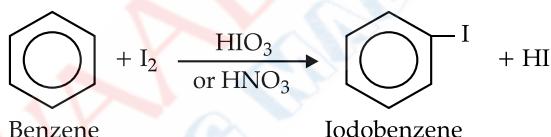


- When two halogens are at 1, 4- positions of benzene ring, it is called *para* substituted derivative. e.g.,

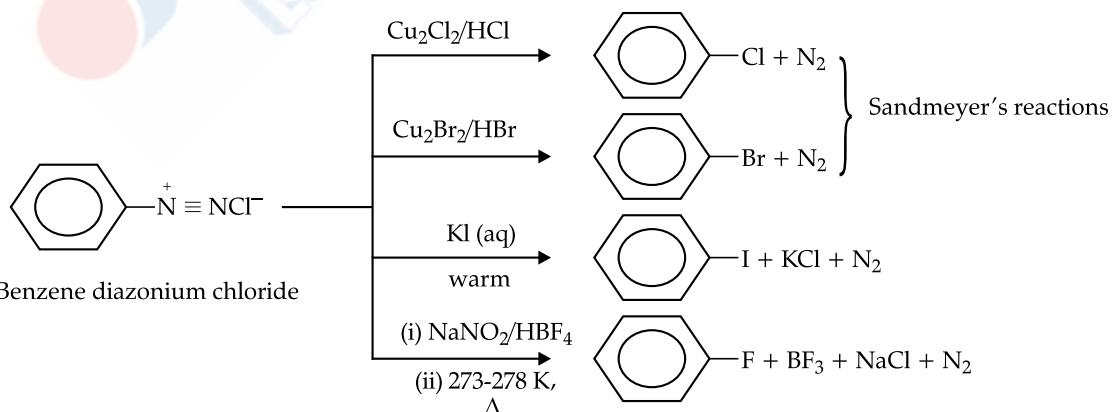
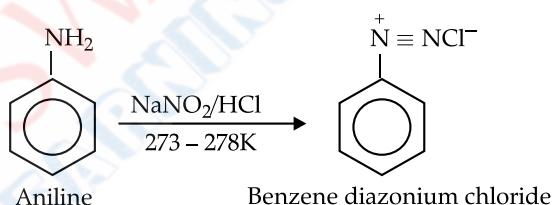


► Methods of preparation of Haloarenes:

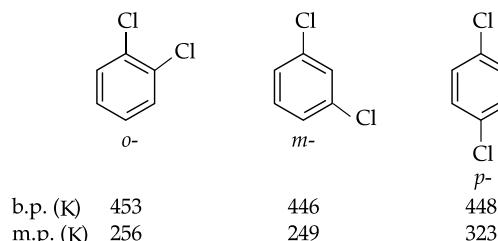
(i) Reacting benzene directly with halogen:



(ii) Starting with diazonium salts:



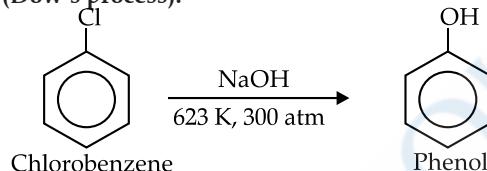
- **Physical properties of Haloarenes:** Isomeric haloarenes have similar boiling points. But *para* isomer has higher melting point than other two *i.e.*, *ortho* and *meta* because of the symmetry in *para* isomer which occupies the crystal lattice better than *ortho* and *meta* isomers.



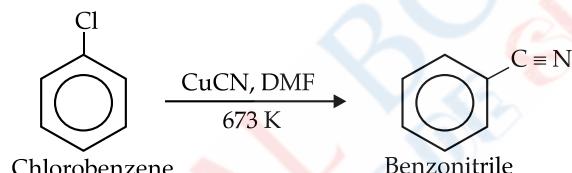
► Chemical properties of Haloarenes:

(a) 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.

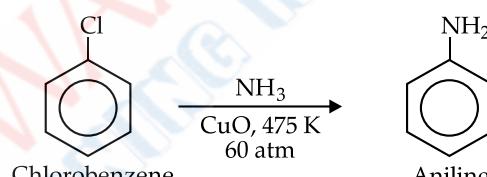
(i) Substitution by —OH group (Dow's process):



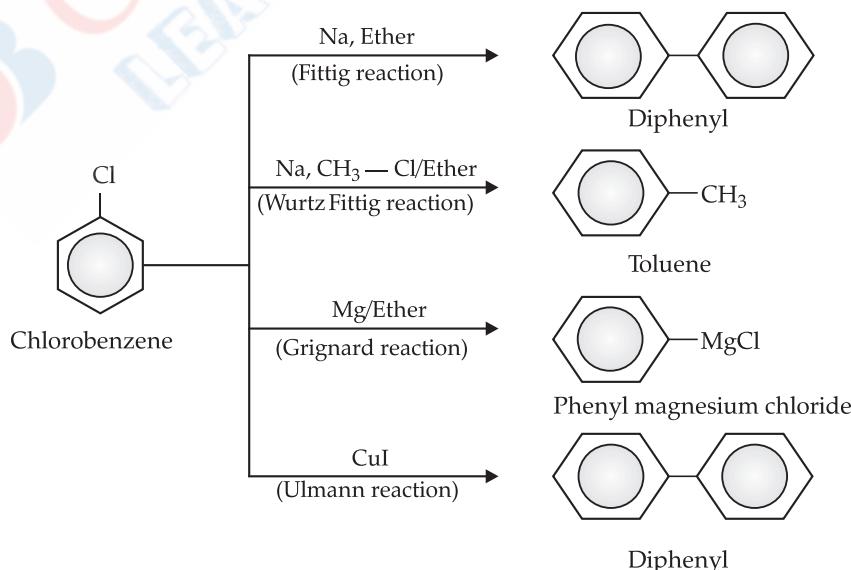
(ii) Substitution by —CN group:



(iii) Substitution by —NH_2 group:

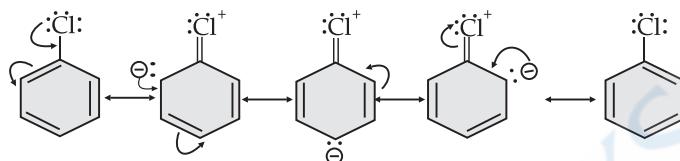


(iv) Reaction with metals:



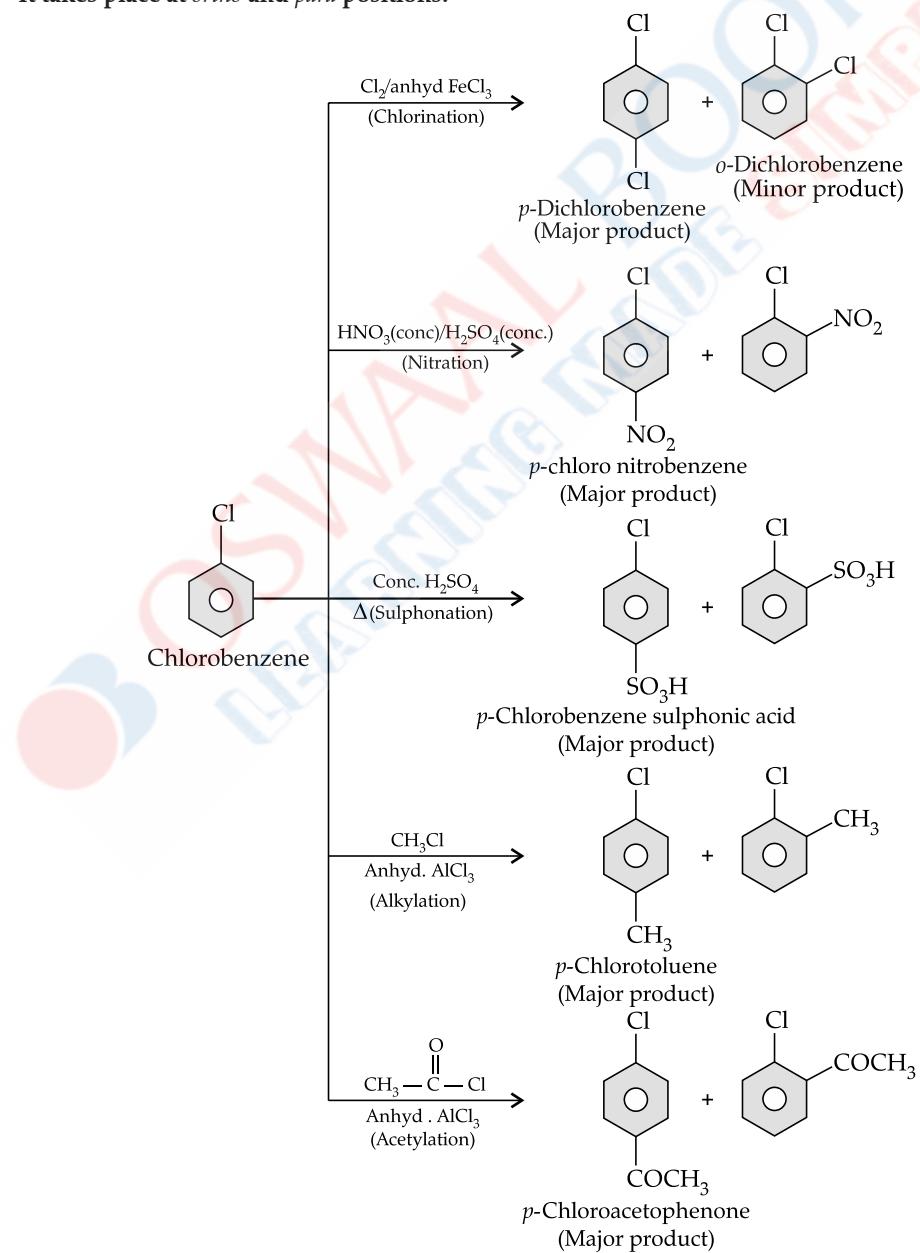
► **Nature of C—X bond in haloarene:** The C—X bond of aryl halide is less reactive than that of haloalkanes. One reason is that in aryl halide, halogen atom is attached to sp^2 -hybrid carbon atom whereas in alkyl halides, it is attached to sp^3 -hybrid carbon atom. Due to more electronegativity of 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.



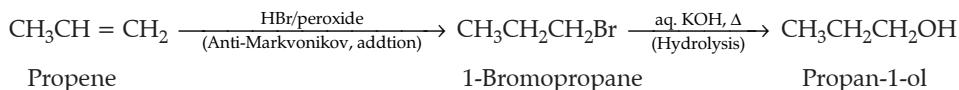
(v) Electrophilic substitution reactions of haloarenes:

It takes place at *ortho* and *para* positions:

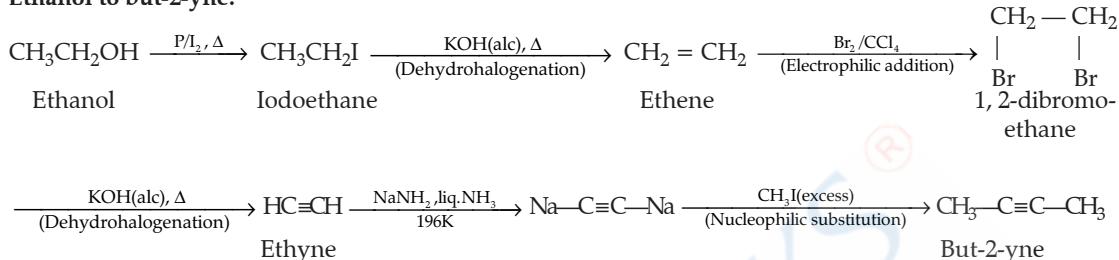


► Some Important Conversions:

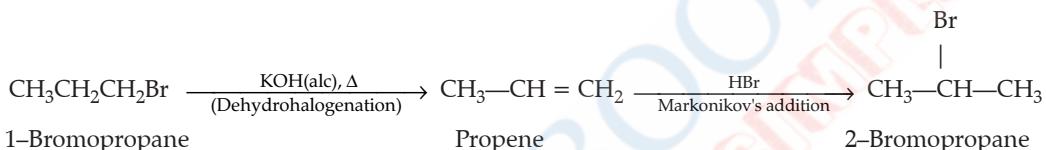
(i) Propene to propan-1-ol:



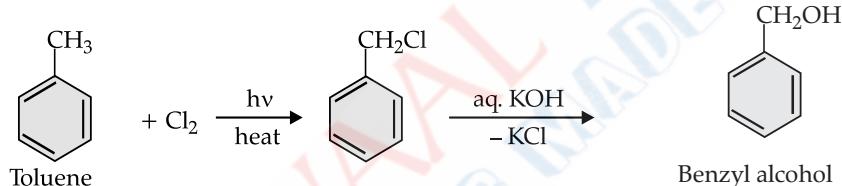
(ii) Ethanol to but-2-yne:



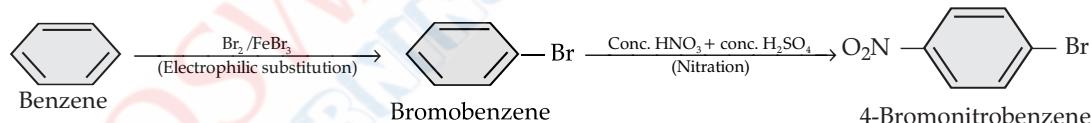
(iii) 1-Bromopropane to 2-bromopropane:



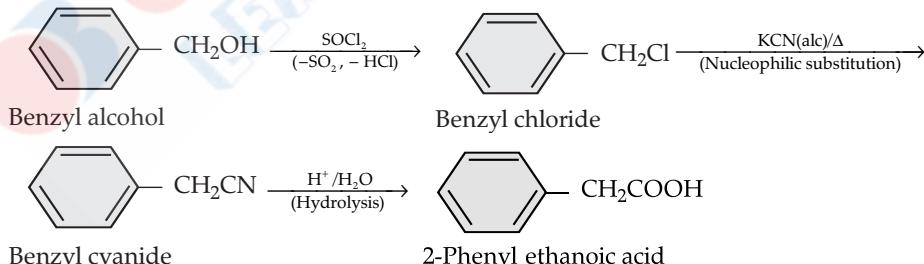
(iv) Toluene to benzyl alcohol:



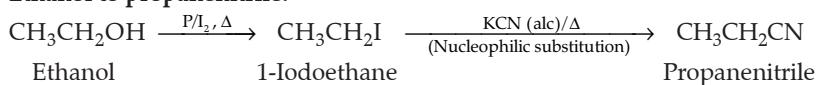
(v) Benzene to 4-bromonitrobenzene:



(vi) Benzyl alcohol to 2-phenylethanoic acid:

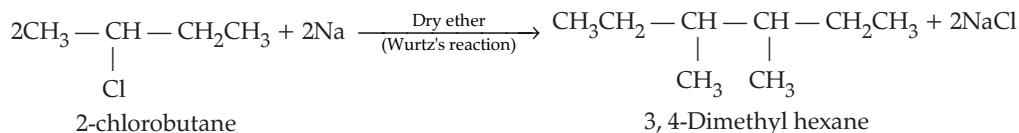
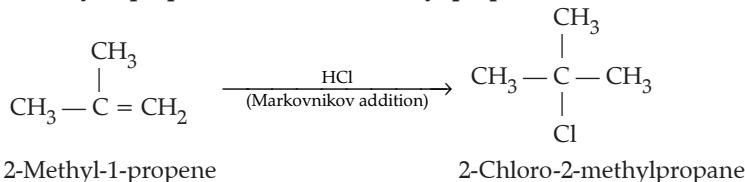
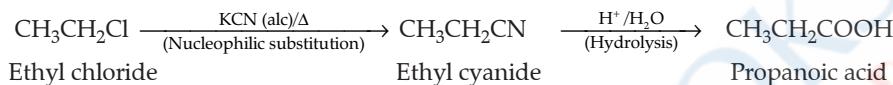
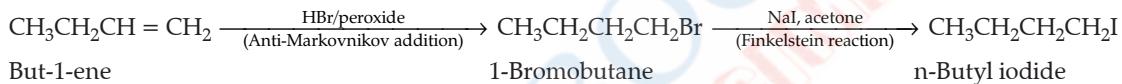
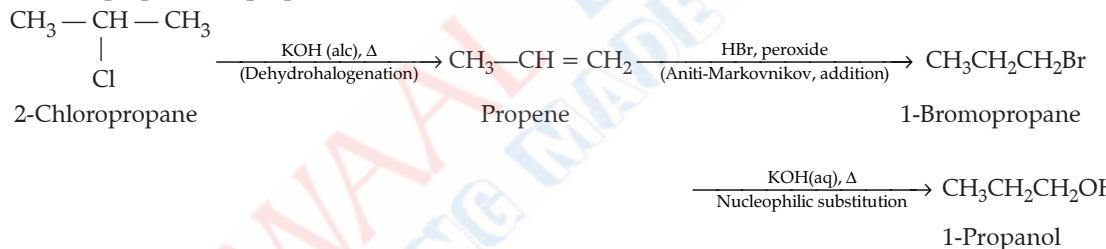
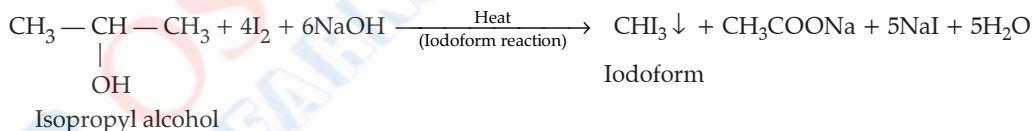
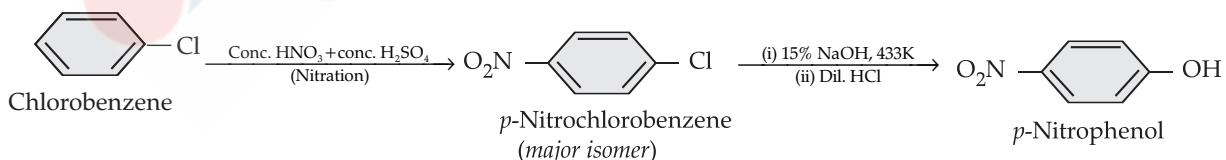
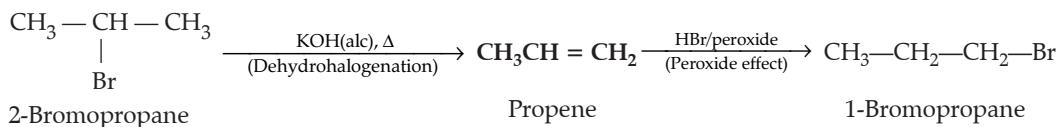
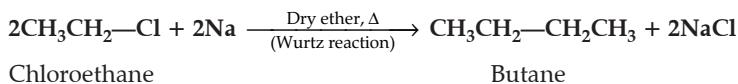


(vii) Ethanol to propanenitrile:

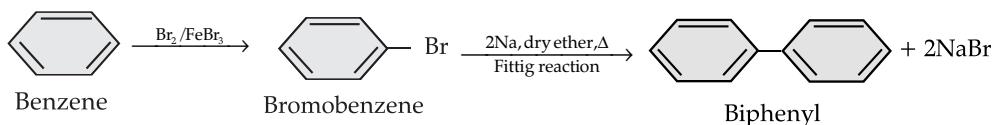


(viii) Aniline to chlorobenzene:

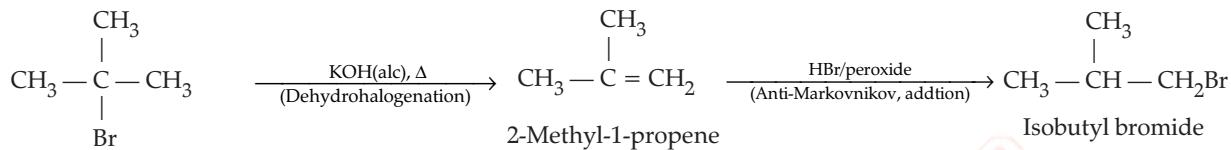


(ix) **2-Chlorobutane to 3, 4-dimethyl hexane:**(x) **2-Methyl-1-propene to 2-chloro-2-methyl propane:**(xi) **Ethyl chloride to propanoic acid:**(xii) **But-1-ene to n-butyl iodide:**(xiii) **2-Chloropropane to 1-propanol:**(xiv) **Isopropyl alcohol to iodoform:**(xv) **Chlorobenzene to p-nitrophenol:**(xvi) **2-Bromopropane to 1-bromopropane:**(xvii) **Chloroethane to butane:**

(xviii) Benzene to diphenyl:

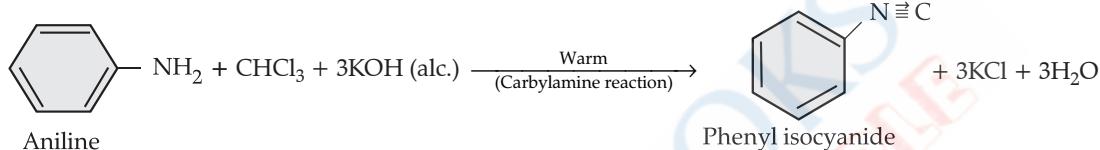


(xix) *tert*-Butyl bromide to iso-butyl bromide:



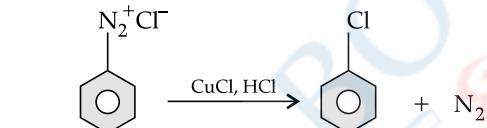
tert-Butyl bromide

(xx) Aniline to phenyl isocyanide:

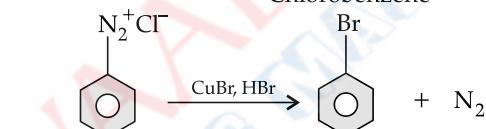


► Important Name Reactions:

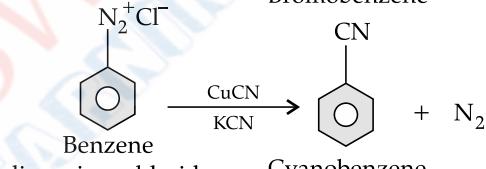
(i) Sandmeyer's Reaction:



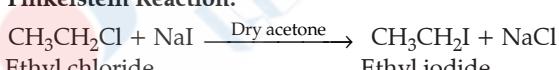
Benzene diazonium chloride



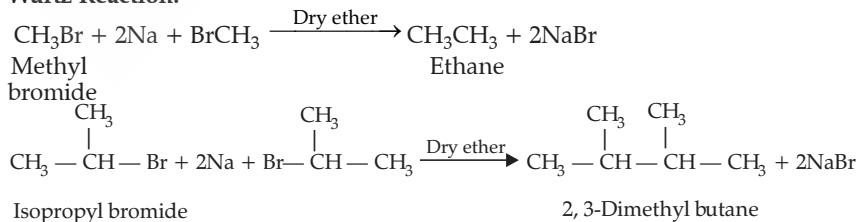
Benzene diazonium chloride



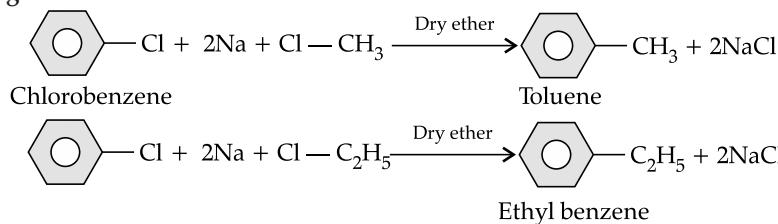
(ii) Finkelstein Reaction:

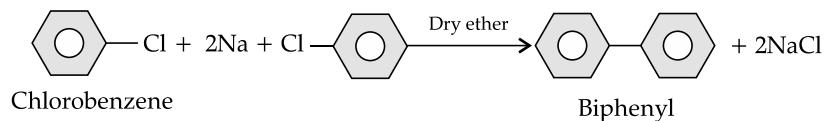
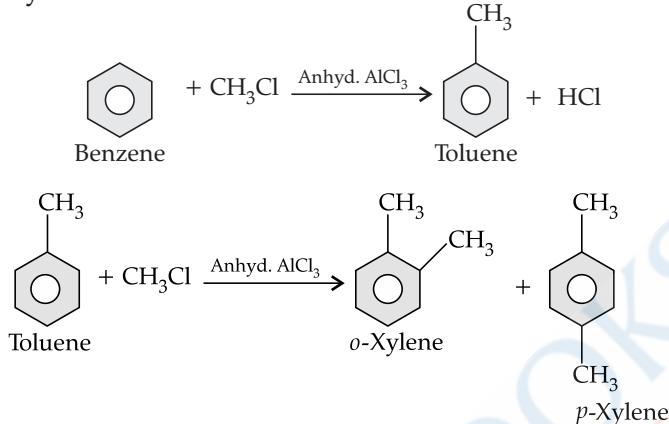
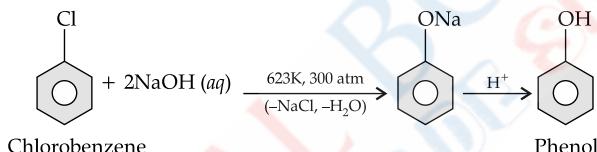


(iii) Wurtz Reaction:

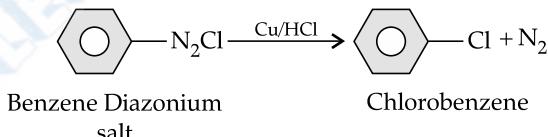


(iv) Wurtz-Fittig Reaction:



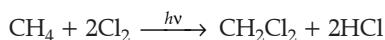
(v) **Fittig's Reaction:**(vi) **Friedel-Crafts Alkylation:**(vii) **Dow's Process:**(viii) **Hunsdiecker's Reaction:****Key Word**

Reflux: It is a technique used in various chemical reactions in which the condensation of vapours takes place to be heated again.

(ix) **Gattermann's Reaction:**

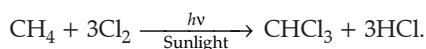
► **Polyhalogen compounds:** Carbon compounds containing more than one halogen atoms are usually referred to as polyhalogen compounds. Many of those compounds are useful in industry and agriculture.

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



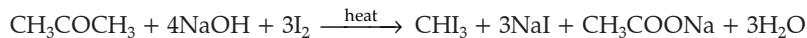
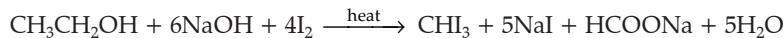
The mixture so obtained is separated by fractional distillation. It is widely used as solvent in pharmaceuticals and food industry.

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



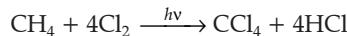
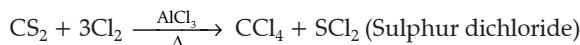
It is extensively used as solvent for waxes, resins, rubber, fats etc. It was earlier used as anaesthetic and swallowing agent, but due to formation of phosgene gas (poisonous gas), it is not used at present.

- (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.



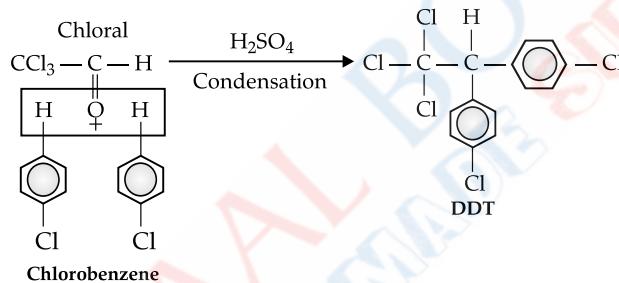
It is used as an antiseptic for dressing wounds.

- (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.



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.



CHAPTER-7

ALCOHOLS, PHENOLS AND ETHERS

Topic-1

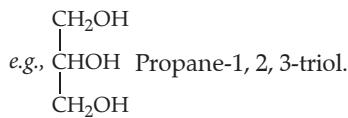
Methods of Preparation and Properties of Alcohols and Phenols

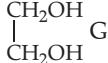
Concepts Covered • General formula, • Nomenclature, • Preparation, • Classification
• Physical properties, • Chemical properties, • Uses of alcohols and phenols.

Revision Notes

- **Alcohol:** When one hydrogen atom of alkane is replaced by $-\text{OH}$ group, the compounds obtained are called alcohols having general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$.
- **Classification of Alcohols:**
 - Based on number of hydroxyl(-OH) group**
 - Monohydric alcohols:** the alcohols which contain one $-\text{OH}$ group.
e.g., CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, etc.
 - Dihydric alcohols:** The alcohols which contain two $-\text{OH}$ groups, also called diols.
general formula = $\text{C}_n\text{H}_{2n}(\text{OH})_2$.
e.g., $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ Ethane-1, 2-diol.
 - Trihydric alcohols:** The alcohols which contain three hydroxyl ($-\text{OH}$) groups, also called triols.

Their general formula is $C_nH_{2n-1}(OH)_3$.

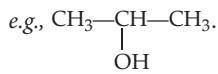


(iv) Polyhydric alcohols: The alcohols which have more than one –OH groups. e.g.,  Glycol.

(b) Based on carbon atom attached to -OH group:

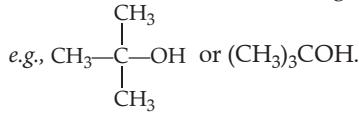
(i) Primary alcohols: The alcohol in which –OH group is attached to primary (1°) carbon atom.
e.g., CH_3OH , C_2H_5OH , etc.

(ii) Secondary alcohols: The alcohol in which –OH group is attached to secondary (2°) carbon atom.



(2-propanol)

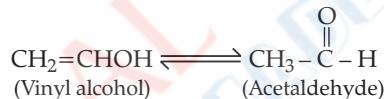
(iii) The alcohol in which –OH group is attached to tertiary (3°) carbon atom is called tertiary alcohol.



(2-methylpropan-2-ol)

(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 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 vinylic alcohols. They are highly unstable and get tautomerised to form aldehydes. e.g.,



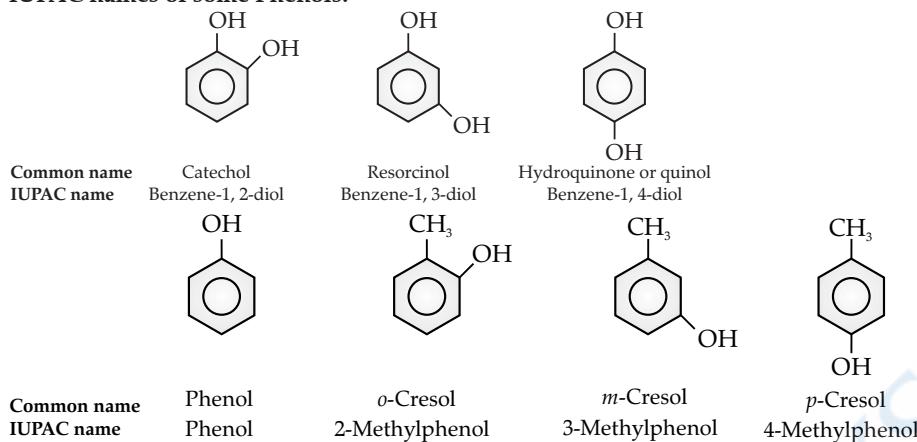
(d) Benzyl alcohol: The alcohol in which –OH group is attached to single bonded sp^3 -hybridised carbon atom attached to aromatic ring is called benzyl alcohol. e.g.,



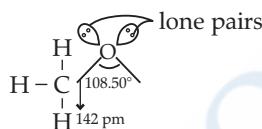
► **Common and IUPAC Names of Some Alcohols**

Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	<i>n</i> -Propyl alcohol	Propan-1-ol
$CH_3CHOHCH_3$	<i>iso</i> -Propyl alcohol	Propan-2-ol
$(CH_3)_2CH-CH_2OH$	<i>iso</i> -Butyl alcohol	2-Methyl-propan-1-ol
$CH_3CH_2CHOHCH_3$	<i>sec</i> - Butyl alcohol	Butan-2-ol
$(CH_3)_3C-OH$	<i>tert</i> - Butyl alcohol	2-Methyl propan-2-ol
CH_2-CH_2 OH OH	Ethylene glycol	Ethane-1, 2-diol
$CH_2-CH-CH_2$ OH OH OH	Glycerol or Glycerine	Propane-1, 2, 3-triol

► IUPAC names of some Phenols:

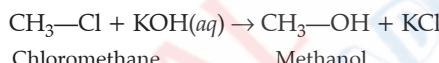


► **Structure of alcohol:** The oxygen of the —OH group is attached to sp^3 hybridised carbon by a σ bond.



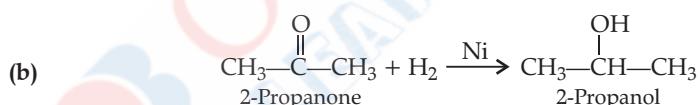
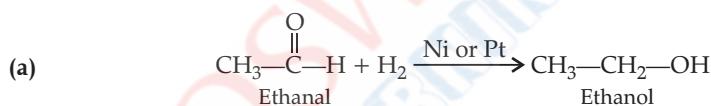
► Methods of preparation of Alcohols:

(1) From haloalkanes: Haloalkanes are hydrolysed to the corresponding alcohols by treatment with aqueous alkali.

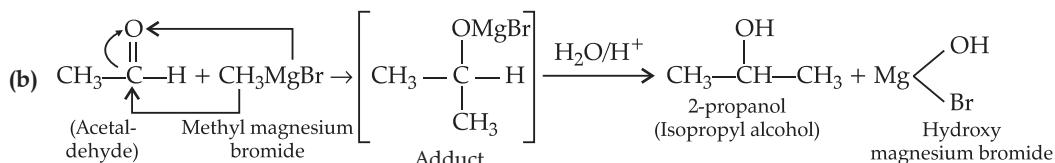
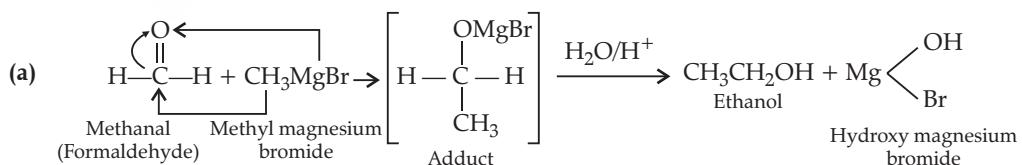


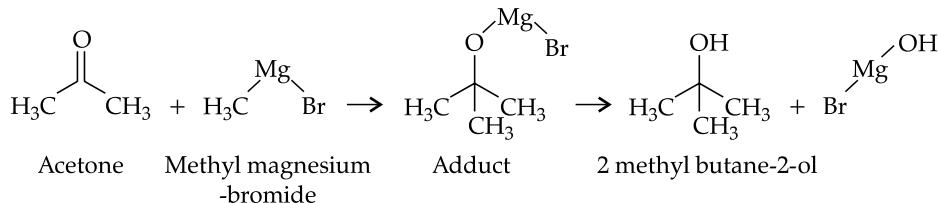
(2) From Aldehydes and Ketones:

(i) **Reduction:** Aldehydes 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.



(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.,



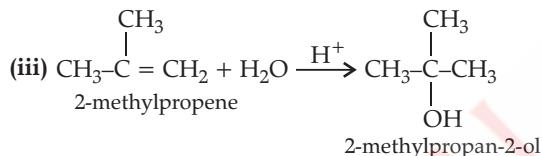
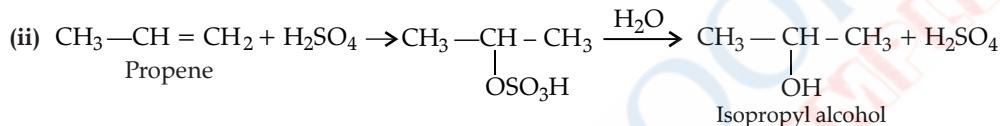
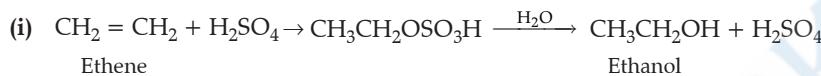


Key Words

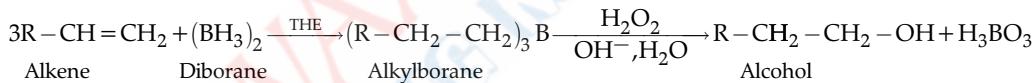
Lithium Aluminium Hydride: It is a powerful reducing agent used in organic synthesis. Its formula is LiAlH_4 .

Grignard Reagent: It is an organomagnesium compound having formula RMgX where R can be an alkyl or aryl group and X is halogen.

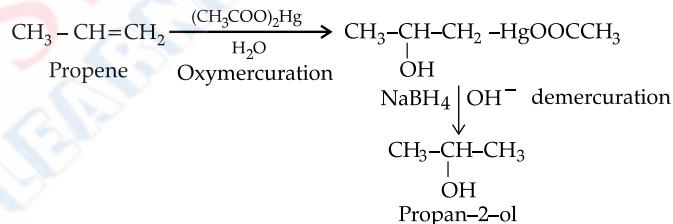
(3) From Alkenes:



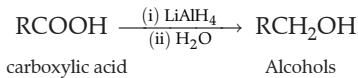
(4) By hydroboration oxidation: As per anti-Markovnikov's rule -



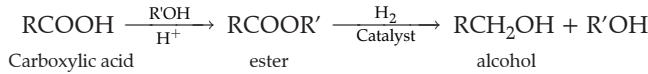
(5) By oxymercuration-demercuration: As per Markovnikov's rule:



(6) Reduction of carboxylic acids and esters: With the help of strong reducing agent, lithium aluminium hydride, carboxylic acids are reduced to primary alcohols.



Commercially, acids are reduced to alcohols by converting them to esters, followed by catalytic hydrogenation.



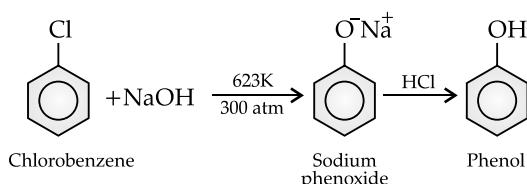
Key Words

Anti- Markovnikov's rule: According to this rule, when a reagent is added to an assymetrical alkene in presence of a peroxide, then the negative part of the addendum goes to the most substituted carbon atom.

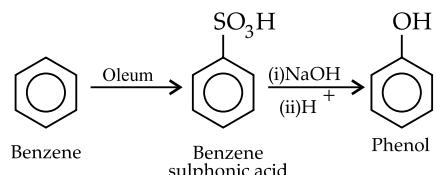
Markovnikov's rule: According to this rule, when a reagent is added to an assymetrical alkene, then the negative part of the addendum goes to the less substituted carbon atom.

► Preparation of Phenols:

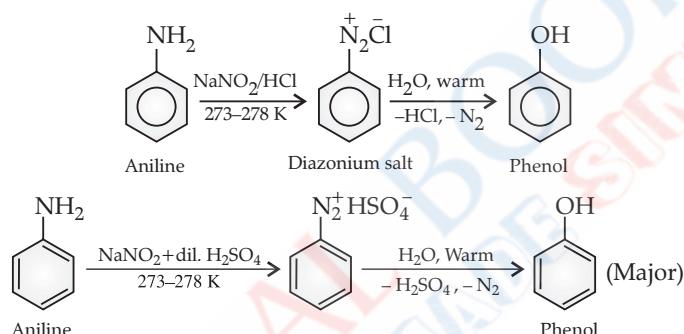
(i) From aryl halides



(ii) From benzene sulphonic acid



(iii) From diazonium salts

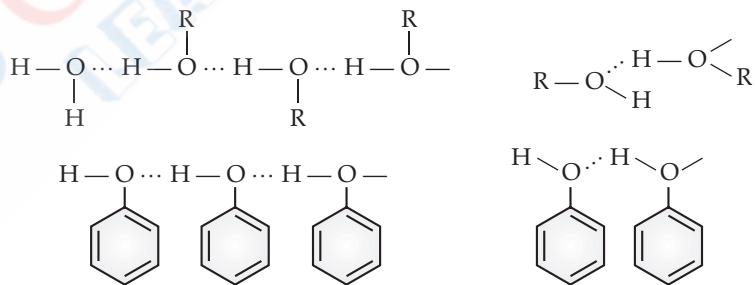


► Physical and Chemical properties of Alcohols and Phenols:

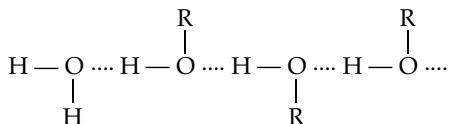
(1) Physical properties:

(i) **Boiling points:** The boiling points of alcohols and phenols increase with increase in the number of carbon atoms due to the increase in van der Waals forces. In alcohols, the boiling points decrease with increase of branching in carbon chain due to decrease in van der Waals forces with decrease in surface area.

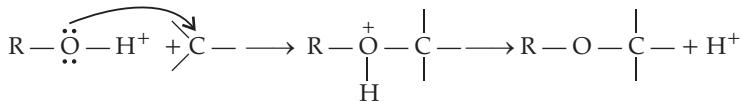
Ethers have low boiling point than Alcohols and phenols due to the absence of -OH group which is involved in intermolecular hydrogen bonding.



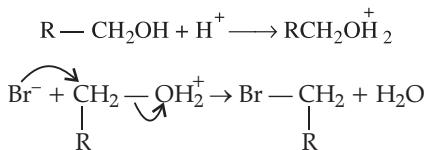
(ii) **Solubility:** Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.



(2) **Chemical properties:** Alcohols and phenols acts both as nucleophiles and electrophiles. The bond between O-H is broken when alcohols react as *nucleophiles*.



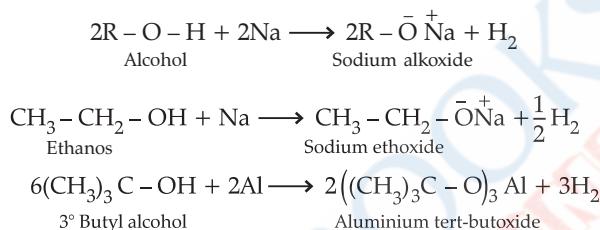
The bond between C–O is broken when they react as *electrophiles*.



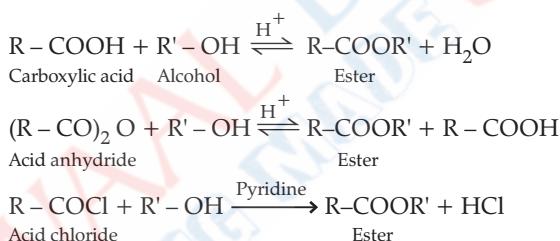
The reactions of alcohols can be classified into:

(a) Reactions involving the cleavage of O–H bond:

(i) Reaction with metals:



(ii) Esterification:

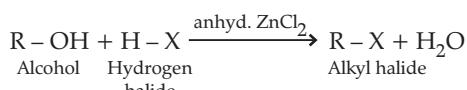


(b) Reactions involving cleavage of C–O bond:

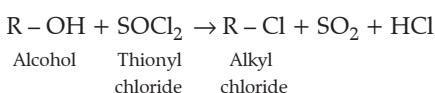
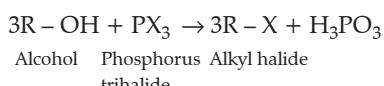
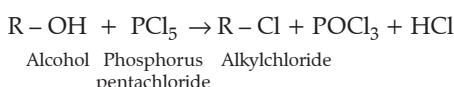
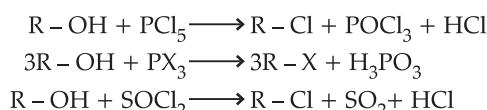
Order of reactivity in such type of reaction is



(i) Reaction with hydrogen halides:

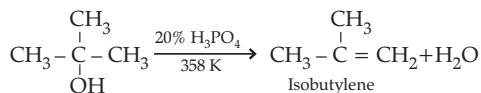
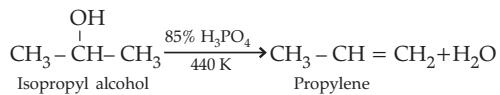
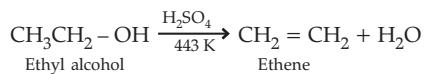


(ii) Reaction with phosphorus halides:



(c) Reactions involving both the alkyl and hydroxyl group:

(i) Dehydration: 3° Alcohol > 2° Alcohol > 1° Alcohol

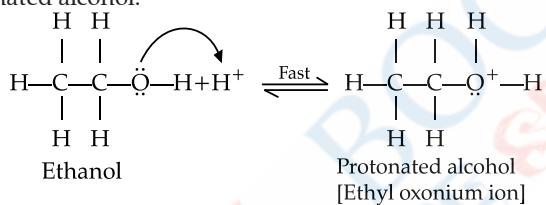


Example 1

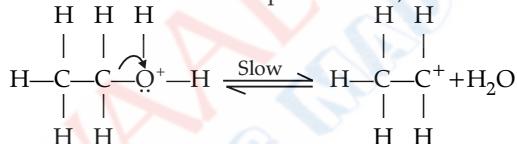
Q. The mechanism of dehydration of ethanol involves the following steps:
Solution:

Mechanism

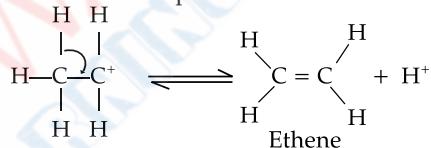
Step I: Formation of protonated alcohol.



Step II: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

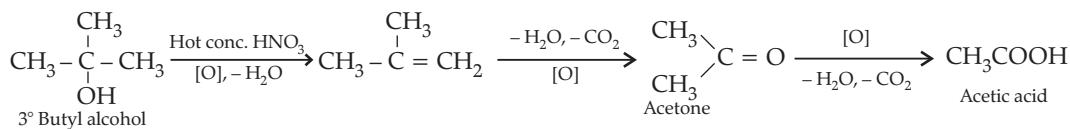
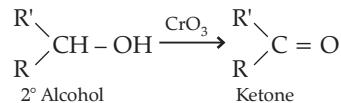
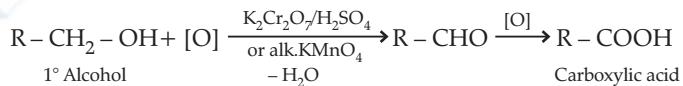


Step III: Formation of ethane by elimination of a proton.

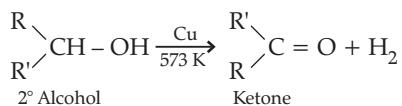
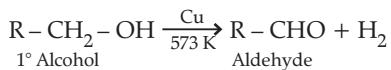


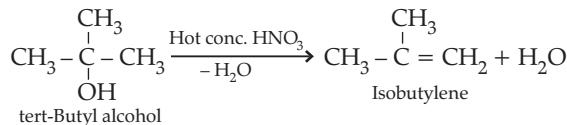
The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

(ii) Oxidation:

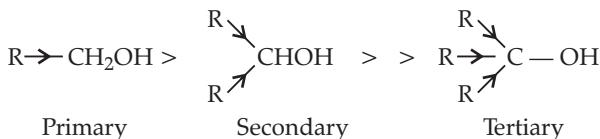


(iii) Dehydrogenation:



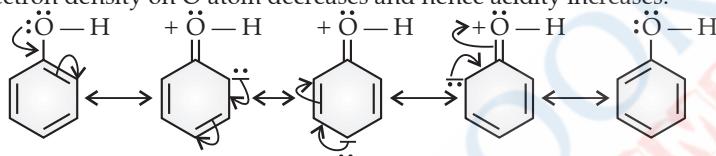


► **Acidity of alcohols and phenols:** The acidic character of alcohols is due to the polar nature of O-H bond. As electron releasing group, i.e., alkyl group increases, electron density on oxygen increases and hence polarity of O-H bond decreases. Therefore order of acidic strength of alcohol will be;

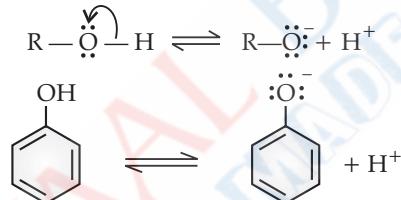


Alcohols can act as Bronsted acids as well as bases due to donation of proton and presence of unpaired electron on oxygen respectively.

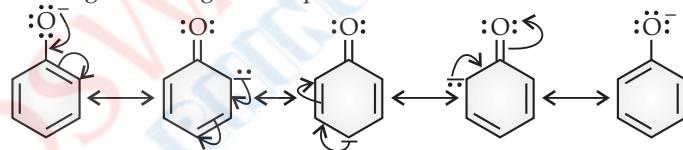
Phenols are more acidic than alcohols and water. The hydroxyl group in phenol is directly attached to the sp^2 -hybridised carbon of benzene ring. As the lone pair on oxygen is delocalised in benzene ring due to resonance, electron density on O atom decreases and hence acidity increases.



The ionisation of an alcohol and a phenol takes place producing alkoxide and phenoxide ions as shown in following equation:



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalization of negative charge makes phenoxide ion more stable and favours the ionisation of phenol.



► Distinction between Primary, Secondary and Tertiary Alcohols:

(i) **Lucas Test:** Alcohol on treating with **Lucas reagent** forms a clear solution. Alkyl chlorides are formed on reaction which being insoluble results in the turbidity in the solution.



Key Word

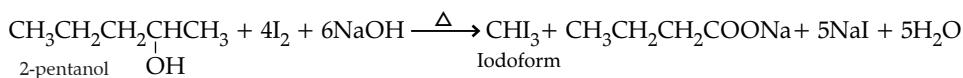
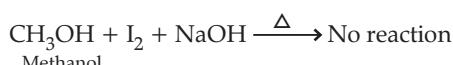
Lucas Reagent: It is an equimolar mixture of HCl and ZnCl_2 .

Tertiary alcohol: Immediate turbidity

Secondary alcohol: Turbidity after 5 minutes

Primary alcohol: No turbidity in room temperature. Turbidity appears on heating.

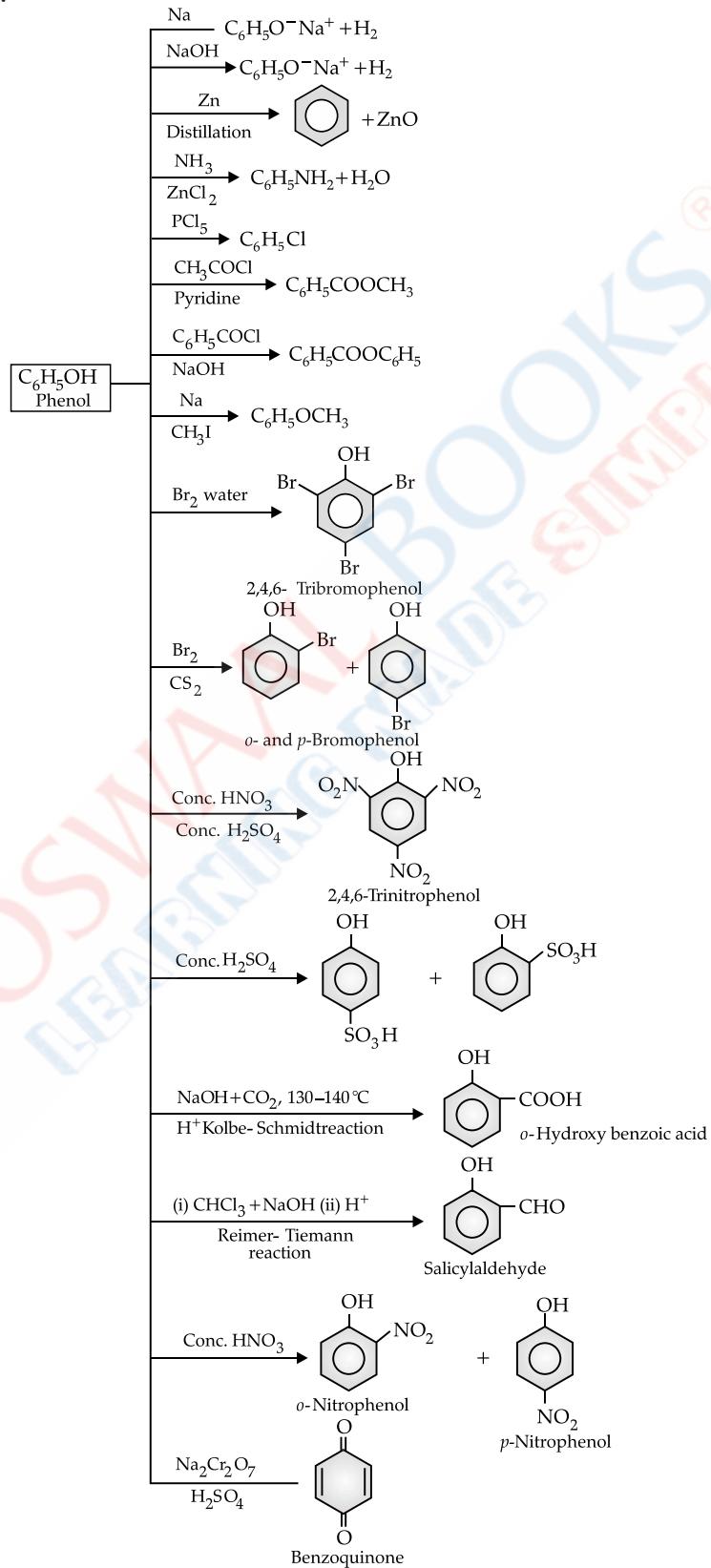
(ii) **Iodoform test:** When ethanol or any alcohol containing the group $\text{CH}_3 - \underset{\text{OH}}{\text{CH}} -$ is heated with iodine and aqueous NaOH or Na_2CO_3 solution at $333 - 343\text{ K}$, a yellow precipitate of iodoform is obtained.



(iii) **Ferric chloride test of phenols:** Phenol gives a violet coloured water soluble complex with ferric chloride.

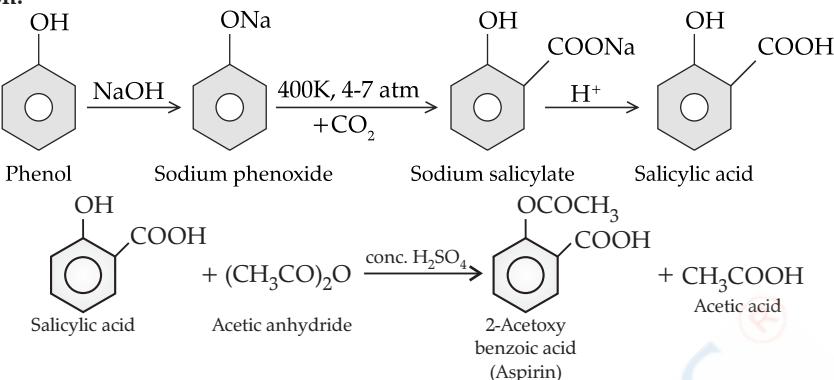


► **Reactions of Phenol:**

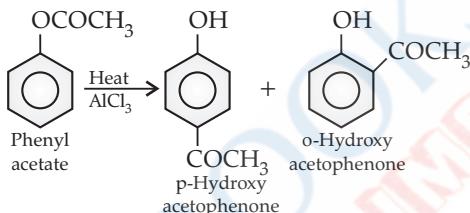


► Some important name reactions:

(i) Kolbe's reaction:



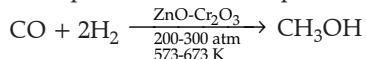
(ii) Fries Rearrangement:



► APPLICATIONS OF ALCOHOLS:

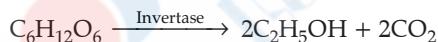
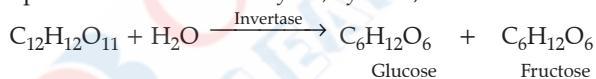
Methanol and ethanol are among the two commercially important alcohols.

1. Methanol: Methanol, (CH_3OH), also known as 'wood spirit', was produced by the destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of $\text{ZnO} - \text{Cr}_2\text{O}_3$ catalyst.



- Methanol is a colourless liquid and boils at 337 K.
 - It is highly poisonous. Ingestion of even small quantities of methanol can cause blindness and large quantities cause even death.
 - Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

2. Ethanol: Ethanol, (C_2H_5OH), is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.



Fermentation takes place in anaerobic conditions *i.e.*, in absence of air. Carbon dioxide is released during fermentation.

If air gets into the fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.

- Ethanol is a colourless liquid with a boiling point of 351 K.
 - It is used as a solvent in the paint industry and in the preparation of several carbon compounds.

The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul-smelling liquid). It is known as the denaturation of alcohol. Nowadays, large quantities of ethanol are obtained by the hydration of ethene.

NOTE:

- The biological oxidation of methanol and ethanol in the body produces the corresponding aldehyde followed by the acid. At times the alcoholics, by mistake, drink ethanol mixed with methanol also called denatured alcohol.

In the body, methanol is oxidised first to methanal and then to methanoic acid, which may cause blindness and death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for the oxidation of aldehyde (HCHO) to acid is swamped allowing time for kidneys to excrete methanol.

► **APPLICATIONS OF PHENOLS:**

1. Phenols are used in plastic manufacturing industries.
The condensation reaction of phenol with acetone produces bisphenol which is extensively used in polymer industries to synthesis various epoxide resins and polycarbonates.
2. The polymerization reaction of phenol with formaldehyde is used to commercially prepare phenolic resins. The resulting resin is known as phenol-formaldehyde resin, commercially it is marketed by the name of bakelite.
3. Phenol is also used in the study and extraction of bio-molecules. Molecular biology finds the application of phenol in the extraction of nucleic acids from tissue samples for further investigations.
4. Phenol is also used in the cosmetic industry in the manufacturing of sunscreens, skin lightening creams and hair colouring solutions.



Key Facts

- 2, 3, 4, 5, 6-pentachlorophenol was being used as a wood preservative.
- 2,4-D and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) were the first herbicides produced commercially for weed control.
- 2,4,5-trichlorophenol acts as a leather and wood fungicide.
- 2,3,4,5,6-pentachlorophenol is used as an insecticide.
- 4-chloro-3,5-dimethylphenol is used as a household and hospital disinfectant.
- 4-chloro-3-methylphenol is used as an antiseptic and preservative.
- Phenol was the main ingredient of the Carbolic Smoke Ball, an ineffective device marketed in London in the 19th century as protection against influenza and other ailments.
- Injections of phenol were used as a means of individual execution by Nazi Germany during the Second World War.

Methods of Preparation and Properties of Ethers

Topic-2

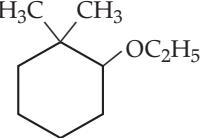
Concepts Covered • General formula of ether. • Physical properties of ethers.
 • Methods of preparation of ethers. • Nomenclature of ethers • Chemical properties of ethers.
 • Rearrangement in ring



Revision Notes

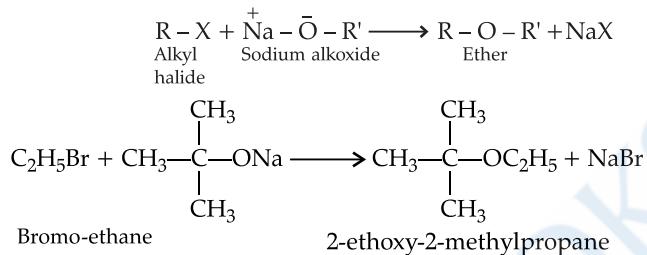
- **Ethers:** Compounds with general formula $C_nH_{2n+2}O$. They are represented by general structure, R-O-R'.
- **Nomenclature of Ethers:** Ethers are named from names of alkyl/aryl/groups written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups 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 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
$CH_3OCH_2CH_2CH_2CH_3$	Methyl n-butyl ether	1-Methoxybutane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene
$C_2H_5—O—C_6H_5$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6—CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O—CH—CH_3$ CH_3	Methyl isopropyl ether	2-Methoxypropane
$C_6H_5—O—CH_2—CH_2—CH—CH_2$ CH_3	Phenyl isopentyl ether	3-Methylbutoxybenzene

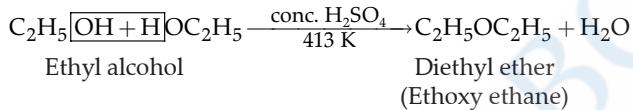
$\text{CH}_3\text{O} - \text{CH}_2 - \text{CH}_2 - \text{OCH}_3$	—	1, 2-Dimethoxyethane
	—	2-Ethoxy-1, 1-dimethylcyclohexane

► **Methods of Preparation of Ethers:**

(i) **Williamson's synthesis:** When alkyl halide reacts with sodium alkoxide, ethers are formed. e.g.,

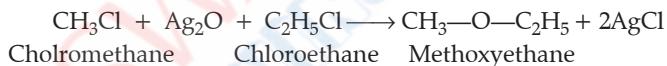
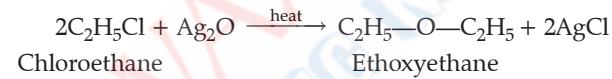


(ii) **Dehydration of alcohols:** Alcohols are dehydrated to ethers in presence of concentrated sulphuric acid at 413 K. The reaction involves the removal of one molecule of water from two moles of alcohols.



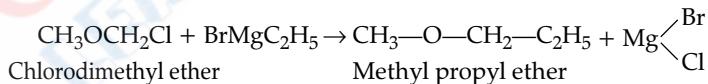
Alcohols can also be dehydrated by heating with alumina at 523 K and high pressure. This method is not suitable for preparation of unsymmetrical ethers.

(iii) **Heating alkyl halides with dry silver oxide:** Ethers can be prepared by heating alkyl halides with dry silver oxide (Ag_2O).

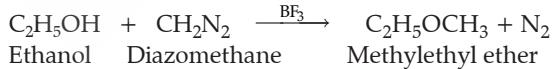


Mixed ethers or unsymmetrical ethers can be prepared by this method.

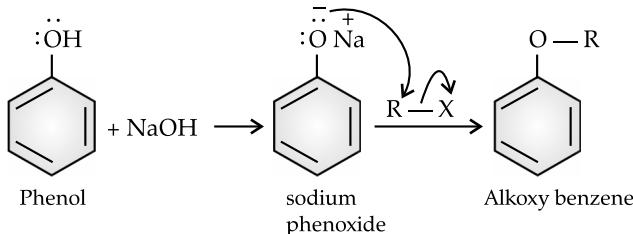
(iv) **Reaction of lower halogenated ethers with Grignard reagent:** Higher homologous ethers can be prepared by action of Grignard reagent on lower halogenated ethers.



(v) **Action of diazomethane on alcohols:** Methyl ethers can be prepared by action of diazomethane on alcohols in the presence of catalysts like BF_3 .



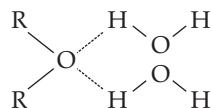
(vi) **From phenol:**



► **Physical Properties:**

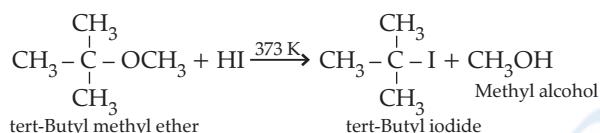
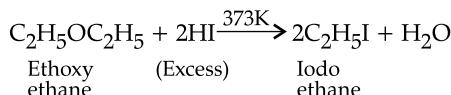
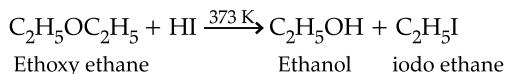
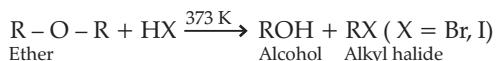
(i) Colourless, pleasant smelling and volatile liquids.

- (ii) Lower boiling points than alcohols.
 - (iii) Solubility is comparable to those of corresponding alcohols due to the ability of their molecules to form hydrogen bond with water molecules.

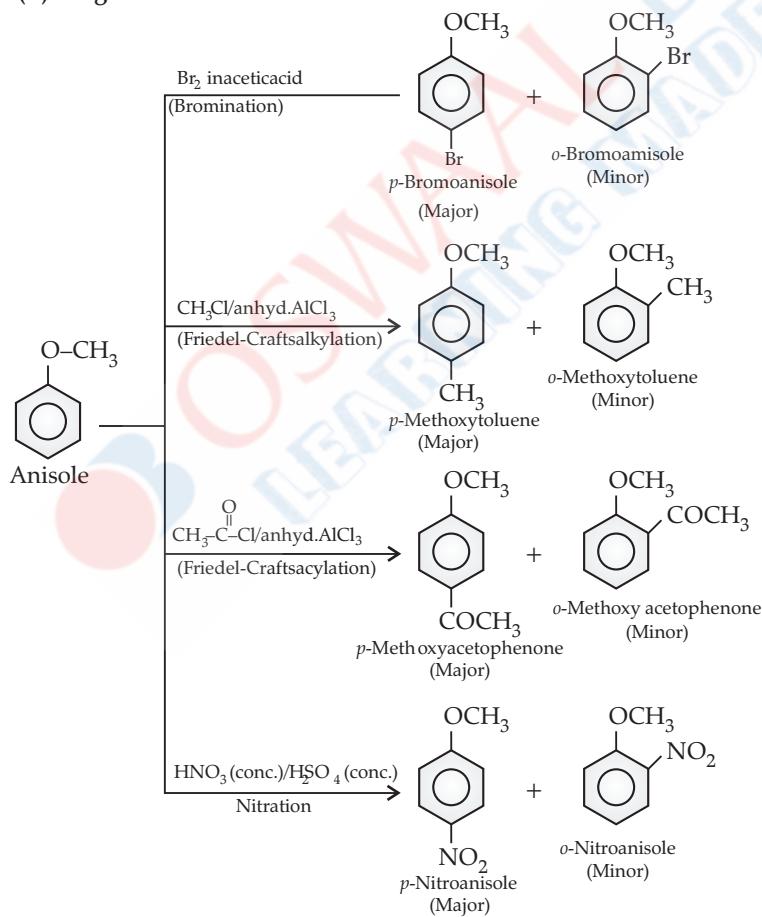


► Chemical properties:

(i) Cleavage with halogen acid:



(ii) Ring substitution in aromatic ethers:



► APPLICATIONS OF ETHERS:

- As ethers are flammable and volatile they are used in cold weather to start a diesel or petrol engine. It is also used as a refrigerant.
 - Ethers are used as an antiseptic

- Ethers are used as disinfectants.
- Diethyl ether is used as an anaesthetic in hospitals. Anaesthetics help in making people go to sleep or become unconscious during surgery.
- Diethyl ether can be used as an anaesthetic, it is an appealing recreational drug.
- It is a controlled substance and can be inhaled by the users to induce euphoria and sedation. But overdose of diethyl ether can cause respiratory paralysis and also result in death.

CHAPTER-8

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

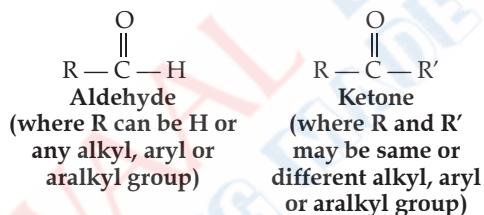
Topic-1

Aldehydes and Ketones

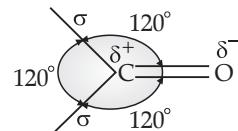
Concepts Covered • Organic compounds containing carbonyl groups, Preparation of aldehydes and ketones, their physical and chemical properties, test for their presence, aldol condensation, Cannizaro reaction.

Revision Notes

- **Carbonyl group:** The functional group $\text{C}=\text{O}$ is called carbonyl group. Organic compounds containing carbonyl group are aldehydes and ketones. The general formulae of these compounds are as follows:



- **Structure of Carbonyl Group:**



- 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. e.g., CH_3CHO , $\text{C}_2\text{H}_5\text{CHO}$, $\text{C}_6\text{H}_5\text{CHO}$, etc.
- 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., CH_3COCH_3 , $\text{CH}_3\text{COC}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$, etc.
- **Nomenclature of Aldehydes and Ketones:**

Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$		
General formula: $\text{R}-\text{C}=\text{O}-\text{H}$, where $\text{R} = \text{C}_n\text{H}_{2n+1}$			
Structural formula	Condensed formula	Common name	IUPAC name
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$	HCHO	Formaldehyde	Methanal
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{H} \end{array}$	CH ₃ CHO	Acetaldehyde	Ethanal

$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$	$\text{CH}_3\text{CH}_2\text{CHO}$	Propionaldehyde	Propanal
$\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	Butyraldehyde	Butanal
$\begin{array}{c} \text{CH}_3-\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H} \\ \\ \text{CH}_3 \end{array}$	$(\text{CH}_3)_2\text{CHCHO}$	Isobutyraldehyde	2-Methylpropanal
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$	$\text{CH}_3(\text{CH}_2)_3\text{CHO}$	Valeraldehyde	Pentanal
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H} \\ \\ \text{CH}_3 \end{array}$	$(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$	Isovaleraldehyde	3-Methylbutanal
$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H} \\ \\ \text{CH}_3 \end{array}$	$(\text{C}_2\text{H}_5)\text{C}(\text{CH}_3)\text{CHCHO}$	α -Methylbutyraldehyde	2-Methylbutanal

Ketones	$\text{General formula: R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}'$ and $\text{R}' = \text{C}_n\text{H}_{2n'+1}$ ($n = n'$, $n \neq 0$)		
Structural Formula	Condensed formula	Common name	IUPAC name
$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$	CH_3COCH_3	Acetone	Propanone
$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_3$	$\text{CH}_3\text{COCH}_2\text{CH}_3$	Ethyl methyl ketone	Butan-2-one or Butanone
$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl <i>n</i> -Propyl ketone	Pentan-2-one
$\begin{array}{c} \text{CH}_3-\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	$(\text{CH}_3)_2\text{CHCOCH}(\text{CH}_3)_2$	Diisopropyl ketone	2, 4-Dimethyl pentan-3-one
$\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	Diethyl ketone	Pentan-3-one
$\begin{array}{c} \text{CH}_3-\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$(\text{CH}_3)_2\text{CHCOCH}_3$	Isopropyl methyl ketone	3-Methylbutan-2-one
$\begin{array}{c} \text{CH}_3-\text{C}=\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	Mesityl oxide	4-Methylpent-3-en-2-one



Key Facts

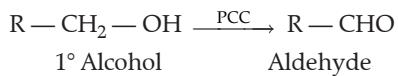
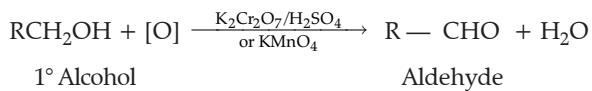
More about aldehydes:

- (a) Aldehydes are a family of reactive, organic compounds that occur in natural products like cinnamon bark (cinnamaldehyde) and vanilla bean (vanillin) and also can be manufactured in laboratories.
- (b) Aldehydes can be obtained as by-products in drinking water disinfection processes, particularly in Ozonisation.

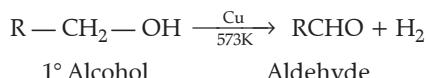
► **Methods of preparation of Aldehydes and Ketones:**

(a) **Preparation of Aldehydes:**

(i) **By oxidation of primary alcohols:** Aldehydes can be prepared by the oxidation of primary alcohols.

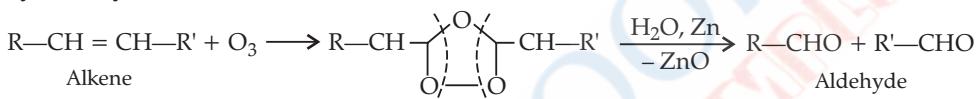


(ii) **By dehydrogenation of alcohols:**

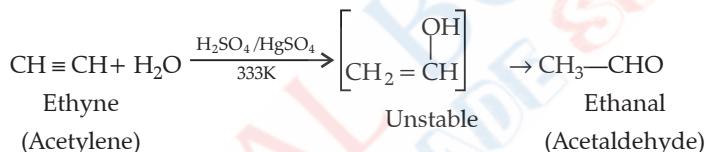


(iii) **From hydrocarbons:** Aldehydes can be prepared either by ozonolysis of alkenes or by hydration of alkynes.

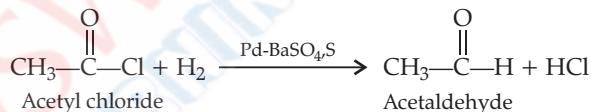
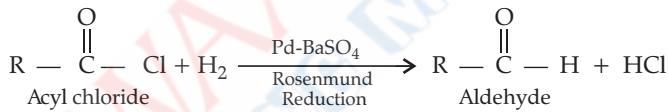
(a) **By ozonolysis of alkenes:**



(b) **By hydration of alkynes:**



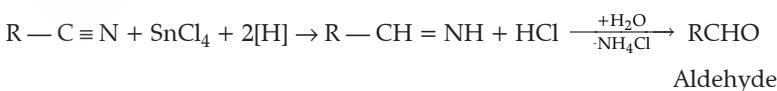
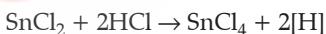
(iv) **From acyl chloride:**



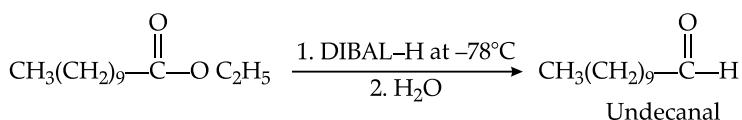
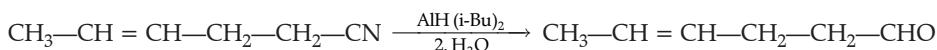
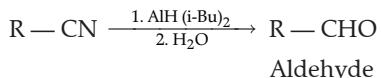
Key Word

Hydrocarbons: The organic chemicals which are made up of only carbon and hydrogen.

(v) **From nitriles and esters:**



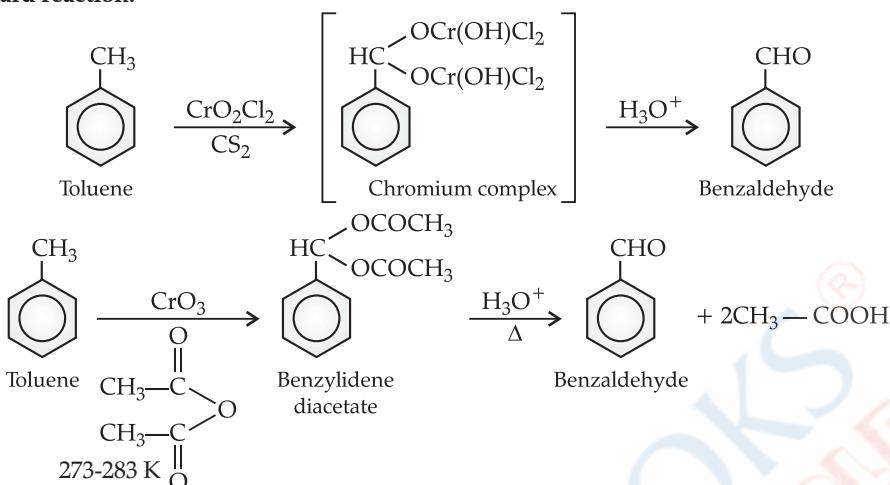
Stephen reaction:



(b) Preparation of Benzaldehyde:

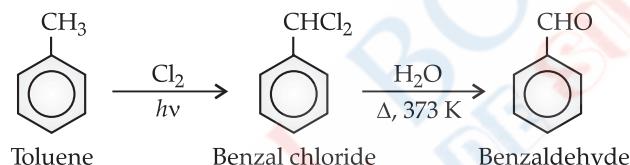
(i) By oxidation of toluene:

Etard reaction:

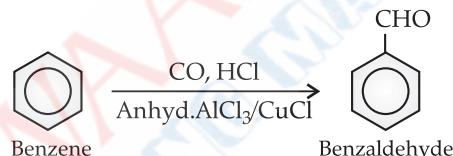


(ii) By side chain chlorination followed by hydrolysis:

Commercial method of preparation

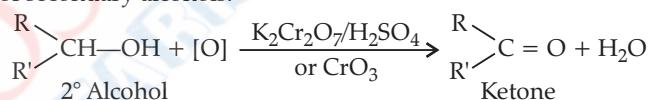


(iii) By Gattermann - Koch reaction:

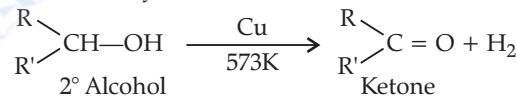


(c) Preparation of Ketones:

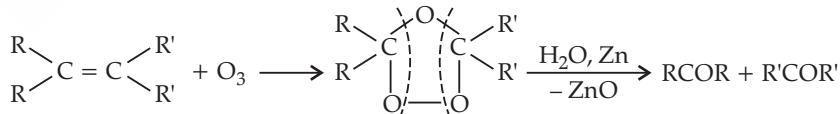
(i) By oxidation of secondary alcohols:



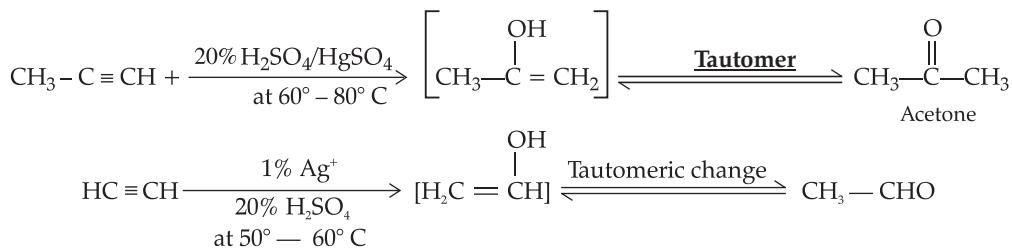
(ii) By dehydrogenation of secondary alcohols:



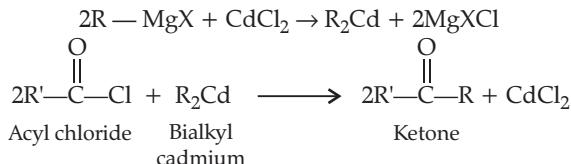
(iii) By ozonolysis of alkenes:



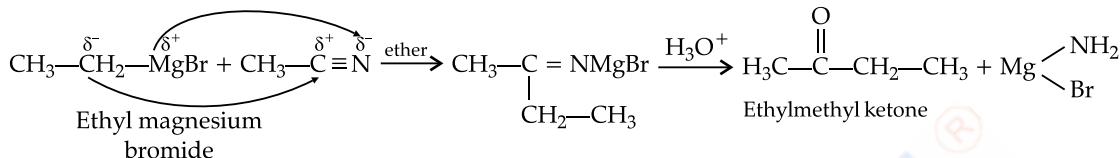
(iv) By hydration of alkynes: (By Kucherov's reaction)



(v) From acyl chlorides:



(vi) From nitriles:

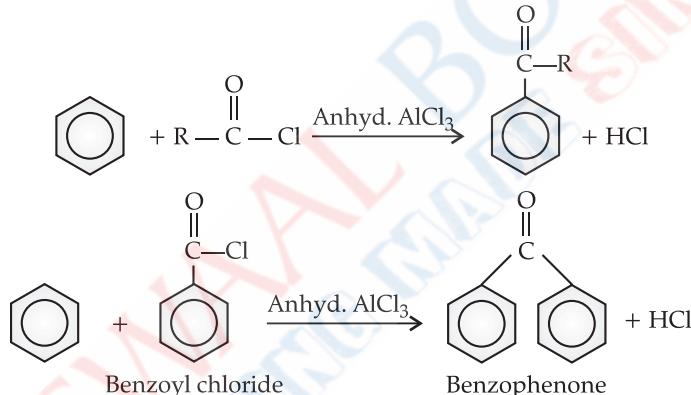


Key Word

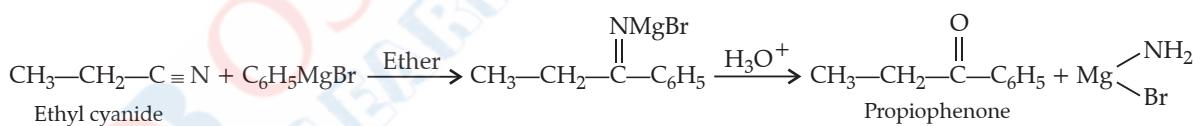
Tautomer: The type of isomerism in which the isomers change into one another with great ease so that they exist together in equilibrium.

(d) Preparation of Aromatic ketones:

(i) By Friedel-Crafts acylation:



(ii) From nitriles:



► Physical properties of Aldehydes and Ketones:

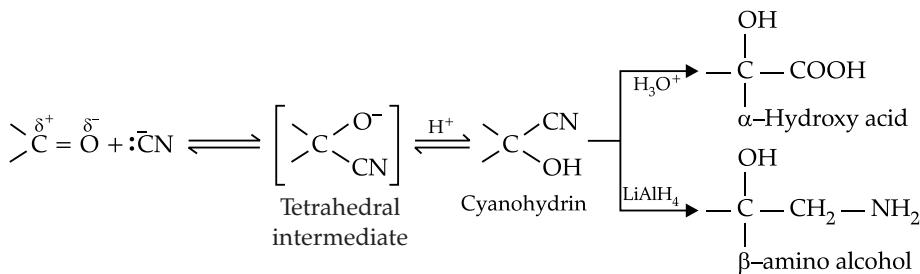
- (i) Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have a pleasant smell.
 - (ii) Both of these have relatively high boiling point as compared to hydrocarbons of comparable molecular masses due to presence of polar carbonyl group. But they have lower boiling point than alcohols of comparable molecular masses.
 - (iii) The lower members of aldehydes and ketones (up to four carbon atoms) are soluble in water due to hydrogen bonding.

- **Chemical properties of Aldehydes and Ketones:** Aldehydes and ketones are highly reactive compounds. Both undergo nucleophilic addition reaction.

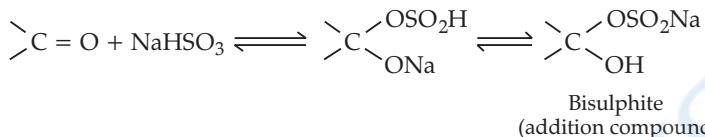
Nucleophilic addition reactions:

(i) Addition of hydrogen cyanide (HCN):

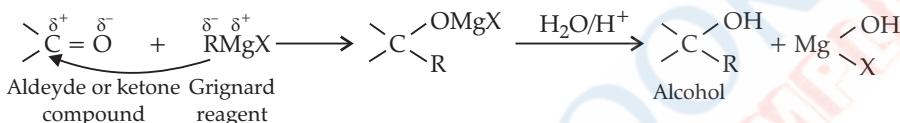




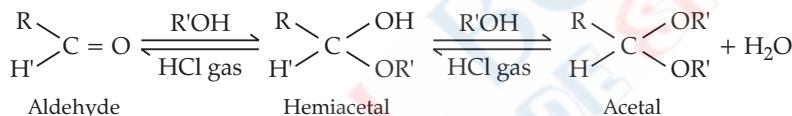
(ii) Addition to sodium hydrogen sulphite:



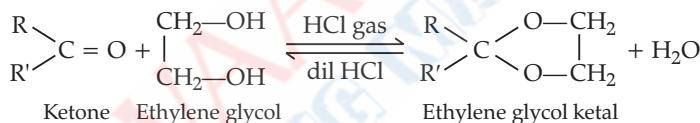
(iii) Addition of Grignard reagent:



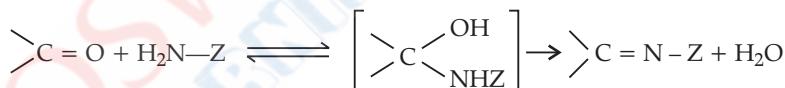
(iv) Addition of alcohols:



Ketones react with dihydric alcohols to give ketals.



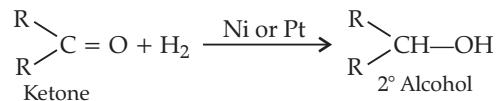
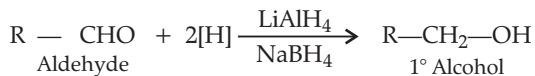
(v) Addition of ammonia and its derivatives:



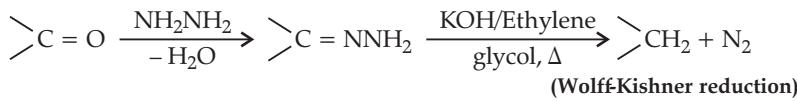
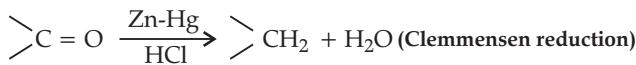
where, Z = Alkyl, aryl, -OH, -NH₂, C₆H₅NH-, -NHCONH₂, etc.

► Reduction:

(i) Reduction to alcohols:



(ii) Reduction to hydrocarbons:





Mnemonics

Concept: To memorise reagents used for converting $\text{C}=\text{O}$ to alkanes in Clemmenson and Wolff-Kishner

Mnemonics: Can Zebra WOo Nightingale

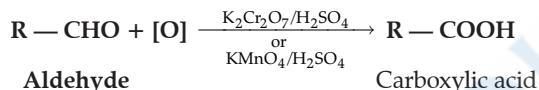
Interpretations:

To memorise regents used for converting $\text{C}=\text{O}$ to alkanes

C and Z- Clemmenson reduction $\rightarrow \text{Zn-Hg/HCl}$

W and N- Wolff- Kishner reduction $\rightarrow \text{N}_2\text{NH}_2/\text{OH}^-$

- 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**.

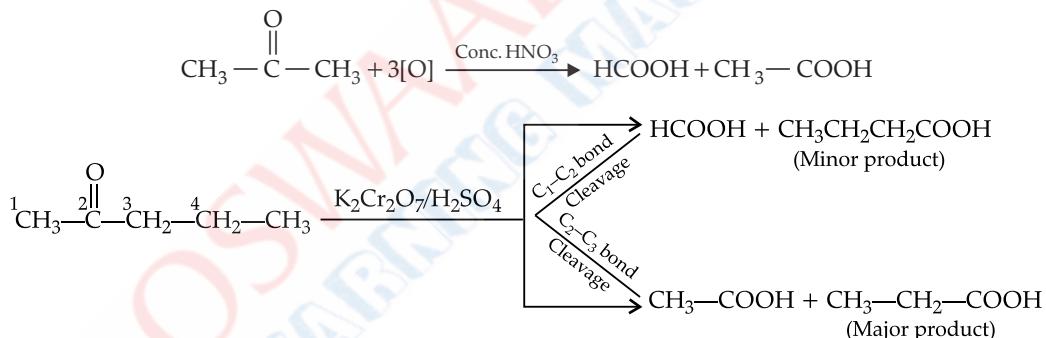


Key Word

Tollen's reagent: Ammonical silver nitrate solution with which aldehyde gives confirmatory silver mirror test.

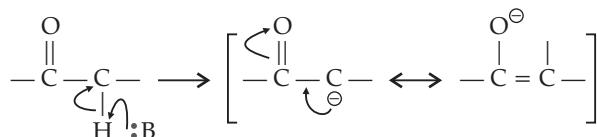
Fehling's Solution: Fehling A (aq. Copper sulphate) solution + Fehling B solution (alk. Sodium potassium tartarate). Aliphatic aldehydes reduce it to give reddish brown precipitate, which is a confirmatory test for aliphatic aldehydes.

Ketones undergo oxidation under vigorous conditions with cleavage of carbon bond.

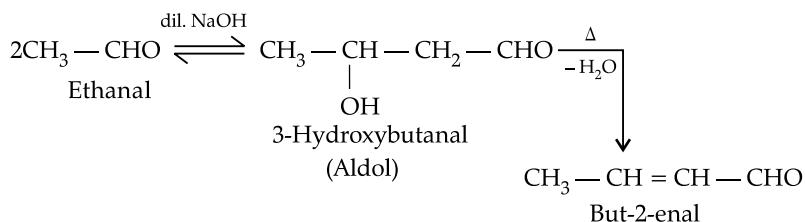


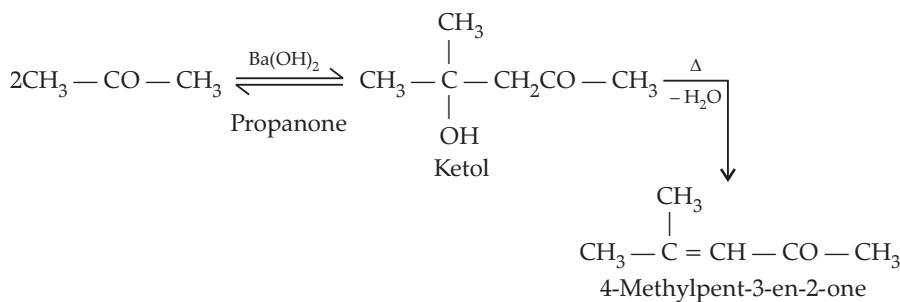
- Reaction due to α -hydrogen:

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.

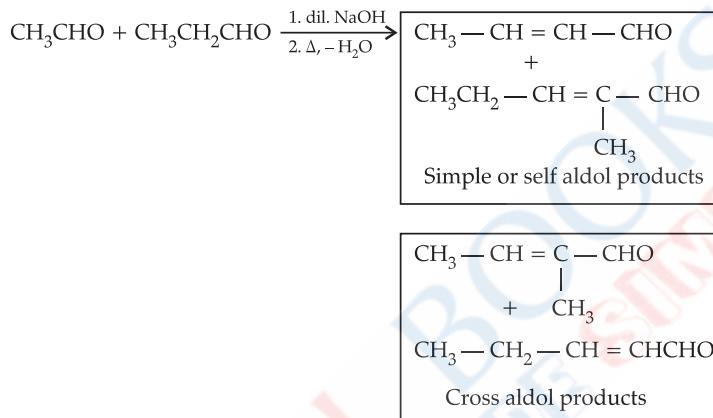


- (i) **Aldol condensation:** Aldehydes and ketones having at least one α -hydrogen react in presence of dilute alkali to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol).

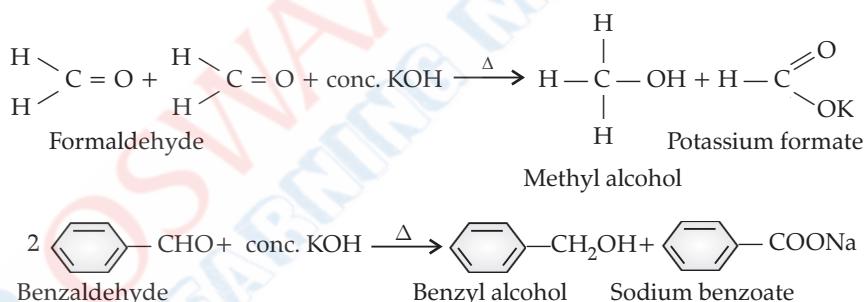




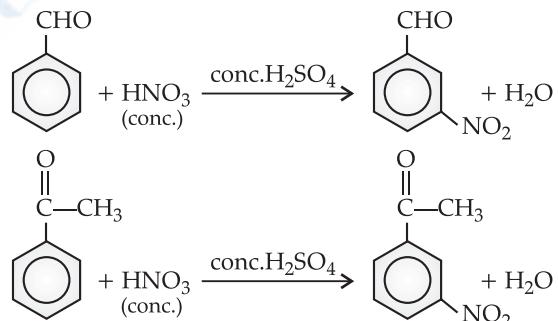
(ii) **Cross aldol condensation:** When two different aldehydes and/or ketones undergo aldol condensation, it is called cross aldol condensation.



(iii) Cannizzaro Reaction: Aldehydes undergo self oxidation and reduction on heating with conc. alkali. The aldehydes which do not have a-hydrogen undergo this reaction.



(iv) Electrophilic substitution reaction:



► Test for Aldehydes and Ketones:

- (i) Both give iodoform test when one α -hydrogen is present.
(ii) **Fehling's test :** Aliphatic aldehydes reduce the Fehling's solution to red cuprous oxide.

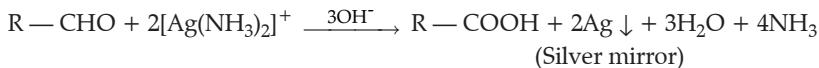
$$\text{R}-\text{CHO} + 2\text{CuO} + 5\text{OH}^- \rightarrow \text{R}-\text{COOH} + \text{Cu}_2\text{O} \downarrow + 3\text{H}_2\text{O}$$

(red ppt.)

Aromatic aldehydes do not respond to this test.

(iii) Ketones are not oxidised by Tollen's reagent.

Aldehydes form silver mirror with ammonical silver nitrate (Tollen's reagent) solution.



Mnemonics

Concept: Cannizaro's Reaction

Mnemonics: CRAKN Reviews

Interpretations: Canizzaro Reaction is given by Aldehydes and Ketones having no α -H atom.

Concept: To distinguish Aldehydes from Ketones. Detection tests - Tollen's and Fehling's

Mnemonics: TASty FAAli Redbrown IMeLY

Interpretations: TASty → Tollen's test, Aldehyde group, Silver mirror

FAAli → Fehling's test, Aliphatic Aldehyde

Red brown → Red brown ppt in Fehling's test

IMeLY → Iodoform test, Methyl group Linked to $\text{C}=\text{O}$ group, Yellow ppt.

► **Uses of aldehydes and ketones:**

- Aldehydes and ketones are used as solvents (such as acetone and ethyl methyl ketone), starting materials and reagents in the synthesis of several products in chemical industries.
- Formaldehyde which is known as formalin (40%) solution, is used to preserve biological specimens. It is also used to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products.
- Benzaldehyde is used in perfumery and in dye industries.
- Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc., are well known for their odours and flavours.

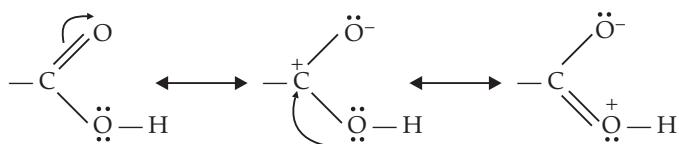
Carboxylic Acids

Topic-2

Concepts Covered • Nomenclature of carboxylic acids, • Methods of preparation of carboxylic acids, • Physical properties of carboxylic acids, • Chemical properties of carboxylic acids, • Uses of carboxylic acids.

Revision Notes

- Carboxylic acids are those compounds which have $\begin{matrix} \text{O} \\ || \\ -\text{C}-\text{OH} \end{matrix}$ group. The carboxyl group is made up of carboxyl, $>\text{C}=\text{O}$ and hydroxyl, $-\text{OH}$ group, hence, its name is carboxyl group.
- **Structure of Carboxyl group:** The bonds to the carboxyl carbon lie in one plane separated by about 120° . The carboxylic carbon is less electrophilic than carbonyl carbon due to possible resonance structures.

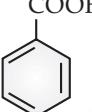
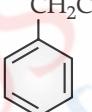
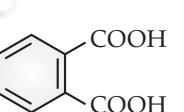


- **Nomenclature of carboxylic acids:** Derived by replacing terminal 'e' of the alkane with 'oic acid'.

Carboxylic acids	$\begin{matrix} \text{O} \\ \\ \text{R}-\text{C}-\text{OH} \end{matrix}$, where $\text{R} = \text{C}_n\text{H}_{2n+1}$		
Structural formula	Condensed formula	Common name	IUPAC name

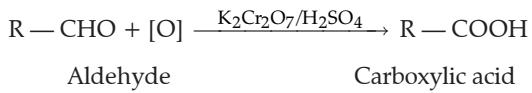
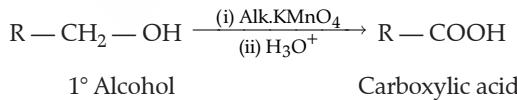
$\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$	HCOOH	Formic acid	Methanoic acid
$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$	CH_3COOH	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$	$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	Butyric acid	Butanoic acid
$\begin{array}{c} \text{CH}_3-\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	$(\text{CH}_3)_2\text{CHCOOH}$	Isobutyric acid	2-Methylpropanoic acid

Dicarboxylic Acids

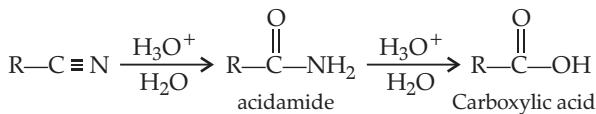
$\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \\ (\text{Oxalic acid}) \\ \text{Ethane-1, 2-dioic acid} \end{array}$	$\begin{array}{c} \text{CH}_2-\text{COOH} \\ \\ \text{CH}_2-\text{COOH} \\ (\text{Malonic acid}) \\ \text{Propane-1, 3-dioic acid} \end{array}$	$\begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{COOH} \\ (\text{Succinic acid}) \\ \text{Butane-1, 4-dioic acid} \end{array}$	$\begin{array}{c} \text{CH}_2-\text{CH}_2\text{COOH} \\ \\ \text{CH}_2-\text{CH}_2\text{COOH} \\ (\text{Glutaric acid}) \\ \text{Pentane-1, 5-dioic acid} \end{array}$
$\begin{array}{c} \text{CH}_2\text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{CH}_2\text{COOH} \\ (\text{Adipic acid}) \\ \text{Hexane-1, 6-dioic acid} \end{array}$	$\begin{array}{c} \text{CH}_2-\text{COOH} \\ \\ \text{CH}-\text{COOH} \\ \\ \text{CH}_2-\text{COOH} \\ (\text{Propene-1, 2, 3-tricarboxylic acid}) \end{array}$	$\begin{array}{c} \text{CH}_3-\text{CH}=\text{CH}-\text{COOH} \\ (\text{Crotonic acid}) \\ \text{But-2-enoic acid} \end{array}$	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{CH}-\text{COOH} \\ (\text{Lactic acid}) \\ \text{2-Hydroxypropanoic acid} \end{array}$
			
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

► Methods of preparation of Carboxylic acids:

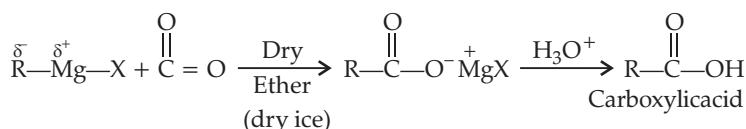
(i) By oxidation of primary alcohols and aldehydes:



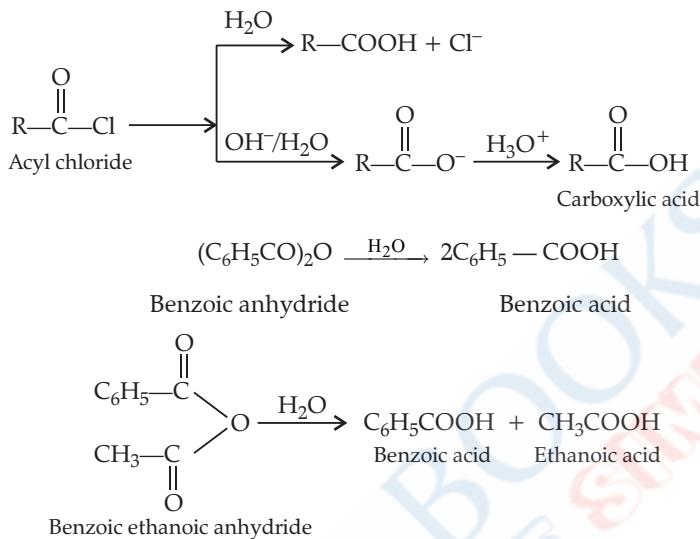
(ii) From nitriles and amides:



(iii) From Grignard reagent:



(iv) From hydrolysis of acyl halide and acid anhydrides:



(v) By hydrolysis of esters:

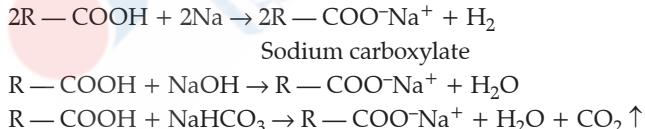


► Physical properties of Carboxylic acids:

- (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 acids have higher boiling point due to their ability to form intermolecular hydrogen bonding.
 - (iv) Carboxylic acid with even number of carbon atoms have higher melting points than those with odd number of carbon atoms above or below it.

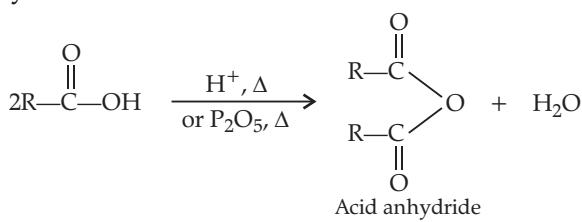
Chemical Properties: Chemical properties of carboxylic acids are classified as follows :

- (i) Reaction involving cleavage of O — H bond: Reactions with metals and alkalis.

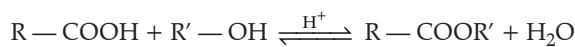


- ### (ii) Reactions involving cleavage of C — OH Bond:

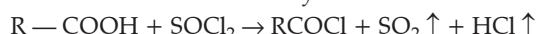
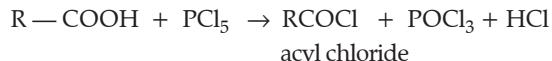
- (a) Formation of anhydride:**



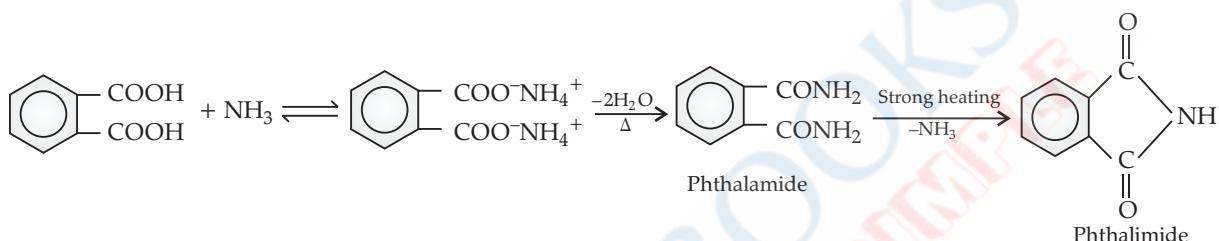
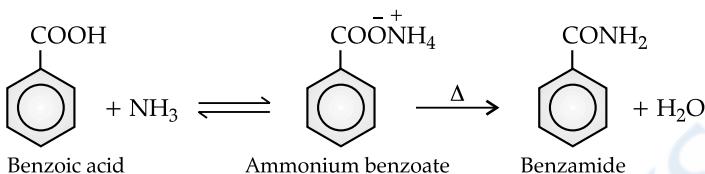
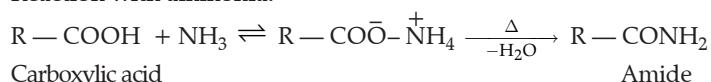
- (b) Esterification:**



(c) Reaction with PCl_5 , PCl_3 and SOCl_2

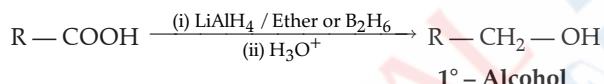


(d) Reaction with ammonia:

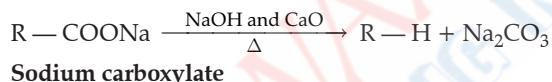


(iii) Reduction involving -COOH group:

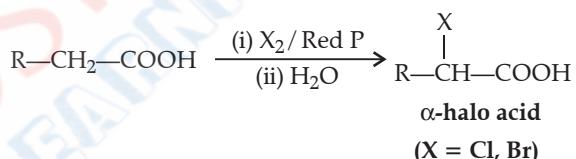
(a) Reduction:



(b) Decarboxylation:

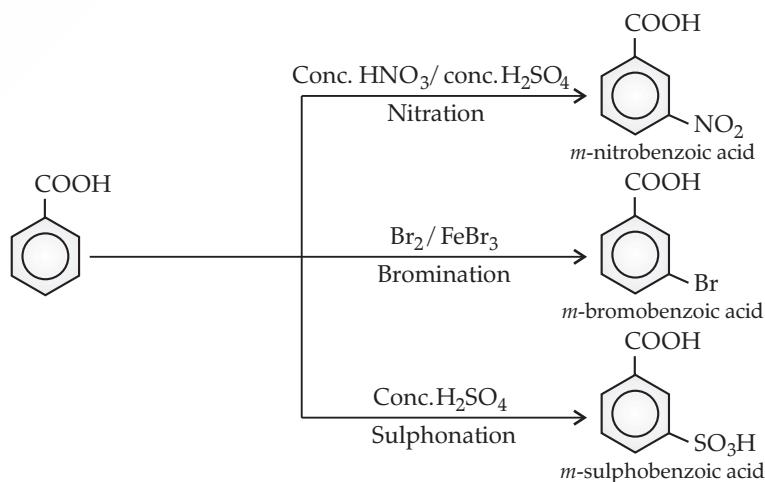


(c) Halogenation:



This reaction is known as Hell-Volhard-Zelinsky(HVZ) reaction.

(iv) Electrophilic Substitution Reaction:



Key Facts

The first part of the ester name comes from the name of the alcohol. The second part of the name comes from the name of the carboxylic acid.

Apple, pear, cherry, mixed fruits are different flavours used by mixing alcohol and carboxylic acid.

Enjoy the flavours:

Carboxylic acid	Propanoic acid	Butanoic acid	Pentanoic acid
Alcohol	Apple		Mixed fruit
Methanol	Methyl propanoate		Methyl pentanoate
	pear	Cherry	Propanoic acid
Ethanol	Ethyl propanoate	Methyl butanoate	Butanoic acid

► **Uses of Carboxylic acids:**

- (i) Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.
- (ii) Ethanoic acid is used as a solvent and as vinegar in the food industry.
- (iii) Hexanedioic acid is used in the manufacture of nylon-6,6. Esters of benzoic acid are used in perfumery.
Sodium benzoate is used as a food preservative.
- (iv) Higher fatty acids are used in the manufacturing of soaps and detergents.

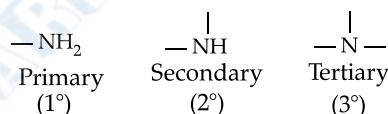
CHAPTER-9

AMINES

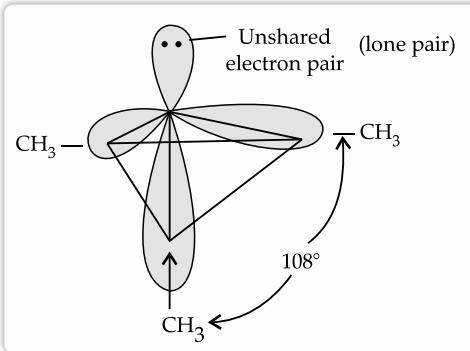


Revision Notes

- **Amines:** Amines are considered as amino derivatives of hydrocarbons or alkyl derivatives of ammonia. In these compounds, one, two or three hydrogen atoms are replaced by alkyl or aryl groups. Aliphatic amino compounds are called amino alkanes and aromatic amines are called amino arenes. e.g., CH_3NH_2 , $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NH}_2$, etc.
- **Classification of amines:**



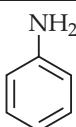
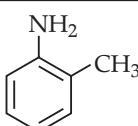
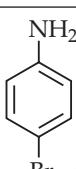
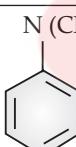
► **Structure of amine:**



Pyramidal shape of trimethylamine

Nitrogen orbitals in amines are sp^3 hybridized and the geometry is pyramidal. Due to the presence of unshared pair of electrons, the angle C—N—E (where E is C or H) is less than 109.5°.

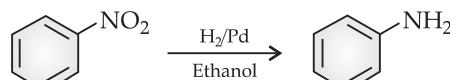
► Nomenclature of some Alkylamines and Arylamines:

Amine	Common name	IUPAC name
$\text{CH}_3\text{—CH}_2\text{—NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—NH}_2$	<i>n</i> -Propylamine	Propan-1-amine
$\begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\ \\ \text{NH}_2 \end{array}$	Isopropylamine	Propan-2-amine
$\begin{array}{c} \text{CH}_3\text{—N—CH}_2\text{—CH}_3 \\ \\ \text{H} \end{array}$	Ethylmethylamine	N-Methylethanamine
$\begin{array}{c} \text{CH}_3\text{—N—CH}_3 \\ \\ \text{CH}_3 \end{array}$	Trimethylamine	N, N-Dimethylmethanamine
$\text{C}_2\text{H}_5\text{—N}\left(\text{C}_2\text{H}_5\right)\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$	N, N-Diethylbutylamine	N, N-Diethylbutan-1-amine
$\text{NH}_2\text{—CH}_2\text{—CH}=\text{CH}_2$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2\text{—}(\text{CH}_2)_6\text{—NH}_2$	Hexamethylenediamine	Hexane-1, 6-diamine
	Aniline	Aniline or Benzenamine
	<i>o</i> -Toluidine	2-Aminotoluene
	<i>p</i> -Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N, N-Dimethylaniline	N, N-Dimethylbenzenamine

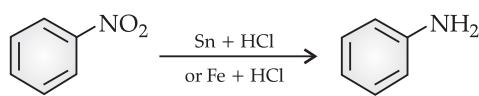
► Preparation of Amines:

(i) By reduction of nitro compounds:

(a)



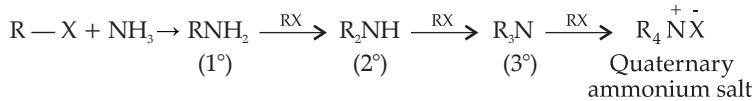
(b)



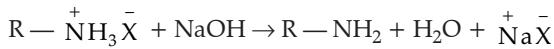
(c)



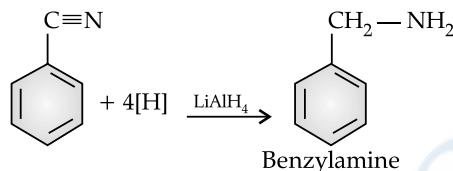
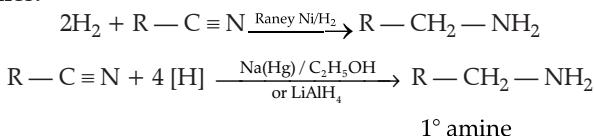
(ii) By ammonolysis of alkyl halides: It is a type of nucleophilic substitution reaction.



The free amine can be obtained from the ammonium salt by treatment with a strong base:

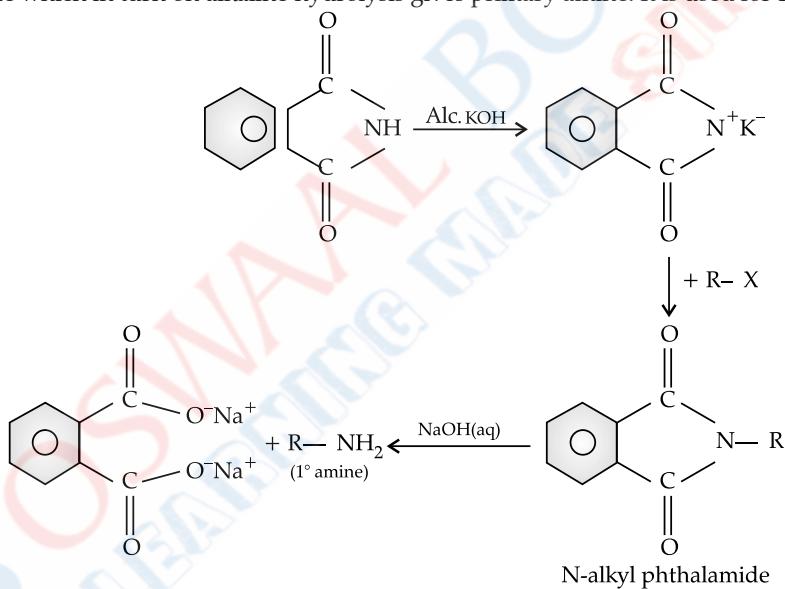


(iii) By reduction of nitriles:

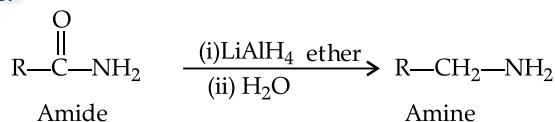


(iv) Gabriel phthalimide synthesis:

Phthalimide gives potassium salt with ethanolic KOH, which on heating with alkyl halide forms N-alkyl phthalimide which in turn on alkaline hydrolysis gives primary amine. It is used for 1° amine synthesis.

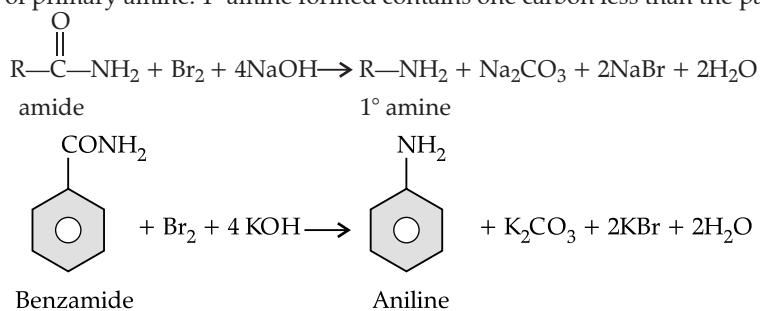


(v) By reduction of amides:



(vi) By Hoffmann bromamide degradation reaction:

Treating amide with bromine in aqueous or ethanolic NaOH solution, results in degradation of amide leading to formation of primary amine. 1° amine formed contains one carbon less than the parent amide.



► **Physical properties:**

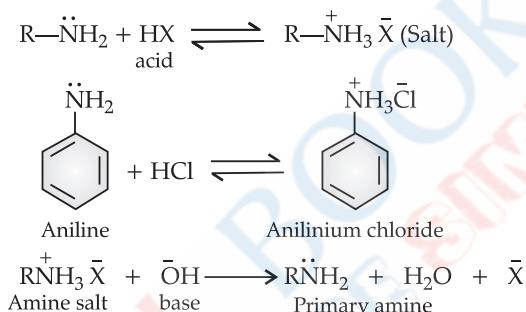
- (i) Lower members are combustible gases, members from C₃ to C₁₁ are volatile liquids and C₁₂ onwards are solid.
Lower aromatic amines are liquids.
- (ii) Pure amines are colourless but develop colour on keeping in air for long time.
- (iii) Boiling point increases with an increase in molecular weight. The order of boiling points of isomeric amines:
Among isomers, boiling point decreases with branching.
Primary > Secondary > Tertiary.
- (iv) Lower members are readily soluble in water which decreases in water and increases in organic solvents with an increase in molecular weight.

► **Chemical properties:**

Reactions due to alkyl group:

Basic Strength of Amines:

Amines are basic in nature because they can undergo **protonation** due to the presence of lone pair of electrons on nitrogen atom of —NH₂ group.



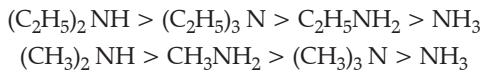
 **Key Word**

Protonation: Addition of proton or hydrogen cation.

Due to presence of the alkyl group, reaction of amines with proton helps to share the proton of the acid and the ammonium ion formed is stabilized by dispersal of positive charge by +I effect of alkyl group. Thus, alkylamines are stronger bases than ammonia. The basic nature of aliphatic amines should increase with increase in the number of alkyl groups. The order of basicity of amines in the gaseous phase follows the expected order:

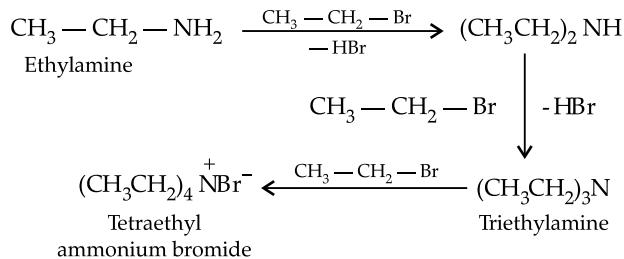
Tertiary amine > Secondary amine > Primary amine > NH₃.

The inductive effect, solvation effect and steric hindrance of the alkyl group decide the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

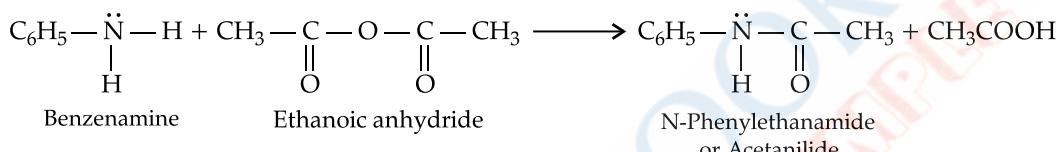
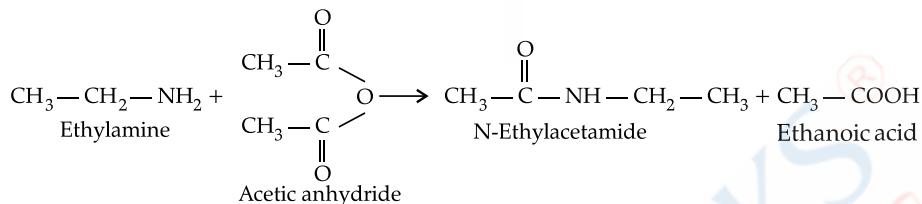
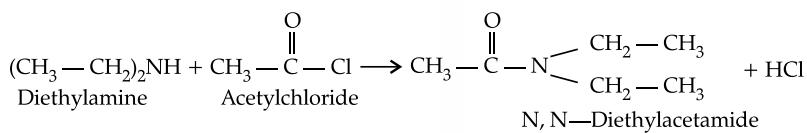
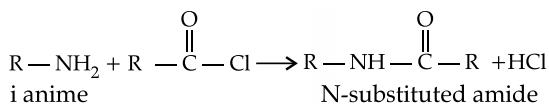


As the —NH₂ group is attached directly to the benzene ring in aryl amines, this results in conjugation of the lone pair of nitrogen with the benzene ring and thus making it less available for protonation. Thus, proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like —OCH₃, —CH₃ increase basic strength whereas electron withdrawing groups like —NO₂, —SO₃H, —COOH, —X decrease the basic strength.

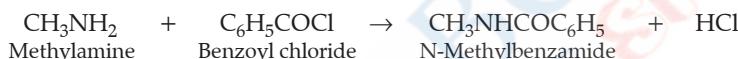
(i) **Alkylation:**



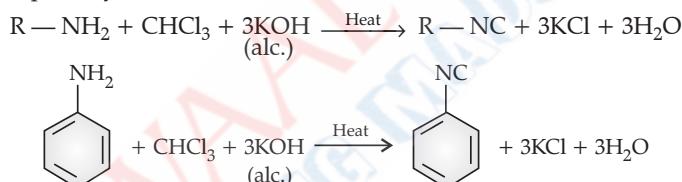
(ii) Acylation:



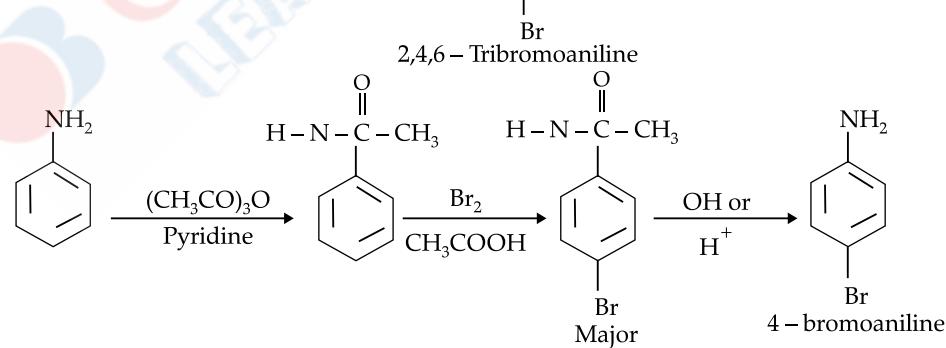
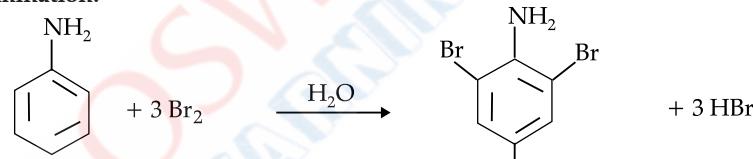
Benzoylation:



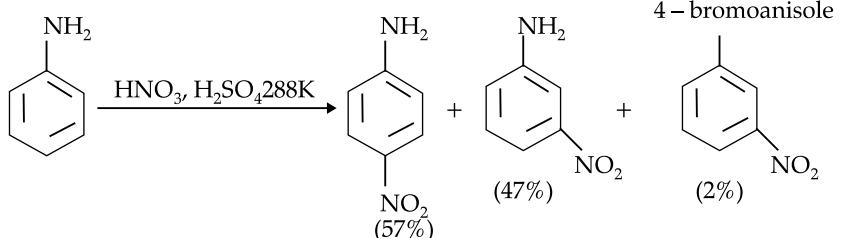
(iii) **Carbylamine reaction:** Secondary and tertiary amines do not give this reaction. This reaction is used to give a positive test for primary amines.



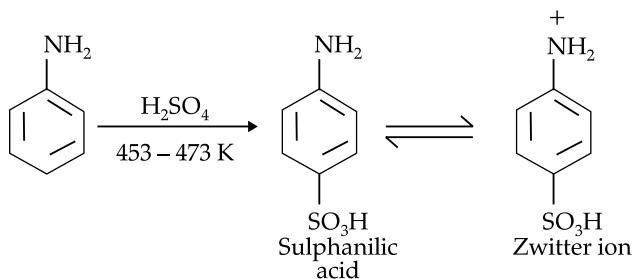
(iv) Bromination:



(v) Nitration



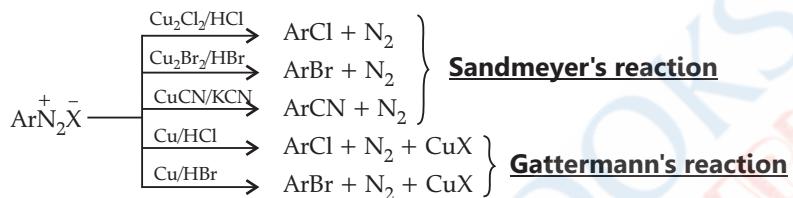
(vi) Sulphonation:



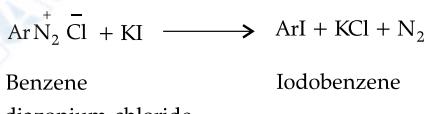
(vii) Chemical properties:

(a) Reactions involving displacement of nitrogen:

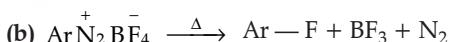
(i) Replacement by halide or cyanide ion-

**Mnemonics****Concept:** Sandmeyer's reaction**Mnemonics:** Diazo and Cupro Came Barking to Sandy in CorNer.**Interpretation:**Diazonium salt \longrightarrow in presence of Cu (I)ion \longrightarrow ArCl/ArBr/ArCNDiazo \longrightarrow Cupro \longrightarrow Cl, Br, CN \longrightarrow Sandmeyer's reaction.**Key Word****Sandmeyer's reaction:** Introduction of nucleophiles Cl^- , Br^- , CN^- to benzene ring in presence of Cu(I) ion.**Gattermann's reaction:** Introduction of Cl^- , Br^- to benzene ring by treating diazonium salts with halogen acids. .

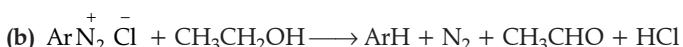
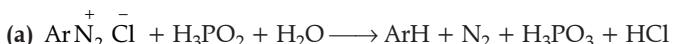
(ii) Replacement by iodide ion-



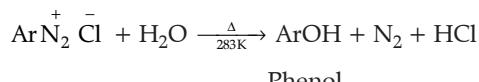
(iii) Replacement by fluoride ion— (Balz-Schiemann reaction)



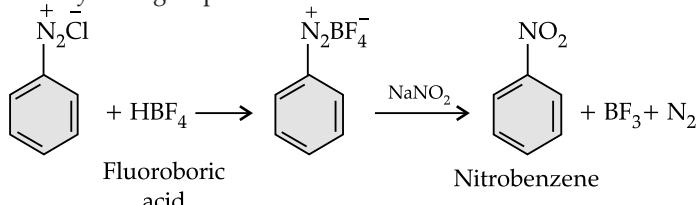
(iv) Replacement by H—



(v) Replacement by hydroxyl group—

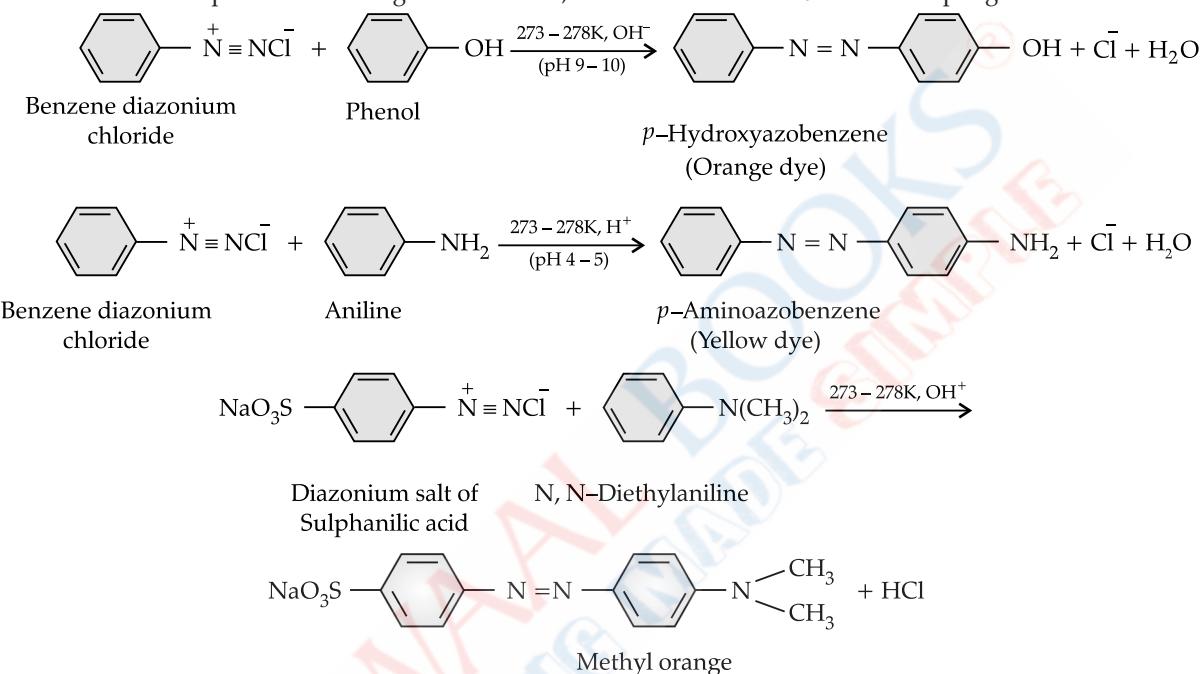


(vi) Replacement by nitro group—



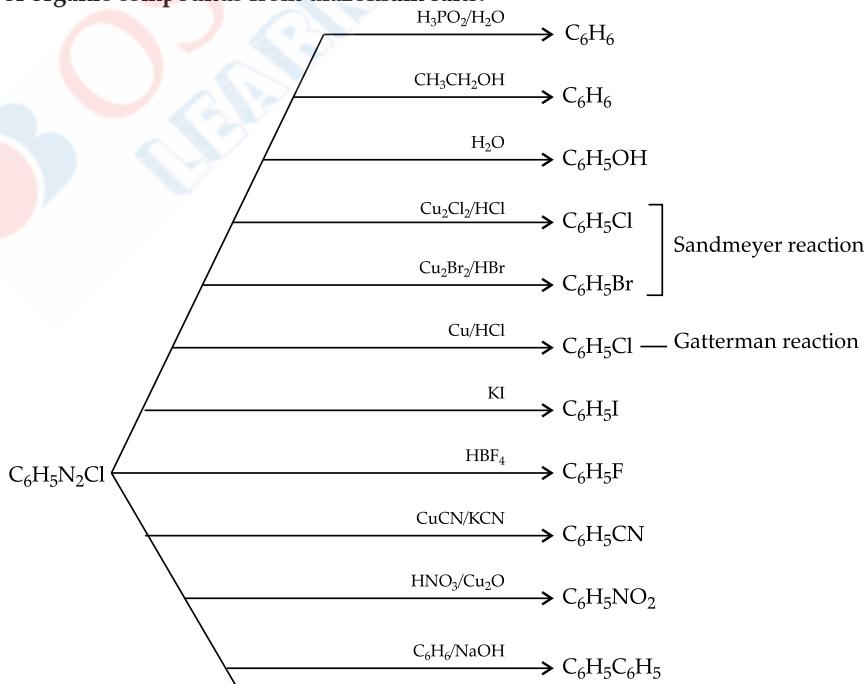
(b) Reactions involving retention of diazo group:

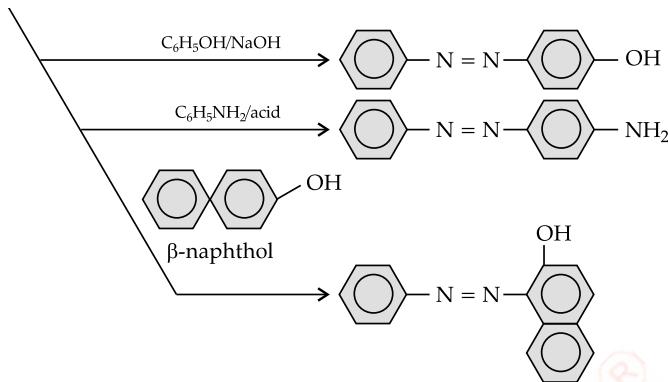
(i) **Coupling reaction:** The reaction of diazonium salts with phenol and aromatic amines to form azo compounds with the general formula, $\text{Ar} - \text{N} = \text{N} - \text{Ar}$ is known as coupling reaction.



(v) **Importance of Diazonium salts:** They are very good intermediates for the introduction of $-F$, $-Cl$, $-Br$, $-I$, $-CN$, $-OH$, $-NO_2$ groups into aromatic ring. Cyanobenzene can be prepared from diazonium salts.

► Synthesis of organic compounds from diazonium salts:





➤ Identification of Primary, Secondary and Tertiary Amines:

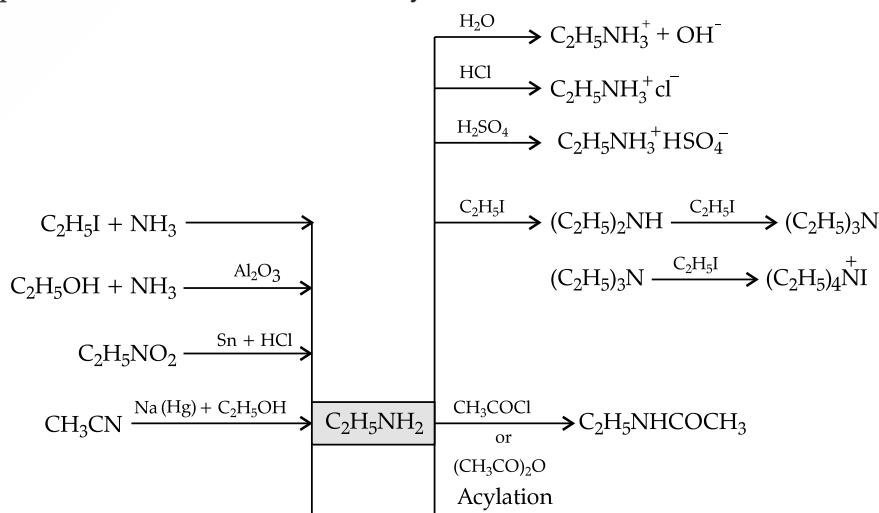
S.No.	Test	Primary amine	Secondary amine	Tertiary amine
(i)	Reaction with nitrous acid.	Gives alcohol with effervescence of N ₂ gas.	Gives oily nitrosoamine which gives Liebermann's test.	Forms nitrite in cold soluble in water and on heating gives nitrosoamine
(ii)	Hinsberg Test: Reaction with benzene sulphonyl chloride (Hinsberg's reagent).	Gives N-alkyl benzene-sulphonamide which is soluble in alkali.	Gives N, N-dialkyl benzene sulphonamide which is insoluble in alkali.	No reaction.
(iii)	Carbylamine test : Reaction with chloroform and alcoholic KOH.	Forms carbylamine or isocyanide (RNC) with characteristic unpleasant odour.	No reaction.	No reaction.
(iv)	Hoffmann's mustard oil reaction : Reaction with CS ₂ and HgCl ₂ .	Forms N-substituted isothiocyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.

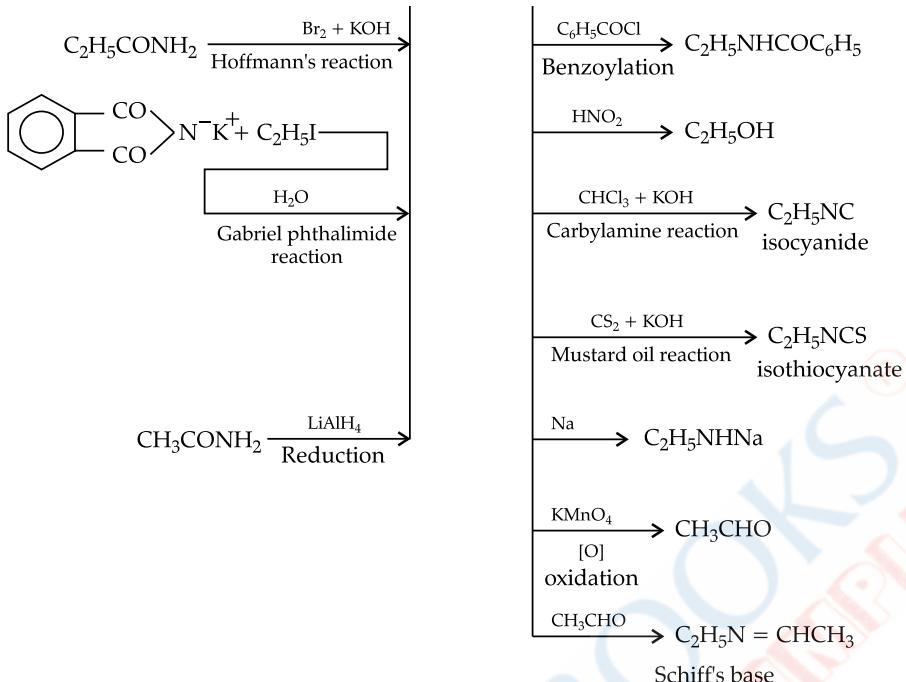


Key Facts

- Primary, secondary and tertiary amines: When applied to amines these terms refer to the number of alkyl (or aryl) substituents bonded to the nitrogen atom, whereas in other cases they refer to the nature of an alkyl group.
- Like ammonia, amines are weak bases due to the presence of lone pair of electrons on nitrogen atoms.
- Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation.

➤ Methods of preparation and chemical reactions of ethylamine:





Key Fact

Serotonin is an important amine that functions as one of the primary neurotransmitters for the brain. It controls the feelings of hunger and is critical for the speed with which the brain operates in general.

CHAPTER-10

BIOMOLECULES

Topic-1

Carbohydrates, their Classification and Importance

Concepts Covered • Classification of Carbohydrates, Monosaccharides - Glucose, its structure and Reactions, Fructose with structure and 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., polysaccharides, proteins, etc.
- **Carbohydrates:** Carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or compounds which produce such units on hydrolysis. e.g., cellulose, glycogen, **starch**, etc.
- **Classification of carbohydrates:** On the basis of the molecular size, carbohydrates have been classified into following four types:
 - 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 example are given in the table as shown below:



Key Words

Hydrolysis: It is a chemical reaction of the interaction of chemicals with water.

Monosaccharides: They are the simplest carbohydrates which cannot be hydrolysed to smaller carbohydrates.

Aldoses: It is a monosaccharide with carbon backbone chain with carbonyl group on the endmost carbon atom.

Ketoses: It is a monosaccharide containing one ketone group per molecule.

Starch: It is polymeric carbohydrate consisting of numerous glucose units joined by glycosidic bonds.

Class	Molecular Formula	Structural formula	Example
Aldoses			
Aldotriose	C ₃ H ₆ O ₃	CH ₂ OH.CH OH.CHO	Glyceraldehyde
Aldotetrose	C ₄ H ₈ O ₄	CH ₂ OH.(CHOH) ₂ .CHO	Erythrose, Threose
Aldopentose	C ₅ H ₁₀ O ₅	CH ₂ OH.(CHOH) ₃ CHO	Arabinose, Ribose, Xylose, Lyxose
Aldohexose	C ₆ H ₁₂ O ₆	CH ₂ OH.(CHOH) ₄ CHO	Glucose, Mannose, Galactose, Talose, Idose, allose, Altrose
Ketoses			
Ketotriose	C ₃ H ₆ O ₃	CH ₂ OH.CO.CH ₂ OH	Dihydroxyacetone
Ketotetrose	C ₄ H ₈ O ₄	CH ₂ OHCO CHOH CH ₂ OH	Erythrulose
Ketopentose	C ₅ H ₁₀ O ₅	CH ₂ OH.CO(CHOH) ₂ CH ₂ OH	Ribulose, Xylulose
Ketohexose	C ₆ H ₁₂ O ₆	CH ₂ OHCO(CHOH) ₃ .CH ₂ OH	Fructose, Sorbose, Tagatose, etc.

(ii) Oligosaccharides: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides.

Disaccharide: Disaccharide also called double sugar, any substance that is composed of two molecules of simple sugars (monosaccharides) linked to each other. Disaccharides are crystalline water-soluble compounds. Example: Sucrose, Lactose, Maltose. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. For example, one molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose gives two molecules of only glucose.

(iii) Polysaccharides: Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc. Polysaccharides are not sweet in taste, hence they are also called non-sugars.

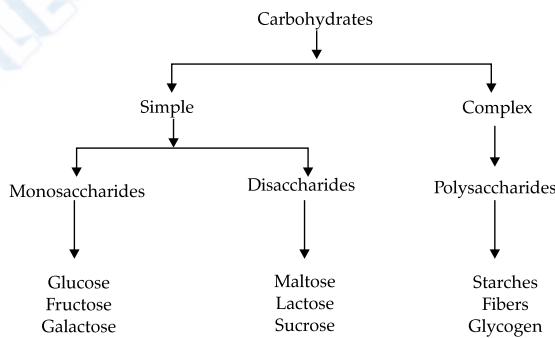
- Sugar:** In general, monosaccharides and oligosaccharides are crystalline solids, soluble in water, sweet in taste. They are collectively called sugars. e.g., glucose, fructose, sucrose, etc. They are of two types:

(i) **Reducing sugars:** Those carbohydrates which contain free aldehydic or ketonic group and reduce Fehling's solution and Tollen's reagent are known as reducing sugars. e.g., all monosaccharides, maltose.

(ii) Non-reducing sugars: Those carbohydrates which do not have free aldehydic or ketonic group and do not reduce Fehling's solution or Tollen's reagent are known as non-reducing sugars. e.g., **sucrose**.

The HP logo, which consists of a stylized lowercase 'h' and 'p' inside a square frame.

Key Diagram

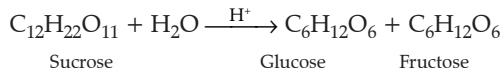


Classification of Carbohydrates

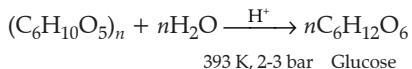
► **Glucose:** Glucose occurs in nature in free as well as in combined form. It is present in sweet fruits and honey.

- Methods of preparation of Glucose:

(i) From sucrose:



- (ii) **From starch:** Commercially, glucose is obtained by hydrolysis of starch by boiling it with dil. H_2SO_4 at 393 K under pressure.



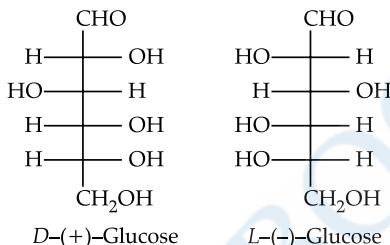
Key Words

Glucose: It is most abundant monosaccharide present in sweet fruits and honey.

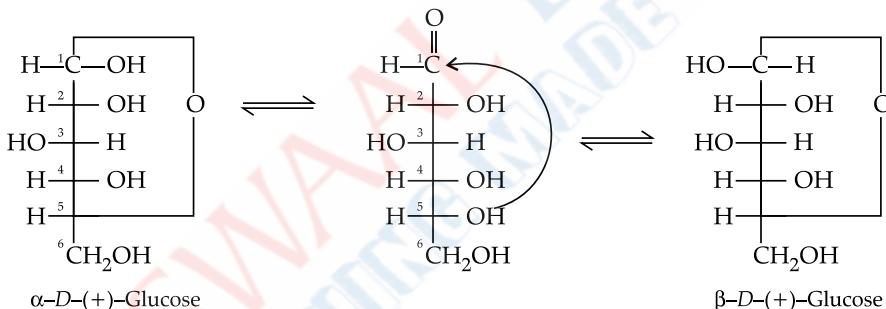
Sucrose: It is diasachharide composed of Glucose and Fructose.

- **Structure of Glucose:** It is a six carbon straight chain aldose which has one aldehydic group ($-\text{CHO}$), one primary hydroxyl group ($-\text{CH}_2\text{OH}$) and four secondary hydroxyl groups ($-\text{CHOH}$).

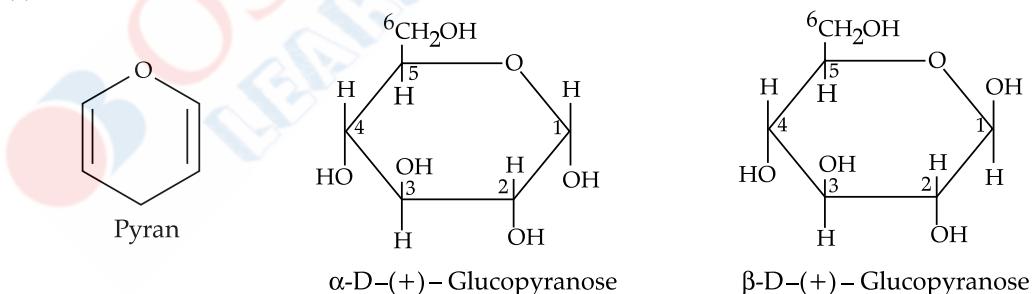
(a) **Open chain structure:**



(b) **Cyclic structure:**

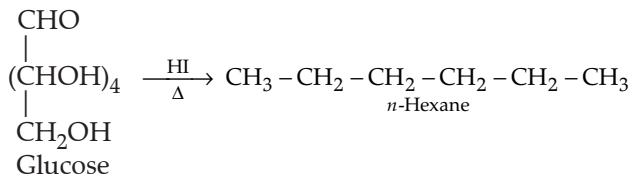


(c) **Haworth structure:**

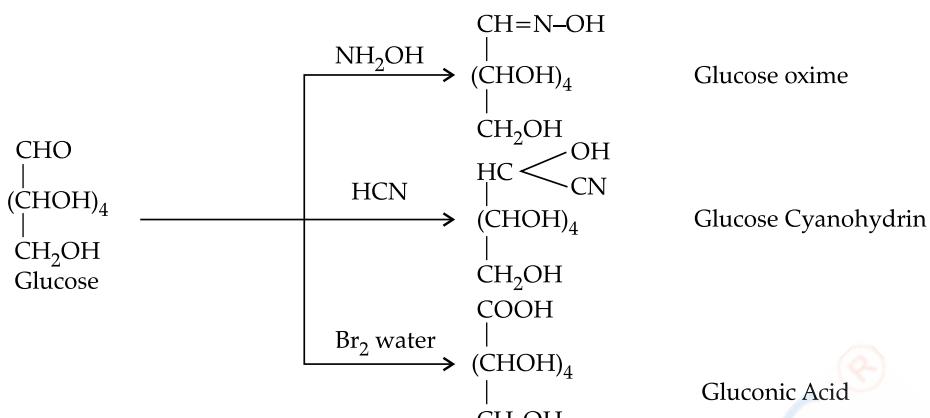


- **Reactions of Glucose:**

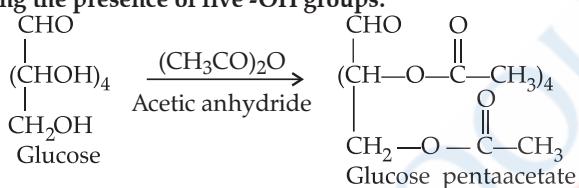
(i) **With HI:**



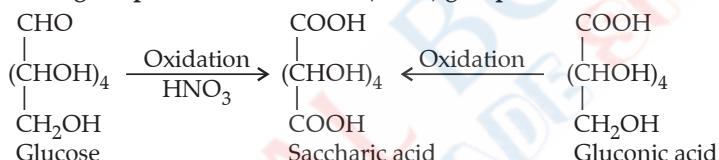
(ii) **Reactions showing the presence of carbonyl group ($>\text{C}=\text{O}$):**



(iii) Reactions showing the presence of five -OH groups:



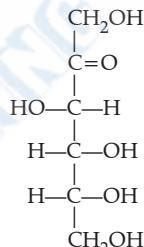
(iv) Reaction showing the presence of alcoholic (-OH) group:



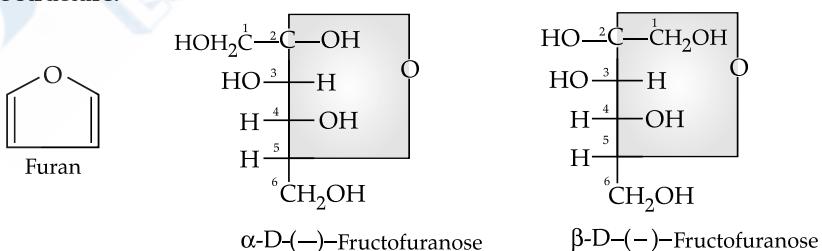
► **Fructose:** It is a ketohexose obtained by hydrolysis of **disaccharide**.

- **Structure of Fructose:**

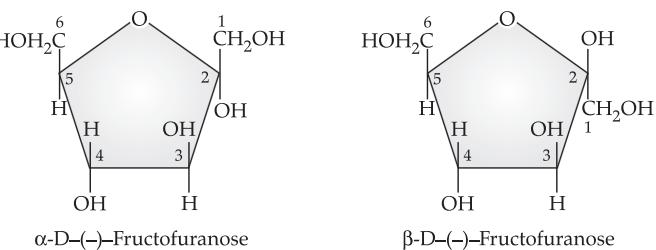
(a) Open chain structure:



(b) Cyclic structure:



(c) Haworth structure:



► Distinction between Glucose (monosaccharide), Sucrose (disaccharide) and Starch (polysaccharide):

S. No.	Test	Glucose (Monosaccharide)	Sucrose (Disaccharide)	Starch (Polysaccharide)
1.	On heating with <u>Fehling's solution</u>	Red precipitate is obtained.	No precipitate.	No precipitate.
2.	On heating with <u>Tollens' reagent (ammonical AgNO₃)</u>	Silver mirror is formed.	No silver mirror is formed.	No silver mirror is formed.
3.	On heating with phenyl hydrazine	Yellow coloured crystals of osazone are formed.	No osazone is formed.	No osazone is formed.
4.	On heating with resorcinol and HCl	No colour.	Wine red colour.	No colour.
5.	On adding NaOH solution and 1-2 drops of cobalt nitrate	No colour.	Violet colour.	No colour.
6.	On adding I ₂ solution in aqueous solution	No colour.	No colour.	Blue-violet colour.
7.	On heating in a dry test tube	Melts into brown coloured substance and smells of burnt sugar. Turns black on heating further.	Melts at 463 K, becomes brown at 473 K, chars at high temperature.	Chars on heating strongly.



Key Word

Tollen's Reagent: It refers to the chemical reagent which is used in the detection of an aldehyde functional group, an aromatic aldehyde functional group, or an alpha hydroxy ketone functional group in a given test substance.

Fehling's solution: It is a deep blue alkaline solution which is used to identify the presence of aldehydes or groups that contain any aldehyde functional group -CHO and in addition with Tollen's reagent to differentiate between reducing and non-reducing sugars.

► **Importance of Carbohydrates:** Carbohydrates are **our body's main source of energy**. They help to fuel our brain, kidneys, heart muscles, and central nervous system. For instance, fibre is a carbohydrate that aids in digestion, helps us feel full, and keeps blood cholesterol levels in check.

Carbohydrates are essential for life in both plants and animals.

Carbohydrates form a major portion of our food. Honey has been used for a long time as a instant source of energy by 'Vaidas' in ayurvedic system of medicine.

Carbohydrates are used as storage molecules as starch in plants and glycogen in animals.

Cell wall of bacteria in plants is made up of polysaccharides(carbohydrates)-.We build furniture from cellulose in form of wood and indeed clothes also are made of cellulose in form of cotton fibre.

Carbohydrates are broken down by the body into glucose – a type of sugar. Glucose is used as fuel by your body's cells, tissues, and organs and hence , it is the main source of energy to the body.

Topic-2

Proteins, Nucleic Acids, Vitamins and Hormones

Concepts Covered • Amino acids- classification and types, Protein structure, Nucleic Acids- DNA and RNA, Vitamins, Hormones and their functions



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 ($\text{---} \overset{\text{O}}{\underset{\parallel}{\text{C}}} \text{---} \text{NH} \text{---}$) bonds.
- **Conjugated proteins:** In this case, a protein part is linked to a non-protein part called prosthetic group which is mostly concerned with the special biological function of protein.
- **Derived proteins:** These are the proteins formed by the partial hydrolysis of simple conjugated proteins such as proteases, peptones, peptides, etc.

- **Transcription:** Process of synthesis of RNA.
- **Replication:** Process by which a single DNA molecule produces two identical copies of itself.
- **Native protein:** Protein found in biological system with a unique 3-dimensional structure and biological activity.
- **Gene:** Sequence of bases or nucleotides in the DNA molecule which regulates the synthesis of a specific protein.
- **Amino Acids:** The compounds which contain carboxylic acid ($-COOH$) group and an amino group ($-NH_2$) are called amino acids. Amino acids form proteins.
- **α -Amino Acids:** Those amino acids in which $-NH_2$ group and $-COOH$ group are attached to same carbon are called α -amino acids. These are obtained by hydrolysis of proteins. e.g., glycine.
- **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 group at the end of amino acid molecule which is known as C-Terminal end.
- **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 groups in their molecule. If equal number of amino and carboxyl groups are present, it is neutral. More number of amino than carboxyl groups makes it basic and more carboxyl groups as compared to amino makes it acidic.
 - **Essential and Non-essential Amino Acids:** The amino acids which can be synthesised in the body are known as non-essential amino acids. e.g., glycine, alanine, glutamine, etc. On the other hand, those which cannot be synthesised in the body and must be obtained by diet are known as essential amino acids.



Mnemonics

Concept: Basic amino acids

Mnemonics: BaLy Likes His Art.

Interpretations: Basic Amino Acids-Lysine, Histidine, Arginine.

- **Classification of Proteins:** Proteins are classified as follows:

(a) **Based on molecular shape:**

(i) **Fibrous proteins:**

They have thread like molecules which tend to lie side by side to form fibres. 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, albumin, haemoglobin, etc.

(b) **Based on structure and shape:**

(i) **Primary structure:** Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is called as primary structure of proteins.

(ii) **Secondary structure:** It refers to the shape in which a long polypeptide chain exists. They are of two types:

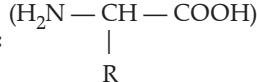
1. α -helix in which polypeptide chain forms intramolecular hydrogen bonds by twisting into a right handed helix with the $-NH$ group of each amino acid residue hydrogen bonded to the $>C=O$ of an adjacent turn of the helix. e.g., keratin in hair, nails.

2. β -pleated sheet has all peptide chains stretched to nearly maximum extension and then arranged side by side held together with intermolecular hydrogen bonding. e.g., silk.

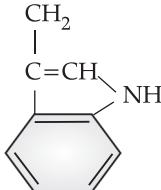
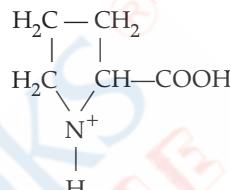
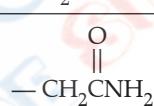
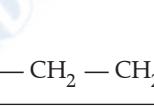
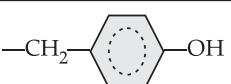
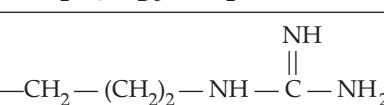
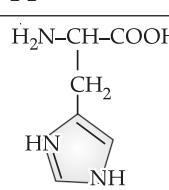
(iii) **Tertiary structure:** It represents overall folding of polypeptide chains by H-bonds, disulphide linkages, van der Waals and electrostatic form of attraction. e.g., Fibrous and globular proteins.

(iv) **Quaternary structure:** The spatial arrangement of two or more polypeptide chains with respect to each other is known as quaternary structure.

- **Name and structure of some naturally occurring α -Amino Acids:**



S. No.	Amino acids	Isoelectric point (Hydrophobic)	One alphabet code	Three alphabet code	$-R$ (Side chain)
1.	Non-polar Glycine	5.97	G	Gly	$-H$
2.	Alanine	6.02	A	Ala	$-CH_3$
3.	Valine*	5.97	V	Val	$-CH(CH_3)_2$
4.	Leucine*	5.90	L	Leu	$-CH_2-CH(CH_3)_2$

5.	Isoleucine*	6.02	I	Ile	$-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$
6.	Phenylalanine*	5.84	F	Phe	$-\text{CH}_2-\text{Ph}$
7.	Methionine*	5.06	M	Met	$-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$
8.	Tryptophan*	5.88	W	Trp	
9.	Proline	6.30	P	Pro	
10.	Polar (Neutral) Serine	5.68	S	Ser	$-\text{CH}_2\text{OH}$
11.	Cysteine	5.02	C	Cys	$-\text{CH}_2-\text{SH}$
12.	Asparagine	5.41	N	Asn	
13.	Glutamine	5.70	Q	Gln	
14.	Threonine*	5.60	T	Thr	$-\text{CH}(\text{OH})-\text{CH}_3$
15.	Tyrosine	5.67	Y	Tyr	
16.	Acidic Aspartic acid	2.98	D	Asp	$-\text{CH}_2-\text{COOH}$
17.	Glutamic acid	3.22	E	Glu	$-\text{CH}_2\text{CH}_2\text{COOH}$
18.	Basic Lysine*	9.47	K	Lys	$-\text{CH}_2-(\text{CH}_2)_3-\text{NH}_2$
19.	Arginine*	10.76	R	Arg	
20.	Histidine*	7.59	H	His	

* These are essential amino acids.



Mnemonics

Concept: Non polar amino acids

Mnemonics: PriVate PhIL Went For A TryM At Glyttery New Parlour.

Interpretations: Non-Polar Amino Acids-Proline, Valine, Phenylalanine, Isoleucine, Leucine, Alanine, Tryptophan, Methionine, Glycine.

► Different Proteins and their functions:

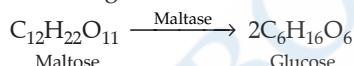
S. No.	Type of Protein	Example	Function
1.	Enzyme	Trypsin, Pepsin	As a catalyst in biochemical reactions.
2.	Structural	Collagen, Keratin	Structural and protective action in teeth, nails and hairs.
3.	Transport	Haemoglobin	Transport of oxygen from lungs by blood stream to different tissues.
4.	Motor	Myosin, Actin	For motion of muscles.
5.	Hormone	Insulin	Regulate body metabolism.
	Storage	Ferritin, Casein	Store nutrients.

- ▶ **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 gets uncoiled and protein loses its biological activity. It is called denaturation of protein. e.g., coagulation of egg white on boiling, curdling of milk, etc.

► **Enzymes:** Enzymes are biocatalysts, basically proteins that catalyse biological reactions. They are very specific in nature and catalyse only a particular reaction for a particular substrate.

Many of the reactions in our body like digestion of food, absorption of molecules, production of energy occurs with the help of these biocatalysts called enzymes.

They are generally named after the compound or class of compounds upon which they work. For example, the enzyme that catalyses hydrolysis of maltose into glucose is named as maltase



Sometimes enzymes are also named after the reaction, where they are used. For example, the enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate are named as oxidoreductase enzymes. The ending of the name of an enzyme is -ase.

Other examples of enzymes:

Examples of specific enzymes

- Lipases – a group of enzymes that help digest fats in the gut.
 - Amylase – helps change starches into sugars.
 - Maltase – also found in saliva; breaks the sugar maltose into glucose. ...
 - Trypsin – found in the small intestine, breaks proteins down into amino acids.

► Nucleic acid: The polymers of nucleotides help in synthesis of protein and transfer genetic traits.

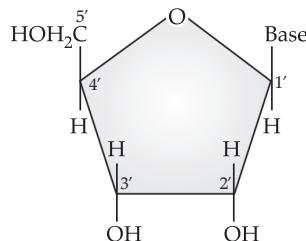
Nucleic acids are of two types:

- (i) Deoxyribonucleic acid (DNA)
 - (ii) Ribonucleic acid (RNA)

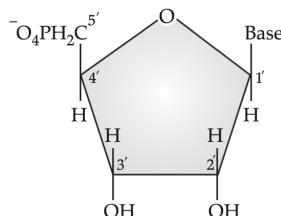
Constituents of nucleic acids: Pentose sugar, phosphoric acid and nitrogenous bases.

► Nitrogen containing bases:

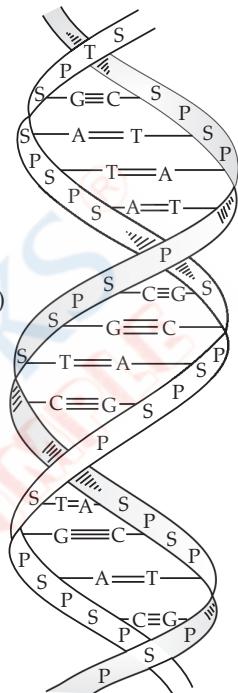
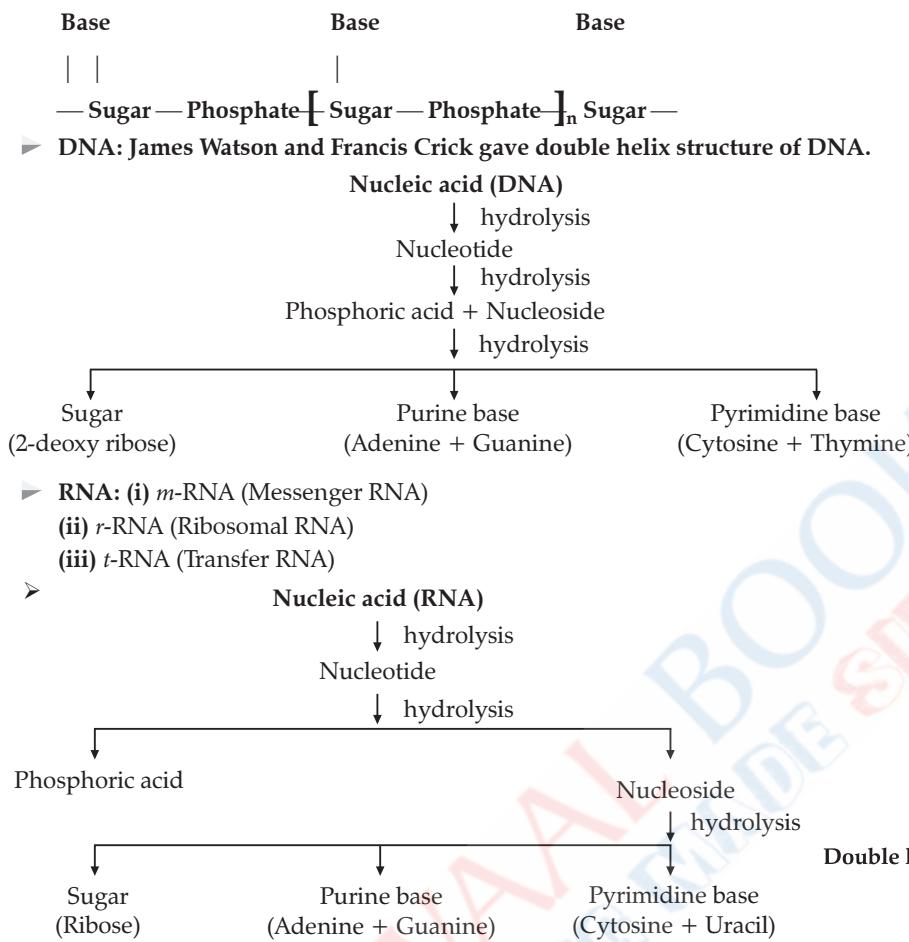
- **Pyrimidines:** These are three bases derived from pyrimidines. These are cytosine (C), thymine (T) and uracil (U). In DNA, T is present but in RNA, U is present.
 - **Purines:** There are two bases derived from purine. These are adenine (A) and guanine (G).
 - **Nucleoside:** A unit formed by the 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:



Double helix structure of DNA molecule

Properties of Nucleic Acids:

- Nucleic acids are very important constituents (polynucleotide) found in nucleus of cell which help in biosynthesis of protein and act as carriers for transfer of hereditary characters.
- A molecule formed by the combination of one pentose sugar unit, a purine or pyrimidine base and a phosphate. Nucleotides combine among themselves to form polynucleotide (nucleic acid).
- A polynucleotide (DNA) which has a thymine base but not a uracil base. It contains deoxyribose sugar but not ribose sugar. It has double helix structure.
- A polynucleotide (RNA) which contains uracil base and ribose sugar but thymine base and deoxyribose sugar are absent. It has single stranded structure.



Mnemonics

Concept: DNA base

Mnemonics: ATGC

Interpretations: Nitrogen Bases Present In DNA = Adenine, Thymine, Guanine And Cytosine.

Concept: RNA Base

Mnemonics: Area Under The Growth Curve

Interpretations: Nitrogen Bases Present In RNA = Adenine, Uracil, Guanine And Cytosine

Hormones and their functions: Hormones are molecules that act as intercellular messengers. These are produced by endocrine glands in the body and are poured directly in the blood stream which transports them to the site of action.

In terms of chemical nature, some of these are steroids, e.g., estrogens and androgens; some are polypeptides for example insulin and endorphins and some others are amino acid derivatives such as epinephrine and norepinephrine.

Functions of hormones: They help to maintain the balance of biological activities in the body.

Example-The role of insulin in keeping the blood glucose level within the narrow limit is an example of this function. Insulin is released in response to the rapid rise in blood glucose level.

Growth hormones and sex hormones play role in growth and development.

Testosterone is the major sex hormone produced in males. It is responsible for development of secondary male characteristics (deep voice, facial hair, general physical constitution) and estradiol is the main female sex hormone. It is responsible for development of secondary female characteristics and participates in the control of menstrual cycle.

S. No.	Name of Endocrine gland	Hormone secreted	Functions
1.	Pituitary gland	(i) Growth hormone (ii) Other Hormones	Regulates normal growth of a person to regulate functioning of (a) Thyroid gland (b) Adrenal gland (c) Production of testosterone by testes and estrogen by ovaries.
2.	Thyroid gland	Thyroxine	Controls body metabolism. Lack of thyroxine causes Goitre. Sufficient iodine in diet prevents goitre.
3.	Pancreas	Insulin	Control carbohydrate metabolism. Lack of insulin secretion causes Diabetes.
4.	Adrenalin	(i) Hormone to keep salt balance (ii) Adrenalin	Maintains correct balance of salt-water in the blood.

► Vitamins:

- The term "Vitamine" was coined from the word vital + amine since the earlier identified compounds had amino groups. Later work showed that most of them did not contain amino groups, so the letter 'e' was dropped and the term vitamin is used these days
 - A vitamin is an organic molecule (or a set of molecules closely related chemically, *i.e.*, vitamers) that is an essential micronutrient which an organism needs in small quantities for the proper functioning of its metabolism.
 - These vitamins perform specific biological functions for normal maintenance of optimum growth.
 - Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them, so they are considered as essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us.
 - Vitamins are named as Vitamin A, B, C, D, etc. Some of them are further named as sub-groups e.g., B1, B2, B6, B12, etc. Excess of vitamins is also harmful and vitamin pills should not be taken without the advice of doctor.
 - Vitamins are classified into two groups depending upon their solubility in water or fat.
 - (i) Fat soluble vitamins: Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.
 - (ii) Water soluble vitamins: B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B12) in our body.
- Some important Vitamins, their Sources and their Deficiency Diseases

Vitamins

Vitamin	What it does ?	Where is it found ?
Vitamin A	<ul style="list-style-type: none"> • Growth and development • Immune function • Reproduction • Red blood cell formation • Skin and bone formation • Vision 	<ul style="list-style-type: none"> • Cantaloupe • Carrots • Dairy products • Eggs • Fortified cereals • Green leafy vegetables (e.g., spinach and broccoli) • Pumpkin • Red peppers • Sweet potatoes

Vitamin B6	<ul style="list-style-type: none"> ● Immune function ● Nervous system function ● Protein, carbohydrate, and fat metabolism ● Red blood cell formation 	<ul style="list-style-type: none"> ● Chickpeas ● Fruits (other than citrus) ● Potatoes ● Salmon ● Tuna
Vitamin B₁₂	<ul style="list-style-type: none"> ● Conversion of food into energy ● Nervous system function ● Red blood cell formation 	<ul style="list-style-type: none"> ● Dairy products ● Eggs ● Fortified cereals ● Meats ● Poultry ● Seafood (e.g., clams, trout, salmon had-dock, tuna)
Vitamin C	<ul style="list-style-type: none"> ● Antioxidant ● Collagen and connective tissue forma-tion ● Immune function ● Wound healing 	<ul style="list-style-type: none"> ● Broccoli ● Brussels sprouts ● Cantaloupe ● Citrus fruits and juices (e.g., oranges and grapefruit) ● Kiwifruit ● Peppers ● Strawberries ● Tomatoes and tomato juice
Vitamin D Nutrient of concern for most Americans	<ul style="list-style-type: none"> ● Blood pressure regulation ● Bone growth ● Calcium balance ● Hormone production ● Immune function ● Nervous system function 	<ul style="list-style-type: none"> ● Eggs ● Fish (e.g., herring, mackerel, salmon, trout, and tuna) ● Fish liver oil ● Fortified cereals ● Fortified dairy products ● Fortified margarine ● Fortified orange juice ● Fortified soy beverages (soya milk)
Vitamin B₆	<ul style="list-style-type: none"> ● Antioxidant ● Formation of blood vessels ● Immune function 	<ul style="list-style-type: none"> ● Fortified cereals and juice ● Green vegetables (e.g., spinach and broccoli) ● Nuts and seeds
Vitamin B₁₂	<ul style="list-style-type: none"> ● Blood clotting ● Strong bones 	<ul style="list-style-type: none"> ● Green vegetables (e.g., broccoli, kale, spinach, turnip greens, collards, Swiss chard, mustard greens)