

CHAPTER-1

ELECTROCHEMISTRY

Revision Notes

Electrolytic Conductivity, Electrolytes and Kohlrausch's Law

- **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 , MgCl_2
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.

- **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 also Ohm-cm is used as a unit.

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

$$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

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

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

$$1\text{S} = 1\text{ Ohm}^{-1} = 1\text{ }\Omega^{-1}$$

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

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

where C = Conductance of the solution

l = Distance or length

A = Area of cross section

Its SI unit is S m^{-1} . 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)
- **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
 - **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.

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

It depends on the:

- (i) Distance between the electrodes
 - (ii) Area of cross section
- The resistance of electrolytic solution is determined by wheatstone bridge method where R_2 is resistance of electrolyte solution. A null point detected by P detector such that,

$$\text{Unknown } R_2 = \frac{R_1 R_4}{R_3}$$

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

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

where κ = Conductivity

C = Concentration of solution.

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

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

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

where Λ° = 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 from its individual ions. If the molar conductivity of the cations is denoted by λ_+^∞ and that of the anions by λ_-^∞ then the law of independent migration of ions is:

$$\Lambda_m^\infty = v^+ \lambda_+^\infty + v^- \lambda_-^\infty \text{ or } \Lambda_m^\circ = v^+ \lambda_+^\circ + v^- \lambda_-^\circ$$

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:

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

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

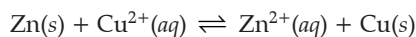
$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$$

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

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

Redox Reactions and Electrochemical Cells, Electrode Potential and Nernst Equation

- **Redox reaction:** A chemical reaction in which oxidation and reduction both processes take 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.
- **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 and Cu) in contact with the solution of its own ion *i.e.*, ZnSO_4 and 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:

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

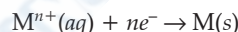
where

$$E_{\text{cathode}}^\circ = \text{standard electrode potential of cathode}$$

and

$$E_{\text{anode}}^\circ = \text{standard electrode potential of anode}$$

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

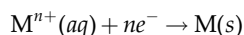


the Nernst equation can be written as

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

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).

For a cell, the electrode potential for any concentration of ions using electrode reactions is



At equilibrium,

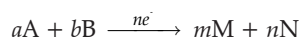
$$E_{\text{cell}}^\circ = \frac{0.059}{n} \log K_c$$

Where,

K_c = Equilibrium constant

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

For the general electrochemical cell with the net reaction,



the Nernst equation at 298 K can be written as

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

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

where

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

➤ **Gibbs energy:**

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

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

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

$$\Delta_r G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

and

$$\Delta_r G = -nFE_{\text{cell}}$$

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

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

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

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

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

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

➤ **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 non-chargeable batteries such as Leclanche cell and Dry cell.

(ii) Secondary batteries are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.

- **Dry cell (Leclanche 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 .

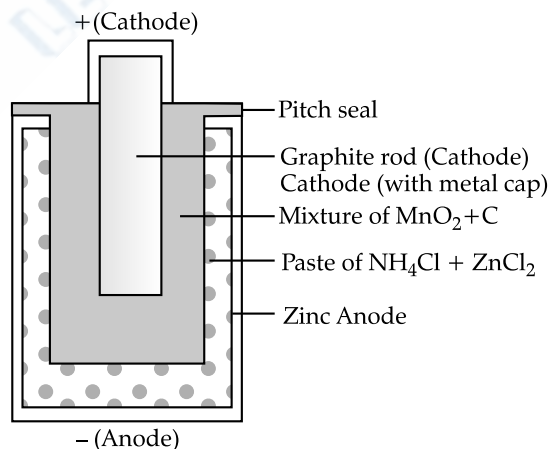


Fig 1: Dry cell

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

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

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%)

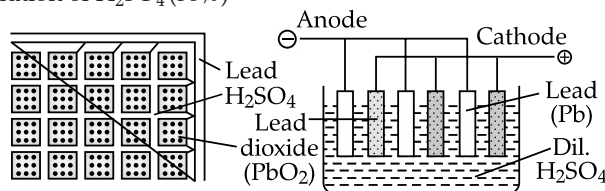
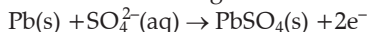


Fig 2: Lead storage battery

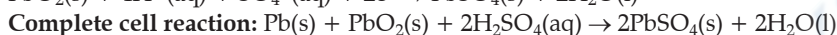
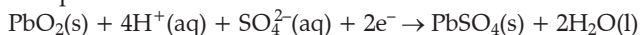
Discharge reaction of cell:

At anode: Following reaction takes place at anode

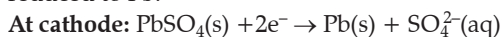


Reaction at cathode: PbO_2 filled in lead grid gets reduced to Pb^{2+} ions which combines with SO_4^{2-} ions to form $\text{PbSO}_4(\text{s})$.

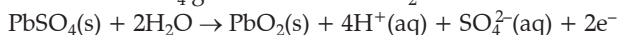
Complete cathode reaction is as follows:



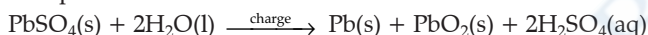
Recharge reaction of cell: It changes the direction of electrode reaction. PbSO_4 accumulated at cathode gets reduced to Pb.



At anode: PbSO_4 gets oxidised to PbO_2



Complete cell reaction would be as follows:



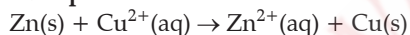
➤ **Conventions for representing the galvanic cell:**

(i) Double vertical line is used for salt bridge. Left hand side of the double line is anode and the cathode is on the right hand side.

(ii) A single vertical line is used to separate metal and the electrolytic solution.

(iii) If there is no metallic surface involved, we write Pt.

Example:



➤ **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:

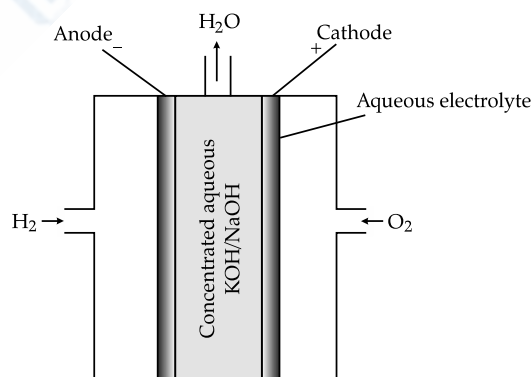
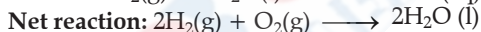
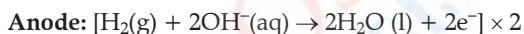
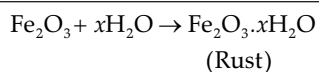
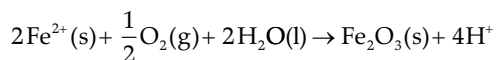
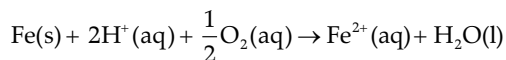


Fig 3: Fuel cell using H_2 and O_2 produces electricity

➤ **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.

Know the Terms

- **Superconductors:** Materials with a zero resistance.
- **Limiting molar conductivity:** Molar conductivity when concentration approaches zero.
- **Electrolyte:** Substance that dissociates into electrically conducting ions.
- **Over voltage:** It is the difference between the potential required for the evolution of a gas and its standard reduction potential.

Know the Formulae

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

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

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

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

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

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

$$\Lambda^\circ = \nu_+ \Lambda_+^\circ + \nu_- \Lambda_-^\circ$$

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

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

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

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

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

Nernst equation:

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

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

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

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

$$Q = It$$

$$m = ZIt$$

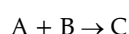
CHAPTER-2

CHEMICAL KINETICS

Revision Notes

Rate of a Chemical Reaction and Factors Affecting Rate of Reactions

- **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.



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

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

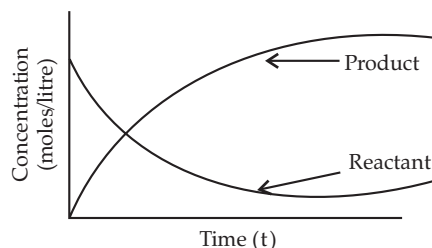
$$\text{and for product } C = \frac{\Delta[C]}{\Delta t}$$

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

- **Unit of rate of reaction:** mol L⁻¹ s⁻¹ or mol L⁻¹ 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.

$$\text{Instantaneous rate} = \frac{dx}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt}$$

- **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.
 - (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.



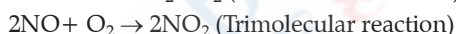
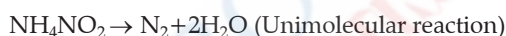
(viii) **Effect of physical state:** Rate of reaction depends upon physical state of the reactant, e.g., $I_2(g)$ reacts faster than $I_2(s)$. $AgNO_3(aq)$ reacts with $NaCl$ but $AgNO_3(s)$ does not react with $NaCl$.

- **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 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.

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

- **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., $\text{Rate} = k[A]^0$. Rate constant of zero order reaction is

$$k = \frac{[A]_0 - [A]}{t}, \text{ where 'k' is rate constant, } [A]_0 \text{ is initial concentration of reactant.}$$

Unit of the rate constant k is $\text{mol L}^{-1} \text{ s}^{-1}$. 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.

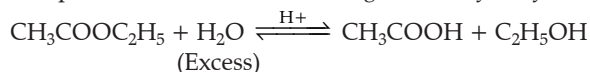
- **First order reaction:** The rate of reaction is directly proportional to the first power of the concentration of reacting substance. i.e., $\text{Rate} = k[A]^1$. Rate constant of the first order reaction is

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

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

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 N_2O_5 and N_2O are some examples.

- **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).



Therefore, Rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5]$

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

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

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:** $\text{A}(\text{g}) \rightarrow \text{B}(\text{g}) + \text{C}(\text{g})$

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

or

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

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

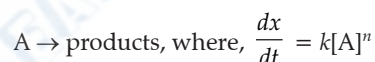
- **Half-life of a reaction:** The time taken for a reaction when half of the initial value has reacted is called **half-life of a reaction**.

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.

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

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



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

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

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

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

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

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

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

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

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

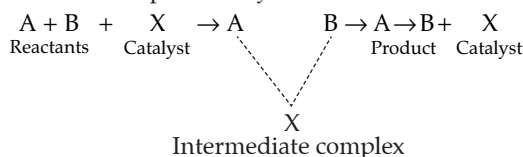
➤ **Integrated rate laws for the reactions of zero and first order:**

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

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

➤ **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:



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.



Mnemonics

- Concept: Zero order
- Mnemonics: ZOR don't CCR
- Interpretation: In zero order reaction, the rate of reaction does not change with concentration of the reactants.
- Concept: Effect of Collision
- Mnemonics: ECFPM
- Interpretation: Effective collisions lead to formation of product molecules.
- Concept: Catalyst
- Mnemonics: CAR
- Interpretation: A catalyst alters the reaction

Know the Formulae

➤ **Integrated Rate Equations:**

(i) For a zero order reaction:

$$t = \frac{[R]_0 - [R]}{k} \quad \text{and} \quad t_{1/2} = \frac{[R]_0}{2k}$$

(ii) For a first order reaction:

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \quad \text{and} \quad t_{1/2} = \frac{0.693}{k}$$

CHAPTER-3

SURFACE CHEMISTRY

Revision Notes

Adsorption and its Types, Factors Affecting Adsorption

- **Surface chemistry:** The branch of chemistry which deals with the phenomenon that occurs at the surface is called surface chemistry. This phenomenon is studied with the help of adsorption and colloidal state.
- **Adsorption** is a surface phenomenon in which the substance gets accumulated on the surface of a solid rather than in the bulk of a solid or liquid. The surface that adsorbs is called **adsorbent** and the one that gets adsorbed is called an **adsorbate**. **For example:** Pt can adsorb large amount of hydrogen gas.
- **Types of adsorption:**
 - (i) **Physisorption:** Physisorption is also called physical adsorption. If the adsorbate is held on a surface of adsorbent by weak Van der Waals forces, the adsorption is called **Physical adsorption or physisorption**.
 - (ii) **Chemisorption:** Chemisorption is also called chemical adsorption. If the forces holding the adsorbate are as strong as in chemical bonds, the adsorption process is known as **Chemical adsorption or Chemisorption**.
- **Desorption:** The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**.
- In **absorption**, molecules of a substance are uniformly distributed throughout the body of solid or liquid. **For example:** Ammonia absorbed by water, water absorbed by anhydrous CaCl_2 .
- **Sorption:** When adsorption and absorption take place simultaneously, it is called sorption, *e.g.*, dyeing of cotton fabrics. The dye is adsorbed initially on the surface of cotton fibre, but later the fibre has uniform concentration of dye throughout.
- **Enthalpy of adsorption:** Adsorption generally occurs with release in energy, *i.e.*, it is exothermic in nature. The enthalpy change for the adsorption of one mole of an adsorbate on the surface of adsorbent is called **enthalpy or heat of adsorption**.
- **Differences between Adsorption and Absorption:**

S. No.	Adsorption	Absorption
(i)	It is a surface phenomenon. Adsorbate molecules are held at the surface of adsorbent.	Absorption occurs in the bulk of absorbing substance.
(ii)	The concentration of the adsorbate at the surface of adsorbent is much more than that in the bulk.	Absorbed material is uniformly distributed throughout the bulk. Thus, concentration is same throughout.
(iii)	Initially rate of adsorption is rapid. It decreases slowly till equilibrium is attained.	Absorption occurs with uniform rate.
(iv)	Example: Water vapours are adsorbed on Silica gel.	Example: Water vapours are absorbed by Anhydrous CaCl_2 . (Calcium Chloride)

- **Factors affecting adsorption of gases on solids:**
 - (i) Nature of gas
 - (ii) Nature of adsorbent
 - (iii) Specific area of the solid
 - (iv) Pressure of the gas
 - (v) Effect of temperature
 - (vi) Activation of adsorbent
- **Adsorption isobar:** A plot of extent of adsorption (x/m) vs temperature at constant pressure is called adsorption isobar.
- **Adsorption isotherm:** The plot of extent of adsorption (x/m) vs pressure (p) at constant temperature is called adsorption isotherm, where, x is the quantity of gas adsorbed by unit mass ' m ' of the solid 'adsorbent'.
- **Freundlich Adsorption Isotherm:** It gives the relationship between magnitude of adsorption (x/m) and pressure at a constant temperature. It can be given by mathematical equation.

$$\frac{x}{m} = kp^{1/n} \quad \dots(i)$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \quad \dots(ii)$$

A plot of $\log \frac{x}{m}$ vs $\log p$ gives a straight line with slope $\frac{1}{n}$

and y intercept = $\log k$

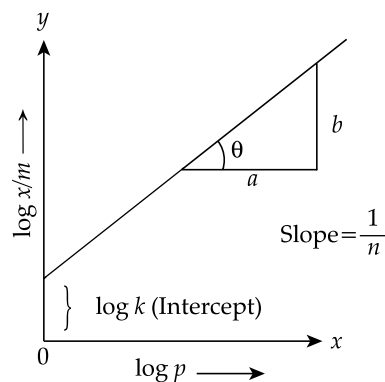
In case of solution, the isotherm takes the form

$$\frac{x}{m} = k(C)^{1/n}; \log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

where x is the amount of adsorbate adsorbed on (m) gram of adsorbent at pressure p or concentration C of the adsorbate, k and n are constants where, $n > 1$.

➤ **Applications of Adsorption:**

- | | |
|--|-------------------------------|
| (i) In removing colouring matter from solution | (vii) In curing diseases |
| (ii) In gas masks | (viii) In dehumidifiers |
| (iii) In separating noble gases | (ix) In adsorption analysis |
| (iv) In dyeing of cloth | (x) In creating high vacuum |
| (v) In chromatography | (xi) In ion-exchange resins |
| (vi) In froth flotation process | (xii) Heterogeneous catalysis |



Colloids, Types of Colloids, Characteristics and Preparation of Colloids

- **Colloids:** A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. The size of colloidal particles is in the range 1–1000 nm.
- **Colloidal solution:** A colloidal solution is a heterogeneous system in which a definite substance is distributed in the form of very small particles as dispersed phase in another substance called dispersion medium, e.g., glue, Ink, smoke, etc.
- **Dispersed phase:** Dispersed phase is the component present in small proportion like solute in the solution. e.g., Sugar Particles in water.
- **Dispersion medium:** The medium in which the colloidal particles are dispersed is called dispersion medium.
- **Crystalloids:** The substances whose aqueous solution can pass through the semi-permeable membrane are called crystalloids.
- **Types of Colloidal solutions:**

S. No.	Dispersed phase	Dispersion medium	Name	Examples
1.	Solid	Gas	Aerosol	Smoke, dust particles.
2.	Solid	Liquid	Sol	As ₂ S ₃ , Gold sol, starch, gum, muddy water.
3.	Solid	Solid	Solid sol	Coloured gem stones, some alloys, pearls, ruby glass.
4.	Liquid	Solid	Gel	Jellies, cheese, butter.
5.	Liquid	Liquid	Emulsion	Milk, Hair cream, Cod liver oil.
6.	Liquid	Gas	Aerosol	Fog, mist, cloud.
7.	Gas	Solid	Solid foam	Pumice stone, foam rubber, cork.
8.	Gas	Liquid	Foam	Whipped cream, froth, soap lather.

➤ **Classification based on nature of interaction between dispersed phase and dispersion medium:**

- (i) **Lyophilic colloids:** Lyophilic means “solvent loving”. Those substances which when mixed with a suitable solvent as the dispersion medium directly form the colloidal solution are called lyophilic substances and the solution thus formed is called lyophilic solution. They are also known as Intrinsic colloids. **For example:** Gum, gelatin, starch, rubber; etc.

(ii) **Lyophobic colloids:** Lyophobic means “solvent hating”. These are the substances, when mixed with dispersion medium do not form colloidal solution. Their solution can be prepared only by special method, such substances are called lyophobic and the solutions formed by them are called lyophobic solutions. They are also known as extrinsic colloids. **For example:** metals and their sulphides.

➤ **Classification based on the type of particles of the dispersal phase: Multimolecular, Macromolecular and Associated colloids:**

(i) **Multimolecular colloids:** Multimolecular colloids contain dispersed particles less than 1 nm made of aggregates of many molecules. These are lyophobic colloids. In multimolecular colloids, particles are held together by weak van der Waals forces. For example: sulphur sol, gold sol etc.

(ii) **Macromolecular colloids:** Macromolecular colloids are molecularly dissolved solutions of a polymer with particle size of colloidal range and are lyophilic colloids. In macromolecular colloids, particles are held by chemical bonds.

For example:

(a) Naturally occurring macromolecular colloids (starch, cellulose, proteins and enzymes).

(b) Man made macromolecular colloids (polythene and nylon).

(iii) **Associated colloids (Micelles)**

Micelles: Those colloids which behave as normal strong electrolytes at low concentrations, show colloidal properties at higher concentrations due to the formation of aggregated particles of colloidal dimensions. Such compounds are also referred to as associated colloids. Surface active agents like soaps and synthetic detergents belong to this class. They also form ions. Micelles may contain 100 molecules or more.

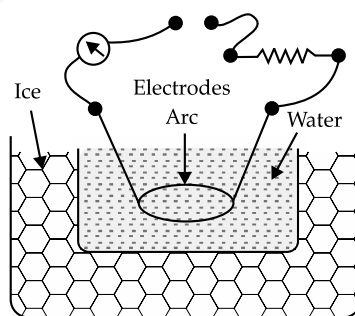
Mechanism of micelle formation: Micelles are generally formed by the specific type of molecules which have lyophilic as well as lyophobic ends. Such molecules are known as surface active molecules or surfactant molecules.

Sodium oleate, $C_{17}H_{33}COO^-Na^+$ (one of the soaps) is a typical example of such type of molecule. The long hydrocarbon part of oleate radical ($C_{17}H_{33}-$) is lyophobic end while COO^- part is lyophilic end. When the concentration of the solution is below its CMC ($3 \times 10^{-3} \text{ mol L}^{-1}$), sodium oleate behaves as normal electrolyte and ionises to give Na^+ and $C_{17}H_{33}COO^-$ ions. As the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and are made to approach each other. However, the polar $C_{17}H_{33}COO^-$ part tend to interact with the solvent. This ultimately leads to the formation of the cluster having the dimensions of the colloidal particles. In each such cluster, a large number of (usually 100 or more) oleate groups are clumped together in a spherical manner so that their hydrocarbon parts interact with one another but $C_{17}H_{33}COO^-$ parts remain projected in water. Hence, the mechanism of micelles formation is same as that of soap.

➤ **Preparation of colloidal solution:** Colloidal solutions can be prepared by following methods:

(i) **Mechanical dispersion:** A suspension of coarsely ground particles prepared in dispersion medium is fed into a colloidal mill and speed of rotation is adjusted so as to get the particles of colloidal size.

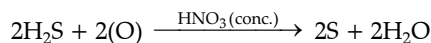
(ii) **Electrodispersion: (Bredig's Arc method):** In this method, two rods of the metal (Au, Cu, Pt, Ag) to be dispersed are kept immersed in cold and a direct electric arc is struck between them. In this way vapours of metal are formed which then immediately condense to form particles of colloidal size.



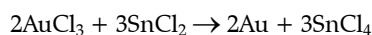
Bredig's Arc method

(iii) **Chemical methods:**

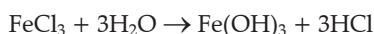
● **Oxidation:** Solutions of non-metals are prepared by this method; e.g., colloidal solution of sulphur.



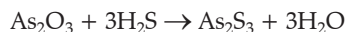
● **Reduction:** Metal sols can be prepared by this method; e.g.; Gold sol



- **Hydrolysis:** Hydroxides sols are prepared by this method; *e.g.*; $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$



- **Double decomposition:** This method is used to prepare colloids from inorganic salts; *e.g.*;



- **Exchange of solvent:** Some substances which form true solution in one solvent, forms colloidal solution in another due to lowering of solubility, *e.g.*; sulphur dissolved in alcohol forms colloidal solution in water and phenolphthalein dissolved in alcohol forms colloidal solution in water.
- **Excessive cooling:** The colloidal solution of ice in CHCl_3 or ether can be obtained by freezing a solution of water in solvent. The molecules of water combine to form particles of colloidal size.

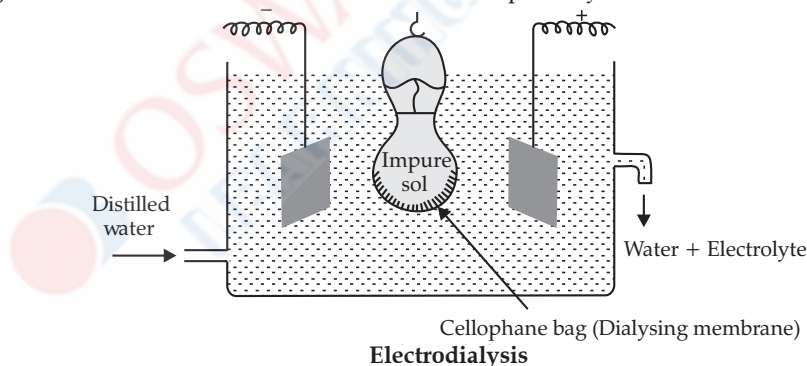
➤ **Peptization:** The conversion of precipitate into colloidal solution in presence of peptizing agent is called Peptization. Peptizing agent is generally an electrolyte.

➤ **Purification methods of colloidal solutions:** Colloidal solution can be purified by following methods:

- (i) **Dialysis:** In dialysis, particles of true solutions can pass through parchment paper or cellophane membrane. On the other hand, Sol particles cannot pass through these membranes. A bag made up of such a membrane is filled with the colloidal solution and is then suspended in fresh water. The crystalloid particles pass out leaving behind the colloidal sol.



- (ii) **Electrodialysis:** Movement of ions across the membrane can be quickened by applying electric potential through two electrodes. This method is faster than simple dialysis and known as electro dialysis.



- (iii) **Ultrafiltration:** The process of separating colloidal particles by specially prepared filter papers whose pore size is reduced by dipping it in colloidal solution (*e.g.*, 4% nitrocellulose in mixture of alcohol and ether) are known as ultrafiltration.

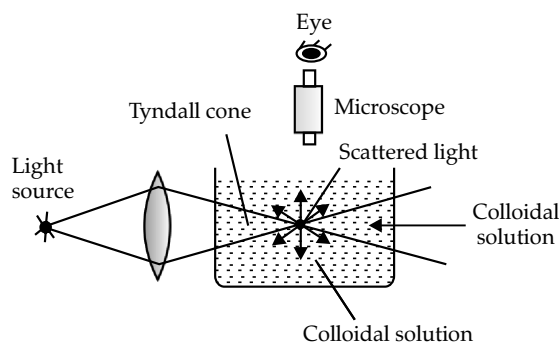
➤ **Properties of colloids:**

- (i) **Brownian movement:** The zig-zag movement of colloidal particles when seen under powerful microscope is called Brownian movement.



Brownian Movement

- (ii) **Tyndall effect:** Scattering of light by colloidal particles is called Tyndall effect.



Tyndall effect

(iii) **Electrophoresis:** The movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution is called electrophoresis.

➤ **Hardy-Schulze rule:**

(i) Opposite charged ions are effective for coagulation.

(ii) The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation. *e.g.;* $Al^{3+} > Ba^{2+} > Na^{+}$ for negatively charged colloids.

$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$ for positively charged colloids.

The reciprocal of coagulation value is called coagulating power. *i.e.*, lower the coagulation value, higher will be coagulating power.

➤ **Electrokinetic potential or Zeta potential:** The potential difference between the fixed layer and diffused layer of opposite charges is called zeta potential.

➤ **Coagulation:** Coagulation which can be reversed by shaking is called flocculation or coagulation.

➤ **Coagulating value:** The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as coagulation value.

$$\text{Coagulation value} \propto \frac{1}{\text{Coagulating power}}$$

➤ **Gold number:** The number of milligram of protective colloids which must be added to 10 ml of given Gold sol to prevent it from coagulation by addition of 1 ml of 10% of NaCl solution.

➤ **Applications of colloids:**

(i) Sewage disposal

(ii) Purification of drinking water

(iii) Smoke precipitation

(iv) Medicines

(v) Tanning

(vi) Rubber industry

➤ **Distinction between True solution, Colloids and Suspension:**

S. No.	True Solution	Colloids	Suspension
1.	It is homogeneous.	It appears to be homogeneous but actually it is heterogeneous.	It is heterogeneous.
2.	Its particle size is less than 1 nm.	Its particle size is 1 nm to 1000 nm.	Its particles are larger than 1000 nm.
3.	It passes through filter paper.	It passes through ordinary filter paper but not through ultrafilter.	It does not pass through filter paper.
4.	It does not show Tyndall effect.	It shows Tyndall effect.	It does not show Tyndall effect appreciably.
5.	It has higher value of Colligative property.	It has low value of Colligative property.	It has very low value of Colligative property.
6.	Its particles cannot be seen even with powerful microscope.	Its particles can be seen by powerful microscope due to scattering of light.	Its particles can be seen even with naked eye.

Know the Terms

➤ **Saturation pressure:** The pressure beyond which adsorption becomes independent of pressure is called as Saturation pressure.

- **Competitive adsorption:** A strong adsorbate gets adsorbed more efficiently as compared to weak adsorbate, that strong adsorbate can displace already adsorbed one from the surface of the adsorbent and is known as Competitive adsorption or Preferential adsorption.
- **Optimum pH:** Particular pH at which the rate of an enzyme catalysed reaction is maximum.
- **Crystalloids:** The substances whose aqueous solution can pass through the Semipermeable membrane.
- **CMC:** Critical Micelle Concentration is the concentration of surfactant above which micelle formation takes place.
- **Streaming potential:** When a liquid is forced through a porous material or a capillary tube, a potential difference is set up between the two sides and is known as Streaming potential.
- **Dorn potential:** When a particle is forced to move through a resting liquid, a potential difference is set up. It is known as Dorn potential also called Sedimentation potential.
- **U-number:** The number of milligrams of a hydrophilic sol which is sufficient to produce the colour change from red to blue in 1 cc of gold sol., and it is called as U-number.



CHAPTER-4

‘d’ AND ‘f’ BLOCK ELEMENTS

Revision Notes

d-Block Elements, their Properties and Compounds

- **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 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:** These elements have incomplete *6d*-orbitals. Known elements of this series are actinium (89) and then from Rf (104) Cn(112).
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
3 <i>d</i> 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) $3d^{10} 4s^2$
4 <i>d</i> 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) $4d^{10} 5s^2$
5 <i>d</i> series	La (57) $5d^1 4f^0 6s^2$	Hf (72) $5d^2 4f^{14} 6s^2$	Ta (73) $5d^3 4f^{14} 6s^2$	W (74) $5d^4 4f^{14} 6s^2$	Re (75) $5d^5 4f^{14} 6s^2$	Os (76) $5d^6 4f^{14} 6s^2$	Ir (77) $5d^7 4f^{14} 6s^2$	Pt (78) $5d^9 4f^{14} 6s^1$	Au (79) $5d^{10} 4f^{14} 6s^1$	Hg (80) $5d^{10} 4f^{14} 6s^2$
6 <i>d</i> series	Ac (89) $5f^0 6d^1 7s^2$	Rf (104) $5f^{14} 6d^2 7s^2$	Db (105) $5f^{14} 6d^3 7s^2$	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) $5f^{14} 6d^{10} 7s^2$

- **General characteristics of Transition Elements:**

Physical Properties:

- (i) All are metals.
- (ii) All are malleable and ductile except mercury (liquid).
- (iii) High thermal and electrical conductivity.

- (iv) **Metallic lustre and sonorous.**
- (v) **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 increases 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**.
- (vi) **Ionic radii:** The ionic radii decrease with increase in oxidation state.
- (vii) **Density:** From left to right in a period, density increases.
- (viii) **Ionisation enthalpy:** Along the series from left to right, there is an increase in ionisation enthalpy. Irregular trend in the 1st 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.
- (ix) **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.
- (x) **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.
- (xi) **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.
- (xii) **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 ($IE_1 + IE_2$), sublimation and hydration enthalpies.
- (xiii) **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 transition metals show multiple oxidation states and have large surface area, so, all metals act as a catalyst.
- (xiv) **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.
Magnetic moment, $(\mu) = \sqrt{n(n+2)}$ 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).
- (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,

+2	+3	+8, +3	+4	+7
MnO	Mn ₂ O ₃	Mn ₃ O ₄	MnO ₂	Mn ₂ O ₇
Basic	Amphoteric	Amphoteric	Amphoteric	Acidic

f-Block Elements : Lanthanoids and Actinoids

- **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 4*f*-orbitals following lanthanum La (*Z* = 57) is called the lanthanoid series. There are 14 elements in this series starting with Ce (*Z* = 58) to Lu (*Z* = 71).

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

● **Physical properties:**

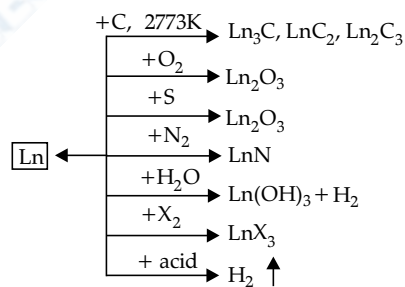
- (i) Highly dense metals, soft, malleable and ductile.
- (ii) High melting point.
- (iii) Forms alloys easily with other metals.
- (iv) **Magnetic properties:** Among lanthanoids, La³⁺ and Lu³⁺ which have 4*f*⁰ or 4*f*¹⁴ electronic configurations are diamagnetic and all other trivalent lanthanoid ions 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:

- (a) It leads to similar physical and chemical properties among lanthanoids.
 - (b) Zr and Hf have same properties due to similar atomic radii.
 - (c) 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 dehydrogenation and petroleum cracking.
- (v) Pyrophoric alloys are used for making tracer bullets and shells.



Mnemonics

3d series
• Concept: First Row Transition Elements-3d series
• Mnemonic: Scary Tiny Vicious Creatures Mingle (with) Fellow Cow Nilgai Cougar Zebra.
• Interpretation: Scandium(Sc), Titanium(Ti), Vanadium(V), Chromium(Cr), Manganese(Mn), Iron(Fe), Cobalt(Co), Nickel(Ni), Copper(Cu), Zinc(Zn)
4d series
• Concept: Second Row Transition Elements-4d series
• Mnemonic: Yesterday Zora Nabbed a Monkey TRicking her Rheumatic Padosan Agnes Cadillac.
• Interpretation: Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd
5d series
• Concept: Third Row Transition Elements-5d series
• Mnemonic: Late Harry Took Walk, Reached Office In Pajamas After an Hour.
• Interpretation: La....., Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg
Lanthanides
• Concept Name: Lanthanide Series
• Mnemonic: Late CEO Promoted Nadia Palmer Smart to Europe so she said Goodbye to Toby a Day before Hoarding Eroding Timber in Yard of Lu.
• Interpretation: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Know the Terms

- **Oxidation state:** The total number of electrons in the valence shell, more than or less than the number of electrons in free atom that an atom either gains or loses in order to form chemical bonds.
- **Ferromagnetic substances:** Substances which are attracted very strongly by the applied magnetic field. *e.g.*, Fe, Co, Ni etc.
- **Transuranic elements:** 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 too short.



CHAPTER-5

COORDINATION COMPOUNDS

Revision Notes

Coordination Compounds : Properties and IUPAC Name

- **Coordination Compound:** A coordination compound contains a central metal atom or ion surrounded by the number of oppositely charged ions or neutral molecules. There is a coordinate bond between metal atom and the ions or molecules, *e.g.*, $[\text{Cu}(\text{NH}_3)_4]^{2+}$.
- **Double Salt:** A salt is formed when two or more salts are added to form a stable solid and dissociate 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 bond in which one of the atoms supplies both the electrons. Coordinate bonds are also called dipolar bonds or dative bonds.

➤ **Central metal atom or ion:** The metal atom or ion surrounded by the fixed number of ions or molecules is called central metal atom or ion, *e.g.*, in $K_4[Fe(CN)_6]$, Fe^{2+} is the central metal ion.

➤ **Ligand:** The neutral molecules or ions (usually anions) which are attached with the central metal atom or ion in the 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.*, $\ddot{N}H_3$, $H_2\ddot{O}$:

(ii) **Bidentate ligands:** Contain two donor atoms. *e.g.*, $(COO^-)_2$, $CH_2 - \ddot{N}H_2$
 $\quad \quad \quad | \quad \quad \quad \ddot{N}H_2$
 $\quad \quad \quad CH_2 - \ddot{N}H_2$

(iii) **Polydentate ligands:** Contain more than two donor atoms. *e.g.*, EDTA.

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

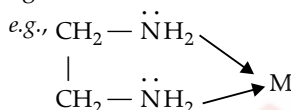
(i) **Cationic ligands:** Carry positive charge. *e.g.*, NO_2^+ , $N_2H_5^+$.

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

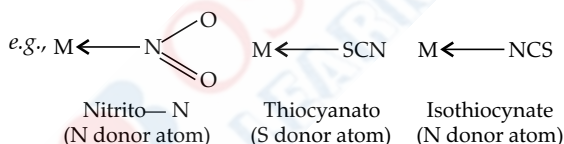
(iii) **Neutral ligands:** Do not carry any charge. *e.g.*, $\ddot{N}H_3$ (ammine), $H_2\ddot{O}:(\text{aqua})$.

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

(i) **Chelate ligands:** A bidentate or polydentate ligand uses its two or more donor atoms to bound 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.



➤ **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 $[Ni(NH_3)_6]^{2+}$, 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.*, $[PtCl_4]^{2-}$ has square planar geometry.

➤ **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:**

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

➤ **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 tetradentate ligand.
- **Oxidation number of central atom:** It is defined as the charge that central metal atom carry if all the ligands are removed along with the electron pairs that are shared with the central atom. It is represented by Roman numeral.
- **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.*, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$. The complexes in which the metal atom or ion is linked to more than one kind of ligands are called heteroleptic complexes. *e.g.*, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$.
- **Homonuclear and Polynuclear complexes:** Complexes in which only one metal atom is present are known as homonuclear complexes. *e.g.*, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$. 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 $\text{K}_4[\text{Fe}(\text{CN})_6]$, K^+ ions are counter ions.
- **Coordination ions:** The coordination entity with charge is called as coordination ion.
- **IUPAC Nomenclature of Coordination compounds:**
 - (i) The cation whether simple or complex is named first followed by anion.
 - (ii) Ligands are named in alphabetical order.
 - (iii) For indicating the number of each kind of ligand within the coordination entity, two kinds of numerical prefixes are used (di, tri, tetra, etc.). For ligands containing any of these prefixes in their names, their numbers are indicated by prefixes bis, tris, tetrakis, etc. Anionic ligands end with -o. Neutral ligands retain their names while cationic end with -ium.
 - (iv) The coordination sphere is written in square bracket.
 - (v) In IUPAC naming, ligands are named first in the alphabetical order followed by the metal atom and then the oxidation state of metal by a Roman numeral in parenthesis.
 - (vi) Name of coordination compounds starts with a small letter and the complex part is written as one word.
 - (vii) Oxidation number of central atom is indicated in Roman numerals. No space is left between the number and the rest of the name.

Werner's Theory, Bonding, Valence Bond Theory (VBT), Crystal Field Theory (CFT)

- **Werner's Theory of Coordination compounds:**

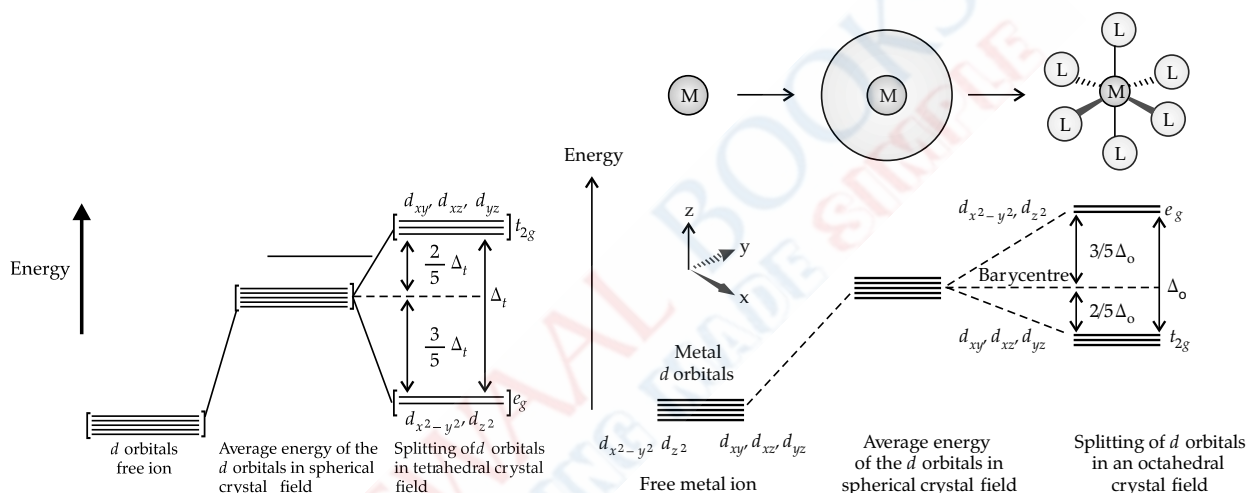
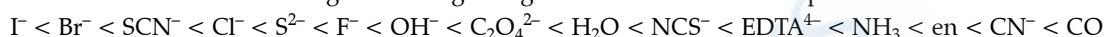
Different postulates of Werner's coordination theory are given below:

 - (i) Metal ions possess two types of valency (a) Primary or ionisable valency and (b) Secondary or non ionisable valency.
 - (ii) Every metal ion has a fixed number of secondary valency and this is known as coordination number.
 - (iii) **Primary valencies** are satisfied by the anions while secondary valencies are satisfied by the negative group or neutral molecules with lone pair of electrons.
 - (iv) **Secondary valencies** are directed in space towards the internal positions.
- **Limitations of Werner's theory:** This theory does not explain the following queries—
 - (i) Why is the complex forming tendency limited to a few elements only ?
 - (ii) Why bonds in the coordination complexes are of directional nature ?
 - (iii) Why are certain complexes of magnetic nature and show geometrical and optical isomerism ?
- **Valence Bond theory:** It was developed by Pauling. The brief points are:
 - (i) A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bond with the ligands.
 - (ii) Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon total number of ligands.
 - (iii) The hybridised orbitals are allowed to overlap with those ligand orbitals that can donate an electron pair for bonding.
 - (iv) The outer orbitals (high spin) or inner orbitals (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.
- **Limitations of Valence bond theory:**
 - (i) It cannot explain the detailed magnetic properties of complex compounds.
 - (ii) It cannot explain the optical absorption spectra of coordination compounds.

- (iii) It cannot predict properly whether a particular coordinate complex is square planar or tetrahedral in geometry.
- (iv) It fails to make distinction between strong and weak ligands.
- (v) It does not explain thermodynamic or kinetic stabilities of coordination compounds.

➤ **Crystal Field Theory (CFT):**

- (i) The ligand is considered as point charge or point dipole.
- (ii) Interaction between metal ion and ligand is considered as electrostatic in nature.
- (iii) Metal ion is supposed to be present at the origin of the axis. Ligands approach to the 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.
- (iv) 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.
- (v) Some ligands are able to produce strong fields in which 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 called as spectrochemical series.



d -orbital splitting in a tetrahedral crystal field

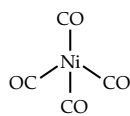
d -orbital splitting in an octahedral crystal field

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

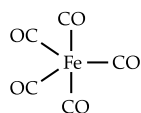
- **Metal carbonyls:** Homoleptic carbonyls are formed by d -block elements and contain carbonyl ligands only. e.g., $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, $[\text{Mo}(\text{CO})_6]$, $[\text{W}(\text{CO})_6]$, $[\text{Mn}_2(\text{CO})_{10}]$, $[\text{Fe}(\text{CO})_5]$, $[\text{Fe}_2(\text{CO})_9]$, $[\text{Co}_2(\text{CO})_8]$, $[\text{Co}_4(\text{CO})_{12}]$, $[\text{Ni}(\text{CO})_4]$, etc. Metal carbonyls from outside the central part of a d -block are unstable.

Properties of Metal carbonyls:

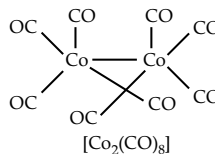
- (i) Metal carbonyls are mostly solids at room temperature and pressure. Exceptionally, iron and nickel carbonyls are liquids.
- (ii) The mononuclear carbonyls are volatile and toxic.
- (iii) Most of the metal carbonyls are soluble in hydrocarbon solvents except $[\text{Fe}_2(\text{CO})_9]$.
- (iv) Mononuclear carbonyls are either colourless or light coloured.
- (v) They are highly reactive due to central metal and the CO ligands.
- (vi) Metal carbonyls are used as industrial catalyst and as a precursor in organic synthesis.

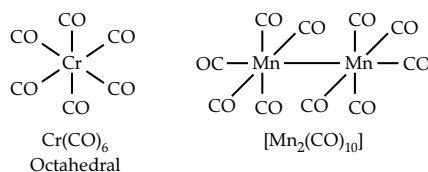


$\text{Ni}(\text{CO})_4$
Tetrahedral



$\text{Fe}(\text{CO})_5$
Trigonal bipyramidal





- **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 the back donation of pair of d -electrons to vacant antibonding orbital of carbonyl.
- **Factors affecting the stability of coordination complexes:**
 - (i) **Nature of the central ion:** Greater the charge density on the central metal ion, greater is the stability of the complex.
 - (ii) **Nature of the ligand:** More basic ligands have a tendency to donate the electron pairs to the central metal ion more easily resulting in a stable complex.
 - (iii) **Chelate effect:** Entropy increases when chelation occurs so the formation of the complex becomes more favourable.



Mnemonics

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

• **Mnemonic:** I Brought SCaNned Classnotes to Study Fundamentals of Chemistry.

• **He Nurtured Excellence in NHew (New) Coordination COmpounds chapter.**

• **Interpretation:** $\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{EDTA}^{4-} < \text{NH}_3 < \text{CN}^- < \text{CO}$

$\text{I}^- = \text{I}$

$\text{SCN}^- = \text{SCaNned}$

$\text{S}^- = \text{Study}$

$\text{OH}^- = \text{Of}$

$\text{H}_2\text{O} = \text{He}$

$\text{EDTA}^{4-} = \text{Excellence}$

$\text{CN}^- = \text{Coordination}$

$\text{Br}^- = \text{Brought}$

$\text{Cl}^- = \text{Classnotes}$

$\text{F}^- = \text{Fundamentals}$

$\text{C}_2\text{O}_4^{2-} = \text{Chemistry (Oxalate ion)}$

$\text{NCS}^- = \text{Nurtured}$

$\text{NH}_3 = \text{NHew}$

$\text{CO} = \text{Compounds (Carbonyl group)}$

Know the Terms

- **Coordination chemistry:** The study of the coordination compounds is known as coordination chemistry.
- **Labile complex:** A complex in which ligand substitution is fast.
- **Inert complex:** A complex in which ligand substitution is slow.
- **Synergic bonding:** A ligand donates a pair of electrons to the metal atom or ion and then accepts a pair of electrons back in its vacant orbital also from d -orbitals of the metal or ion. This is called synergic bonding and the ligands involved are known as π -donor ligands.
- **Effective Atomic Number (EAN):** It can be calculated for the metal atom or ion in the coordination complex by using following relation:

$$\text{EAN} = \text{Atomic no. (Z) of metal atom} - \text{Oxidation number} + 2 \text{ C.N. where, C.N. is coordination number.}$$
- **Perfect or penetrating complexes:** These are the complexes in which complex ion is fairly stable and either completely or feebly dissociates in solution.
- **Imperfect or abnormal complexes:** These are the complexes in which the complex ion is less stable and is dissociated reversibly to give enough simple ions.
- **Homogeneous catalysis:** Organometallic compounds or intermediates derived from soluble transition metal complexes catalyse a variety of reaction in solutions. This is known as homogeneous catalysis.

- **Macrocyclic effect:** Multidentate ligands happen to be cyclic in nature without causing any steric hindrance, the stability of the complexes is further increased. This is known as macrocyclic effect.
- **Metal carbonyl:** Organometallic compounds in which carbon monoxide acts as the ligand.



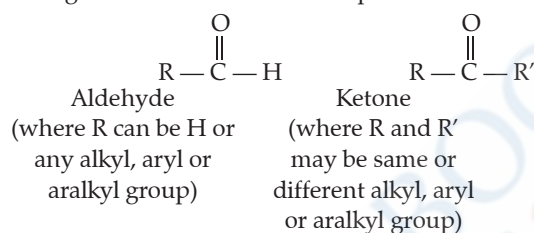
CHAPTER-6

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

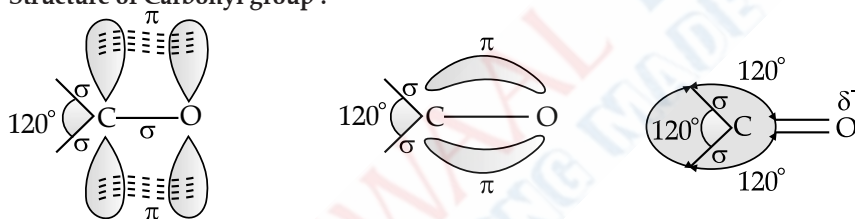
Revision Notes

Aldehydes and Ketones

- **Carbonyl group :** The functional group >C=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	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{H}, \text{ where } \text{R} = \text{C}_n\text{H}_{2n+1} \end{array}$ General formula :		
Structural formula	Condensed formula	Common name	IUPAC name
$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{H} \end{array}$	HCHO	Formaldehyde	Methanal
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{H} \end{array}$	CH_3CHO	Acetaldehyde	Ethanal
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CHO}$	Propionaldehyde	Propanal
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	Butyraldehyde	Butanal
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{CH}-\text{C}-\text{H} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CHO} \\ \\ \text{CH}_3 \end{array}$	Isobutyraldehyde	2-Methylpropanal

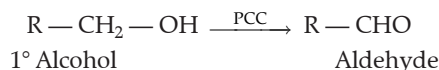
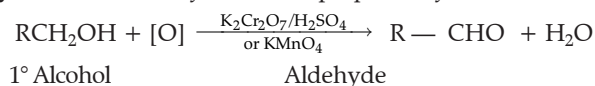
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{H}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	Valeraldehyde	Pentanal
$\text{CH}_3\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—CH}_2\text{C}(=\text{O})\text{H}$	$\text{CH}_3\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—CH}_2\text{CHO}$	Isovaleraldehyde	3-Methylbutanal
$\text{CH}_3\text{—CH}_2\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—C}(=\text{O})\text{H}$	$\text{CH}_3\text{—CH}_2\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—CHO}$	α -Methylbutyraldehyde	2-Methylbutanal

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

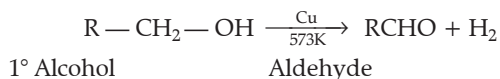
➤ **Methods of preparation of Aldehydes and Ketones :**

(a) **Preparation of Aldehydes :**

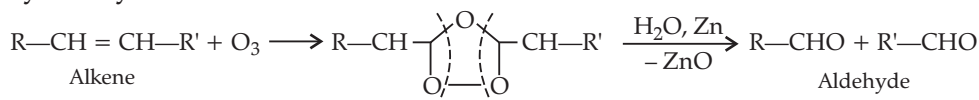
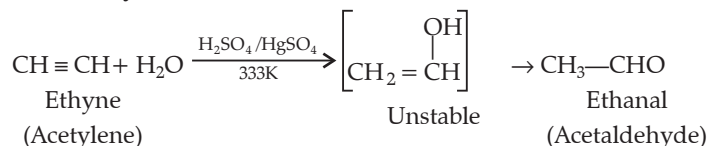
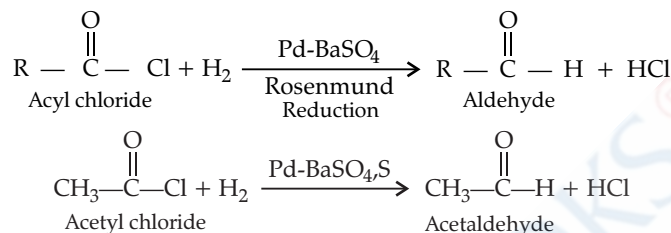
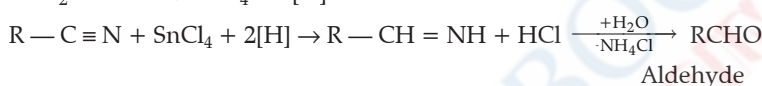
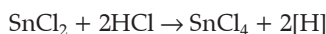
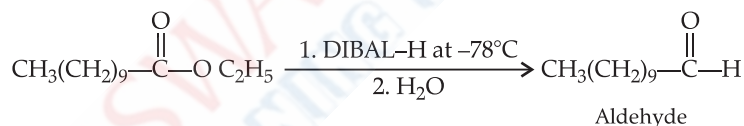
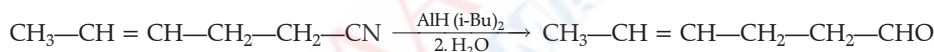
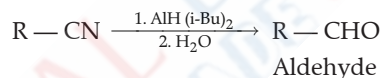
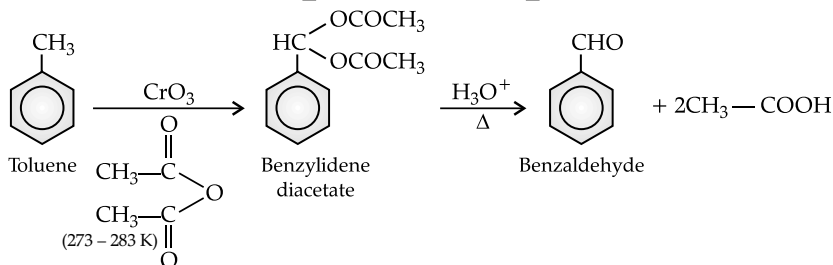
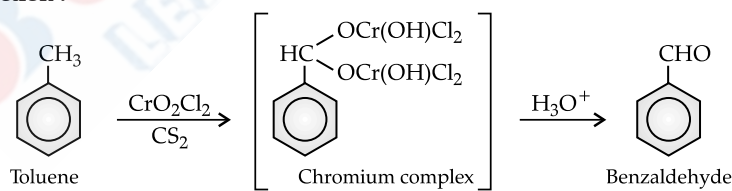
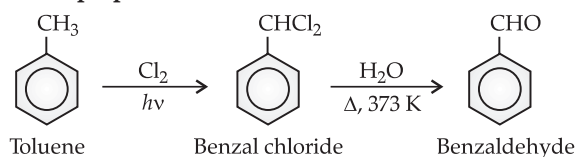
(i) **By oxidation of primary alcohols :** Aldehydes can be prepared by the oxidation of primary alcohols.

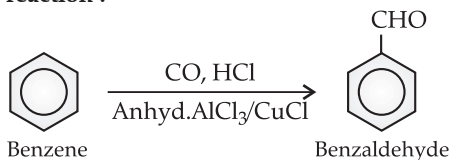
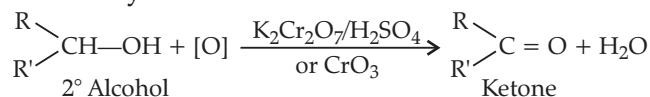
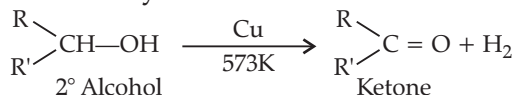
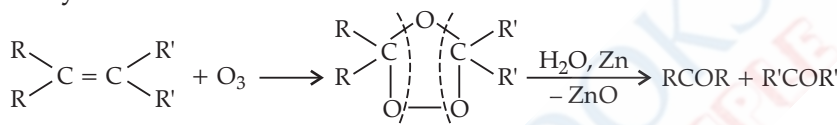
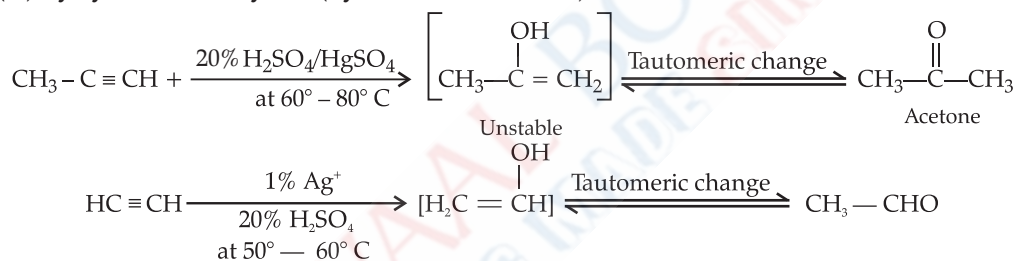
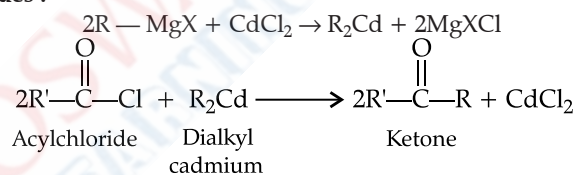
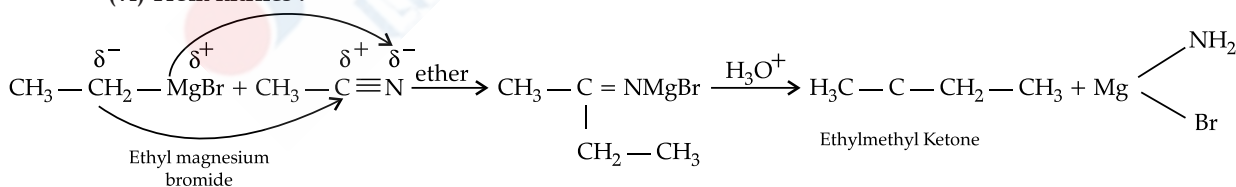
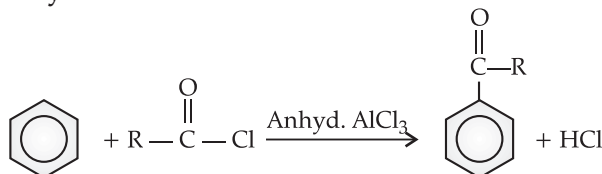


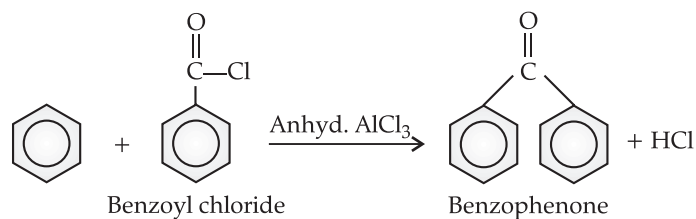
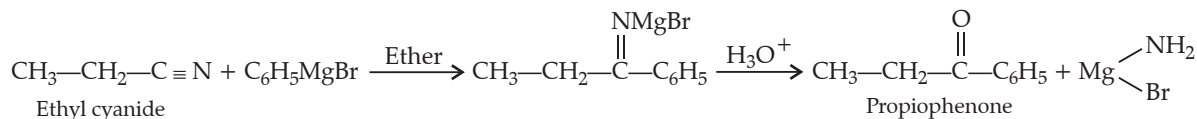
(ii) **By dehydrogenation of alcohols :**



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

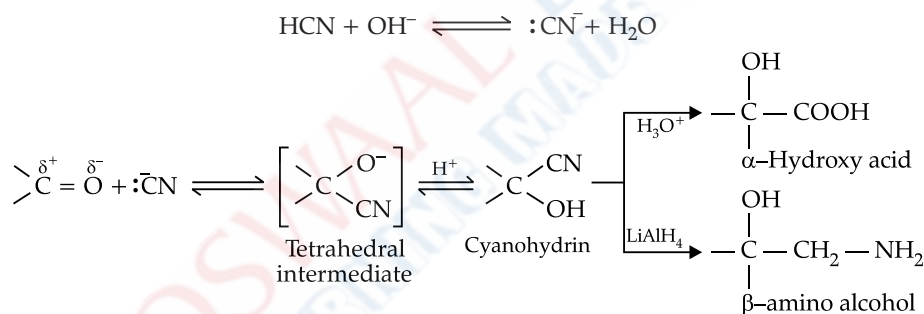
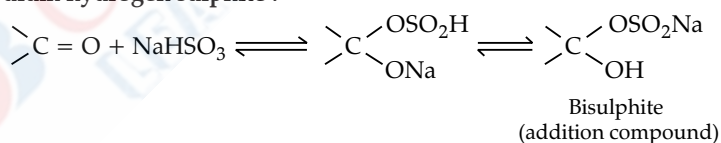
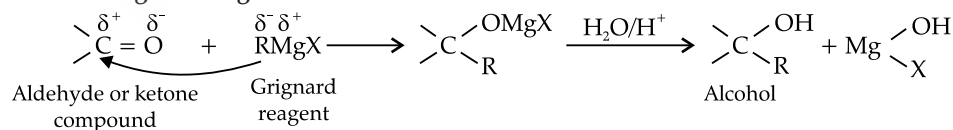
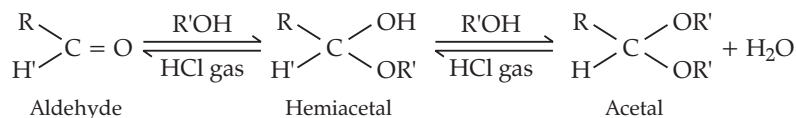
(a) By ozonolysis of alkenes :**(b) By hydration of alkynes :****(iv) From acyl chloride :****(v) From nitriles and esters :****Stephen reaction :****(b) Preparation of Benzaldehyde :****(i) By oxidation of toluene :****Etard reaction :****(ii) By side chain chlorination followed by hydrolysis :****Commercial 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 :****(d) Preparation of Aromatic ketones :****(i) By Friedel-Crafts acylation :**

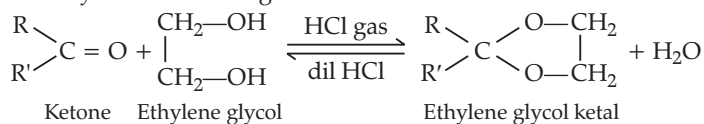
**(ii) From nitriles :****➤ Physical properties of Aldehydes and Ketones :**

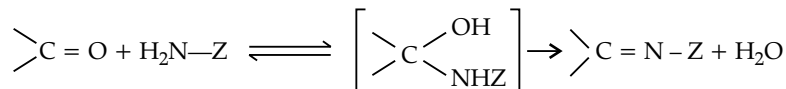
- (i) Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have a pleasant smell.
- (ii) Both of these have relatively high b.p. as compared to hydrocarbons of comparable molecular masses due to presence of polar carbonyl group. But they have lower b.p. 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.

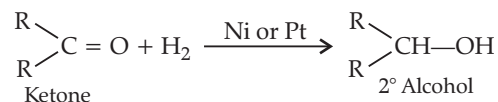
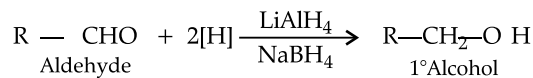
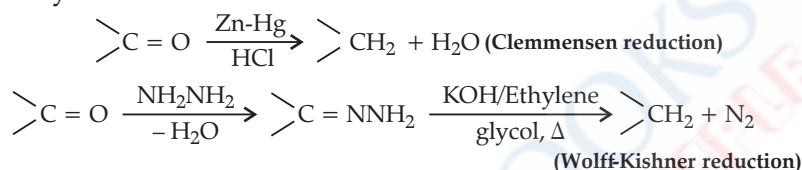
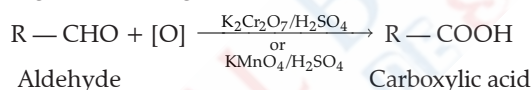
Nucleophilic addition reactions :**(i) Addition of hydrogen cyanide (HCN) :****(ii) Addition to sodium hydrogen sulphite :****(iii) Addition of Grignard reagent :****(iv) Addition of alcohols :**

Ketones react with dihydric alcohols to give ketals.

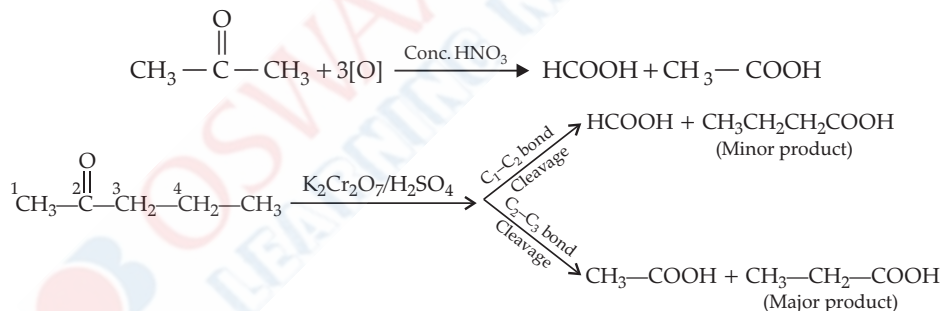


(v) Addition of ammonia and its derivatives :

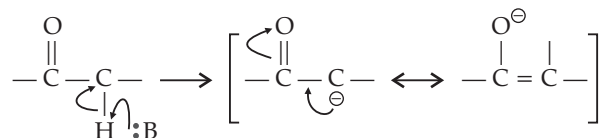
where, Z = Alkyl, aryl, -OH, -NH₂, C₆H₅NH-, -NHCONH₂, etc.

➤ Reduction :**(i) Reduction to alcohols :****(ii) Reduction to hydrocarbons :****➤ 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.

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).

➤ **Test for Aldehydes and Ketones :**

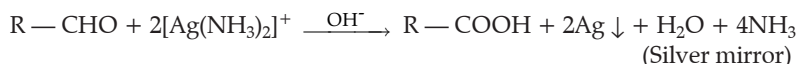
- (i) Both give iodoform test when one α -hydrogen is present.
 (ii) **Fehling's test :** Aliphatic aldehydes reduce the Fehling's solution to red cuprous oxide.

$$R-CHO + 2CuO + 5OH^- \rightarrow R-COOH + Cu_2O \downarrow + 3H_2O$$
 (red ppt.)

Aromatic aldehydes do not respond to this test.

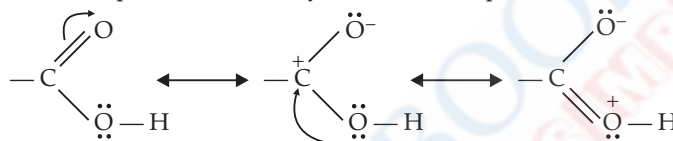
- (iii) Ketones are not oxidised by Tollen's reagent.

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



Carboxylic Acids

- Carboxylic acids are those compounds which have $-\overset{\overset{O}{\parallel}}{C}-OH$ group. The carboxyl group is made up of carboxyl, $>C=O$ and hydroxyl, $-OH$ 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.


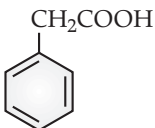
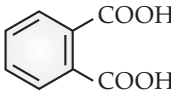
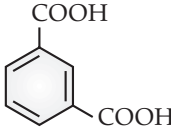
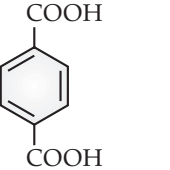


- **Nomenclature of carboxylic acids :** Derived by replacing terminal 'e' of the alkane with 'oic acid'.

Carboxylic acids Structural formula	General formula : $R-\overset{\overset{O}{\parallel}}{C}-OH$, where $R = C_nH_{2n+1}$		
	Condensed formula	Common name	IUPAC name
$R-\overset{\overset{O}{\parallel}}{C}-OH$	HCOOH	Formic acid	Methanoic acid
$CH_3-\overset{\overset{O}{\parallel}}{C}-OH$	CH ₃ COOH	Acetic acid	Ethanoic acid
$CH_3CH_2-\overset{\overset{O}{\parallel}}{C}-OH$	CH ₃ CH ₂ COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2-\overset{\overset{O}{\parallel}}{C}-OH$	CH ₃ CH ₂ CH ₂ COOH	Butyric acid	Butanoic acid
$CH_3-\underset{\underset{CH_3}{ }}{CH}-\overset{\overset{O}{\parallel}}{C}-OH$	(CH ₃) ₂ CHCOOH	Isobutyric acid	2-Methylpropanoic acid

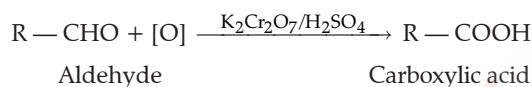
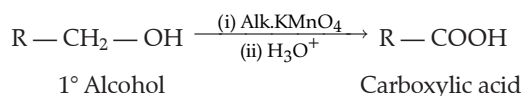
Dicarboxylic Acids

$\begin{array}{c} COOH \\ \\ COOH \end{array}$ (Oxalic acid) Ethane-1, 2-dioic acid	$\begin{array}{c} COOH \\ / \\ CH_2 \\ \backslash \\ COOH \end{array}$ (Malonic acid) Propane-1, 3-dioic acid	$\begin{array}{c} CH_2COOH \\ \\ CH_2COOH \end{array}$ Butane-1, 4-dioic acid (Succinic acid)	$\begin{array}{c} CH_2COOH \\ / \\ CH_2 \\ \backslash \\ CH_2COOH \end{array}$ (Glutaric acid) Pentane-1, 5-dioic acid
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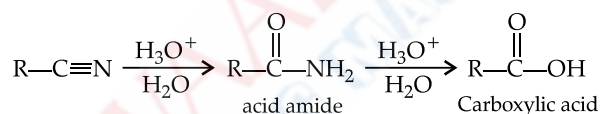
$\begin{array}{c} \text{CH}_2\text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{CH}_2\text{COOH} \\ \text{(Adipic acid)} \\ \text{Hexane-1, 6-dioic acid} \end{array}$	$\begin{array}{c} \text{CH}_2 - \text{COOH} \\ \\ \text{CH} - \text{COOH} \\ \\ \text{CH}_2 - \text{COOH} \\ \text{Propane- 1, 2, 3-} \\ \text{tricarboxylic acid} \end{array}$	$\begin{array}{c} \text{CH}_3 - \text{CH} = \text{CH} - \text{COOH} \\ \text{(Crotonic acid)} \\ \text{But-2-enoic acid} \end{array}$	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 - \text{CH} - \text{COOH} \\ \text{(Lactic acid)} \\ \text{2-Hydroxypropanoic acid} \end{array}$	
 <p>Benzoic acid or Benzene carboxylic acid</p>	 <p>Phenylacetic acid or 2-Phenylethanoic acid</p>	 <p>Phthalic acid or Benzene-1, 2- dicarboxylic acid</p>	 <p>Isophthalic acid or Benzene-1, 3- dicarboxylic acid</p>	 <p>Terephthalic acid or Benzene-1, 4- dicarboxylic acid</p>

➤ **Methods of preparation of Carboxylic acids :**

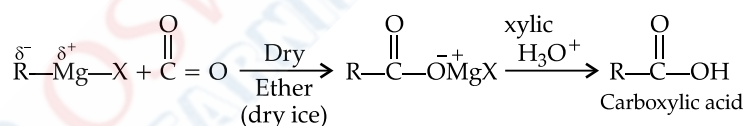
(i) **By oxidation of primary alcohols and aldehydes :**



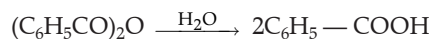
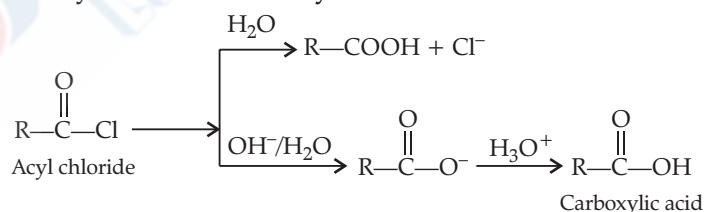
(ii) **From nitriles and amides :**



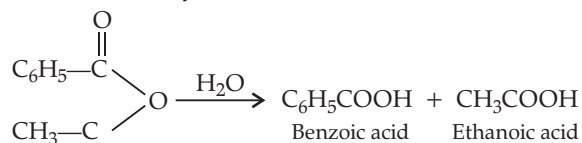
(iii) **From Grignard reagent :**



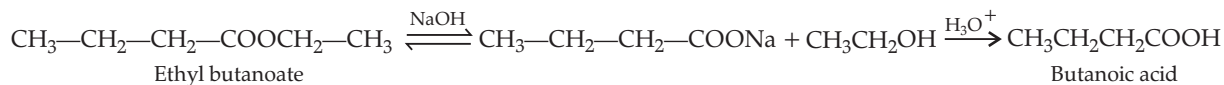
(iv) **From hydrolysis of acyl halide and acid anhydrides :**



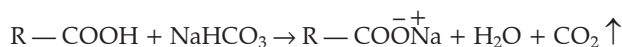
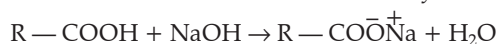
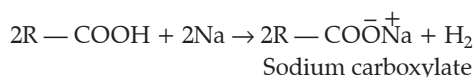
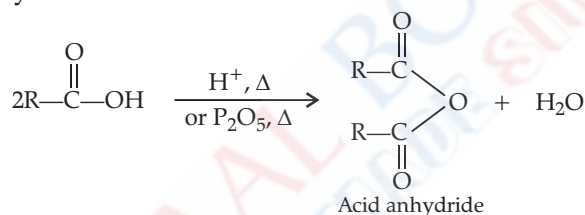
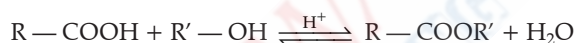
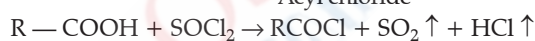
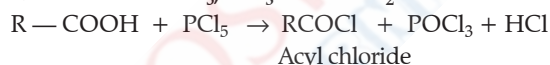
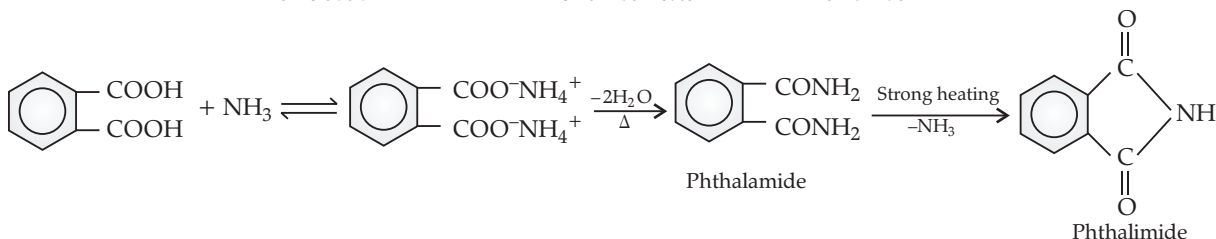
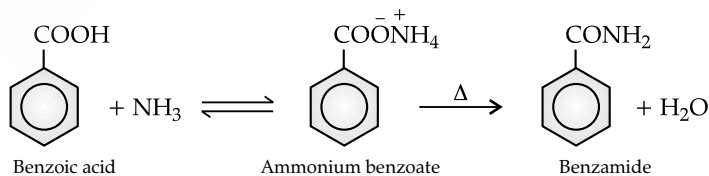
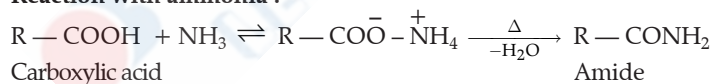
Benzoic anhydride Benzoic acid

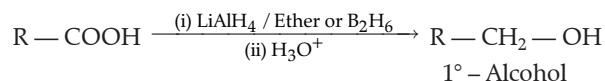
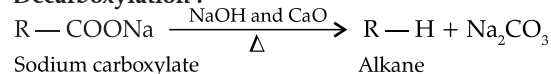
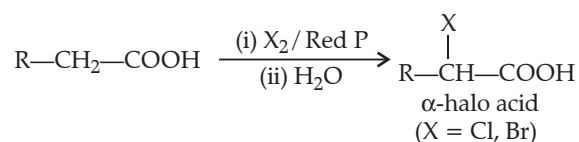


Benzoic ethanoic anhydride

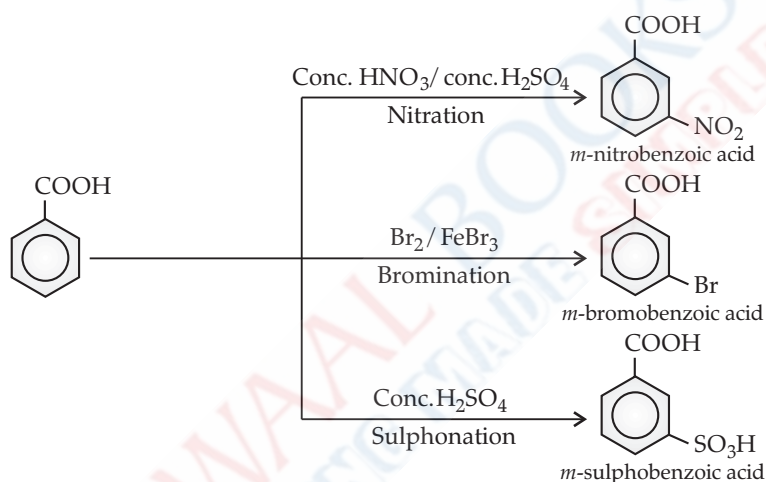
(v) By hydrolysis of esters :**➤ Physical properties of Carboxylic acids :**

- (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 PCl₅, PCl₃ and SOCl₂****(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 :

Mnemonics

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

• **Mnemonic:** TASTy FAAlI Redbrown IMeLY

• **Interpretation:** 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 -C=O- group, Yellow ppt

• **Concept:** Cannizaro's Reaction

• **Mnemonic:** CRAKN Reviews

• **Interpretation:** Cannizzaro Reaction is given by Aldehydes and Ketones having no α-H atom.

• **Concept:** To memorise reagents used for converting -C=O- to alkanes in Clemmensen and Wolff-Kishner reduction

• **Mnemonic:** Can Zebra WOO Nightingale

• **Interpretation:** To memorise reagents used for converting -C=O- to alkanes

C and Z- Clemmensen reduction → Zn-Hg/HCl

W and N- Wolff- Kishner reduction → NH₂NH₂/OH⁻

Know the Terms

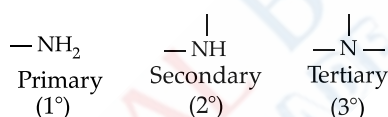
- **Tollen's Reagent** : Ammonical silver nitrate solution with which aldehydes give confirmatory silver mirror test.
- **Fehling's Solution** : Fehling A (aq. Copper sulphate) solution + Fehling B solution (alk. Sodium potassium tartarate). Aliphatic aldehydes reduce it to give reddish brown precipitate, which is a confirmatory test for aliphatic aldehydes.
- **Aldol Condensation**: Aldehydes and ketones having α -hydrogen in presence of dil. alkali form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol).
- **Cannizzaro Reaction**: Aldehydes which do not contain α -hydrogen undergo self oxidation and reduction on heating with conc. alkali resulting in an alcohol and a carboxylic acid.



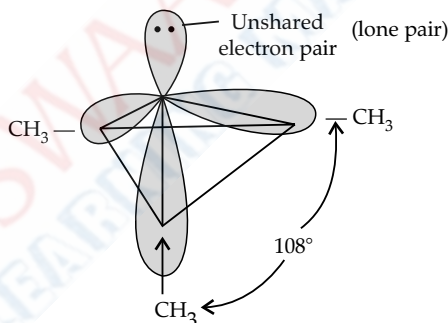
CHAPTER-7 AMINES

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**:

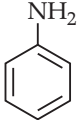
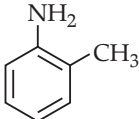
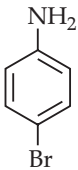



Pyramidal shape of trimethylamine

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

- **Nomenclature of some Alkylamines and Arylamines**:

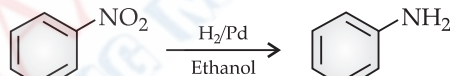
Amine	Common name	IUPAC name
$\text{CH}_3\text{—CH}_2\text{—NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—NH}_2$	<i>n</i> -Propylamine	Propan-1-amine
$ \begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\ \\ \text{NH}_2 \end{array} $	Isopropylamine	Propan-2-amine
$ \begin{array}{c} \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

$\begin{array}{c} \text{C}_2\text{H}_5-\text{N}-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}_2}-\overset{3}{\text{CH}_2}-\overset{4}{\text{CH}_3} \\ \\ \text{C}_2\text{H}_5 \end{array}$	N, N-Diethylbutylamine	N, N-Diethylbutan-1-amine
$\text{NH}_2-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}}=\overset{3}{\text{CH}_2}$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2$	Hexamethylenediamine	Hexane-1, 6-diamine
	Aniline	Aniline or Benzenamine
	<i>o</i> -Toluidine	2-Aminotoluene
	<i>p</i> -Bromoaniline	4-Bromobenzylamine or 4-Bromoaniline
	N, N-Dimethylaniline	N, N-Dimethylbenzenamine

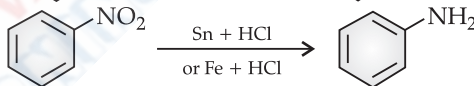
➤ **Preparation of Amines:**

(i) **By reduction of nitro compounds:**

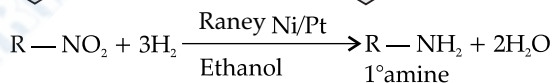
(a)



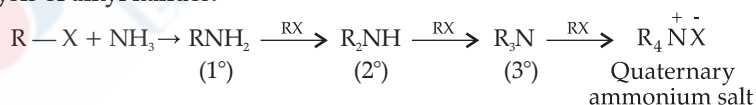
(b)



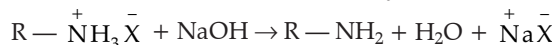
(c)



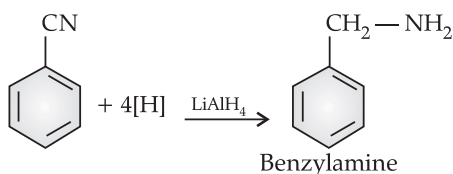
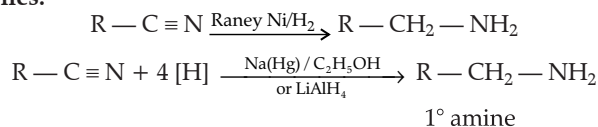
(ii) **By ammonolysis of alkyl halides:**

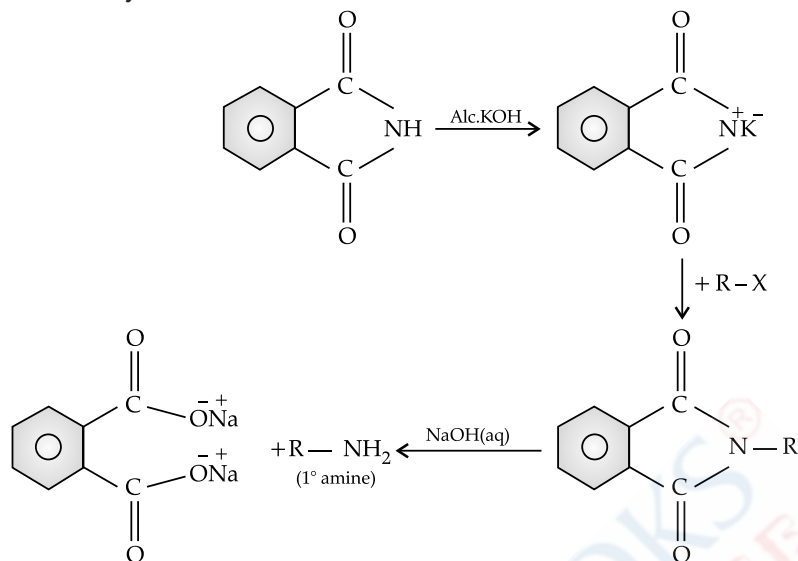
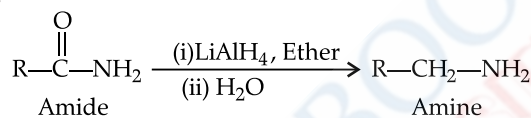
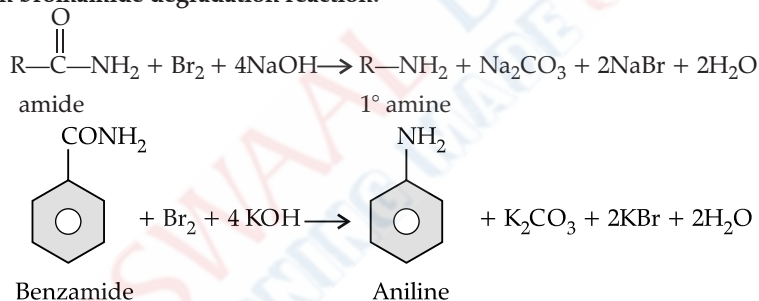


The free amine can be obtained from the ammonium salt by treatment with a strong base:



(iii) **By reduction of nitriles:**

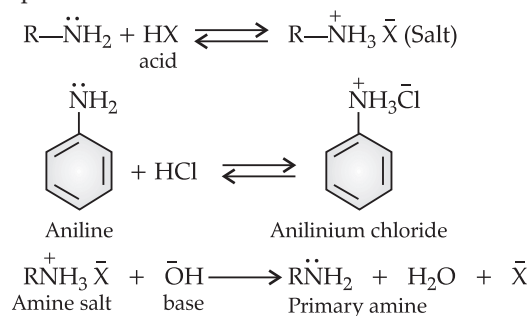


(iv) Gabriel phthalimide synthesis:**(v) By reduction of amides:****(vi) By Hoffmann bromamide degradation reaction:****➤ Physical properties:**

- (i) Lower members are combustible gases, members from C₃ to C₁₁ are volatile liquids and C₁₂ onwards are solids. 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: 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:**

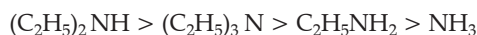
Amines are basic in nature because they can undergo protonation due to the presence of lone pair of electrons on nitrogen atom of —NH₂ group.



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 stabilised 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:

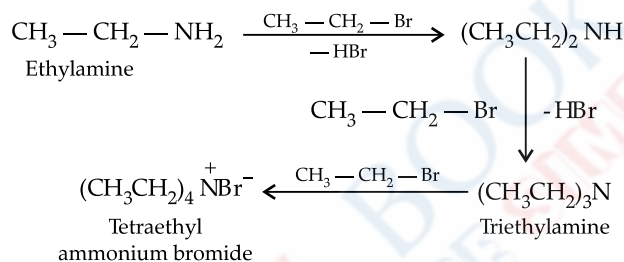


The inductive effect, solvation effect and steric hindrance of the alkyl group decide the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

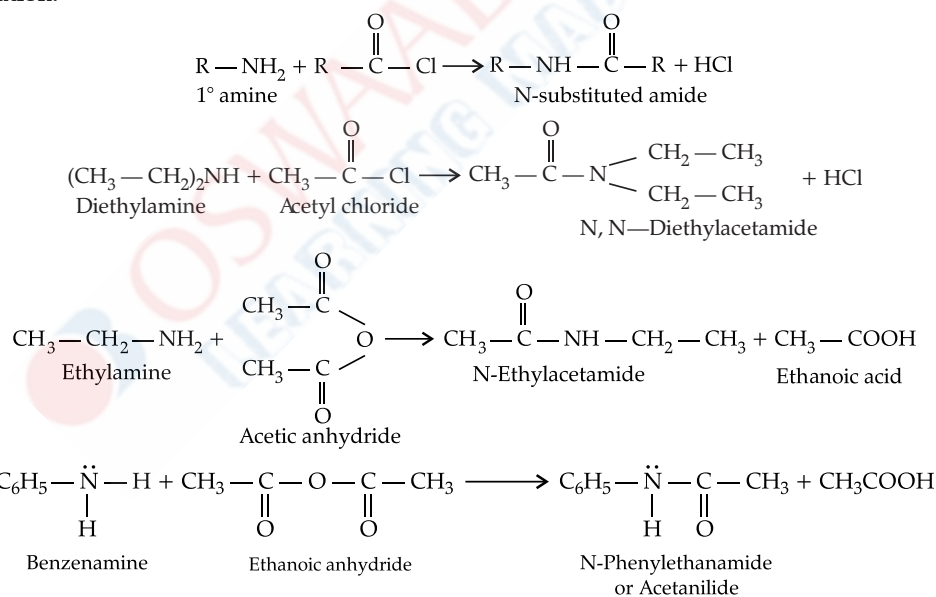


As the $-\text{NH}_2$ group is attached directly to the benzene ring in aryl amines, this results in conjugation of the lone pair of nitrogen with the benzene ring and thus making it less available for protonation. Thus, proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like $-\text{OCH}_3$, $-\text{CH}_3$ increase basic strength whereas electron withdrawing groups like $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{X}$ decrease basic strength.

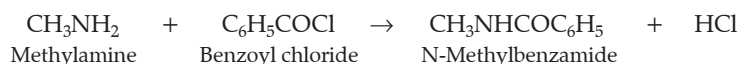
(i) Alkylation:



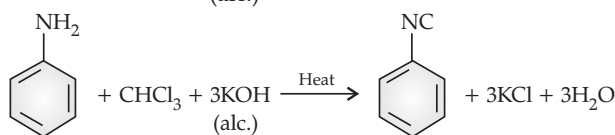
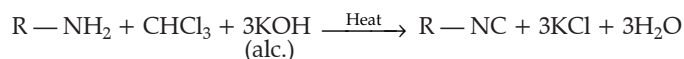
(ii) Acylation:



Benzoylation:



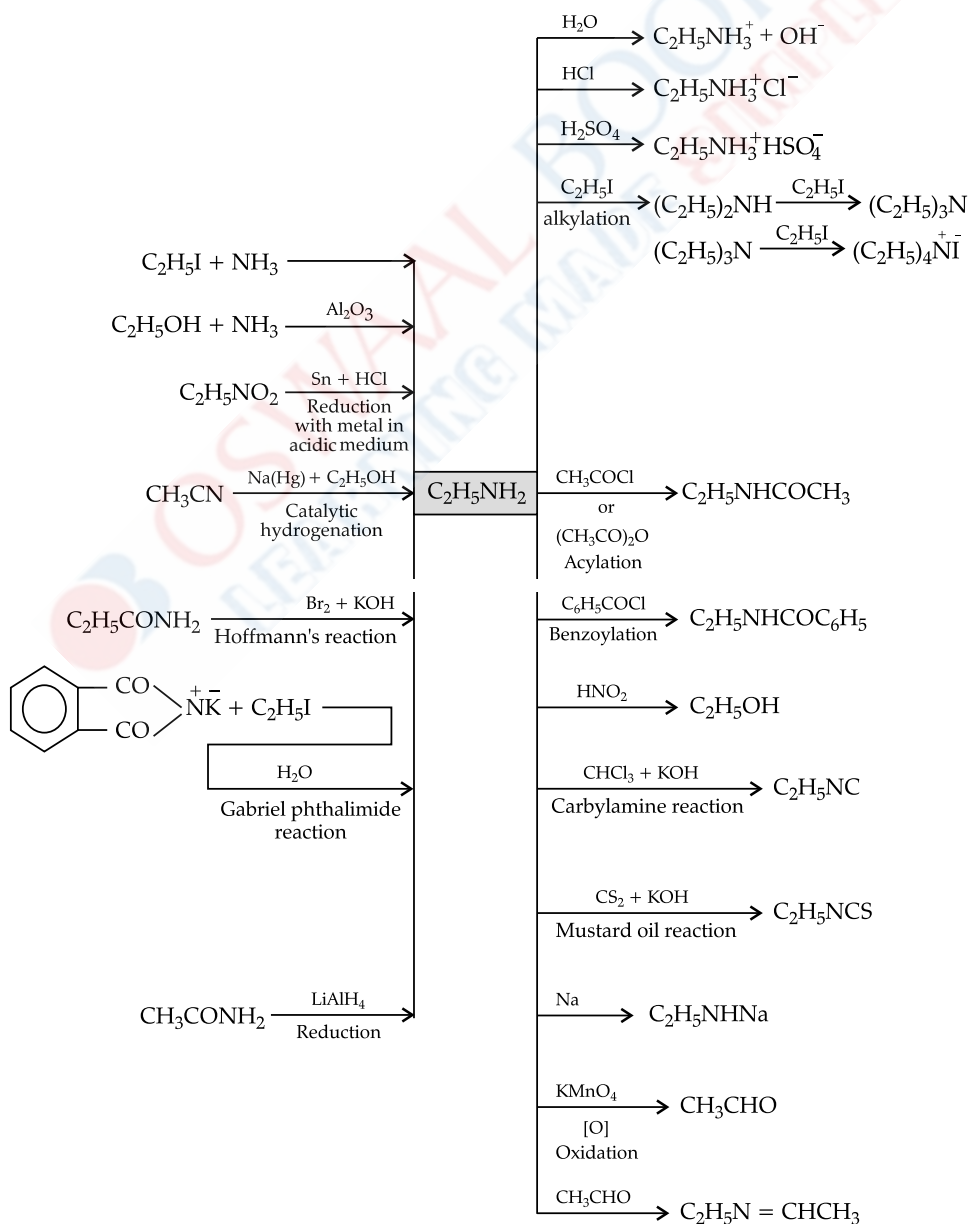
(iii) Carbylamine reaction: Secondary and tertiary amines do not give this reaction. This reaction is used to give a positive test for primary amines.



➤ Identification of primary, secondary and tertiary amines:

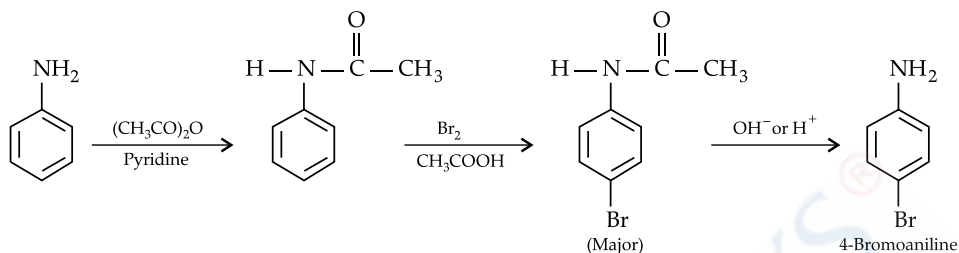
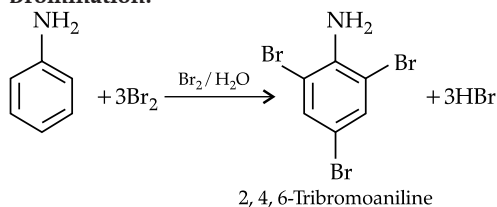
S.No.	Test	Primary amine	Secondary amine	Tertiary amine
(i)	Reaction with nitrous acid.	Gives alcohol with effervescence of N ₂ gas.	Gives oily nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold soluble in water and on heating gives nitrosoamine
(ii)	Hinsberg Test: Reaction 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.

➤ Methods of preparation and chemical reactions of ethylamine:

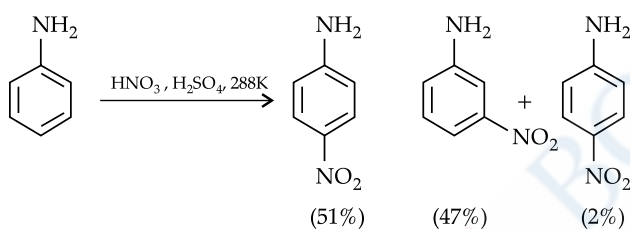


➤ **Electrophilic substitution reactions for aniline**

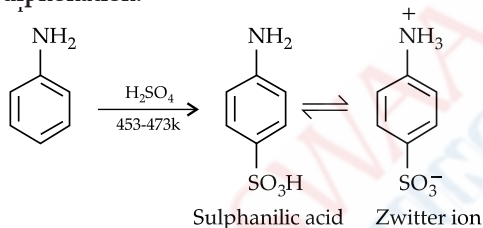
(i) **Bromination:**



(ii) **Nitration:**



(iii) **Sulphonation:**



Mnemonics

- Concept: Amines
- Mnemonic: **P**assive **A**voidance **C**onditioned **R**eflex
- Interpretation: Primary amines give Carbylamine reaction.

Know the Terms

- **Zwitter ion:** It contains both positive and negative ions. It contains acidic as well as basic groups in the same molecule, e.g.,



- **Gabriel phthalimide synthesis:** Phthalimide gives potassium salt with ethanolic KOH, which on heating gives alkyl halide which in turn on alkaline hydrolysis gives primary amine. It is used for 1° amine synthesis.
- **Hoffman Bromamide degradation:** 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.
- **Sandmeyer's reaction:** Introduction of nucleophiles Cl⁻, Br⁻, CN⁻ to benzene ring in presence of Cu(I) ion.
- **Schotten Baumann reaction:** Benzoylation of amines with benzoyl chloride is known as Schotten Baumann reaction.