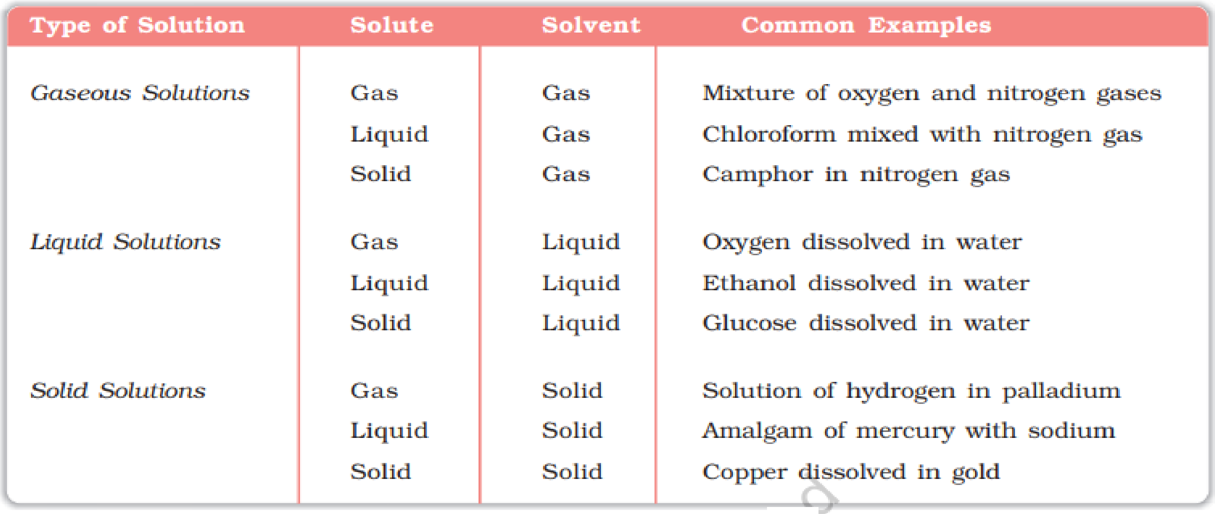
CHAPTER - 1 SOLUTIONS
SUMMARY

TYPES OF SOLUTIONS:



Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

CONCENTRATION OF SOLUTIONS

Some basic formulae	**Mole fraction**	**Molarity (**M)
Mass percentage. **w/w%** **For liquid solutions** w/w%=massof component/total mass of solution	For solvent $X_A=n_A/n_A+n_B$ For solute $X_B=n_B/n_A+n_B$ $X_A+X_B = 1$ **ppm (parts per million)=** mass of solute x10^6/total mass of solution	no. of moles of solute/volume of solution (L) Unit=mole/litre [mol/L] **Molality (m) =** no. of moles of solute/mass of solvent(kg) Unit=mole/Kilogram [mol

Henry's law: - Statement: - Mole fraction of gas in the solution is directly proportional to partial pressure of gas in the vapour phase.

$P \alpha X_B$ $P= K_HX_B$ (K_H= Henry's constant)(greater the **K_H**value lower the solubility

APPLICATIONS: 1. Soft drinks are sealed under high pressure to increase solubility of CO_2.

2. To avoid **Bends**, the tanks used by scuba divers are filled with air diluted with helium (less soluble than N_2)

Anoxia,problem at higher altitudes due to low pressure low concentration of O_2 in Blood cells.

- **Vapour pressure: -**The pressure exerted by the vapours in the equilibrium with liquid at a given temperature is called vapour pressure
- **Raoult's law: -** The partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

$$P_A \alpha X_A \qquad P_B \alpha X_B$$

$$P_A=P_A^oX_AP_B^oX_A$$

$$P_T=P_A+P_B \text{ (Daltons Law)}$$

Ideal solutions	**Non-Ideal solutions**

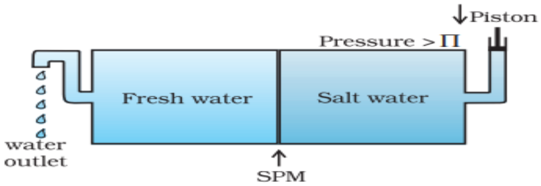
Obeys Raoult's law over the entire range of concentration e.g. Solution of n-hexane and n-heptane	Don't Obey **Raoult's law**
A-A , B-B = A-B interactions	A-A , B-B ≠ A-B interactions
$P_{Total}= P_A+ P_B, P_{Total}= P^0_A X_A+ P_B^0 X_B$	$P_{Total} \neq P_A+ P_B, P_{Total} \neq P^0_A X_A+ P_B^0 X_B$
$\Delta_{mix} H= 0$ $\Delta_{mix} V = 0$	$\Delta_{mix} H \neq 0$, $\Delta_{mix} V \neq 0$
Can be separated by fractional distillation	Cannot be separated by fractional

Positive deviation	**Negative deviation**
$P_{Total} > P_A+ P_B$ ΔV_{mix}=+ve,ΔH_{mix}=+ve	PTotal< PA+ PB ΔVmix=-veΔHmix=-ve
A – B interaction is weaker than A – A and B – B interactions. EXAMPLE-ethanol+water,acetone+ethanol	A – B interaction is stronger than A – A and B – B interaction Chloroform+acetone,water+HCl
Minimum boiling Azeotrope	Maximum boiling Azeotrope

- **Azeotrope**(Greek: boiling without change) Mixtures having same composition in liquid and vapour phase, boil at a constant temperature and cannot be separated by fractional distillation
- **Colligative properties: -** The properties of solutions which depend only on the number of particles of the solute (molecules or ions) dissolved in a definite amount of the solvent and do not depend on the nature of solute

Relative lowering in vapour pressure	**Elevation in boiling point**	**Depression in freezing point**	**Osmotic pressure**
$P^o_A - P_s/P^o_A = X_B$ $X_B = n_B/n_A + n_B$ [for a very dilute solution $n_B << n_A$] $P_A^o - P_S/P_A^o = n_B/n_A$	**$\Delta T_b = T_b - T_b^o$** **$\Delta T_b = K_b m$** **K_b =** molal elevation or EBULLIOSCOPIC constant. It is the elevation in boiling point of 1 molal solution.	**$\Delta T_f = T_f - T_f^0$** **$\Delta T_f = K_f m$** **K_f=** molal depression or CRYOSCOPIC constant. It is the depression in freezing point of 1 molal solution.	**π=CRT** **$\pi = \frac{nRT}{V}$** The excess pressure on solution side which just prevents the flow of solvent molecules is called OSMOTIC PRESSURE.

- **OSMOSIS**-The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semipermeable membrane is called **OSMOSIS.**
- **REVERSE OSMOSIS**-The process of movement of solvent through a semipermeable membrane from the solution to the pure solvent by applying pressure more than osmotic pressure on the solution side is called reverse osmosis.



- **Application**-desalination of sea water
- **NOTE:** The **osmotic pressure** method **advantages** over other colligative properties.
- The measurement of osmotic pressure is around the room temperature,
- Gives large measurable value for dilute solution

ISOTONIC SOLUTION	HYPOTONIC SOLUTION	HYPERTONIC SOLUTION
Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. $\pi_1 = \pi_2$	solutions having different osmotic pressure at a given temperature, the one with lower osmotic pressure is called **hypotonic** solution	Solution with higher osmotic pressure is called **hypertonic** solution

- **Abnormal molar mass: ELECTROLYTIC SOLUTIONS:** - When the molar mass of a substance (solute) become higher or lower after its association or dissociation in the solution it is called abnormal molar mass.
- **Van't Hoff factor: i =** Normal molar mass/Abnormal(observed)molar mass

Colligative property after abnormal molar masses: -

- Lowering of vapour pressure: - $X_B = i\ P^o_A - P_s/P^o_A$
- Elevation in boiling point: - $\Delta T_b = i\ K_b\ m$
- Depression in freezing point: - $\Delta T_f = i\ K_f\ m$
- Osmotic pressure: **-** $\pi = iCRT$

PROPERTY	ASSOCIATION	DISSOCIATION
Colligative property	Lowers	Increases
Molar mass	Greater than theoretical value	lesser
i=1	i < 1	i > 1
α (extent) =degree of dissociation / association	$\alpha = i-1/1/n-1$ [n = no. of particles associated]	$\alpha = i-1/n-1$ [n = no. of dissociated particles.]

SECTION -A (1 Mark)

Q1. The value of Henry's Law constant is:

(a) larger for gases with higher solubility (b) larger for gases with lower solubility

(c) Constant for all gases (d) Not related to the solubility of gases

Q2. If a molecule AB undergoes dimerization in Benzene, its Van't Hoff factor is found to be 0.60. The degree of dissociation of AB is

(a) 20% (b) 60% (c) 80% (d) 50%

Q3.Select the property that is not colligative in nature.

(a) Osmotic pressure (b) Lowering of vapour pressure

(c) Depression in freezing point (d) Molal elevation constant

Q4.An unripe mango placed in a concentrated salt solution to prepare pickles shrinks because

2. ELECTROCHEMISTRY

SUMMARY

Electrochemistry is a branch of chemistry which deals with inter-conversion of chemical energies and electrical energy

⇨ Before going into details of the chapter , you must know……

Redox reaction: In a redox reaction, both oxidation and reduction reaction takes place simultaneously
Direct redox reaction : Both oxidation and reduction in same vessel.
Indirect redox reaction :oxidation and reduction in different vessels.

Conductors: Materials that allow flow of electrons . these are of two types

Electronic or Metallic Conductors	**Electrolytic or Solution conductors**
1.Movement of electrons in the metallic lattice, e.g., Cu, Ag, etc	1. Movement of ions in molten state or in aqueous solution of electrolytes, e.g., NaCl (aq) or NaCl (fused).
2. Passage of current brings only physical change.	2. Chemical and physical change both.
3. No transfer of matter	3. Transfer of matter takes place.
4. Generally show increase in resistance with increase in temperature.	4. Generally show decrease in resistance due to decrease in viscosity of medium and degree of hydration of ions.

In this chapter we will focus on Electrolytic conduactance and electrochemical cell

ELECTROLYTES:	**ELECTRODE :**
The substance that in solution or in the molten state, conducts electric current and is simultaneously decomposed. Their extent of dissociation may vary.	To pass the current through an electrolytic conductor, two rods or plates are conducted with the battery. These are called electrodes.
Strong electrolytes : That are 100% decomposed in normal solution. **eg.:All salts (except $CdBr_2$, $HgCl_2$), mineral acids like HCl, H_2SO_4, HNO_3, etc. and bases like NaOH, KOH, etc.**	**Active Electrodes:** (Basically used in electroplating.) Actively participate in the electrochemical reaction, either by donating or accepting ions. eg.Zn, Cu,,Pb and Ag electrodes.
Weak electrolytes : which dissociate only to a small extent in aqueous solution. **eg : All organic acids (except sulphonic acids), inorganic acids like HCN, H_3BO_3, etc. and bases like NH_3, amines, etc.**	**Inert Electrodes:** (basically used in electrolysis, and electrolytic cells) do not actively participate in the reaction but facilitate the transfer of electrons **eg :Pt, Au, graphite, rhodium etc.**

Electrical Conductance	**Specific Conductance or Conductivity**
The property of the conductor (metallic as well as electrolytic) which facilitates the flow of	In a conductor if length is 1 cm. And

electricity through it.
Conductance =1/ Resistance
Unit : mho^{-1}

area is 1 cm^2 , the resistance offered is known as resistivity .R = ρ
The reciprocal of specific resistance or resistivity is known as specific conductance or conductivity (κ)kappa.

$$R = \rho \frac{l}{A} = \frac{1}{k} \frac{l}{A}$$

Where l /A is called cell constant
Unit of (κ) is Siemen Cm^{-1}

Molar Conductance

the conductance of all the ions produced by ionization of 1 g-mole of an electrolyte when present in V ml of solution. It is denoted by Λm.

$$\Lambda_m = \frac{k \text{ x } 1000}{M}$$

Unit : Siemen Cm^{2}mol^{-1}

variation	With temp increase	With conc. decrease
conductivity	Increaseas	decreases
Molar conductivity	increases	increases
conductance	increases	decreases

Kohlrausch' law of independent migration of ions:

Molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions.
If the limiting molar conductivity of the cations is denoted by λ_+^0 and that of the anions by λ_-^0, then the limiting molar conductivity of electrolyte is:

Molar conductivity, $\Lambda_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$

Where v+ and v- are the number of cations and anions per formula of electrolyte

<u>Applications of </u>Kohlrausch's Law :

1. Determining Λ^0 m of a weak electrolyte:
2. Degree of dissocition,
   α=**Λm/Λ^{0}m**
3. Determination of solubility of sparingly soluble salt:

$$\Lambda^0 m = \frac{1000k}{C}$$

where, C is molarity of sol'n and hence solubility

4. Determination of ionic product of water

$$\Lambda^0 m \ (H_2O) = \lambda^0_{H+} + \lambda^0_{OH-}$$

(complete dissocition of water)

$$\Lambda^0 m = \frac{K}{C}$$

Then. **K_W=C^2**

<u>Ionic mobility</u> :For aqueous solution, greater the charge or smaller the size of gaseous ion, greater will be the size of aqueous ion. When such a big ion moves in solution, it experiences greater resistance by the size of solvent particles. This results in a decrease in its conductance as well as ionic mobility. Following are the increasing order of ionic mobilities of some ions:

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$; $< F^- < Cl^- < Br^- < I^-$;$< Al^{+3} < Mg^{+2} < Na^+$

Weak electrolytes : These are not completely ionized in polar solvents like water and hence an equilibrium between ions and unionised salt exists

$$AB+ \rightleftharpoons A^+ + B^-.$$

We can calculate degree of dissociation(α) and equilibrium constant (K),using expression **$K = c\alpha^2 /(1-\alpha)$, if $\alpha << 1$** then use **$K = c\alpha^2$**

Electrode Potential: A metal placed in a solution of its ions obtains either a positive or negative charge with respect to the solution. On account of this, a definite potential is developed between the metal and the solution. This potential difference is called electrode potential.

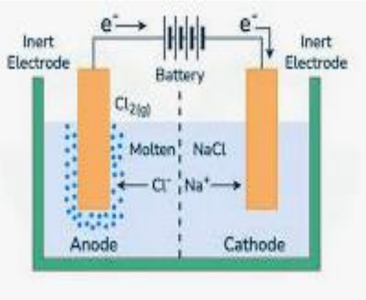
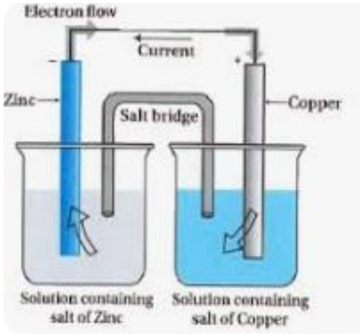
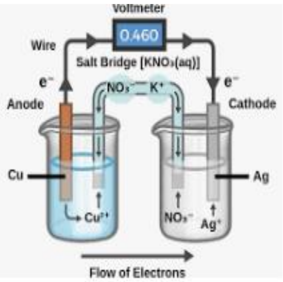
Standard Electrode Potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25ºC (298 K).

EMF of a cell: It is the difference in the potential across left and right electrodes due to which electrons flow from anode to cathode.

Standard EMF: The EMF values of an electrode under standard conditions (1 atm, 298 K) and the unit concentrations of its ions

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \text{ or } E^\circ_{cell} = E^\circ_{right\ electrode} - E^\circ_{left\ electrode}$$

ELECTROCHEMICAL CELLS

ELECTROLYTIC CELLS	DANIEL CELLS	GALVANIC CELLS
Devices in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done. (non spaontaneous redox reaction is carried out) 	A specific type of **voltaic cell** with a copper cathode and zinc anode, using copper sulfate and zinc sulfate solutions, respectively. It is known for its reliable and consistent voltage output. 	A broader term encompassing any electrochemical cell that converts chemical energy to electrical energy through a spontaneous redox reaction. 
Cell reaction : $NaCl + H_2O \rightleftharpoons Na^+ + OH^- + H_2 + Cl_2$ **QUICK COMPARISION** **1. Redox reaction** **Non spontaneous** **2.E^O^cell is negative** **3.Anode is +ve** **4.Cathode is -ve** **5.flow of electron anode to cathode** **6.Electrolysis, electroplating**	**Cell representation :** **Zn/Zn^{+2} (aq.) II Cu^{+2}(aq.)/Cu** **Redox reaction** **Spontaneous** **E^Ocell ispositive** **Anode is -ve** **Cathode is +ve** **Anode to cathode**	**Cell representation :** **Cu/Cu^{+2} (aq.)IIAg+/Ag** **Redox reaction** **Spontaneous** **E^Ocell is positive** **Anode is -ve** **Cathode is +ve** **Anode to cathode**

	Cell	**Batteries**

Faraday's law of electrolysis

First law:the amount of substance deposited at electrode is proportional to quantity of charge passed through the electrolyte.

W=zit

z is electrochemical equivalent

$$z = \frac{Eq.Wt}{F} = \frac{M}{nF}$$

$$W = \frac{M}{nF} * i * t$$

Second law :the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses,when same quantity of current is passed.

W =Z x Q,

When Q = 96500 coulomb

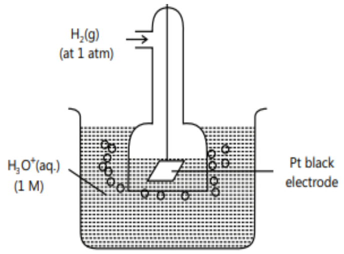
W becomes gm equivalent mass E,

$$Z = \frac{E}{96500} \; ; \; \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Faraday's first law and second

Reference Electrode To determine the cell potential of individual half cell , reference electrode is required. The electrode cell potential of reference electrodes are known.a and on coupling with other electrode, a **voltaic cell** is constituted.

Standard Hydrogen Electrode, SHE or NHE



Electrode : Platinized Platinum
Electrolyte: 1M HCl
(freshly prepared)
Temperature : 298 K
Hydrogen gas
Pressure : 1 atm or 1 bar

SHE half reaction	**Electrode potential**
$H_2 \longrightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \longrightarrow H_2$	0.0 V (Cathode)

Nernst Equation :

Suppose, we reduced the conc. of Zn $^{+2}$ in the Zn/Cu cell from its unit activity value of around 0.5 M to a much smaller value:

Zn/Zn^{+2} (0.001M) II Cu^{+2} /Cu

This will reduce the value of Q for the cell reaction

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

ΔG more negative than ΔG^0 , so

E would be more positive than

$\Delta G^0 = -nFE^o$; $\Delta G = -nFE$

Using $\Delta G = \Delta G^0 + RT\ lnQ$;

$$E = E^{\circ} - \frac{RT}{nF} lnQ$$

For a general reaction;

$$aA + bB \longrightarrow cC + dD$$

$$E_{cell} = E^{\circ}_{(cell)} - \frac{RT}{nF} lnQ = E^{\circ}_{(cell)} - \frac{RT}{nF} ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Salt bridge completes the

The overall reaction and ΔGº for each cell is same.
E^0_{cell} and 'n' values are different for each cell.
E^0_{cell} × n is same for each cell.
ΔGº depends on cell reaction and E^0_{cell} depends upon making up of a cell.

up of a cell

law can be combined $W = ZQ = \frac{E}{F} \times Q = \frac{Q}{F} \times E = \frac{Q}{F} \times \frac{M}{z} = \frac{C \times t}{F} \times \frac{M}{z}$	circuit, maintains electroneutrality and also minimises liquid junction potential.

Preferential Discharge Theory: Electrolysis of solutions containing more than two ions, the ion that requires the least energy (or has the highest reduction potential) to be discharged will be preferentially discharged at the respective electrode.

Cont.

electrolyte	electrode	Cathodic reaction	Anodic reaction	Remarks if any
1. Molten NaCl	Pt	$2Na^+ + 2e^- \rightarrow 2Na$	$2Cl^- \rightarrow Cl_2 + 2e^-$	One cation and on anion
2.Molten $PbBr_2$	Pt	$Pb \rightarrow Pb^{+2} + 2e^-$	$2Br^- + 2e^- \rightarrow Br_2$	**--do---**
3.NaCl aq. (two competing reactions are possible both at cathode and anode) **The products vary with concentration.**	Pt	**AT pH 7** At cathode : Na+ and water both can be reduced $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^o = -1.0$ V $Na^+(l) + e^- \rightarrow Na(l)$ $E^o = -2.71V$ At anode : both water and chloride ion can be oxidised. $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ $E^o = -1.42$ V $2Cl^- \rightarrow Cl_2 + 2e^-$ $E = -1.36V$		

A.) Very dilute aq. NaCl solution

water with high reduction potential is reduced at cathode

At cathode: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^o = -1.0$ V

At anode: $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ $E^o = +1.4$ V

In small conc.the electrolysis of water becomes more predominant yielding **oxygen at anode.**

B. **)High Concentration of Sodium Chloride :** **Hydrogen at cathode**

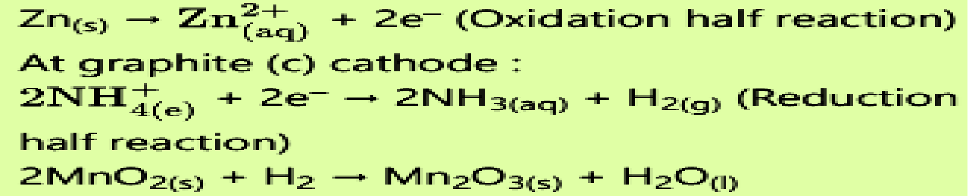
At anode oxidation of water being more positive is more feasible, so the evolution of oxygen gas should happen at the anode. But, the evolution of oxygen from water has an overvoltage of -0.6V, making the voltage for the oxidation of water as -1.4V.So, chloride is, oxidised to **chlorine at the anode**.

BATTERIES : Consist of two or more galvanic cells.these are of two types.

PRIMARY BATTERY

When the reactants have been converted to products, no more electricity is produced.the cell reaction can not be reversed and cell becomes dead.

A.) DRY CELL



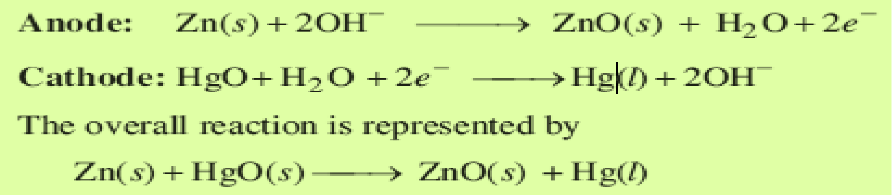
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (Oxidation half reaction)

At graphite (c) cathode :

$2NH^{+}_{4(e)} + 2e^- \rightarrow 2NH_{3(aq)} + H_{2(g)}$ (Reduction half reaction)

$2MnO_{2(s)} + H_2 \rightarrow Mn_2O_{3(s)} + H_2O_{(l)}$

B. **)** MERCURY CELL



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

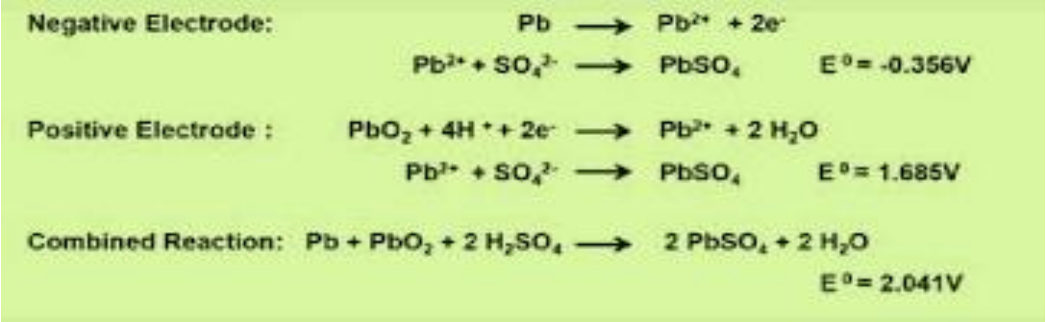
Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

The overall reaction is represented by

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

SECONDARY BATTERY : The cell reaction can be reversed by passing electricity through the battery(charging).It can be used again and again.

LEAD STORAGE BATTERY :



Negative Electrode: $Pb \longrightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$ $E^0 = -0.356V$

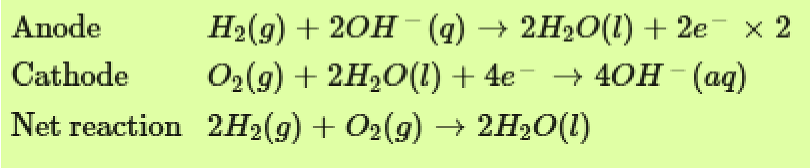
Positive Electrode : $PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$ $E^0 = 1.685V$

Combined Reaction: $Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

$E^0 = 2.041V$

FUEL CELLS : Electrical cells that are discharged to convert the energy from the combustion of fuels (hydrogen, carbon monoxide, methane, etc.) directly into the electrical energy are called fuel cells.



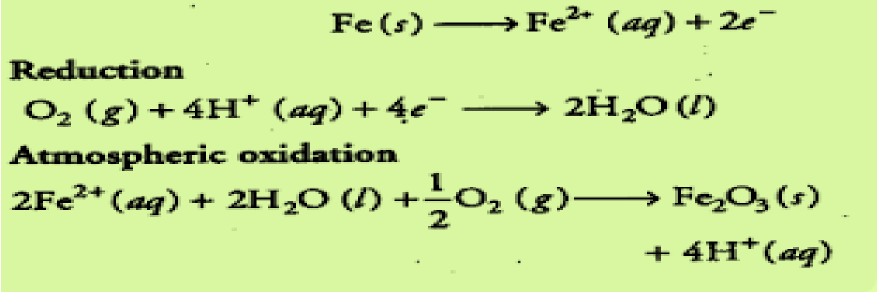
Anode $H_2(g) + 2OH^-(q) \rightarrow 2H_2O(l) + 2e^- \times 2$

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

Net reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Corrosion of Iron (Rusting)

Rusting of iron which is the most commonly seen example happens when iron comes in contact with air or water. The reaction could be seen as a typical electrochemical cell reaction..



$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Reduction

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

Atmospheric oxidation

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

PREVENTION OF RUSTING :

BARRIER COATINGS : Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds.

HOT-DIP GALVANIZATION : The iron in the steel reacts with the zinc to create a tightly bonded alloy coating which serves as protection.

CATHODIC PROTECTION : To prevent corrosion, the active sites on the metal surface are converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

IMPORTANT LINKS : Representation of electrochemical cell :
https://diksha.gov.in/play/content/do_3129961045697904641131?referrer=utm_source%3Dmobile%26utm_campaign%3Dshare_content
Electrochemistry at a glance :
https://diksha.gov.in/play/content/do_3134757780802928641239?referrer=utm_source%3Dmobile%26utm_campaign%3Dshare_content

QUESTION BANK
SECTION- A (1 MARK)

Q.1) Which device converts chemical energy of a spontaneous redox reaction into electrical energy?
(a) Galvanic cell (b) Electrolytic cell
(c) Daniell cell (d) Both (a) and (c)

Q.2) The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called
(a) Cell potentials (b) Cell emf
(c) Potential difference (d) Cell voltage

Q.3) The most durable metal plating on iron to protect against corrosion is
(a) nickel plating (b) copper plating
(c) tin plating (d) zinc plating

Q.4) The electric charge for electrode decomposition of one gram equivalent of a substance is
(a) one ampere per second (b) 96500 coulombs per second
(c) one ampere for one hour (d) charge on one mole of electrons

Q.5) The ion of least limiting molar conductivity among the following is
(a) SO_4^{2-} (b) H^+ (c) Ca^{2+} (d) CH COO^-

Q.7) Which of the following batteries cannot be reused?
(a) Lead storage battery (b) Ni-Cd cell
(c) Mercury cell (d) Both (b) and (c)

Q.8) Specific conductance of 0.1 M HNO_3 is 6.3×10^{-2} ohm^{-1} cm^{-1}.The molar conductance of the solution is
(a) 100 ohm^{-1} cm^2 (b) 515 ohm^{-1} cm^2
(c) 630 ohm^{-1} cm^2 (d) 6300 ohm^{-1} cm^2

Q.9) If salt bridge is removed from two half-cells the voltage
(a) drops to zero (b) does not change
(c) increases gradually (d) increases rapidly

Q.10) For the galvanic cell Zn | Zn^{2+} (0.1M) || Cu^{2+} (1.0M)|Cu; the cell potential increase if:
(a) [Zn^{2+}] is increased (b) [Cu^{2+}] is increased
(c) [Cu^{2+}] is decreased (d) surface area of anode is increased

B.)ASSERTION-REASON TYPE QUESTIONS: In the following questions Q.11 to Q.15, each of these questions contain two statements, Assertion and Reason. Each of these

Chapter- 3 Chemical Kinetics

Summary

- **Rate of a Chemical Reaction**: It is the change in concentration of a reactant or product per unit time.

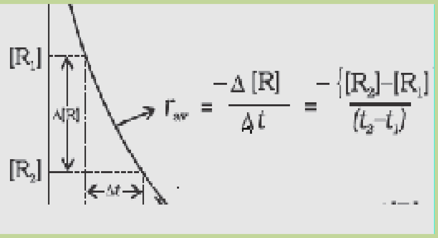
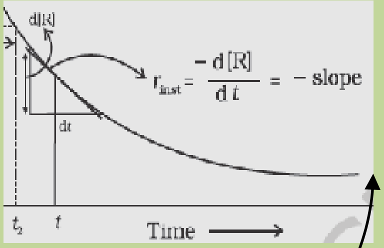
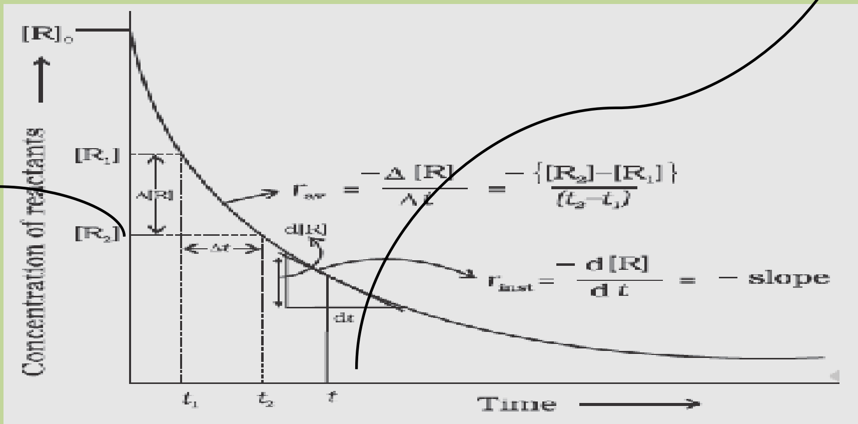
Expression for rate of reaction:

Consider a reaction,

$$R \rightarrow P$$

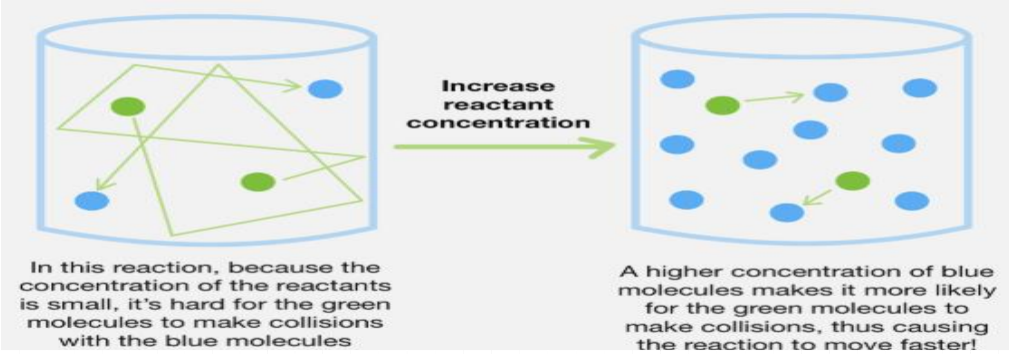
Units of rate of a reaction: mol $L^{-1}s^{-1}$

$$\frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

Average Rate	**Instantaneous Rate**
It is the change in concentration of reactants in a given interval of time.	Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.
 	
 	

- **Factors Influencing Rate of a reaction:**

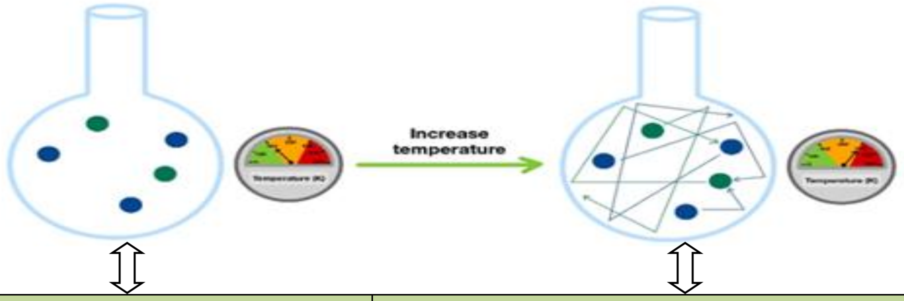
(i) Effect of concentration of reactants (pressure in case of gases).



In this reaction, because the concentration of the reactants is small, it's hard for the green molecules to make collisions with the blue molecules

A higher concentration of blue molecules makes it more likely for the green molecules to make collisions, thus causing the reaction to move faster!

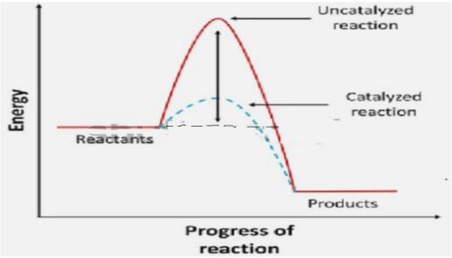
(ii) Effect of temperature



The molecules in this reaction Moving very slowly, which makes it hard for collisions to occur. This iscausing the reaction to proceed at a very slow rate	Increasing the temperature causes the K.E. of the molecules to increase thus causing the molecules tomove faster which causing collisions tooccur more frequently. More collision meansthe rate increases

(iii) Effect of catalyst

(a) A catalyst does not alter Gibbs energy.
(b) It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.
(c) It is also found that a catalyst does not change the equilibrium constant ofa reaction rather, it helps in attaining the equilibrium faster.



- **Rate Law Expression:** It is a mathematical expression in which rate of reaction is expressed in terms of molar concentration of reactants with each term raised to power, which may or may not be equal to the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Zero order reaction (n = 0) = mol L^{-1} s^{-1}

Rate = $k\,[A]^x\,[B]^y$

Units of rate constant

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

x+ y = n ; n = order of reaction.

(concentration)$^{1-n}$ time^{-1}

On considering S.I.unit of concentration as **mol L^{-1}** and time as **seconds**, the unit of

k = (mol L^{-1})$^{1-n}$ s^{-1}

first order reaction (n = 1) = s^{-1}

Second order reaction (n = 2) = mol^{-1} L s^{-1}

- **Order of a Reaction**: The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero-order reaction means that the rate of reaction is independent of the concentration of reactants.

When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions.

The reactions taking place in one step are called elementary reactions.

Molecularity of a reaction

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

The slowest step in a reaction called the rate determining step.

The integrated rate equations

Zero order reaction

$$k = \frac{[R]_0 - [R]}{t}$$

First order reaction

$$k = \frac{2.303}{t}\log\frac{[R]o}{[R]}$$

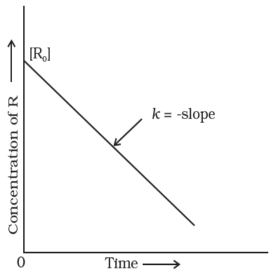
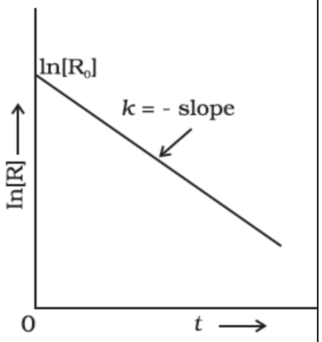
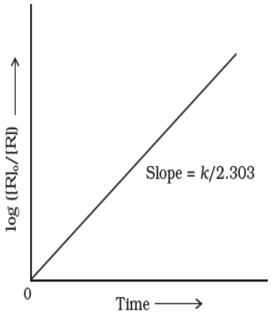
Where

$[R]_0$ = initial concentration of reactant,

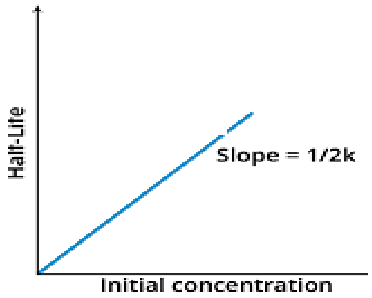
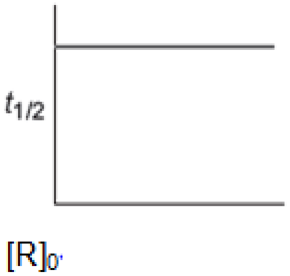
[R] = the final concentration at time 't' ,

t = time taken

- **<u>Important Graph plots for zero order and first order reaction-</u>**

	Graph -1 (zero order reaction)	Graph -2 (First order reaction)	Graph -3 (First order reaction)
Line equation	$[R] = -kt + [R]_0$	$\ln[R] = -kt + \ln[R]_0$	$\log\frac{[R]_0}{[R]} = \frac{kt}{2.303}$
Figure			
Plot	[R] vs time	In[R] vs time	Log $\frac{[R]0}{[R]}$ vs time
Slope	–k	-k	k/2.303
Intercept	$[R]_0$	In $[R]_0$	0

- **Half life period:** The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.
- The *half life period* for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.
- For a first order reaction, half-life period isconstant, i.e., it is independent of initial concentration of the reactingspecies.
- **Graph plots for half life period of reaction-**

	Graph -1 for zero order reaction	Graph-2 for First order of reaction
Line equation	$t_{1/2} = \frac{[R]0}{2k}$	
Figure		
Plot between	$t_{1/2}$ vs $[R]_0$	$t_{1/2}$ vs $[R]_0$
Slope	$\frac{1}{2k}$	No slope (independent to initial concentration of reactant)
Intercept	0	

- **pseudo first order reactions**.The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction.Such reactions are called **pseudo first order reactions**.
  Inversion of cane sugar is pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

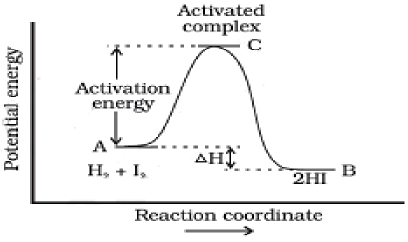
$$\text{Rate} = k\,[C_{12}H_{22}O_{11}]$$

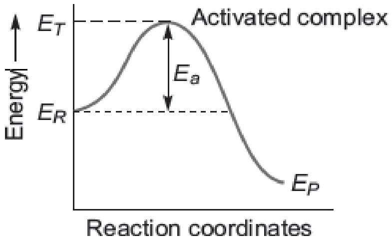
- **Activation Energy**: The energy required to form this intermediate, called activated complex(C), is known as activation energy (Ea).
- According to Kinetic theory of Molecular gases, the average kinetic energy of reacting gaseous molecules is directly proportional to absolute temperature.

$$K.E \propto T$$

  As temperature increases, speed of reacting molecules increases. Thereby, the frequency of collisions also increases and hence rate of reaction increases.
- Experimental evidence shows that for every 10 degree rise in temperature, the rate of a reaction will be doubled.
- If ‘E’ is the energy barrier, then the number of molecules that crosses over the energy barrier is more at higher temperature than at low temperature.
- **Activated complex (Transition State theory)**:It is the reaction intermediate possessing energy that correspond to top of energy barrier.

- **Threshold energy(E_T)**:The minimum amount of energy whichthe reactant must possess in order to convert into products is known as**threshold energy**.





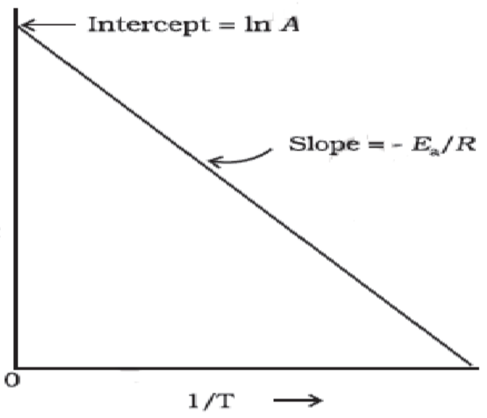
- **Important formula to relate activation energy , temperature and rate constant-**

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Where: k_1 and k_2 are the values of rate constants attemperatures T_1 and T_2 respectively

E_a= Activation energy, R= Gas constant

- **Graph:-**

	**Plot between ln k vs 1/T** ,
	Straight line equation $$\ln k = -\frac{E_a}{RT} + \ln A$$
	slope = $-\frac{Ea}{R}$and intercept = ln$A$

- **Effect of Catalyst:** A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
- Catalyst help to increase the rate of chemical reaction. It carries the reaction through the path of lower activation energy.
- **Collision frequency**: The number of collisions persecond per unit volume of the reaction mixture is known ascollision frequency (Z).
- **Effective collisions**:To facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

****

QUESTION BANK

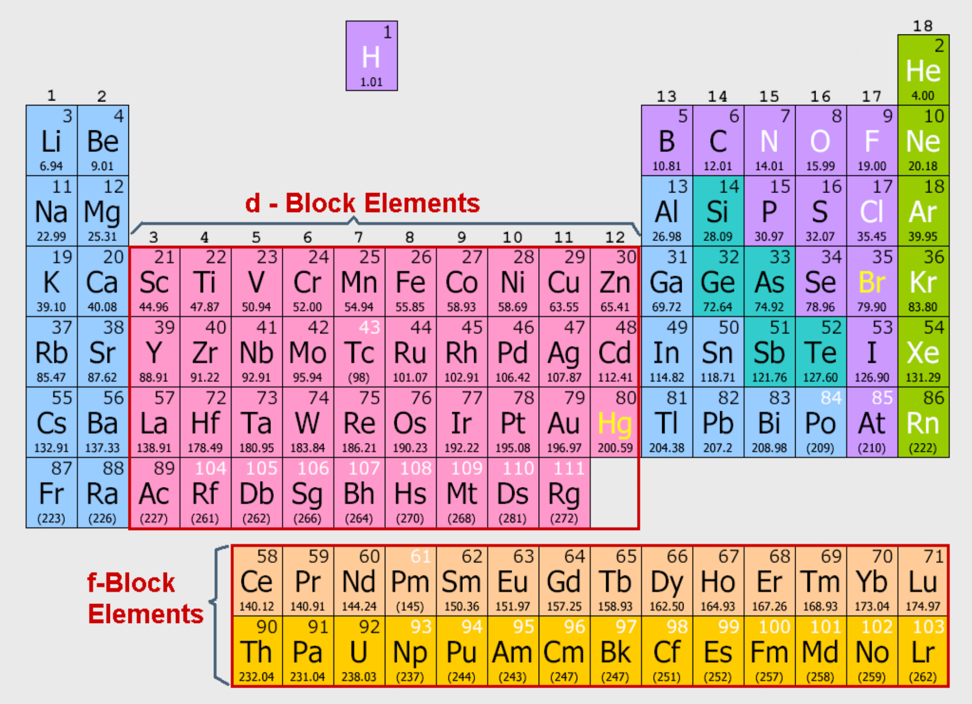
Section – A (1 Mark)

Q.1"For the reaction 2A + B → A_2B, the order with respect to each reactant is 1 .what will be the effect on the reaction rate if the concentration of reactant A is doubled and the concentration of reactant B is decreased by half?"

(a) increase 2 times	(b) increase 4 times
(c) decrease 2 times	(d) remain the same

CHAPTER-8 d & f-BLOCK ELEMENTS

SUMMARY



d - Block Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
						1 H 1.01											2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 25.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)							

f-Block Elements

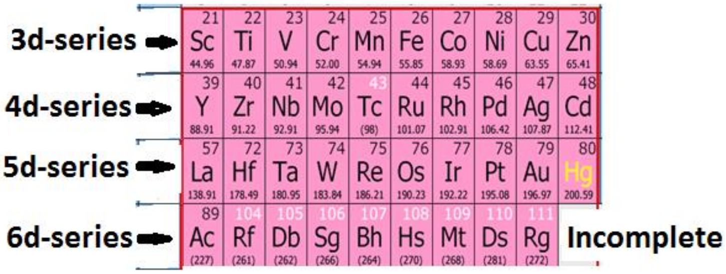
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

General introduction-

- The TRANSITION ELEMENTS are those elements which have partially filled d-sub shell in their elementary form or in their commonly occurring oxidation states.
- Zn, Cd and Hg not regarded as transition elements because they do not have partially filled d- subshell

ELECTRONIC CONFIGURATION - (n-1) d^{1-10} ns^{1-2}

There are four transition series in d-Block of elements –



3d-series	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	
4d-series	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	
5d-series	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	
6d-series	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)		Incomplete

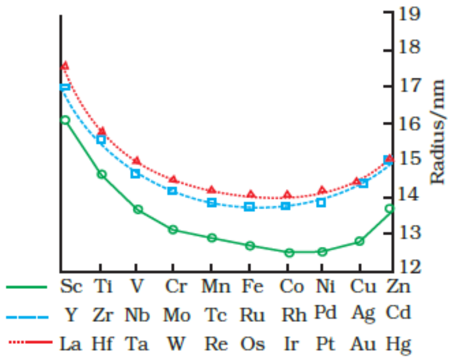
GENERAL CHARACTERISTICS OF d- BLOCK ELEMENTS

- Metals with high tensile strength, ductility, malleability, thermal and electrical conductivity.
- Solids except Mercury with high Melting and Boiling Points.

1. Atomic Radii

- The atomic radii decrease with increase in atomic number.
- In the middle of the series atomic radii become almost constant.
- At the end of the series the atomic radii show a small increase.
- On moving down the atomic radii increase due to increase in number of shells.

- However the atomic radii of second and third transition series are almost same. due to ‘LANTHANOID CONTRACTION’.



2. Metallic Character and Enthalpy of Atomisation

- Metallic character is due to low ionisation energies.
- These are hard metals with high enthalpies of atomisation. This is due to strong bonding due to overlap of unpaired electrons of different atoms.
- Values of enthalpies of atomisation increase with increase in number of unpaired electrons.

3. Densities

- All transition metals have high density due to small size and high atomic mass.
- Densities increase in a series due to increase in atomic mass and decrease in atomic size.

4. Melting and Boiling Points

- In general transition metals have high melting and boiling points. This is due to strong metallic bonds.
- The melting points in a series rise to a maximum value in middle and then decrease. This can be explained on basis of number of unpaired electrons.

5. Ionisation Enthalpies and Electrode Potentials

- IE_1 of d-block elements is higher than s-block elements but lower than p-block elements.
- In a series ionisation enthalpies generally increase from left to right due to increase in nuclear charge.
- The stability of a particular oxidation of an element depends on total value of all of its ionisation enthalpies. Lower is the total of ionisation enthalpies for a particular oxidation state, more is the stability of that oxidation state.
- The stability of a particular oxidation in aqueous solution depends on values of electrode potentials. Higher is the value of oxidation potential of a metal more is stability of its particular oxidation state in aqueous solution.
- The oxidation potential of a metal involves the following process –

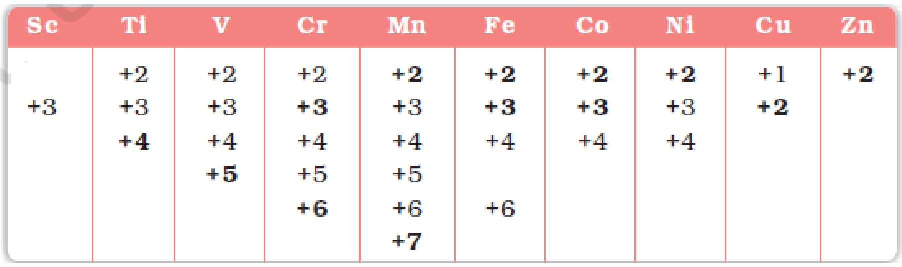
$$M(s) \rightarrow M^+(aq) + e^-$$

6. Oxidation States

- Most of the transition elements show variable oxidation states.
- The variable oxidation is due to the participation of (n-1)d electrons beside ns electrons. This is due to the fact that ns and (n-1)d electron differ very less in energy and (n-1)d electron can also participate in bond formation beside ns electrons.
- The highest oxidation states are found in their fluorides and oxides.

- Except Sc, the most common oxidation state for first transition state is +2.

- The elements with highest oxidation state lies in or near middle of the series.
- For all elements the lowest oxidation state is equal to number of ns electrons while the highest oxidation state is equal to sum of ns and (n-1)d electrons only for first five elements.
- In +2 and +3 oxidation states the bonds are mostly ionic while in higher oxidation states these are essentially covalent.
- Within the group highest oxidation state increase down the group.



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

7. Formation of coloured ions

- Most of the compounds of transition elements are coloured in solid/solution form.
- This can be explained on basis of presence of incomplete (n-1)d sub-shell/presence of unpaired electrons/d-d transition.

8. Magnetic Properties

- Most of the compounds of transition elements are paramagnetic in nature.
- This can be explained on basis of presence of unpaired electrons in (n-1)d sub-shell.
- Higher is the number of unpaired electrons in a substance, the greater is its paramagnetic character.
- $\mu = \sqrt{n(n+2)}$, where n is the number of unpaired electrons and μ is the magnetic
  moment in units of Bohr magneton (BM).

9. Formation of Complexes

- Transition elements form a large number of coordination complexes. This tendency of transition elements is due to-
  1. Small size of atoms and ions of transition metals.
  2. High nuclear charge.
  3. Availability of vacant d-orbitals of suitable energy to accept lone pair of electrons from other groups.

  `For example- $[Ni(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Zn(OH)_4]^{2-}$

10. Formation of Interstitial Compounds

- Transition elements form large number of interstitial compounds with H, B, C, and N.
- This is because the small atoms of these elements get trapped in vacant spaces of the lattice of the metal.
- Interstitial compounds are generally non-stoichiometric e.g. $TiH_{1.7}$, $VH_{0.56}$, etc.

11. Catalytic Properties

Many transition elements and their compounds act as catalysts in various chemical reactions.The transition elements have ability to form reaction intermediates due to variable oxidation states. The formation of reaction intermediates leads the reaction to a path of lower activation energy increasing the rate.In some cases transition metals provide adsorption surface to reactants and increase their concentrations.

12. Alloy Formation

- Transition metals form a large number of alloys e.g. steel, bronze, brass, etc.
- This is because the transition elements are quite similar in size and their atoms can easily accommodate themselves in each other's lattice.

13. **Preparation of Potassium dichromate ($K_2Cr_2O_7$): It is prepared by fusion of chromate ore ($FeCr_2O_4$) with sodium carbonate in excess of air.**

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$$

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

- **Effect of pH on chromate and dichromate ions: The chromates and dichromates are inter-convertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.**

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

- **Potassium dichromate acts as a strong oxidizing agent in acidic medium:**

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$6\,I^- \rightarrow 3I_2 + 6\,e^-$; $3\,Sn^{2+} \rightarrow 3Sn^{4+} + 6\,e^-$

$3\,H_2S \rightarrow 6H^+ + 3S + 6e^-$; $6\,Fe^{2+} \rightarrow 6Fe^{3+} + 6\,e^-$

14. Preparation of Potassium permanganate ($KMnO_4$):

a) Potassium permanganate is prepared by fusion of MnO4 with alkali metal hydroxide (KOH) in presence of O2 or oxidising agent like KNO_3. It produces dark green K_2MnO_4 which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$4H^+ + 3MnO_4^{2-} \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

b) Commercially, it is prepared by the alkaline oxidative fusion of MnO2 followed by the electrolytic oxidation of manganate (VI).

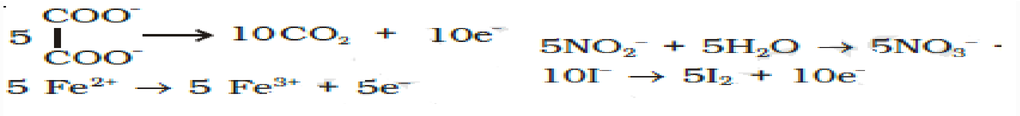
$$\underset{Green}{MnO_4^{2-}} \xrightarrow{electrolytic \text{ oxidation in alkaline medium}} MnO_4^-(Purple)$$

c) In laboratory, Mn^{2+} salt can be oxidized by peroxodisulphate ion to permanganate ion.

Potassium permanganate acts as a strong oxidizing agent in acidic medium, neutral or faintly basic medium:

In acidic medium: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:



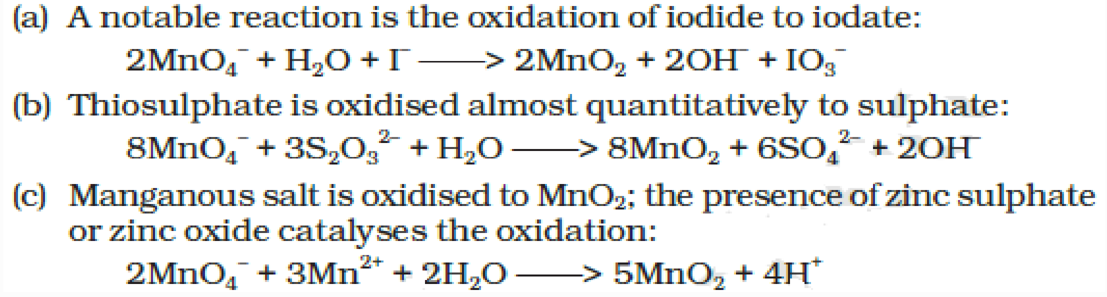
$$5\begin{array}{c}COO^-\\|\\COO^-\end{array} \longrightarrow 10CO_2 + 10e^-$$

$$5NO_2^- + 5H_2O \rightarrow 5NO_3^- -$$

$$5\ Fe^{2+} \rightarrow 5\ Fe^{3+} + 5e^-$$

$$10I^- \rightarrow 5I_2 + 10e^-$$

In neutral or faintly basic medium: $MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$



(a) A notable reaction is the oxidation of iodide to iodate:

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(c) Manganous salt is oxidised to MnO_2; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

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

15. Properties of the lanthanoids:

- General electronic configuration is [Xe] $4f^{1-14}\ 5d^{0-1}\ 6s^2$.
- The metals are silvery-white in colour, malleable, ductile, having low tensile strength and are good conductors of heat and electricity.
- They have relatively high density and possess high melting points.
- The lanthanides exhibit a principal oxidation state of + 3. However, some elements also exhibit + 2 (Eu^{2+}) and + 4 (Ce^{4+}) oxidation states.
- Many of the lanthanide ions are coloured due to the electronic transition between different 4 f-levels.
- The majority of the lanthanide ions exhibit paramagnetism due to the presence of unpaired electrons. The lanthanoid ions that do not exhibit paramagnetism are those with either no 4f-electrons, e. g., La^{3+} and Ce^{4+} or with a completed 4f-level, e.g., Yb^{2+} and La^{3+}..
- The lanthanoid compounds are generally predominantly ionic.

lanthanoid contraction

- Steady decrease in the atomic and ionic (Ln^{3+}) radii with the increase in atomic number of the lanthanoid elements is called lanthanoid contraction.

Cause of lanthanoid contraction

- This is because the additional electron goes to 4*f*-subshell which have poor shielding effect.

Consequences of Lanthanoid Contraction

- There is decrease in basic strength of hydroxides from La to Lu.
- Lanthanoid contraction causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series.
- a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

Properties of actinoids:

- General electronic configuration is [Rn] $5f^{1-14}\ 6d^{0-1}\ 7s^2$.
- The elements are all silvery-white metals.
- The melting points of the actinoids are moderately high.
- The ionic size of the actinoids decreases gradually along the series.
- The actinoids have the ability to exhibit several oxidation states. However, +4 oxidation state is preferred in actinides.

- Some actinoid elements can exist in + 6 oxidation state, e.g., uranium, neptunium and plutonium.
- Many actinoid elements are radioactive. The elements beyond uranium are man-made.
- The actinides have a much greater tendency to form complexes than lanthanides.
- Actinoid contraction is greater from element to element than lanthanoid contraction resulting from poor shielding by 5*f* electrons.

Mischmetall : It is a well-known alloy which consists of a lanthanoid metal $(\sim 95\%)$ and iron $(\sim 5\%)$and traces of S, C, Ca and Al.

QUESTIONS AND ANSWERS

Section A (1 MARK)

1. For a catalyst which condition is not essential?
(a) Variable valency (b) High ionisation energy
(c) Empty orbitals (d) Free valency on the surface

2. Which element is having lowest melting and boiling point?
(a) Ti (b) Cu (c) Zn (d) Mn

3. Density of which of the following element is highest:
(a) Pt (b) Hg (c) Mn (d) Cu

4. The adsorption of hydrogen by platinum black is called:
(a) Hydrogenation (b) Reduction (c) Occlusion (d) Hydration

5. To which of the following series the transition element from Z = 39 to Z = 48 belong:
(a) 3d series (b) 4d series (c) 5d series (d) 6d series

6. Permanent magnets are generally made of alloys of:
(a) Co (b) Zn (c) Mn (d) Pb

7. The reaction of O_2 and CO with haemoglobin gives:
(a) Only oxygen-haeme complex (c) Both but oxygen-haeme-complex is more stable
(b) Only CO-haeme complex (d) Both but CO-haeme-complex is more stable

8. Which of the following statement is not correct:
(a) Fe, Ni, Co form interstetial compound
(b) $CuSO_4 + Ca(OH)_2$ is called Bordeaux mixture
(c) Verdigris is basic copper acetate $[Cu(COOCH_3)_2Cu(OH)_2]$
(d) 24 carat gold is an alloy of Au and Cu

9. Chromium forms most stable compound in the following oxidation state:
(a) Cr (I) (b) Cr(II) (c) Cr (III) (d) Cr (IV)

10. Not more than one oxidation state is shown by:
(a) Mn (b) Cr (c) Fe (d) Sc

Ques	1	2	3	4	5	6	7	8	9	10
Ans	B	C	A	C	B	A	D	D	C	D

Section B (Assertion-Reason questions)

ASSERTION & REASON QUESTIONS

These questions contains Assertion and Reason

Chapter 5: CO-ORDINATION COMPOUNDS

Summary –

- **Coordination Compounds**

  Compounds in which a central metal atom or ion is linked to a number of non metal ions or neutral molecules by coordinate bonds
- **Type of addition compounds-**

1. Double Salt	2.Complex compound
Dissociate into simple ions completely when dissolved in water.	Do not dissociate into simple ions in water
e.g. Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ Potash Alum $K_2SO_4Al_2SO_4.24H_2O$	e.g. $K_4[Fe(CN)_6]$.Complex ion $[Fe(CN)_6]^{4-}$ does not dissociate into Fe^{2+} and CN^- ions.

- **IMPORTANT TERMINOLOGY OF COMPLEX COMPOUND.**

(i) Coordination entity: It constitutes the central metal ion or atom bonded to a fixed number of ions or molecules represented within a square bracket.

(ii) Central atom/ion: The atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

iii) **Ligands**: Ligands are the neutral or negative ions donate lone pairs to the central metal ion via coordinate bonds, acting as Lewis bases. Its may be classified as-

Monodentate/ Unidentate:	Ligands which Contain only one donar atom Ex-Cl^- ;H_2O; NH_3 ; NO_2^-.
Didentate	Ligands which Contain two donor atoms. Ex-$C_2O_4^{2-}$(ox); $NH_2CH_2CH_2NH_2$(en)
Polydentate	which Contain two or more donor atoms present in a single ligand. Ex-$(EDTA)^{4-}$
Chelating ligands	Di-or polydentate ligands that uses two or more donor atoms to bind to a single metal ion to form ring-like complexes.(Ox); (edta)
Ambidentate ligand	A ligand that can ligate through two different atoms, one at a time. Ex-NO_2^-; SCN^- ,CN^-

Coordination number: The no.of ligand donor atoms to which the metal is directly bonded through coordinate bond. It determine the geometry of coordination complex.

Counter ions: The ionisable groups written outside the square bracket. Ex- K^+ in $K_4[Fe(CN)_6]$ OR 3 Cl^- in $[Co(NH_3)_6]Cl_3$

Coordination Polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion. They are commonly Octahedral, Square-planar or Tetrahedral.

Oxidation number: The charge that the central atom would carry if all the ligands are removed along with their pairs of electrons shared with the central atom.

Homoleptic complexes: Complexes in which only one kind of Ligand . Ex-$[Co(NH_3)_6]^{3+}$

Heteroleptic complexes: Complexes in which more than one kind of Ligand Ex-$[Co(NH_3)_4 Cl_2]^+$

- **Key Points of Werner's theory of coordination theory-**

  Developed by Alfred Werner in 1893.in coordination compounds metals show two types of valencies-Primary and Secondary.

  IUPAC NOMENCLATURE- The following rules are used when naming complex.

(i) The cation is named first in both positively and negatively charged Complex.

(ii) The ligands are named in an alphabetical order before the name of the central metal.

(iii) Names of the anionic ligands end in –o.

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used.

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $\{Co(SCN)_4\}^{-2}$ is called cobaltate.

IUPAC names of some coordination compounds

1	$K_2[Zn(OH)_4]$	Potassium tetrahydroxozincate(II)
2	$K_3[Al(C_2O_4)_3]$	Potassium trioxalatoaluminate(III)
3	$[Pt(NH_3)BrCl(NO_2)]^-$	Amminebromidochloridonitrito-N-platinate(II) ion
4	$[CoCl_2(en)_2]Cl$	Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
5	$[Ni(CO)_4]$	Tetracarbonylnickel(0)

- **ISOMERISM IN COORDINATION COMPOUNDS**
- Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism.
- Coordination compounds show two main types of isomerism-

A) Structural Isomerism B) Stereoisomerism

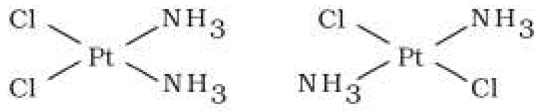
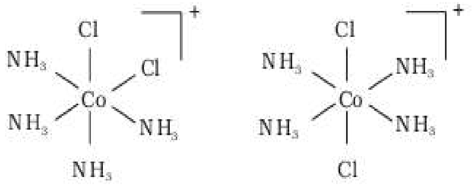
A) Summary of Structural Isomerism:

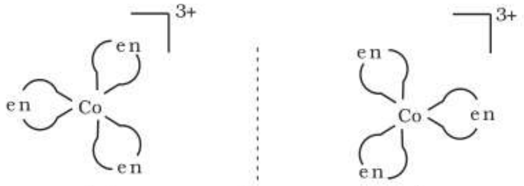
Sr.No.	Type	Description
1	Ionisation Isomerism	Exchange of counter-ions between the coordination sphere and ionizing sphere. $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
2	Linkage Isomerism	Ligand binds through different atoms (e.g., NO_2 binds through nitrogen or oxygen). $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$
3	Coordination Isomerism	Distribution of ligands between two metal centers differs. [Co(NH3)6][Cr(CN)6] and [Cr(NH3)6][Co(CN)6]
4	Solvation Isomerism	Arises due to the presence of solvent molecules as a ligand or as free solvent molecules in the crystal lattice. $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$

B) Summary of Stereo Isomerism: Stereoisomers have the same chemical formula and chemical bonds but theyhave different spatial arrangement.They are of two kinds

A. Geometrical isomerism B.Optical isomerism

Geometrical Isomerism -This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands

COORDINATION NO-4 (Square planar complexes)	$[Ma_2b_2][Pt(NH_3)_2Cl_2]$	 *cis* *trans*
Tetrahedral complexes do not show geometrical isomerism. Reason: The relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other		
COORDINATION NO 6 (Octahedral Complexes	$[Ma_2b_4]=[Co(NH_3)_4Cl_2\ ]^+$	 *cis* *trans*
	$[Ma_3b_3]$ $[Co(NH_3)_3(NO_2)_3]$	 *fac–* *mer–*

Optical Isomerism: Optical isomers are mirror images that cannot be superimposed on one another and are called as enantiomers.
Optical isomers of $[Co(en)_3]^{+3}$  *dextro* mirror *laevo*

Bonding in Coordination Compounds (Valence Bond Theory) : Key Points of VBT

1. The central metal atom/ion provides empty hybrid orbitals (equilivalent energy orbitals) to accept lone pairs from ligands, forming coordinate bonds.

2. **Hybridization and Geometry of the complex-**

Coordination number	Type of hybridisation	Acquired geometry
4	**sp^3**	Tetrahedral
4	**dsp^2**	Square planar
6	**sp^{3}d^2**	Octahedral
6	**d^{2}sp^3**	Octahedral

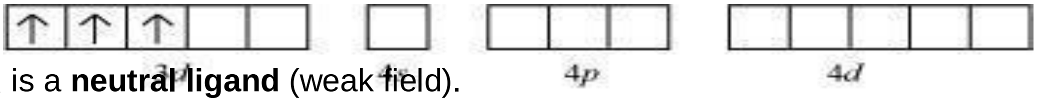
3. **Magnetic Behavior**: VBT to explain paramagnetic (unpaired electrons) or diamagnetic (all paired electrons) nature.

4. **Spectro chemical series:** The arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

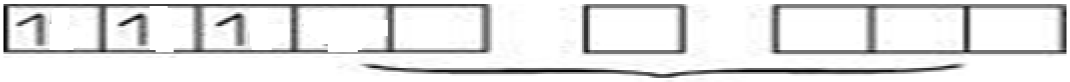
$I^- < Br^- < S2- < SCN^- < Cl\text{-}^- < N3\text{-} < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-} < NO_2 < phen < CO$

Examples: **1. $[Cr(NH_3)_6]^{3+}$**

Atomic no. of Cr = 24 → Cr^{3+} = 21 electrons → $3d^3$



NH_3 is a **neutral ligand** (weak field).



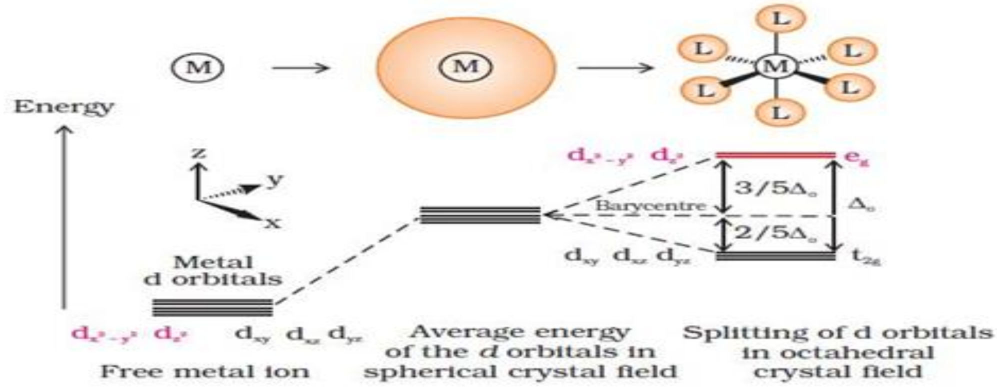
Hybridization: **d^2sp^3** ; Geometry: **Octahedral;** Magnetic: **Paramagnetic** (due to 3 unpaired electrons)

Some more example:-

Sr.No.	**Complex**	**Oxidation State**	**Type of Ligand**	**Hybridization**	**Geometry**	**Magnetic Nature**
1	$[Cr(NH_3)_6]^{3+}$	+3	Weak	d^2sp^3	Octahedral	Paramagnetic
2	$[Ni(CN)_4]^{2-}$	+2	Strong	dsp^2	Square planar	Diamagnetic
3	$[Fe(CN)_6]^{4-}$	+2	Strong	d^2sp^3	Octahedral	Diamagnetic
4	$[FeF_6]^{3-}$	+3	Weak	sp^3d^2	Octahedral	Paramagnetic

Crystal Field Theory - Key Points of CFT

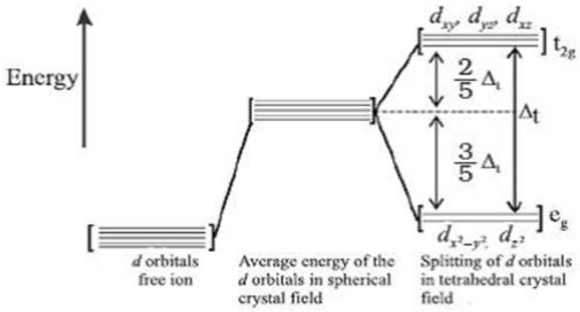
1. Electrostatic Model: CFT treats ligands as point charges (or dipoles in the case of neutral ligands like NH_3 or H_2O). The interaction between these ligands and the metal's *d*-orbitals causes splitting of energy levels.
2. Degeneracy of *d*-orbitals is Lifted: In a free metal ion, the five *d*-orbitals are degenerate (have the same energy). In a complex, due to the ligand field, these orbitals split into groups with different energies.
3. Geometry-Dependent Splitting:
4. Octahedral field (common for 6 ligands): The *d*-orbitals split into two sets: Lower energy: t_2g → (d_{xy},d_{xz},d_{yz}), Higher energy: eg→ (d_{z2}, dx^2-y^2), Energy difference = **Δ_0 (octahedral splitting energy)**



The splitting of degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting**

Weak field ligands	Strong field ligands
Δo < P	Δo > P
Form high spin complexes	Form low spin complexes

5. Tetrahedral field (4 ligands): Lower energy: eg→ (dz^2,dx^2-y^2), Higher energy: t_2g → (dxy,dxz,dyz), Energy difference = **Δt (Tetrahedral splitting energy)**



Why Coordination Compounds are Colored-

1. d–d Transitions: In transition metal complexes, the d-orbitals split in the presence of ligands (crystal field splitting). Electrons can be excited from a lower-energy d orbital to a higher one using visible light.

2. Charge Transfer Transitions:Electrons are transferred between the metal and ligands. These transitions also absorb light in the visible region, producing color.

3. Ligand Field Effect: Different ligands cause varying d-orbital splitting (Δ). Strong-field ligands like CN^- cause more splitting than weak ones like H_2O, affecting the colour of complexes. For example, $[Ti(H_2O)_6]^{3+}$ is violet because Ti^{3+} ($3d^1$) absorbs blue-green light, promoting the electron from t_2g to e_g level($t_2g^1 eg^0 \rightarrow t_2g^0\ eg^1$). Without ligands, no crystal field splitting occurs, so the substance remains colourless.

Note: (i) For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour.

(ii) Zn^{2+}, Cd^{2+}, Sc^{3+}, etc.: These are **colorless** in solution because they have **no d–d transitions** (either d^0 or d^{10} configuration).

BONDING IN METAL CARBONYLS: *In metal carbonyls, the M–C bond has both σ and π character. The σ bond forms by donation of a lone pair from CO to the metal vacant d orbital, and the π bond forms by back-donation from the metal's d-orbital to the CO* π^* antibonding orbital. This two-way interaction creates a synergic effect, strengthening the M–CO bond.

QUESTION BANK

SECTION –A (1 MARK EACH)

1. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl (s). The structure of the complex is

(a) $[Co(NH_3)_3Cl_3]. 2NH_3$ (b) $[Co(NH_3)_4Cl_2]\ Cl\ .\ NH_3$

(c) $[Co(NH_3)_4Cl]\ Cl_2.\ NH_3$ (d) $[Co(NH_3)_5Cl]\ Cl_2$

2. In the coordination compound, K4[Ni(CN)4], the oxidation state of nickel is

(a) 0 (b) +1 (c) +2 (d) –1

3. $[EDTA]^{4-}$ is a :

(a) monodentate ligand (b) bidentate ligand

(c) quadridentate ligand (d) hexadentate ligand

4. Which one of the following is not a ligand ?

(a) PH_3 (b) NO^+ (c) Na^+ (d) F^-

5. Some salts although containing two different metallic elements give test for only one of them in solution. Such salts are

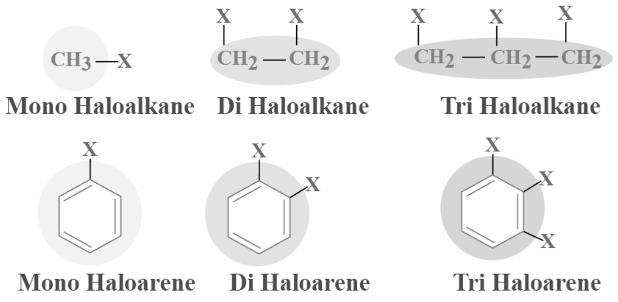
(a) complex (b) double salts (c) normal salts (d) None of these

6. Choose the correct statement.

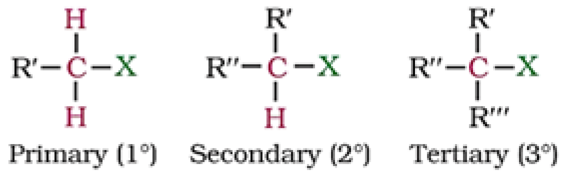
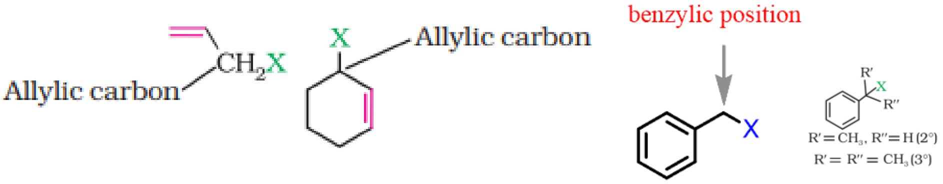
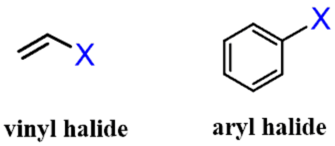
HALOALKANES AND HALOARENES

SUMMARY

- When one or more hydrogen atoms in a hydrocarbon—either aliphatic or aromatic—are replaced by halogen atoms, the resulting compounds are known as alkyl halides (haloalkanes) and aryl halides (haloarenes), respectively.
- **CLASSIFICATION OF HALOALKANE AND HALOARENE**
- Based on the number of Halogen Atoms

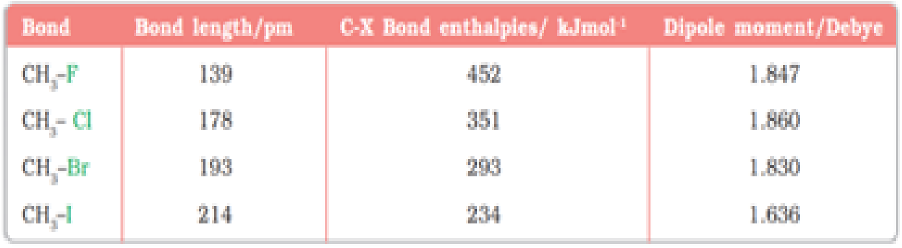


- Based on the type of carbon atom to which the halogen is attached

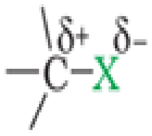
Halogen attached to sp^3 carbon	 Primary (1°) Secondary (2°) Tertiary (3°)
	
Halogen attached to sp^2 carbon	 vinyl halide aryl halide

- **Nature of C-X bond**: Carbon-halogen bond of alkyl halide is polar in nature because chlorine is more electronegative in nature. The carbon atom has a partial positive charge and halogen atom has a partial negative charge.

Table 6.2: Carbon-Halogen (C—X) Bond Lengths, Bond Enthalpies and Dipole Moments



Bond	Bond length/pm	C-X Bond enthalpies/ kJmol^{-1}	Dipole moment/Debye
CH_3-F	139	452	1.847
CH_3- Cl	178	351	1.860
CH_3-Br	193	293	1.830
CH_3-I	214	234	1.636



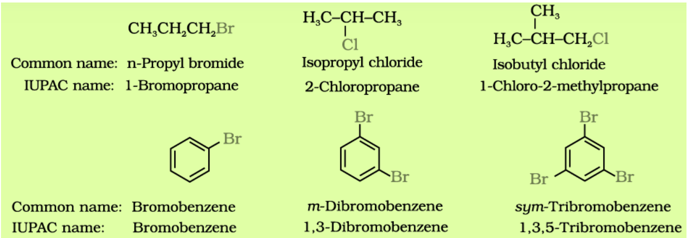
Bond Polarity

important Trends

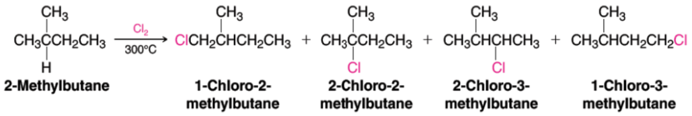
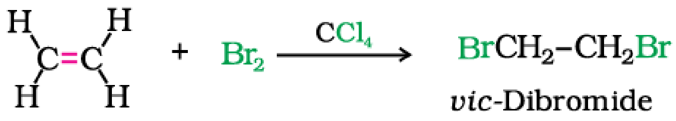
➢ Nomenclature:

Rules

(I) Identify the longest carbon chain and number it to get the lowest set of locants
(II) Follow alphabetical order for substituents (halogens and alkyl groups)
(III) Use prefixes like di-, tri- as needed.
(IV) Halogen is indicated as a prefix (fluoro-, chloro-, bromo-, iodo-) to the name of the parent

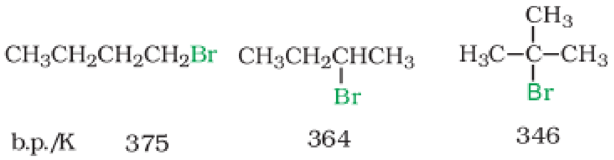


➢ Methods of Preparation for Haloalkane:

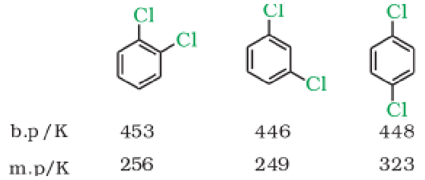
1. From Alcohol	$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$ $R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$ $3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3$ $(X = Cl, Br)$ $R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$ $R\text{–}OH \xrightarrow[X_2=Br_2,I_2]{\text{red } P/X_2} R\text{–}X$ $R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$	Important Point: (i) Thionyl chloride($SOCl_2$) is preferred because the other two side products are escapable gases. Hence the reaction gives pure alkyl halides. (ii) The order of reactivity of alcohols with a given haloacid(HCl) is 3°>2°>1°.
2. From Hydrocarbons	$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$  2-Methylbutane 1-Chloro-2-methylbutane 2-Chloro-2-methylbutane 2-Chloro-3-methylbutane 1-Chloro-3-methylbutane	(i) Reaction follows free radical substitution reaction. (ii) if a molecule has different types of carbon atoms (primary, secondary, tertiary), different products will be formed.
	$CH_3CH = CH_2 + H\text{–}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$	(i) Alkene reacts with hydrogen halide (ii) Major and minor product is given by Markovnikov's rule.
	 $BrCH_2\text{–}CH_2Br$ *vic*-Dibromide	In this reaction, brown color of bromine water disappears, indicating the presence of unsaturation (C=C or C≡C).
3. Halogen Exchange	$R\text{–}X + NaI \xrightarrow{\text{dry acetone}} R\text{–}I + NaX$ $X=Cl, Br$	(i) Name reaction: Finkelstein Reaction (ii) NaCl or NaBr formed as side product is precipitated in dry acetone and facilitates the forward reaction.
	$H_3C\text{–}Br + AgF \longrightarrow H_3C\text{–}F + AgBr$ Other metallic halide AgF, Hg_2F_2 , CoF_2 or SbF_3	(i) Name reaction: Swarts Reaction

➢ Physical Properties

- Haloalkanes have higher boiling points than alkanes due to stronger intermolecular forces of attraction, including dipole-dipole and dispersion forces.
- For the same alkyl group, boiling points of alkyl halides decrease as RI > RBr > RCl > RF due to stronger van der Waals forces with heavier halogens.
- The boiling points of isomeric haloalkanes decrease with increase in branching. Example is given below:



- Melting and boiling point order for dihalobenzene is given below:

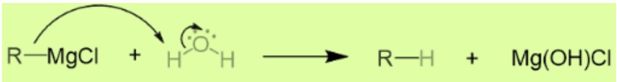


Note: Para-isomers have higher melting points than ortho- and meta-isomers due to their symmetrical structure, allowing better crystal lattice packing.

- Solubility: Despite of polar nature of alkyl halides, they are insoluble in water due to the inability to form hydrogen bonds. Still, they are soluble in non-polar solvents.
- Density: The density increases with an increase in the number of carbon atoms, halogen atoms, and atomic mass of the halogen atoms.

➢ CHEMICAL PROPERTIES

1. Reaction with Metal:

(a) Haloalkanes react with magnesium in dry ether to form RMgX, a compound known as a Grignard reagent. The reaction is given below: $CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$ Note: Traces of moisture must be avoided as Grignard reagents are highly reactive due to their nucleophilic nature and react with proton sources like water, alcohols, or amines to form hydrocarbons. Hence, the reaction is carried out in dry ether. 	(b) Wurtz reaction: This reaction produces symmetrical alkanes with twice the number of carbon atoms as in the original alkyl halide. The reaction is given below: $\underset{\textbf{Alkyl halide}}{R{-}X + 2Na + X{-}R} \xrightarrow{\text{Dry ether}} \underset{\textbf{Alkane}}{R{-}R + 2NaX}$ $\underset{\textbf{Methyl bromide}}{CH_3{-}Br + 2Na + Br{-}CH_3} \xrightarrow{\text{Dry ether}} \underset{\textbf{Ethane}}{CH_3CH_3} + 2Na$

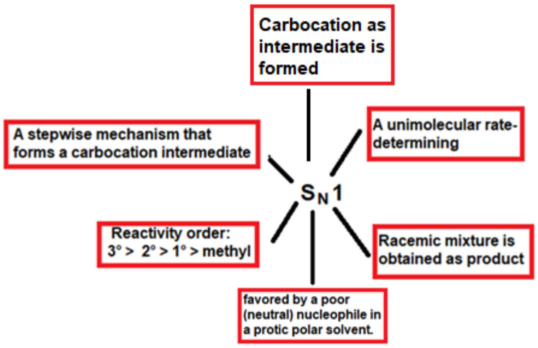
2. Nucleophilic substitution reaction:

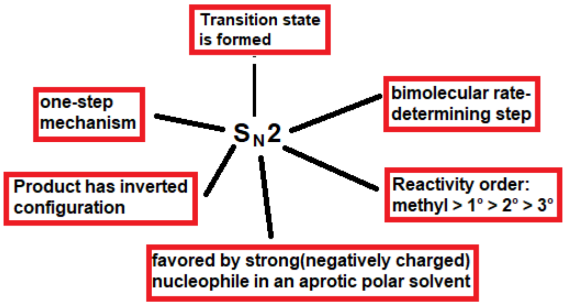
- General definition: The reaction in which a strong nucleophile replaces the already existing weak nucleophile in a molecule is called nucleophilic substitution reaction.

- Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. The example is given below:

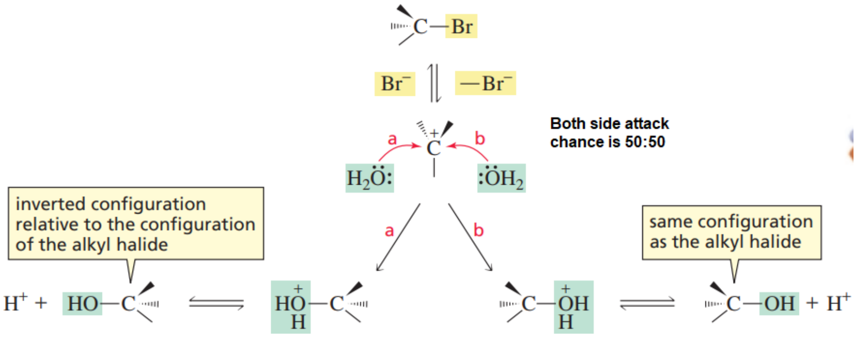
  R-X + AgCN → R-NC ; R-X + KCN → R-CN

- **Substitution nucleophilic unimolecular (S_N1) and Substitution nucleophilic bimolecular (S_N2)**

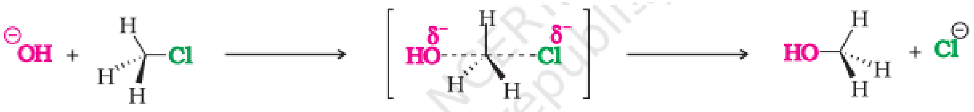




- **Mechanism:**



= S_N1



= S_N2

Note: (i) Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles.

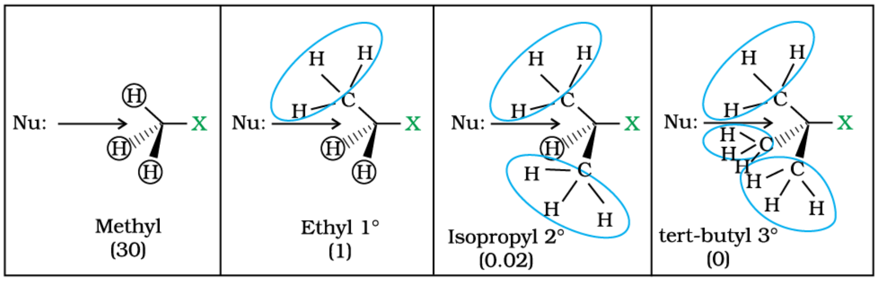
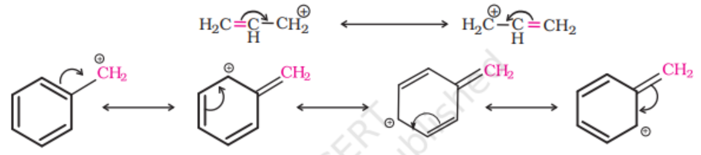


Fig.10.3: Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

(ii) In S_N1 rate of reaction depends on the stability of carbocation. Allylic and benzylic halides are highly reactive in S_N1 reactions due to resonance-stabilized carbocations.



(ii) For a given alkyl group, the reactivity of the alkyl halide R-X, follows the same order in both the mechanisms R–I> R–Br>R–Cl>>R–F

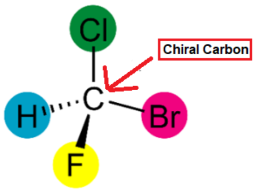
➢ STEREOCHEMICAL ASPECTS OF NUCLEOPHILIC SUBSTITUTION REACTIONS

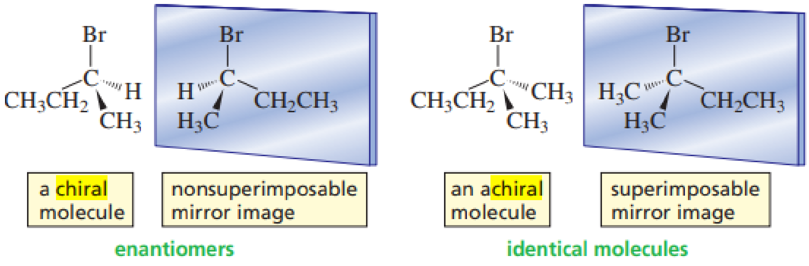
- Some important Terms

  (i) A tetrahedral carbon bonded to four different substituents is called a chiral carbon/chiral center/ asymmetric carbon/stereocentre.

The objects or molecule which are non-superimposable on their mirror image are said to be chiral and property is known as chirality. Optically active	The objects or molecule which superimposable on their mirror images are called achiral. Optically inactive

(ii) Nonsuperimposable mirror-image molecules are called **enantiomers.**





(a) Enantiomers rotate the plane polarized light in opposite direction hence it is known as optical isomers.	(b) Enantiomers possess identical physical properties namely, melting point, boiling point, refractive index, etc.	(c) They only differ with respect to the rotation of plane polarised light. (i) If rotates plane-polarized light to the right (clockwise) is called **dextrorotatory (d-form)** and marked with a **(+)** sign. (ii) If it rotates light to the left (anticlockwise), it is **laevorotatory (l-form)** and marked with a **(–)** sign.

(iii)

Racemic Mixture

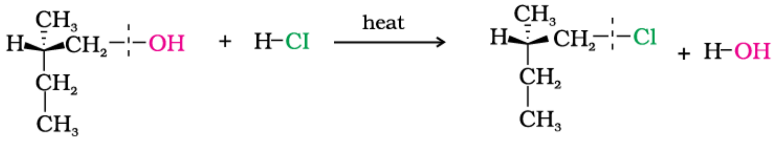
A mixture with equal amounts of two enantiomers shows no optical rotation because one rotates light to the right and the other to the left, canceling each other out.

Racemic mixture is represented by prefixing dl or (±). Example: (±) butan-2-ol

The process of conversion of enantiomer into a racemic mixture is known as racemisation.

INVERSION, RETENTION AND RACEMISATION

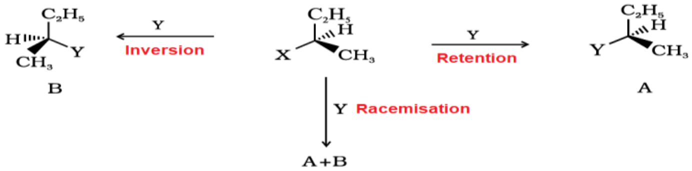
- Inversion: (a) A process in which the relative configuration of an atom in a molecule changed. (b) Inversion takes place in S_N2.
- Retention: It is the process in which configuration of substrate and product remains the same.



(–)-2-Methylbutan-1-ol (+)-1-Chloro-2-methylbutane

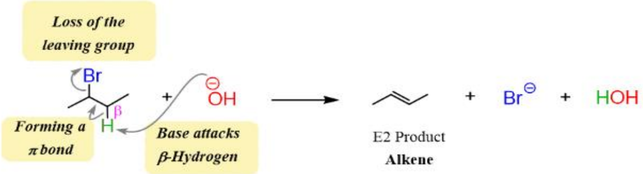
(I) Here, + and - indicate different optical activity.
(II) Configuration at a symmetric centre in the reactant and product is same

- Racemisation: (a) The process in which optically active compounds are converted into optically inactive compounds with zero optical activity.
  (b) Racemisation takes place in S_N1.

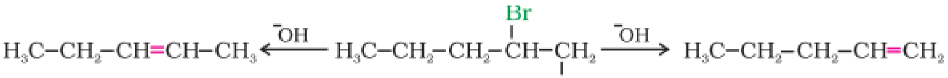


3. Elimination reaction/Dehydrohalogenation/ β-elimination

- Elimination of hydrogen atom from β -carbon and a halogen atom from the α-carbon atom simultaneously takes place.
- The strong base like alcoholic KOH is used in this reaction.
- Mechanism:



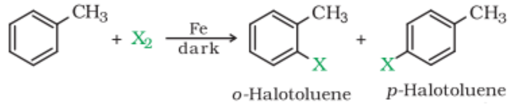
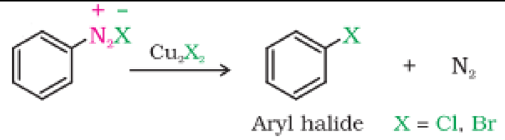
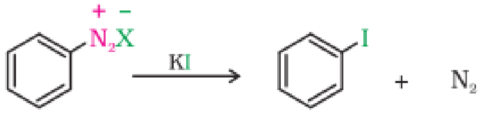
Note: If more than one α-hydrogen is available, multiple alkenes may form. The major product is predicted by Saytzeff's rule. The example is given below:



$$H_3C-CH_2-CH{=}CH-CH_3 \xleftarrow{^-OH} H_3C-CH_2-CH_2-\underset{H}{\overset{Br}{CH}}-CH_2 \xrightarrow{^-OH} H_3C-CH_2-CH_2-CH{=}CH_2$$

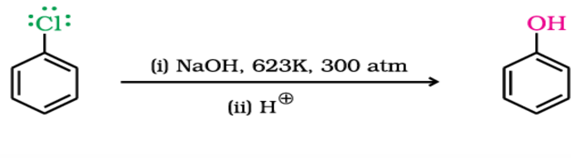
Pent-2-ene (81%) 2-Bromopentane Pent-l-ene (19%)

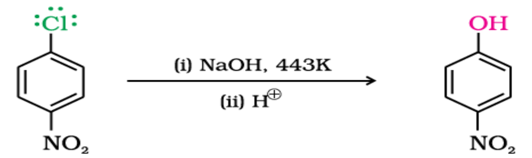
➢ PREPARATION OF HALOARENE:

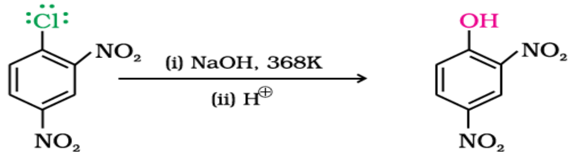
 Electrophilic substitution reaction	(i) The given reaction is an example of an electrophilic aromatic substitution reaction, where X_2 can be Cl_2 or Br_2. (ii) The ortho and para isomers can be easily separated due to large difference in their melting points.
 For Chloro or bromobenzene	(i) Name Reaction: Sandmeyer's reaction  For iodobenzene

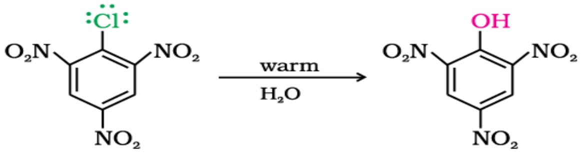
➢ CHEMICAL PROPERTIES OF HALOARENE:

1. When chlorobenzene reacts with aqueous NaOH at high temperature and pressure, a substitution reaction occurs, forming phenol.
Introducing NO_2 groups at the ortho and para positions makes the reaction condition milder and increases the reactivity towards substitution reactions. The reactions are given below:





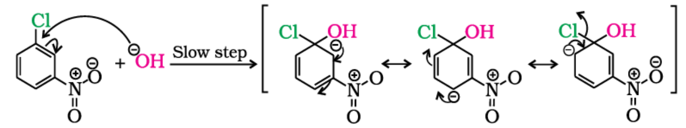




Picric Acid

Note: The effect is not observed when the NO₂ group is attached at the meta position because in meta-nitrobenzene, none of the resonance structures place a negative charge on the carbon with the –NO₂ group.

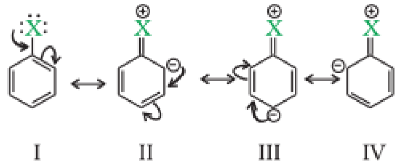
So, the nitro group at the meta position doesn't help stabilize the negative charge, and it doesn't increase the reactivity of the ring. The reaction in given below:



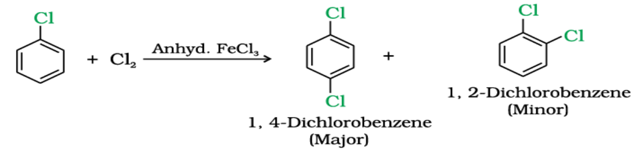
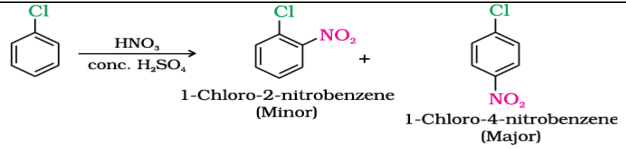
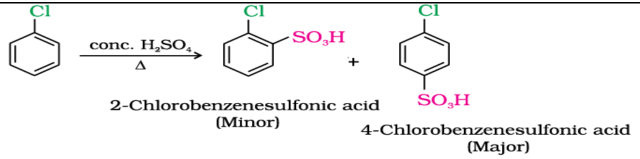
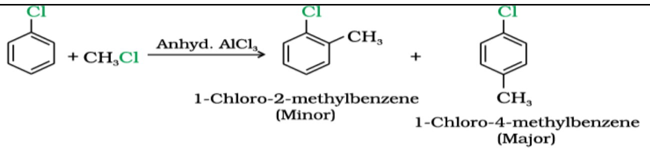
m-isomer

2. Electrophilic substitution reactions:

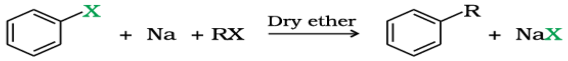
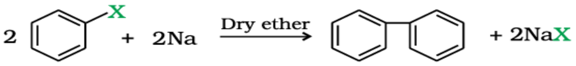
(a) Haloarenes undergo electrophilic substitution. The halogen is slightly deactivating due to –I effect but directs new groups to the ortho and para positions due to resonance, which increases electron density at these sites.



(b) The major product is the para-substituted compound, as it is favored over the ortho product.

(a) Halogenation	
(b) Nitration	
(c) Sulphonation	
(d) Friedel-Crafts reaction	

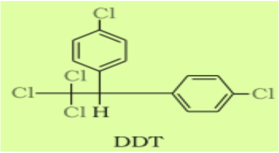
3. Reactions with Metals

(a) Wurtz-Fittig reaction	
(b) Fitting reaction	

Polyhalogen Compounds

(a) Dichloromethane (Methylene chloride)	Used as a solvent(in drug industry), paint remover, propellant in aerosols Harms the central nervous system, Skin contact causes intense burning and mild redness. Eye contact can burn the cornea.
(b) Trichloromethane (Chloroform)	The main use of chloroform today is to produce the refrigerant Freon R-22. Chloroform slowly oxidizes in air and light to form poisonous phosgene gas(carbonyl chloride). It is stored in dark, tightly sealed bottles to keep air out. $2CHCl_3 + O_2 \xrightarrow{light} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$
(c) Triiodomethane (Iodoform)	Iodoform was once used as an antiseptic, but its effects come from releasing free iodine, not iodoform itself, and its unpleasant smell has led to its replacement by other iodine-based formulations.
(d) Tetrachloromethane (Carbon tetrachloride)	Use in the manufacture of refrigerants and propellants for aerosol cans, feedstock in the synthesis of chlorofluorocarbons. used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. It cause dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells.
(e) Freons	Chlorofluorocarbon compounds of methane and ethane. Eg: Freon 12 (CCl_2F_2) Extremely stable, unreactive, non-toxic, noncorrosive and easily liquefiable gases. It is manufactured from tetrachloromethane by Swarts reaction. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.
(f) p,p'Dichlorodiphenyltrichloroethane (DDT)	DDT is chemically stable and fat soluble. It is not metabolized very rapidly by animals; it is deposited and is stored in the fatty tissues. Being non-biodegradable its residues accumulate in environment and are toxic to mammals etc.

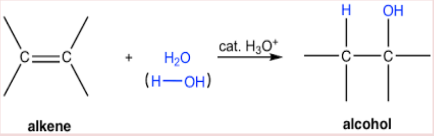
Structure of DDT is given below:



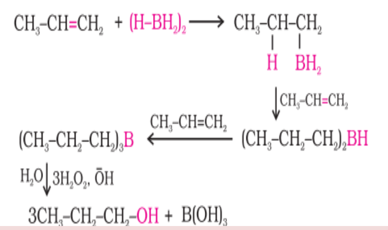
7.ALCOHOLS, PHENOLS AND ETHERS
SUMMARY

PREPARATION OF ALCOHOLS

I)FROM ALKENE (BY ACID CATALYSED HYDRATION)



II)FROM ALKENE (BY HYDROBORATION–OXIDATION:)

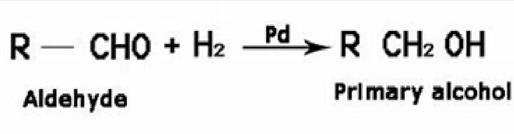


$CH_3\text{-}CH\text{=}CH_2 + (H\text{-}BH_2)_2 \longrightarrow CH_3\text{-}\underset{H}{CH}\text{-}\underset{BH_2}{CH_2}$

$\xrightarrow{CH_3\text{-}CH\text{=}CH_2} (CH_3\text{-}CH_2\text{-}CH_2)_2BH \xrightarrow{CH_3\text{-}CH\text{=}CH_2} (CH_3\text{-}CH_2\text{-}CH_2)_3B$

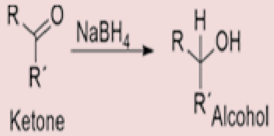
$\xrightarrow{H_2O \mid 3H_2O_2,\ \bar{O}H} 3CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + B(OH)_3$

III) FROM CARBONYL COMPOUNDS(FROM ALDEHYDES)

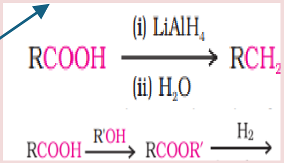


$R - CHO + H_2 \xrightarrow{Pd} R\ CH_2\ OH$

IV)FROM CARBONYL COMPOUNDS(FROM KETONES)



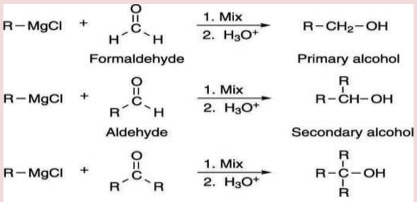
v)FROM CARBONYL COMPOUNDS(FROM CARBOXYLIC ACIDS AND ESTERS:



$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2$

$RCOOH \xrightarrow{R'OH} RCOOR' \xrightarrow{H_2}$

VI) FROM GRIGNARD REAGENTS



$R{-}MgCl + HCHO \xrightarrow[2.\ H_3O^+]{1.\ Mix} R{-}CH_2{-}OH$

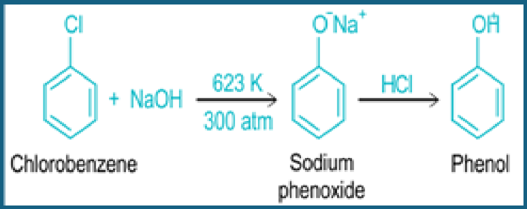
$R{-}MgCl + RCHO \xrightarrow[2.\ H_3O^+]{1.\ Mix} R{-}CH(R){-}OH$

$R{-}MgCl + RCOR \xrightarrow[2.\ H_3O^+]{1.\ Mix} R{-}C(R)_2{-}OH$

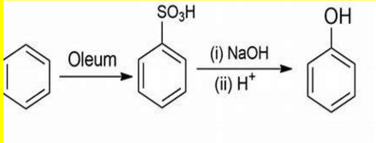
PREPARATION

OF PHENOLS

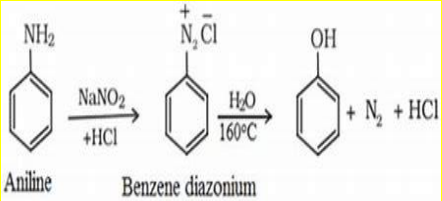
i)From haloarenes



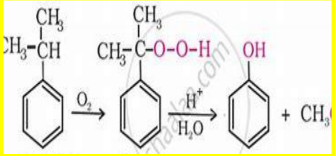
ii) From benzenesulphonic acid



iii)Fromdiazonium salts



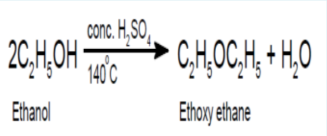
iv)Fromcumene



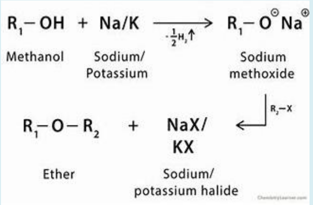
PREPARATION

OF ETHERS

i)By dehydration of alcohols



ii) Williamson synthesis



PHYSICAL PROPERTIES OF ALCOHOL ,PHENOL AND ETHERS-(KINDLY GO THROUGH THE DIKSHA LINK GIVEN)-

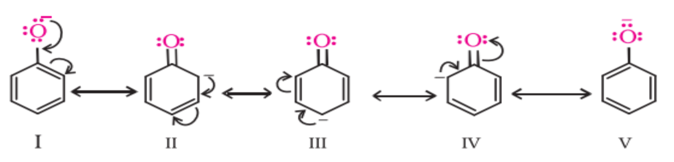
https://diksha.gov.in/play/content/do_3134757718146990081159

CHEMICAL REACTIONS OF ALCOHOL AND PHENOLS

I)Reactions involving cleavage of O – H Bond

(a) Acidity of alcohols and phenols:

- $2R-OH + 2Na \rightarrow 2R-ONa + H_2$
- $2C_6H_5-OH + 2Na \rightarrow 2C_6H_5-ONa + H_2$
- Alcohols are weaker acids than water due to (+I effect) group present in alcohols, which decreases the polarity of -O-H bond
- Acid strength of alcohols: 1° > 2° > 3°
- Phenol is more acidic than alcohols due to stabilization of phenoxide ion through resonance



- Presence of electron withdrawing groups increases the acidity of phenol by stabilizing phenoxide ion
- presence of electron releasing groups decreases the acidity of phenol by destabilizing phenoxide ion.

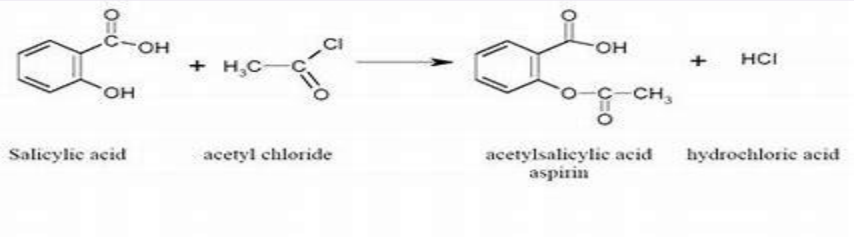
(b)Esterification

$$Ar/ROH + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{\text{Pyridine}} R/ArOCOR' + HCl$$

Acetylation of salicylic acid produces aspirin.



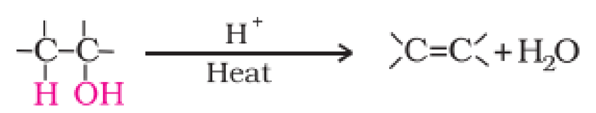
CHEMICAL REACTIONS OF ALCOHOL AND PHENOLS(ii)Reactions involving cleavage of carbon – oxygen (C–O) bond in Alcohols

(a) Reaction with hydrogen halides:
Alcohols react with hydrogen halides to form alkyl halides.
ROH + HX →R–X + H_2O
Reactivity of Alcohols: Tertiary > Secondary > Primary
Lucas Test: - Used to distinguish primary, secondary and tertiary alcohols
Lucas reagent (conc. HCl and $ZnCl_2$)
Alcohols are soluble in Lucas reagent while Alkyl halides (RX) are immiscible and produce turbidity in solution. tertiary alcohols- Immediate turbidity ,Secondary alcohols- Turbidity appears After 5 minutes, Primary alcohols- No turbidity at room temperature.

(b)Reaction with phosphorus trihalides:

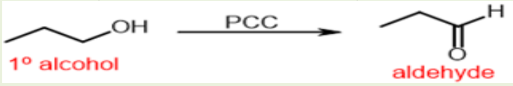
$CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$

(C)Dehydration:

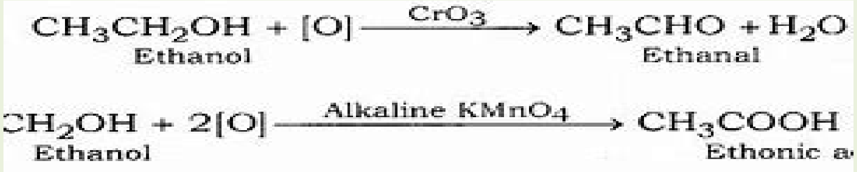


The relative ease of dehydration of alcohol is Tertiary > Secondary >

(d)Oxidation- it involves loss of dihydrogen from an alcohol molecule
Primary alcohol → Aldehyde → Carboxylic acid



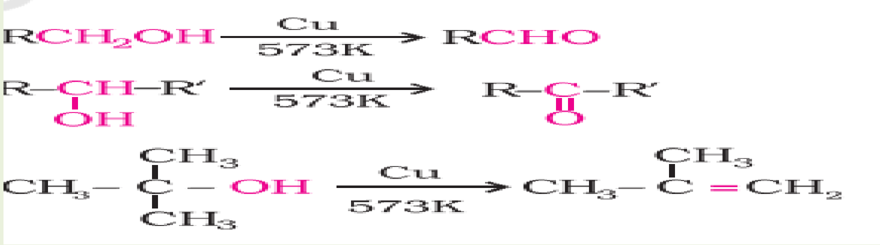
Primary alcohol → Carboxylic acid (strong oxidizing agent, acidified $KMnO4$)



$$\underset{\text{Ethanol}}{CH_3CH_2OH} + [O] \xrightarrow{CrO_3} \underset{\text{Ethanal}}{CH_3CHO} + H_2O$$

$$\underset{\text{Ethanol}}{CH_2OH} + 2[O] \xrightarrow{\text{Alkaline } KMnO_4} \underset{\text{Ethonic a}}{CH_3COOH}$$

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place.

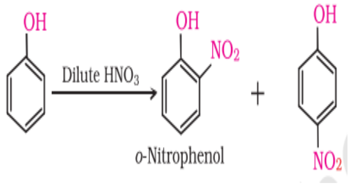
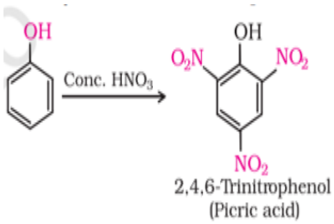
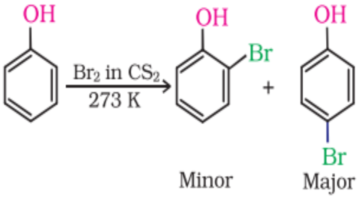
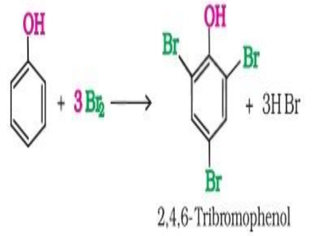
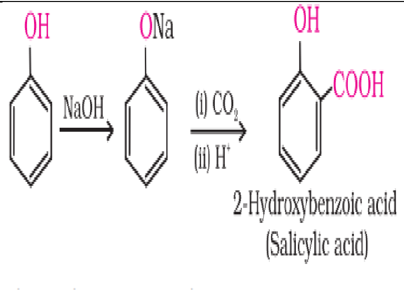
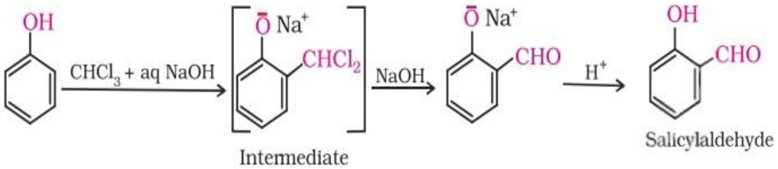
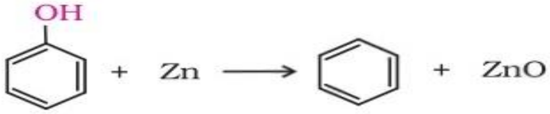


$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$

$$R{-}\underset{OH}{CH}{-}R' \xrightarrow[573K]{Cu} R{-}\underset{O}{\overset{}{C}}{-}R'$$

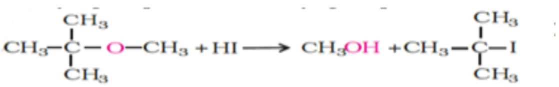
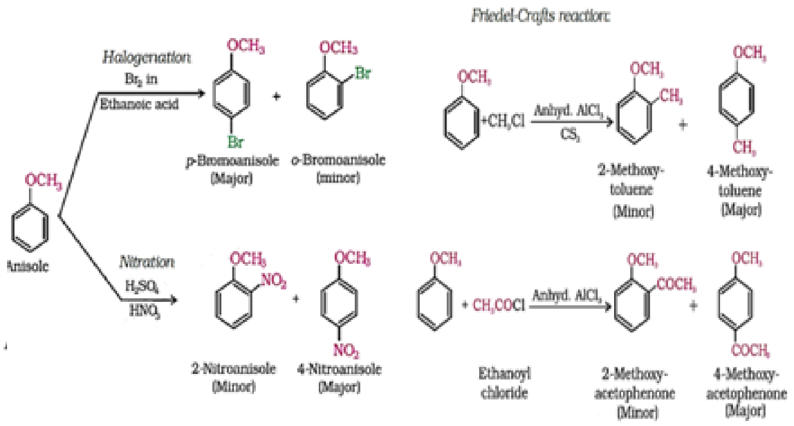
$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH \xrightarrow[573K]{Cu} CH_3{-}\overset{CH_3}{C}=CH_2$$

CHEMICAL REACTIONS OF PHENOL

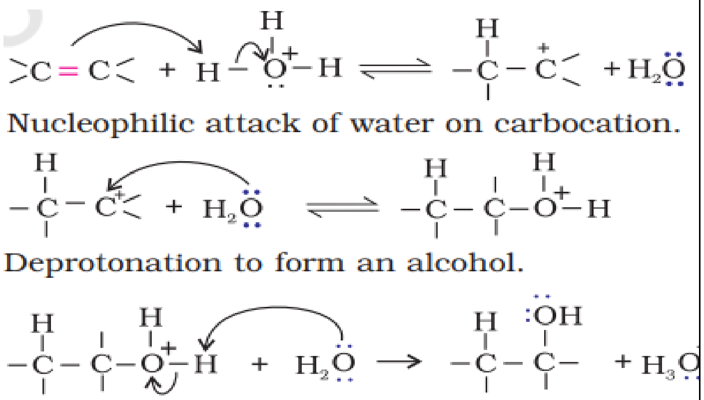
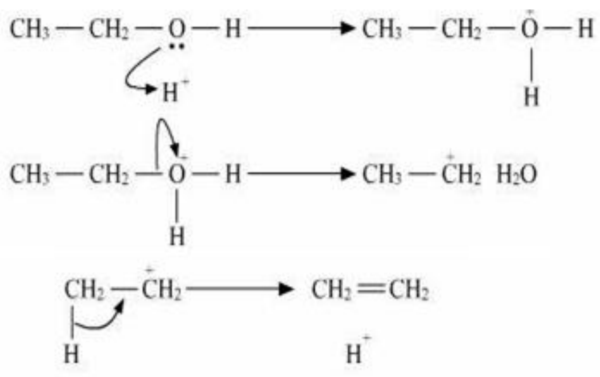
CHEMICAL REACTIONS OF PHENOLS **(a)Electrophilic aromatic substitution on aromatic ring of Phenol**	**i)Nitration**   - The ortho and para isomers can be separated by steam distillation. - o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is
	ii)Halogenation (Bromination).   -When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, mono-bromophenols are formed. -When phenol is treated with bromine water, 2,4,6-
(b)Kolbe's reaction	 -Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide,
(C) Reimer-Tiemann reaction	
(d)Reaction of phenol with zinc dust	

(e) Oxidation	 Oxidation of phenol with chromicacid /$Na_2Cr_2O_7$ produces a conjugated diketoneknown as benzoquinone.

CHEMICAL REACTIONS OF ETHERS

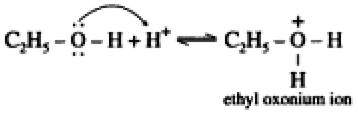
(a) Reactions involving Cleavage of C–O bond in ethers	- Reactions involving Cleavage of C–O bond in ethers $R{-}O{-}R + HX \longrightarrow RX + R{-}OH$ $R{-}OH + HX \longrightarrow R{-}X + H_2O$ - When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (SN2 reaction). $CH_3{-}\ddot{\underset{\cdot\cdot}{O}}{-}CH_2CH_3 + H{-}I \longrightarrow CH_3{-}I + CH_3CH_2{-}OH$ • when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide (SN1reaction)  $CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O{-}CH_3 + HI \longrightarrow CH_3OH + CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}I$
(b) Electrophilic substitution-alkoxy group (-OR) is ortho, para directing	

MECHANISM OF REACTIONS-

I)**Preparation of Alcohols (From alkenes)- By acid catalysed hydration** Protonation of alkene to form carbocation by electrophilic attack of H_3O^+  	II) **Dehydration of Alcohols** 

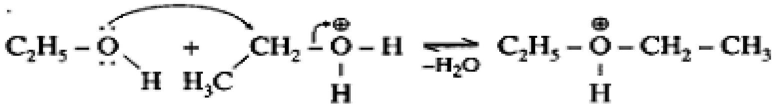
III) FORMATION OF ETHER

Step 1 Protonation



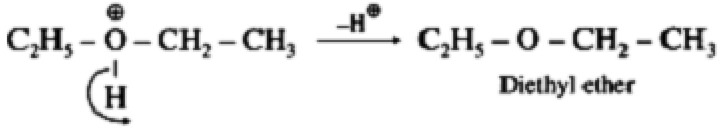
$C_2H_5-\ddot{O}-H+H^+ \rightleftharpoons C_2H_5-\overset{+}{O}(H)-H$

Step 2 S_N2 mechanism



$C_2H_5-\ddot{O}H + H_3C-CH_2-\overset{\oplus}{O}H_2 \xrightleftharpoons[-H_2O]{} C_2H_5-\overset{\oplus}{O}(H)-CH_2-CH_3$

Step 3 Deprotonation



$C_2H_5-\overset{\oplus}{O}(H)-CH_2-CH_3 \xrightarrow{-H^{\oplus}} C_2H_5-O-CH_2-CH_3$

QUESTION BANK
SECTION - A (1 MARK)

Q1.One mole of ethyl acetate on treatment with an excess of $LiAlH_4$ in dry ether and subsequent acidification produces

(a) 1 mole acetic acid + 1 mole ethyl alcohol

(b) 1 mole ethyl alcohol + 1 mole methyl alcohol

(c) 2 moles of ethyl alcohol (d) 1 mole of 2-butanol

Q2.Which of the following reagents can not be used to oxidise primary alcohols to aldehydes ?

CHAPTER-8

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

SUMMARY:

Nature of Carbonyl Group

- The carbon and oxygen of the carbonyl group are sp^2 hybridised and the carbonyl double bond contains one sigma-bond and one π-bond with the bond angle 120^0.
- The electronegativity of oxygen is much higher than that of the carbon, so their electron cloud is shifted towards the oxygen. Therefore, C—O bond is polar in nature .

  In carboxylate ion –ve charge is delocalized on two electronegative O-atoms hence shows resonance which indicate that CO group is not a true carbonyl group in carboxylic acids.

Nomenclature

(i) Nomenclature of **Aldehydes IUPAC** system, the suffix 'e' of alkane is replaced by the suffix 'al'. **e.g.**

Compound	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal

(ii) Nomenclature of **ketones IUPAC** system, the suffix "e" of alkane is replaced by 'one'**. e.g.**

Compound	Common name	IUPAC name
H_3CCOCH_3	Dimethyl ketone (acetone)	Propanone
$H_3CCOC_2H_5$	Ethyl methyl ketone	Butanone

(iii) Nomenclature of carboxylic acids **IUPAC** system, the suffix "e" of alkane is replaced by 'oic'acid. **e.g.**

Compound	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
H_3CCOOH	Acetic acid	Ethanoic acid
$CH_3(CH_2)_2COOH$	Butyric acid	Butanoic acid

Reactivity of aldehyde and Ketones :

$HCHO > RCHO > RCOR > RCOOR > RCONH_2$.

Physical Properties of Aldehydes and Ketones

1. **Methanal (HCHO**) is a gas at room temperature, and its 40% aqueous solution is known as f**ormalin**, which is used to preserve biological specimens .

It is used in silvering of mirrors and decolourising vat dyes.

2. **Ethanal (CH_3CHO)**

It is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.

- The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.
- Aldehydes and ketones have lower boiling point than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
- The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.

- Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.
- Lower members are soluble in water because they can form H-bond with water. Higher members are insoluble in water due to large size of their hydrophobic group.
- **Preparation of Aldehydes** :

  a. Dehydrogenation of primary alcohols

  b. Controlled oxidation of primary alcohols.

  c. Controlled and selective reduction of acyl halides Aromatic aldehydes can be prepared by-

  (i) Oxidation of toluene with chromyl chloride or CrO_3 in the presence of acetic anhydride

  (ii) Formylation of arenes with carbon monoxide and Hydrochloric acid in the presence of anhydrous aluminium chloride / Cuprous chloride

  (iii) Hydrolysis of benzal chloride
- **Preparation of Ketones** :

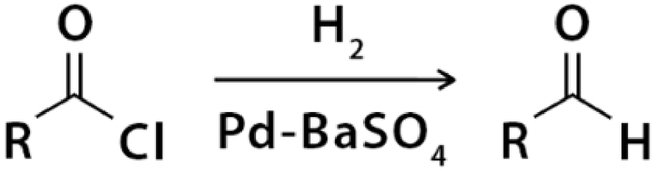
  a. oxidation of secondary alcohols b. Hydration of alkenes

  c. Reaction acyl chlorides with dialkylcadmium d. By friedel crafts reaction
- **Preparation of Carboxylic acids** :

  a. oxidation of primary alcohols, aldehydes and alkenes b. hydrolysis of nitriles

  c. Treatment of grignard reagent with carbon dioxide.
- **IMPORTANT NAMED REACTIONS**

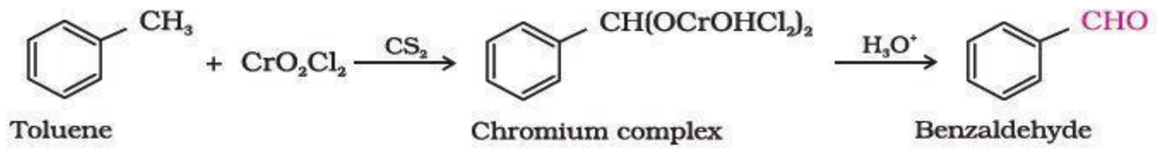
.1. **ROSENMUND REDUCTION**:



2. STEPHEN REACTION

RCN + $SnCl_2$ + HCl → RCH=NH $\xrightarrow{H_3O^+}$ RCHO

3. ETARD REACTION:



This reaction is called **Etard reaction.**

4. CLEMMENSEN REDUCTION

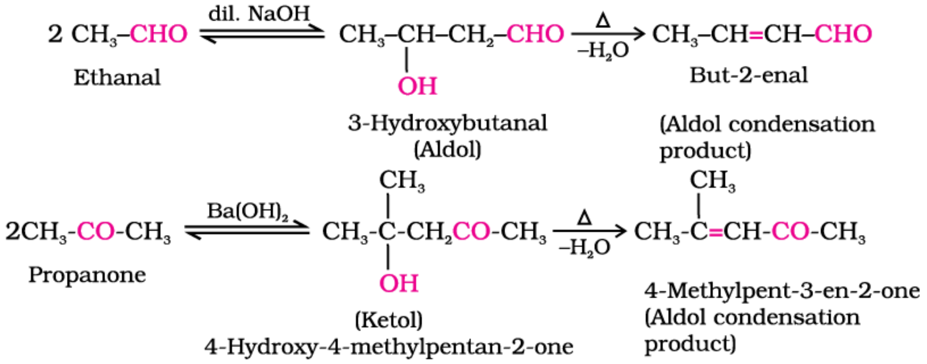
$>C=O \xrightarrow{Zn-Hg/HCl} >CH2 + H2O$

5. WOLFF-KISHNER REDUCTION

$>C=O \xrightarrow{NH_2NH_2} >C=NNH_2 \xrightarrow{KOH/ethylene\ glycol\ /H_2O} >CH_2 + N_2$

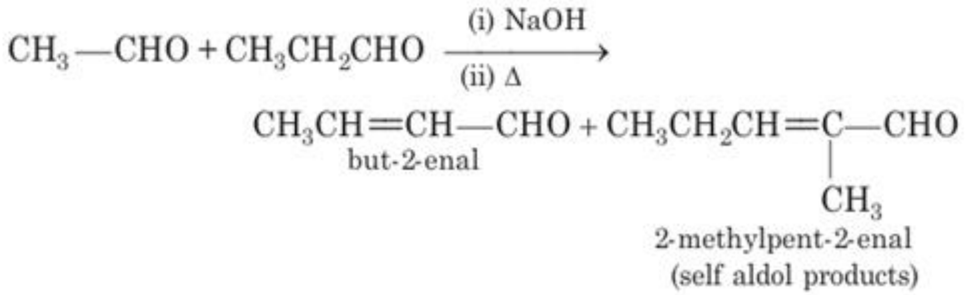
6. ALDOL CONDENSATION

Aldehydes and ketones having at least one α-hydrogen condense in the presence of dilute alkali as catalyst to form β-hydroxyaldehydes (aldol) or β-hydroxy ketones (ketol). The reaction is given below:



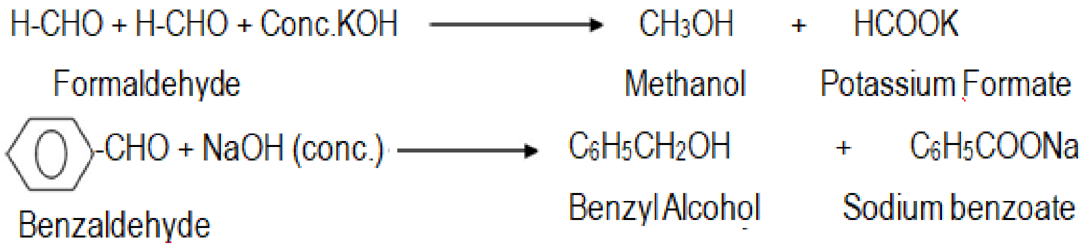
7. CROSS- ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.



8. CANNIZZARO REACTION

Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (dispropotionation) reaction on treatment with concentrated alkali,to yield carboxylioc acid salt and an alcohol respectively.



ADDITION OF AMMONIA AND ITS DERIVATIVES:

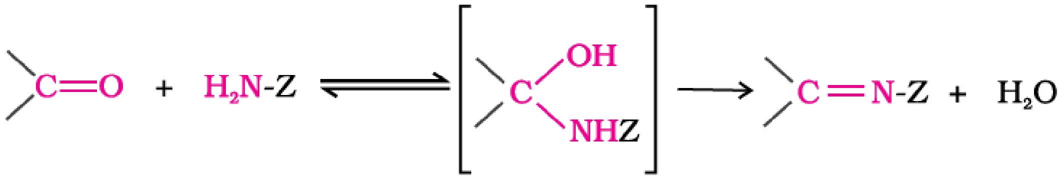
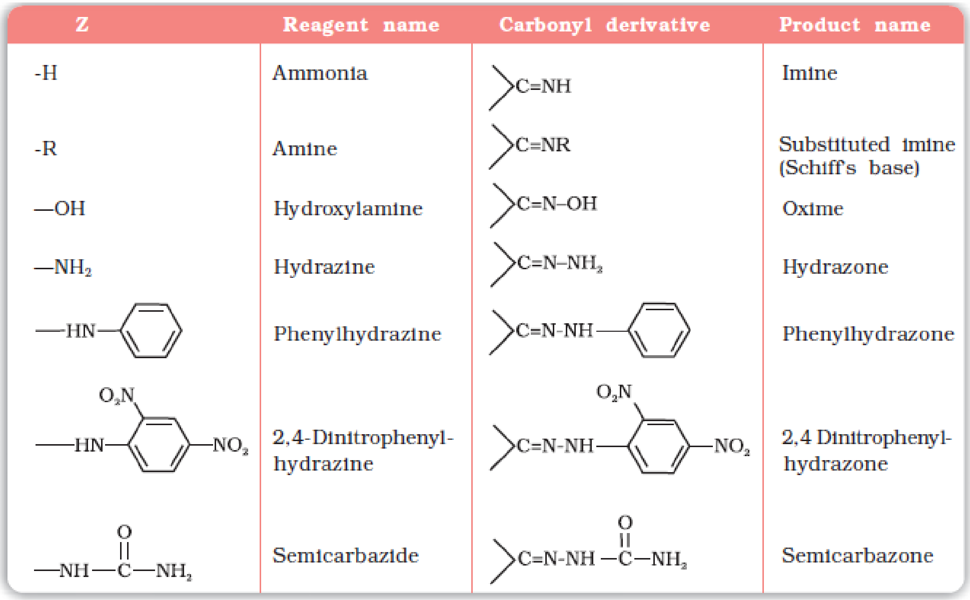


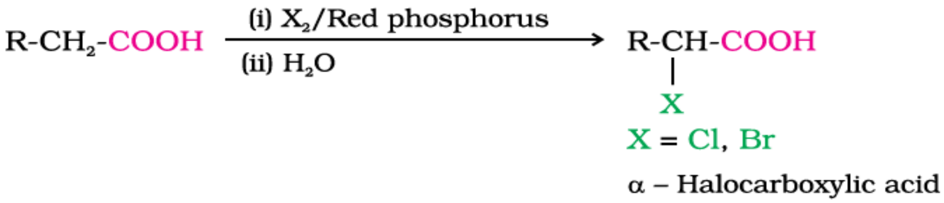
Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)



Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	>C=NH	Imine
-R	Amine	>C=NR	Substituted imine (Schiff's base)
—OH	Hydroxylamine	>C=N–OH	Oxime
$—NH_2$	Hydrazine	$>C=N–NH_2$	Hydrazone
—HN—	Phenylhydrazine	>C=N-NH—	Phenylhydrazone
O_2N —HN— $—NO_2$	2,4-Dinitrophenyl-hydrazine	O_2N >C=N-NH— $—NO_2$	2,4 Dinitrophenyl-hydrazone
$—NH—\overset{O}{\overset{\|\|}{C}}—NH_2$	Semicarbazide	$>C=N-NH—\overset{O}{\overset{\|\|}{C}}—NH_2$	Semicarbazone

REACTIONS OF CARBOXYLIC ACID:

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)



$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} R\text{-}\underset{\underset{X}{|}}{CH}\text{-}COOH$$

X = Cl, Br

α – Halocarboxylic acid

2. ESTERIFICATION

$$RCOOH \quad + \quad R'OH \overset{H^+}{\rightarrow} \quad RCOOR \quad + \quad H_2O$$

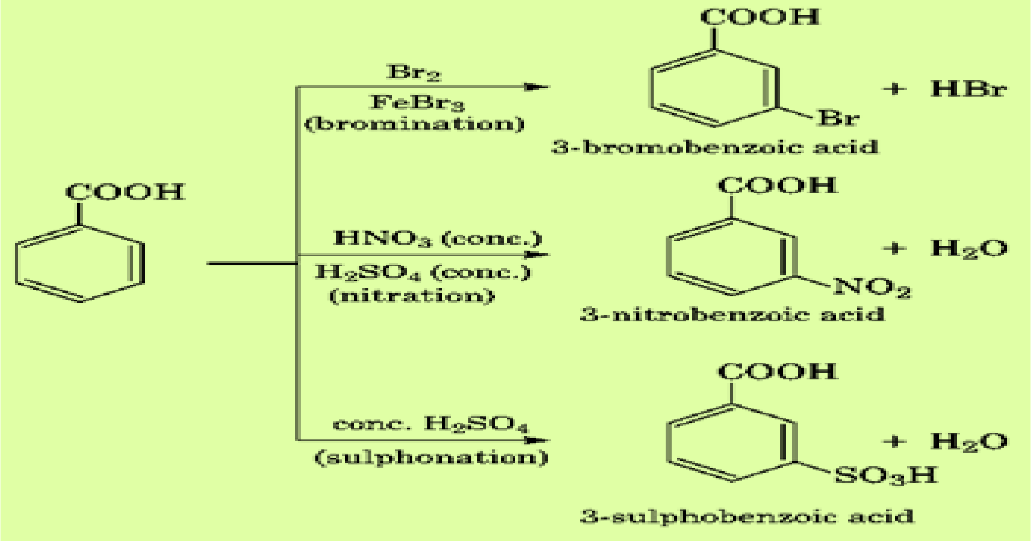
Carboxylic acid alcohol

3. DECARBOXYLATION

$$R\text{-}COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R\text{-}H + Na_2CO_3$$

sodalime = NaOH and CaO in the ratio of 3 : 1

REACTIONS OF BENZOIC ACID



DISTINCTION OF ORGANIC PAIRS

Distinguish between :-

Alcohol	**Phenol**
It does not give $FeCl_3$ test	It gives neutral $FeCl_3$ (violet) test
Benzaldehyde	**Acetophenone**
It give Fehling's solution test and Tollens reagent test	It doesn't give Fehling's solution test and Tollens reagent test
Acetic acid	**Formic acid**
It doesn't gives tollen's reagent and fehling's solution test	It gives tollen's test and fehling's solution test
Ethanal	**Propanal**
It gives iodoform test	It doesn't give iodoform test
Propanol	**Ethanol**
It doesn't give iodoform test	It gives iodoform test
Pentan-2-one	**Pentan-3-one**
It gives iodoform test	It doesn't gives iodoform
Benzoic acid	**benzene**
On adding $NaHCO_3$ effervescence of CO_2 produced	No effervescence obtained

Note: Learn properly since one question on distinguish between organic pairs is ask

SECTION –A (1 MARK)

1. Name the compound $CH_3COCH(CH_3)_2$ as per the IUPAC nomenclature:
(a) 2-methyl-3-butanone (b) 4-methylisopropyl ketone
(c) 3-methyl-2-butanone (d) Isopropylmethyl ketone

2 . Predict the acid which cannot be prepared by Grignard reagent:
(a) Acetic acid (b) Succinic acid (c) Formic acid (d) All of the above

3. Which is highly soluble in water:
(a) Methanal (b) Propanal (c) Propanone (d) Butanone

4. Benzaldehyde reacts with ethanoic KCN to give product :
(a) $C_6H_5CHOHCN$ (b) $C_6H_5CHOHCOC_6H_5$
(c) $C_6H_5CHOHCOOH$ (d) $C_6H_5CHOHCHOHC_6H_5$

5. Name the compound not responding to the Iodoform test :
(a) 2-Pentanone (b) Ethanol (c) Ethanal (d) 3-Pentanone

6. Precipitate produced when acetaldehyde is heated with Fehling's solution :
(a) Cu (b) CuO (c) Cu_2O (d) $Cu(OH)_2$

7. Test used to distinguished between Aldehydes and ketones would be :
(a) Lucas test (b) Tollen's test (c) KMnO4 solution (Baeyer's test) (d) None of these

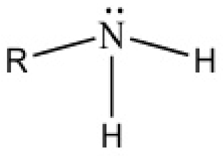
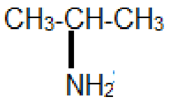
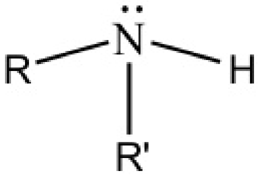
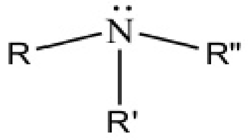
8. Name the compound called Imine derivatives of aldehyde and ketones :
(a) Schiff's reagent (b) Fehling's reagent (c) Schiff's base (d) Schiff's acid

9.Predict the pair of compounds will undergo Aldol and Cannizzaro reaction respectively :
(i) acetone; benzaldehyde (ii) acetaldehyde; butan–2–one
(iii) propanone; formaldehyde. (iv) cyclopentanone, benzaldehyde :
(a) (i) and (iii) (b) (ii) and (iii) (c) (ii), (iii) and (iv) (d) (iii) and (iv)

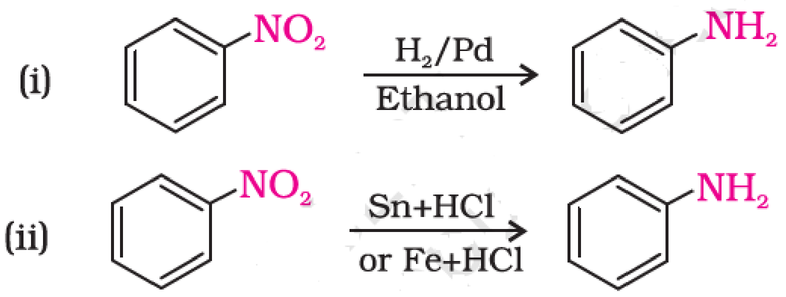
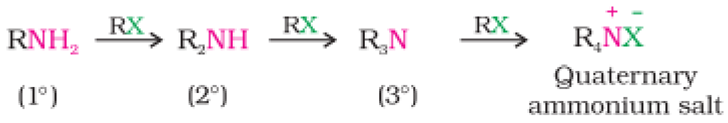
CHAPTER : 9 AMINES

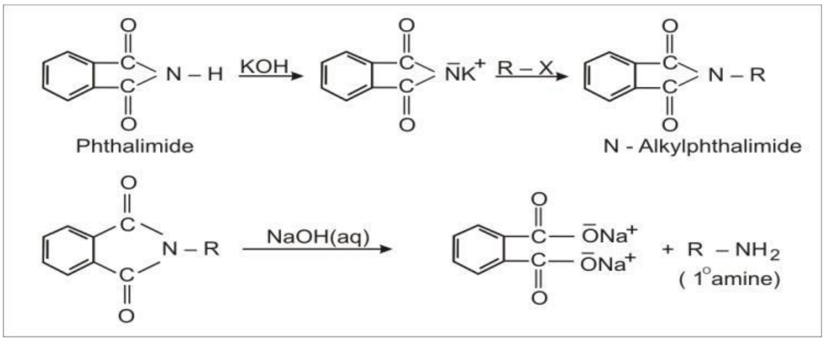
SUMMARY

1. Amines are alkyl / aryl derivatives of ammonia. In amines nitrogen atom is sp3 hybridized and contains one lone pair.
2. Amines can be classified as 10, 20 and 30 based on the number of hydrogen atom present on nitrogen.

1^0 Amine	2^0 Amine	3^0 Amine
 CH_3-NH_2 = Methanamine  $CH_3\text{-}\underset{\displaystyle NH_2}{CH}\text{-}CH_3$ Propan-2-amine	 CH_3-NH- CH_3 N-methylmethanamine	 $(CH_3)_3N$ N,N-dimethylmethanamine

➢ **PREPRATION OF AMINES**

.. Reduction of Nitro compound gives aliphatic and aromatic amines (reducing agent Sn/HCl,Fe/HCl) Reduction with Fe/HCl is preferred as $FeCl_2$ is formed during reduction get hydrolyzed to release HCl	
. **Ammonolysis of alkyl halides**: - Reagent: Ethanolic solution of ammonia.	 Disadvantage: Mixture of amines formed
. **Reduction of nitriles** Reducing agents: - $LiAlH_4$, H_2/Ni, Na/C_2H_5OH	$R - CN \xrightarrow{(H_2/Ni \text{ or } Na(Hg)/C_2H_5OH} R{-}CH_2NH_2$
. **By the reduction of amides**	$CH_3CONH_2 + (LiAlH_4 + H_2O) \rightarrow CH_3CH_2NH_2$

5. **Hoffmann bromamide** Reaction: An amide is heated with Bromine in aq. solution of NaOH/KOH gives primary amine.	$R-CONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
6. **Gabriel phthalimide synthesis**: Only primary aliphatic amines are prepared by this method, primary aromatic amine cannot be prepared because aryl halides do not undergo substitution reaction.	

PHYSICAL PROPERTIES: (i) Primary amines are water soluble as H-bonding follows $1^0 > 2^0 > 3^0$.

(ii) The order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary (Directly depends on the extent of hydrogen bonding)

CHEMICAL PROPERTIES:

1. **Basic Nature-** Amines are basic in nature, it accepts proton from an acid.

- $3^0>2^0>1^0>NH_3$(Basic nature in gaseous phase)
- $2^0>3^0>1^0>NH_3$(Basic nature of ethyl substituted amines in aqueous phase)
- $2^0>1^0>3^0>NH_3$(Basic nature of Methyl substituted amines in aqueous phase)
- Aniline is weaker base than ammonia (Its pKb value is large, lone pair of electrons are involved in resonance)

Acetylation: Replacement of H-atom from $-NH_2$ or >NH by Acid chloride, anhydride and esters

$(C_2H_5)_2NH + CH_3COCl \rightarrow CH_3CON(C_2H_5)_2 + HCl$

3. **Reaction with Nitrous acid:** Forms aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols after reacting with water

4. **Reaction with Hinesberg reagent($C_6H_5SO_2Cl$): (Test for 1^0,2^0, and 3^0 amines)**

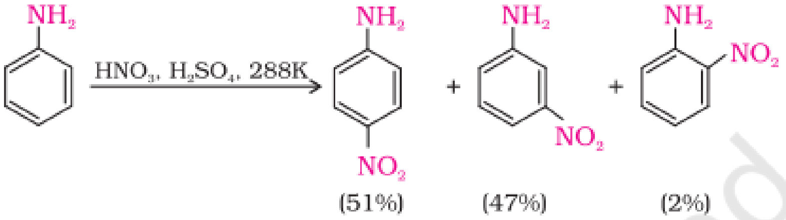
a. 1^0 amine forms a salt which is soluble in alkali
b. 2^0 amine forms a salt which is insoluble in alkali
c. 3^0amine do not react with Hinsberg reagent

5. **Carbylamine reaction: (i)** Primary aliphatic and aromatic amine reacts with chloroform and KOH to form alkyl/aryl isocyanides(foul smell compound distinguish test for primary amine from secondary and tertiary amine

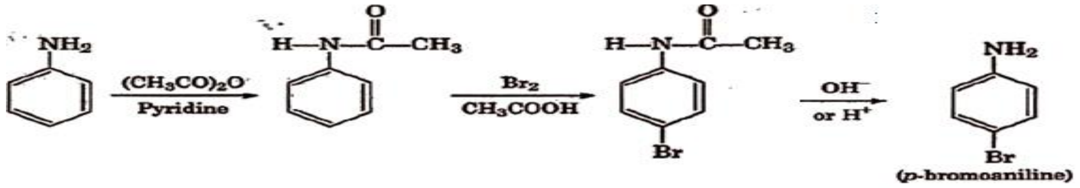
$$R-NH_2 + CHCl_3 + 3KOH \rightarrow R-NC + 3KCl + 3H_2O$$

6. **REACTIONS OF ANILINE**

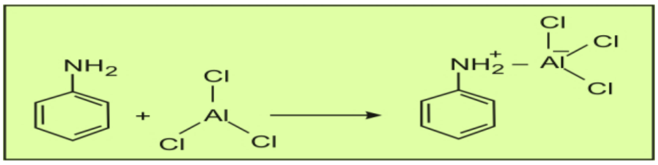
$-NH_2$ group is ortho and para directing and a powerful activating group. Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives.



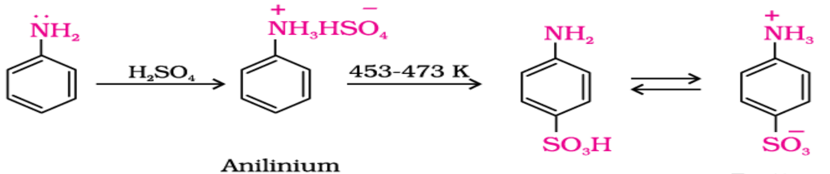
Aniline is converted into acetanilide by acetylation with acetic anhydride and then the desired substitution is carried out followed by hydrolysis the lone pair on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of -$NHCOCH_3$ group is less than that of amino group.



- Aniline do not undergo Friedel craft reaction as it forms salt with the catalyst $AlCl_3$



Sulphonation: Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate, which on heating at 453–473 K yields p-aminobenzene sulphonic acid (sulphanilic acid) as the major product.

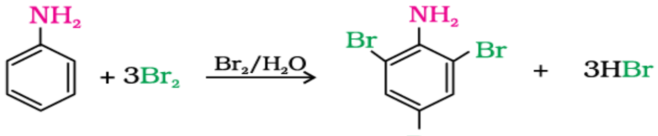


Anilinium hydrogensulphate

Sulphanilic acid

Zwitter ion

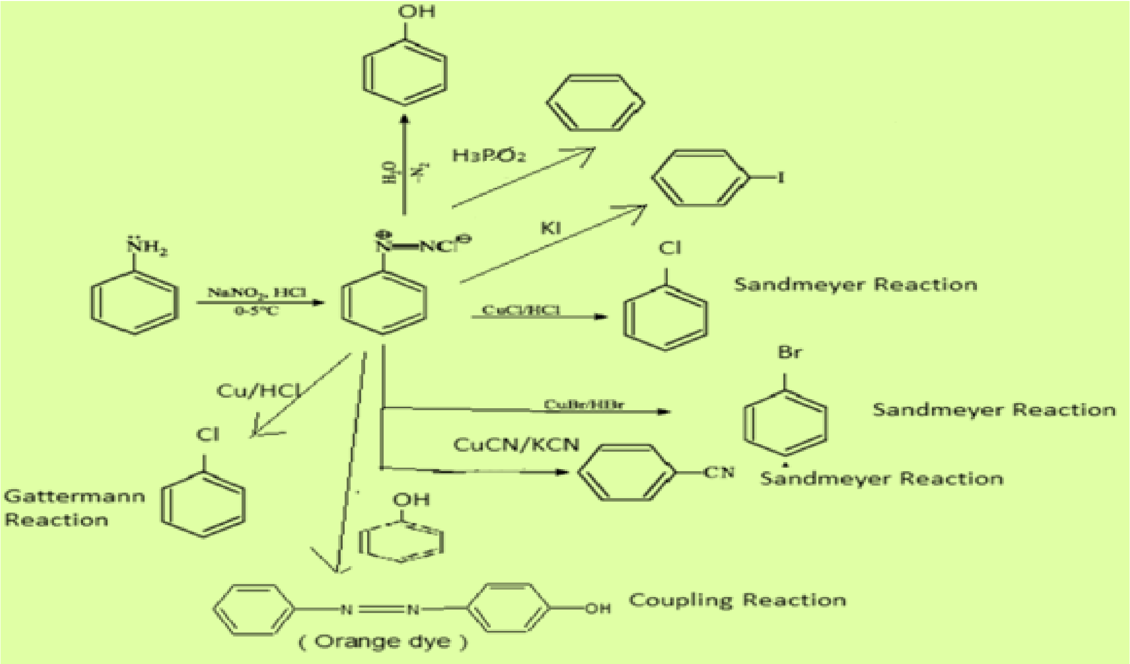
Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



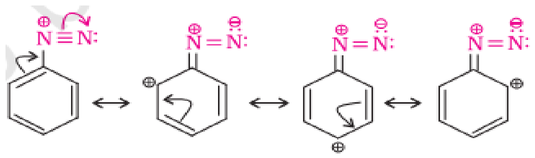
Aniline

2,4,6-Tribromoaniline

7..REACTIONS OF BENZENE DIAZONIUM CHLORIDE



Note: Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



SECTION – A (1 Mark)

Q1. A compound which is formed when hydrogen gas is passed through nitrobenzene in the presence of finely divided nickel is…

(a) Aniline (b) 2-Nitroaniline (c) 3-Nitroaniline (d) 2,4- dinitroaniline

Q2. Aniline reacts with Br_2 water to give……

(a) 1-bromoaniline (b) 1,2- dibromoaniline (c) 2,4,6-tribromoaniline (d) No reaction

Q3. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is…………….

(a) excess H_2 (b) Br_2 in aqueous NaOH

(c) iodine in the presence of red phosphorus (d) $LiAlH_4$ in ether

Q4**.** ……….. of the following compound will not undergo azo-coupling reaction with benzene diazonium chloride**?**

(a) Aniline (b) Phenol (c) Anisole (d) Nitrobenzene

Q5.The correct IUPAC for $CH_3CH_2CH_2NCH_3C_2H_5$ is……..

(a) N-methyl-N-ethylpropan-1-amine (c) N-ethyl-N-methylpropan-1-amine

(b) N,N diethylpropane-1-amine (d) N,N-dimethylpropan-1-amine

Q6. Raghu heated a mixture of primary amine and chloroform with ethanolic potassium hydroxide (KOH) to form isocyanides which has foul smelling. What is the name of the reaction involved in the statement?

(a) Hoffmann bromide degradation reaction (b) Hinsberg's Test

(c) Gabriel Phthalimide reaction (d) Carbylamine reaction

Q7. The correct increasing order of basic strength for the following compounds

(i) CH_3NH_2 (ii) $(CH_3)_2NH$ (iii) $C_6H_5NH_2$ (iv) NH_3

(a) i,ii,iii,iv (b) ii,iii,i,iv (c) iv,iii,i,ii (d) iii,iv,ii,i

Q8. Hinsberg's reagent is:

(a) Phenylisocyanide (b) p- toluenesulphonic acid

(c) benzensulphonyl chloride (d) o-dichlorobenzene

Q9.The conversion of benzene diazonium chloride to bromobenzene can be accomplished by

(a) Reimer-Tiemann reaction (b) Friedel-Crafts reaction

(c) Gattermann reaction (d) Azo-Coupling reaction

Q10. Identify the false statement about amines.

(a) Alkylamines are stronger bases than arylamines.

(b) Alkylamines react with nitrous acid to produce alcohols.

(c) Alkylamines are stronger bases than ammonia.

(d) Arylamines react with nitrous acid to produce phenols

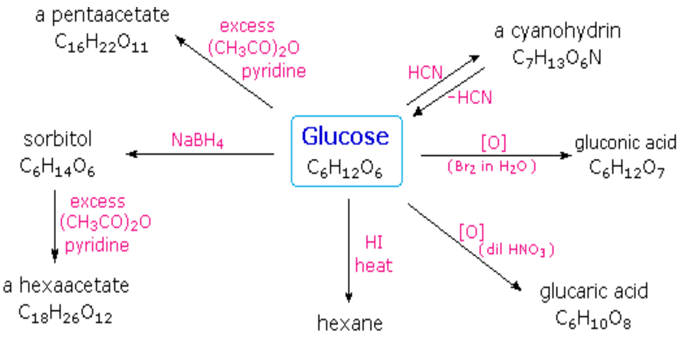
The following questions has two statements; one is assertion and second is reason write;

(a) If assertion and reason both are true and R is correct explanation of A

(b)Assertion and reason both are correct but R is not the correct explanation

10 BIOMOLECULES

- **Monosaccharides** : Cannot be hydrolysed further to simpler molecules. Example: Glucose, fructose, Ribose etc.
- **Reactions of glucose (Open Chain structure):**



- **Reactions of glucose could not be explained by open chain structure.**
  1. Glucose does not give Schiff's test and it does not form the hydrogensulphite.
  2. The pentaacetate of glucose does not react with hydroxylamine (due to absence of free —CHO group.)
  3. Glucose is found to exist in two different crystalline forms which are named as α and β.

Reducing sugars	**Non reducing sugars**
Aldehydic/ ketonic groups free so reduce Fehling's/ Tollens solution and. Eg- maltose and lactose.	Aldehydic/ ketonic groups are bonded so cannot reduce Fehling's solution and Tollens' reagent. Eg- Sucrose Anomers

Anomer: The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon. Such isomers, i.e., α –form and β -form, are called anomers.

Invert sugar:

- Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory.
- Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar

Disaccharides: Hydrolysis, they generally give two monosaccharides unit. The linkage between two monosaccharide units through oxygen atom is called **glycosidic linkage**. Example:

Disaccharides	Monomers
(i) Sucrose	α-D-glucose and of β-D-fructose
(ii) Lactose	β-D-galactose and β-D-glucose.
(iii) Maltose	Two α-D-glucose

Polysaccharides: Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages.

Starch (i) Main storage of plants
(ii) polymer of α-glucose and consists of two components— Amylose and Amylopectin.

Amylose	**Amylopectin**
It is water soluble which constitutes about 15-20% of starch.	It is insoluble in water and constitutes about 80-85% of starch.
It is a long unbranched.	It is a branched chain polymer
α-D-(+)-glucose units held together by C1– C4 glycosidic linkage.	branching occurs by C1–C6 glycosidic linkage

Cellulose: it is the most abundant organic substance in plant kingdom and main constituents of cell wall.Cellulose is a straight chain polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

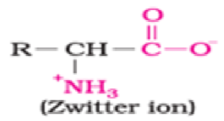
Glycogen: The carbohydrates are stored in animal body as glycogen. It is also known as animal starch. It is present in liver, muscles and brain. It is polysaccharides of α-D glucose.

Proteins: All proteins are polymers of α-amino acids.

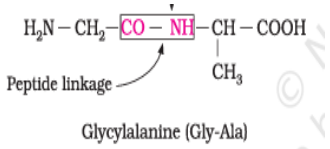
Amino Acids:

Essential amino acids	Non- essential amino acids
• which cannot be synthesised in the body and must be obtained through diet, • eg- Valine, Leucine.	• which can be synthesised in the body • eg - Glycine, Alanine

Zwitter ion: In aqueous solution, amino acids exist as a dipolar ion known as Zwitter ion



Peptide linkage: peptide linkage is an amide formed between –COOH group and NH_2 group of two successive amino acids in peptide chain.



Primary (1^0) structure of proteins	Secondary (2^0) structure of proteins	Tertiary (3^0) structure of proteins
sequence of amino acids that is said to be the primary structure of protein.	(i) Secondary structure of protein refers to the shape in which a long polypeptide chain can exist. (ii) Exist in two types of structures viz. α -helix and β -pleated sheet structure and the binding force is hydrogen bond	**:** (i) Further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. (ii) The main **forces** which stabilise the 3° structures of proteins are **hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction**

Fibrous proteins	Globular proteins
Polypeptide chains run parallel and water insoluble.	Globular proteins chains of polypeptides coil around to give a spherical shape. water soluble.
Eg- are keratin(in hair, wool, silk) and myosin (present in muscles).	Eg-Insulin and albumins Stab.

Denaturation of Proteins: (i) When a protein is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.eg- The coagulation of egg white on boiling, curdling of milk
(ii) During denaturation 2° and 3° structures are destroyed but 1° structure remains intact.

Enzymes: Enzymes are essential biological catalysts which are required to catalyse biological reactions, e.g., maltase, lactase, invertase, etc. Almost all the enzymes are globular proteins

Vitamins: Organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

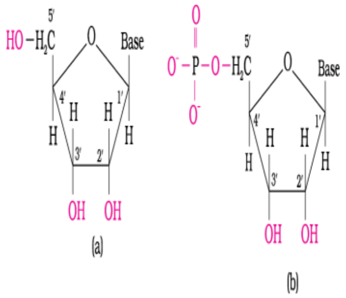
Fat soluble vitamins: These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

Water soluble vitamins: Vitamin B, C. these vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot stored in human body.

Vitamin	Deficiency diseases	Vitamin	Deficiency diseases
Vitamin A	Xerophthalmia (hardening of cornea of eye) Night blindness	Vitamin B6	Convulsions
Vitamin B1 (Thiamine)	Beriberi	Vitamin C(Ascorbic acid)	Scurvy (bleeding gums)
Vitamin B 2	Cheilosis	Vitamin D	Rickets, osteomalacia
Vitamin B12	Pernicious anaemia	Vitamin E	fragility of RBCs and muscular weakness
Vitamin K	Increased blood clotting time		

Nucleic acid

- Particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids.
- Two types of nucleic acid that is deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).nucleic acids are long chain polymers of nucleotides, so they are also called polynucleotides.
- Complete hydrolysis of DNA (or RNA) produces a pentose sugar, phosphoric acid, and nitrogen-containing heterocyclic compounds known as bases.
- A unit formed by the attachment of a base to 1' position of sugar is known as nucleoside.When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide.

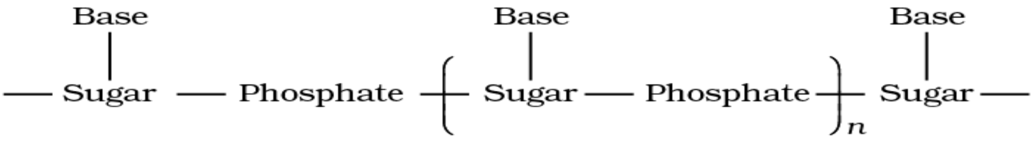


Structure of (a) a nucleoside and (b) a nucleotide

DNA	RNA
β-D-2-deoxyribose sugar is present.	**β-** b-D-ribose sugar is present
DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T)	RNA also contains four bases adenine (A), guanine (G), cytosine (C) and uracil (U).
DNA has a double strand helix structure. The two strands are complementary to each other. The two strands held together by hydrogen bonds between pairs of bases	RNA has a single stranded **α-helix structure.** RNA molecules are of three types and they perform different functions. They are (i) messenger RNA(m-RNA), (ii) ribosomal RNA (r-RNA) and (iii) transfer RNA (t-RNA).
DNA has a unique property of replication	RNA usually does not replicate.
DNA controls the transmission of hereditary effects	RNA controls the synthesis of proteins.

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar.

A simplified version of nucleic acid chain is as shown below.



$$—\underset{}{\overset{\text{Base}}{\overset{|}{\text{Sugar}}}} — \text{Phosphate} \left\{ \overset{\text{Base}}{\overset{|}{\text{Sugar}}} — \text{Phosphate} \right\}_n \overset{\text{Base}}{\overset{|}{\text{Sugar}}} —$$