ExamsRoad.com

Chemistry Notes
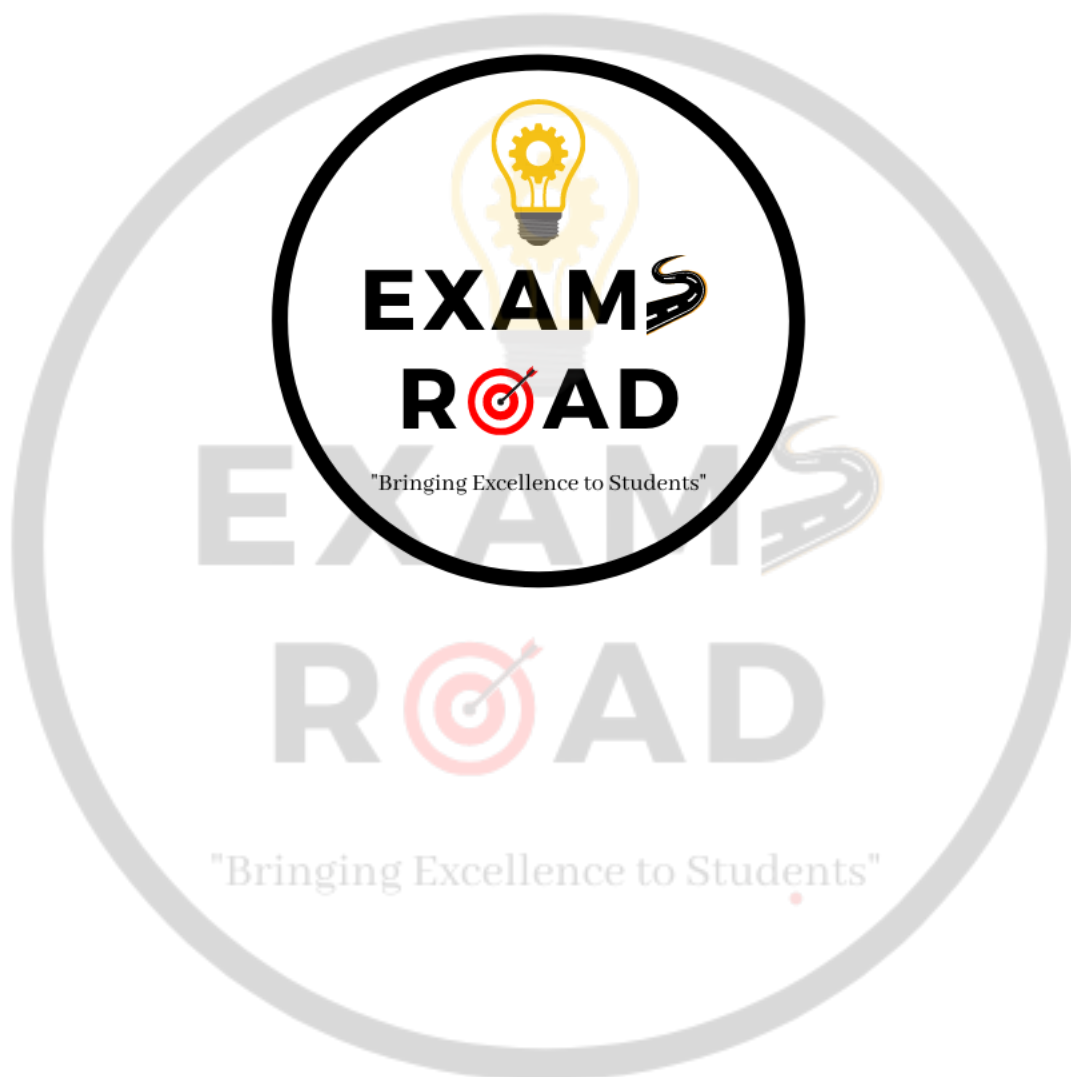
Solution

It is a homogeneous mixture of two or more than two substance e.g sugar solution, salt solution.

Types of solution

Solute	Solvent	Name	Nature	Example
solid	liquid	S in L	liquid	sugar soln
liquid	liquid	L in L	liquid	Alcohol + water
Gas	liquid	G in L	liquid	Aerated drinks
Solid	Solid ~~Solid~~ ~~liquid~~	S in S	solid	Alloys
liquid	Solid ~~liquid~~ ~~liquid~~	L in S	solid	Hydrated salt
Gas	Solid ~~Gas~~	G in S	solid	Rusted iron
Solid	Gas	S in G	Gas	smoke
liquid	Gas	L in G	Gas	fogg
Gas	Gas	G in G	Gas	Air

Mass Percentage

Mass of a component to the per 100 parts mass of solution

Mass % of A $= \dfrac{W_A}{W_A + W_B} \times 100$

10% HCl by mass means 10 g HCl in 100 g solution

Volume Percentage

Volume of a component to the per 100 parts volume of solution

Vol. % of B $= \dfrac{\text{Vol. of B}}{\text{Vol. of soln}} \times 100$

10% HCl by volume means 10 ml HCl in 100 ml solution.

Mass by Volume Percentage

$\dfrac{\text{Mass of component}}{\text{Volume of solution}} \times 100$

10% HCl mass by Volume means 10 g HCl in 100 ml solution.

Mass fraction

$x_1 = \dfrac{W_1}{W_1 + W_2}$, $x_2 = \dfrac{W_2}{W_1 + W_2}$

Parts per million

$\dfrac{W_2}{W_1 + W_2} \times 10^6$

Mole fraction

$x_1 = \dfrac{n_1}{n_1 + n_2}$ or $x_2 = \dfrac{n_2}{n_1 + n_2}$

$\boxed{x_1 + x_2 = 1}$

In gases only

$y_1 = \dfrac{p_1}{p_1 + p_2}$ or $y_2 = \dfrac{p_2}{p_1 + p_2}$ $\boxed{y_1 + y_2 = 1}$

Molarity M

Defined as no. of moles of a solute dissolved in per litre of solution.

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

$$\boxed{Unit = \frac{Moles}{litre}}$$

Molality m

Defined as no. of moles of solute dissolved in per kg of solvent

$$m = \frac{W_B}{M_B} \times \frac{1000}{W_A(g)}$$

$$\boxed{Unit = \frac{Moles}{kg}}$$

Difference b/w molarity and molality

Molarity	Molality
No. of moles of solute dissolved in one litre solution	No. of moles of solute dissolved in one kg solvent
$M = \dfrac{n_B}{V(in\,L)}$	$m = \dfrac{n_B}{W_A(kg)}$
Molarity depends on temperature	Molality is independent of temp.
Molarity decreases with rise in temperature	Molality does not changes with temperature

Molarity & Molality of pure water is 55.5

Solubility → Maximum amount of substance that can be dissolved in a specified amount of a solvent at a specified temp. is called its solubility.

Factors affecting solubility of a Solid in a liquid

→ Nature of solute and Solvent → Polar solutes dissolve in polar solvents and non polar solutes in non polar solvents (i.e like dissolve like)

→ Effect of temperature →

→ If the dissolution process is endothermic (ΔH > 0) the solubility increases with rise in temperature

− If dissolution process is exothermic (ΔH < 0), the solubility decrease with rise in temperature

→ Effect of pressure → Pressure does not have any significant effect on solubility of solids in liquid as these are highly incompressible

Henry's law and its Application

amount of liquid is proportional to its pressure solubility of a gas in a given

$$M = K_H p$$ (OR)

Partial pressure of a gas is directly proportional to the mole fraction of gas

Application

$$p = K_H x$$

- It is used to make carbonated soft drinks
- It is used to explain function of lungs.
- People living at high altitude suffering from disease Anoxia.
- It is used to minimise the painful effects of deep sea diving by replacing N_2 by He gas

K_H is Henry's constant and different for different gases at particular temp.

Value of K_H increases with temp

Higher the value of K_H lower the solubility of gas

Raoult's law → It states that partial pressure of a component in solution is directly proportional to its mole fraction in solution. multi $P_A = P_A^° \times x_A$ $P_B = P_B^° \times x_B$

1.) for Volatile Solute

$$P_S = P_A + P_B$$
$$= P_A^° \times x_A + P_B^° \times x_B$$
$$= P_A^° (1-x_B) + P_B^° \times x_B$$
$$= P_A^° - P_A^° x_B + P_B^° \times x_B$$
$$= P_A^° + (P_B^° - P_A^°) x_B$$

2.) for Non-Volatile Solute

$$P_S = P_A$$
$$P_S = P_A^° \times x_A$$
$$\frac{P_S}{P_A^°} = x_A$$
$$1 - \frac{P_S}{P_A^°} = 1 - x_A$$

Relative lowering in V.P

$$\Rightarrow \frac{P_A^° - P_S}{P_A^°} = x_B$$

→ **Ideal and Non-ideal Solution**

· Those solution which obey Raoult's law are called **ideal** solution

· $P_A = P_A^° \times x_A$
  $P_B = P_B^° \times x_B$

· $\Delta V_{mix} = 0$
· $\Delta H_{mix} = 0$
· Interaction of A-B is same as interaction of A-A and B-B
eg n-hexane + n heptane

Those solution which does **not** obey Raoult's law are called non-ideal

$P_A \neq P_A^° \times x_A$ $P_B \neq P_B^° \times x_B$

· $\Delta V_{mix} \neq 0$
· $\Delta H_{mix} \neq 0$
· interaction of A-B is not same as interaction of A-A and B-B
acetone + ethanol

Azeotropes :- The mix. of liquids boil at constant temp. like a pure liquid and possess same composition of components in liq. as well as vapour phase are called constant boiling mix. and azeotropes

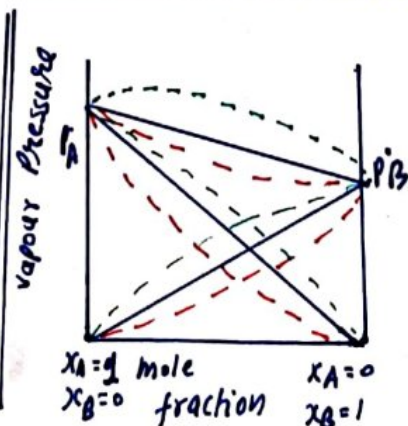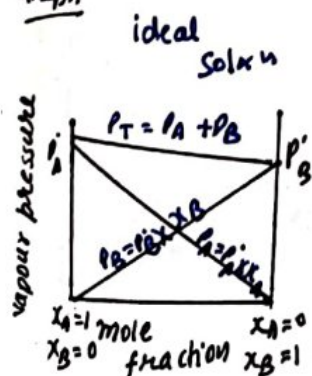| Positive Deviation	Negative Deviation	
· Interaction of A-B is less than interaction of interaction of A-A & B·B	Interaction of A-B is High than interaction of A·A and B-B	- Min. boiling azeotrops formed by those liquid which show positive deviation from ideal behaviour e.g $H_2O + C_2H_5OH$
· $P_A > P_A^° \times x_A$ $P_B > P_B^° \times x_B$	$P_A < P_A^° \times x_A$ $P_B < P_B^° \times x_B$	- Max. Boiling Azeotropes By those liquid pairs which show negative deviation. from ideal behaviour e.g $HNO_3 + H_2O$
· $\Delta V_{mix} > 0$ $\Delta H_{mix} > 0$	$\Delta V_{mix} < 0$ $\Delta H_{mix} < 0$	
· water + methanol acetone + ethanol	- acetone + aniline - acetone + chloroform	

Graph

ideal Soln

$P_T = P_A + P_B$

$x_A = 1$ mole
$x_B = 0$ fraction $x_B = 1$ $x_A = 0$

- negative deviation
- positive deviation
- ideal solution

$x_A = 1$ mole
$x_B = 0$ fraction $x_A = 0$ $x_B = 1$

(4)

Colligative Property

Properties which depends only on the number of solute particles not on the nature of solute particles

1. Relative lowering in v.p
2. Elevation in B.P
3. Depression in freezing pt.
4.) Osmotic Pressure

Relative lowering in v.p

when a non volatile solute dissolved in a solvent, vapour pressure of the solution is lower than that of pure solvent which is known as lowering of V.P.

Relative lowering of v.p is equal to the mole fraction of the solute in the solution

$$\frac{P_A° - P_s}{P_A°} = X_2 = \frac{n_2}{n_1 + n_2}$$

$P_A° - P_s \Rightarrow$ lowering in v.p $\frac{P_A° - P_s}{P_A°} = $ Relative lowering in v.p

Elevation in Boiling Point

The b.pt of a solution containing a non volatile solute is always higher than the b.pt of pure solvent. This increase in B.pt is termed as elevation in B.Pt.

$$\Delta T_b = T_b - T_b°$$
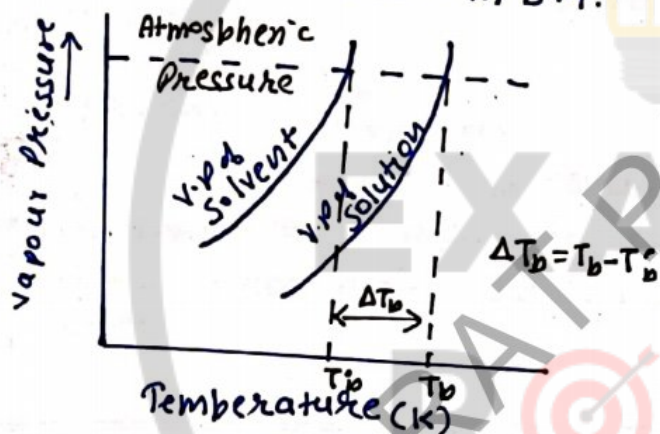
$\Delta T_b \rightarrow$ elevation in B.pt
$T_b \rightarrow$ B.Pt of solution
$T_b° \rightarrow$ B.Pt of pure solvent

$\Delta T_b \propto m$ $\Delta T_b = K_b m$

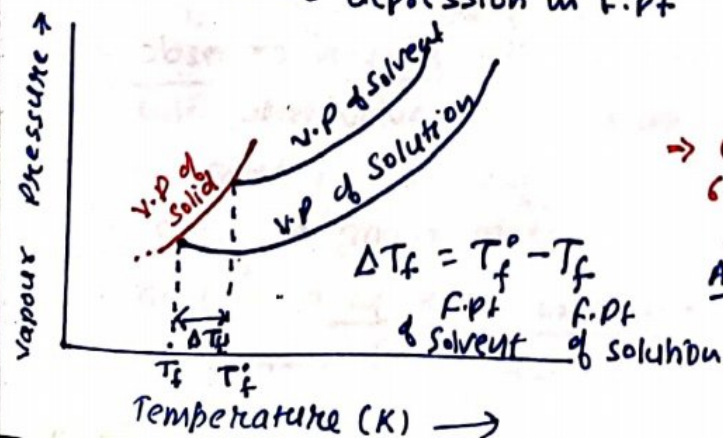$$\Delta T_b = K_b \left(\frac{W_B}{M_B} \times \frac{1000}{W_A(g)} \right)$$

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

$K_b \rightarrow$ ebullioscopic constant or molal elevation constant

Unit = K Kg mol⁻¹

find the B.pt of soln containing 0.520 g of glucose ($C_6H_{12}O_6$) dissolved in 80.2 g of water ($K_b = 0.52$ K/m) [2010]

Ans. $\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A(g)}$

$= \frac{0.52 \times 0.520 \times 1000}{180 \times 80.2}$

$= 0.019$ K

B.Pt of solution $\Delta T_b = T_b - T_b°$

$\Rightarrow T_b = \Delta T_b + T_b°$
$= 0.019$
$+ 373$
$\Rightarrow 373.019$ K

Depression in Freezing Point

The f.Pt of a solution containing a non-volatile solute is always less than the f.Pt of the pure solvent. This decrease in f.pt is termed as depression in f.pt

$$\Delta T_f = T_f° - T_f$$

f.pt of solvent   f.pt of solution

$\Delta T_f \propto m$ $\Delta T_f = K_f m$

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

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

Unit = K Kg mol⁻¹

K_f = molal depression constant or cryoscopic constant

→ Calculate the f.pt of a solution cont. 60 g of glucose (M_B = 180 g mol⁻¹) in 250 g water (K_f = 1.86 K Kg mol⁻¹) [2018]

Ans. $\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A(g)}$

$= \frac{1.86 \times 60 \times 1000}{180 \times 250} = 2.48$ K

$T_f = T_f° - \Delta T_f$
$= 273 - 2.48$
$= 270.52$ K

Osmosis and osmotic pressure The movement of solvent molecules from less concenterated solution to more conc solution through semipermeable membrane is termed as osmosis

The pressure abblied to stop osmosis is called osmotic pressure (p or π)

OSMOSIS

High conc. ↑ low conc.

Semi Permeable membrane

Osmotic Pressure

High conc.↑ low Conc.

Semi Permeable Membrane
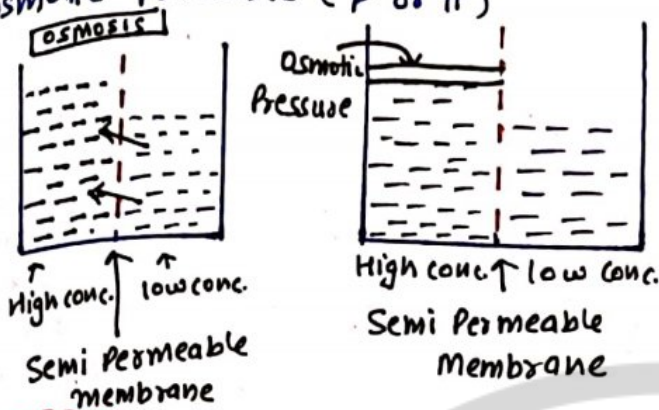
$\pi = C \times R \times T$ ($C \to$ molar conc.)
$R \to$ Gas Constant 8.314 $JK^{-1}mol^{-1}$

$= \dfrac{n_B}{V} \times R \times T$ $T \to$ Temberature

$\pi V = \dfrac{\omega_B}{M_B} \times R \times T$ $\boxed{M_B = \dfrac{\omega_B \times R \times T}{\pi \times V}}$

ISOTONIC Two solution having same pressure at a given tempare called isotonic solution $\boxed{\pi_A = \pi_B}$

Hypertonic If one solution having higher osmotic pressure than other called Hypertonic solution

$$\pi_A > \pi_B$$
Hypertonic   Hypotonic

Reverse Osmosis If more than osmotic pressure abblied on solution side, reverse of osmosis takes place, used in Desalination of water

(N-1) Determine the osmotic press-ure of a solution prebared by dissolving 2.5×10^{-2} g of K_2SO_4 in 2 L of water at $25°C$. Assuming that it is completely dissociated ($R = 0.0821$ L atm $K^{-1}mol^{-1}$)
$M_B = 174$ g mol^{-1} [D-2013]

Ans. $\Delta T_f = i K_f m$
$= i \times K_f \times \dfrac{\omega_B \times 1000}{M_B \times \omega_A(g)}$

$\pi = \dfrac{\omega_B}{M_B} \times \dfrac{R \times T}{V}$

$= \dfrac{2.5 \times 10^{-2} \times 0.0821 \times 298}{174 \times 2}$

$= 0.1758 \times 10^{-2}$ atm

Abnormal Molar Mass when the molecular mass of a substance deter-mined by any of the colligative property comes out to be different than the expected value, the substance is said to show Abnormal molar mass

→ Abnormal molar mass is observed when the solution is non-ideal

Van't Hoff factor → It is the ratio of experimental value of Colligative property to the calculated value of colligative property.

$i = \dfrac{\text{observed value of colligative Prop}}{\text{Calculated value of Collig. Prop.}}$

$= \dfrac{\text{Calculated molar mass}}{\text{observed molar mass}}$

$= \dfrac{\text{no. q moles after ass. or diss.}}{\text{no. q moles before ass. or diss.}}$

If $i > 1$ → dissociation
$i = 1$ → no ass. or diss.
$i < 1$ → association

$\alpha_{diss} = \dfrac{i-1}{n-1}$ $\alpha_{ass.} = \dfrac{1-i}{1-\dfrac{1}{n}}$

Van't Hoff & Colligative Property

$\dfrac{P_A^° - P_s}{P_A^°} = i \times x_B$

$\Delta T_f = i \times K_f m$
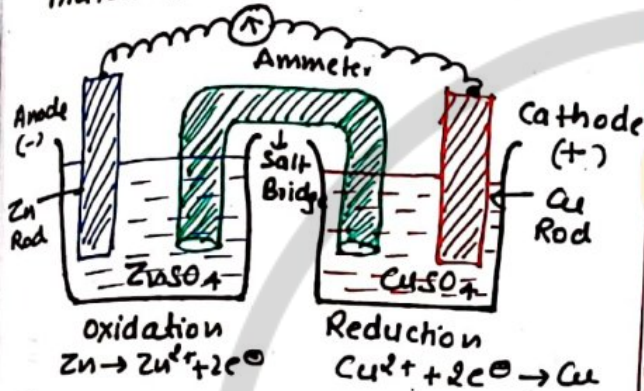$\Delta T_b = i \times K_b m$
$\pi = i \times C \times R \times T$

Electrochemistry

It is that branch of chemistry in which we are studies about the relationship b/w electrical energy and chemical energy and their interconversion.

Cell

smallest device which is used to convert one form of energy into another form of energy

1) Electrochemical cell (Galvanic) or Voltaic	Electrolytic cell
- It is a device which converts chemical energy into electrical energy	It is a device which converts electrical energy into chemical energy.
- Redox Reaction is spontaneous	Redox Rxn is non-spontaneous
Two electrolytes are taken	only one electrolyte is taken
The electrodes taken are of diff. materials	The electrodes taken may be of the same or different materials

Galvanic cell:
- Anode (-), Zn Rod, ZnSO₄
- Cathode (+), Cu Rod, CuSO₄
- Salt Bridge, Ammeter

oxidation $Zn \rightarrow Zn^{2+} + 2e^{\ominus}$

Reduction $Cu^{2+} + 2e^{\ominus} \rightarrow Cu$

Electrolytic cell:
- Impure Cu
- Pure Cu
- CuSO₄
- Anode mud
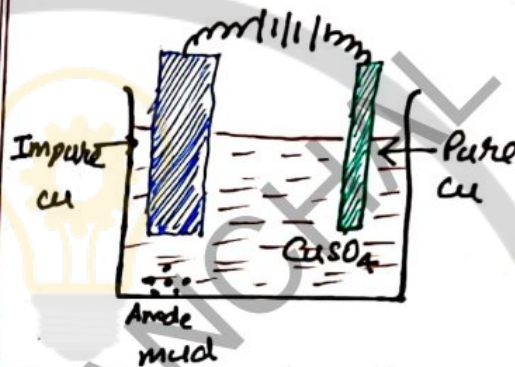
- electrical energy is produced	- electrical energy is used
Anode is −ve	Anode is +ve
Cathode is +ve	Cathode is −ve

Salt Bridge

It is an inert U-shaped glass tube which is filled with the paste of KCl or KNO₃ or K₂SO₄ in agar agar form

Application
(i) It is used to connect both the beakers
(ii) It is used to maintain the electrical neutrality
(iii) It is used to prevent the passage of one electrolyte into another
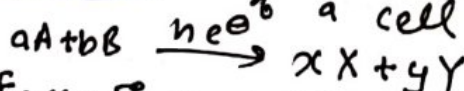(iv) It is used to complete the inner cell circuit.

Nernst Equation

Used to give electrode potential when conditions are not standard

$$E_{metal} = E^{\circ}_{Metal} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[Oxi]}{[Red]}$$

Application
1) To calculate electrode potential of a cell

$$aA + bB \xrightarrow{ne^{\ominus}} xX + yY$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

2) To calculate equilibrium constant

$$E^{\circ}_{cell} = \frac{0.0591}{n} \log K_c$$

3) Gibbs Free Energy and cell potential
$$\Delta G^{\circ} = -nF E_{cell} \quad \text{or} \quad \Delta G^{\circ} = -2.303 RT \log K_c$$

Ⓝ Calculate ΔG° and $\log K_c$ for the following reaction. (2019)

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

Given $E^{\circ}_{Cd^{2+}/Cd} = -0.403V$
$E^{\circ}_{Zn^{2+}/Zn} = -0.763V$

Ans:

$$E_{cell} = E^{\circ}_{Red} - E^{\circ}_{Oxi}$$
$$-0.403 - (-0.763) = 0.36V$$

$$\Delta G^{\circ} = -nF E_{cell} \Rightarrow -2 \times 96500 \times .36$$
$$= -69480 J = -69.48 KJ$$

$$\log K_c = \frac{n E_{cell}}{0.059}$$
$$= \frac{2 \times 0.36}{0.059} = 12.20$$

$$K_c = \text{antilog}(12.20)$$
$$= 1.58 \times 10^{12}$$

Conductance G $\frac{1}{R} = \frac{a}{\rho \ell} = \frac{K \cdot a}{\ell}$ Unit = ohm^{-1} or Ω^{-1} or siemen

on dilution conductance increases as no. of ions are produced

Specific Conductance or Conductivity (K) $\frac{1}{\rho}$ or $G \frac{\ell}{a}$ Unit = ohm^{-1} c·m^{-1} or S·c·m^{-1}

on dilution, specific conductance decrease as no. of ions per c.m³ decreases

Equivalent Conductivity Λ_{eq} $K \times V$ or $K \times \frac{1000}{N}$ Unit = Ω^{-1} c·m² or S c·m² eq^{-1}

on dilution, equivalent conductivity increases with dilution due to increase in V

Molar Conductivity Λ_M $K \times V$ or $K \times \frac{1000}{M}$ Unit = Ω^{-1} c·m² mol^{-1} or S c·m² mol^{-1}

Increase with dilution due to large increase in V

(N-1) The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the soln. **[2014]**

Ans: Conductivity $(K) = \frac{1}{R} \times G = \frac{1}{200} \times 1 = 5 \times 10^{-3}$ Ω^{-1} c·m^{-1}

Molar Conductivity (Λ_m)

$$= \frac{K \times 1000}{M} = \frac{5 \times 10^{-3} \times 1000}{0.01} = 500 \ \Omega^{-1} \ c·m² \ mol^{-1}$$

(N-2) The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 c·m and length is 50 c·m is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity **[2013]**

Ans: $a = \pi r² = 3.14 \times \left(\frac{1}{2}\right)² = \frac{3.14}{4}$ c·m²

Resistivity, $\rho = R \frac{a}{\ell} = 5.5 \times 10^3$ ohm $\times \frac{3.14}{4 \times 50}$ $\Rightarrow$ 86.35 ohm c·m

Again, conductivity $K = \frac{1}{\rho} = \frac{1}{86.35} = 1.158 \times 10^{-2}$ ohm^{-1} c·m^{-1}

And molar conductivity, $\Lambda_m = \frac{K \times 10^3}{M} = \frac{1.158 \times 10^{-2} \times 10^3}{5 \times 10^{-2}} = 231.6$ ohm^{-1} c·m² mol^{-1}

(N-3) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S·c·m^{-1}? **[2012]**

Ans: conductivity $(K) = 0.146 \times 10^{-3}$ S·c·m^{-1} resistance $(R) = 1500 \ \Omega$

cell constant $= \frac{Conductivity}{Conductance} \Rightarrow$ Conductivity $\times$ Resistance

$\Rightarrow K \times R \Rightarrow 0.146 \times 10^{-3} \times 1500 = 0.219$ c·m^{-1}

Limiting molar Conductivity when concentration approaches zero i.e at infinite dilution, the molar conductivity is known as limiting molar conductivity (Λ_m)

Kohlrausch law It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte

$$\Lambda_m° AB = \lambda_m° A^+ + \lambda_m° B^-$$

Application of Kohlrausch law

1.) Calculation of molar conductivity of weak electrolyte

$$\Lambda_m° CH_3COOH = \lambda_m° CH_3COO^- + \lambda_m° H^+$$

2.) Calculation of degree of dissociation

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m°} = \frac{\text{Molar conductance at conc. C}}{\text{Molar conductance at infinite dilution}}$$

3.) Calculation of dissociation constant

$$K_c = \frac{C\alpha²}{1-\alpha}$$

Electrolysis — It is the process of decomposition of an electrolyte by passing (8) electricity through its aqueous solution or molten state

Faraday's first law — The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity through the electrolyte

$$W \propto Q$$
$$W = ZQ$$
$$W = Z \times I \times t$$
$$W = \frac{At. Mass}{n \times 96500} \times I \times t$$

where, Z is electrochemical equivalent of the substance deposited

Faraday's Second law — The amount of different substance liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weight

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

where E is equivalent wt.

(N-1) How much charge is required for the reduction of 1 mol Zn^{2+} to Zn? [2015]

Ans: $Zn^{2+} + 2e^{\ominus} \longrightarrow Zn$ one mole of Zn^{2+} requires 2 moles of $e^{\ominus}$

$$Q = 2 \times F = 2 \times 96500 = 193000 \, C$$

(N-2) Silver is uniformly electrodeposited on a metallic vessel of surface area of 900 $C \cdot m^3$ by passing a current of 0.5 ampere for 2 hours. Calculate the thickness of silver deposited (Given density of silver is 10.5 $g \cdot m^3$, At of Ag = 108 Mass atm) [2013]

Ans: electrode reaction $Ag^+ + e^{\ominus} \rightarrow Ag$

quantity of electricity passed = Current × time
$$= 0.5 \times 2 \times 60 \times 60 = 3600 \, C$$

96500 C of electricity deposit = 108g Ag

3600 C $= \frac{108}{96500} \times 108 = \boxed{4.03g \, Ag}$

let the thickness of deposit be x cm

Mass = volume × density = Area × thickness × density [∵ Vol. = area × thickness]

∴ $4.03g = 900 \times x \times 10.5$

$$\boxed{x = 4.26 \times 10^{-4} \, C \cdot m}$$

(N-3) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given: $1F = 96500 \, C \, mol^{-1}$) [2017]

Ans: Given $I = 0.5 A$, $t = 2 hrs$

Number of $e^{\ominus} = ?$

$$= 0.5 \times 2 \times 60 \times 60 = 3600 \, C$$

Total Charge $(Q) = I \times t$

∴ No. of $e^{\ominus} = \frac{Total \, charge}{charge \, of \, one \, e^{\ominus}}$

$$= \frac{3600}{1.6 \times 10^{-19}} = 2.25 \times 10^{22} \, e^{\ominus}$$

Some Commercial cells

- **Primary cells** :- cells once exhausted can not be used again eg dry cell, mercury cell
- **Secondary cell** :- Rechargable cell can be used again and again e.g lead-storage battery
- **Fuel cell** cell which can convert the energy of combustion of fuels such as H_2, CO, CH_4 etc. into electrical energy e.g H_2-O_2 fuel cell

Corrosion It is the process of slow eating away of metals when exposed to the atmosphere is called corrosion

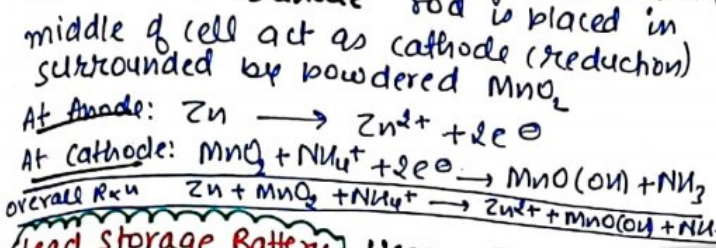**Rusting** It is an electrochemical phenomenon which occurs in the presence of moisture and oxygen

At Anode :- $2Fe \longrightarrow 2Fe^{2+} + 4e^{\ominus}$

At Cathode :- $O_2 + 4H^+ + 4e^{\ominus} \longrightarrow 2H_2O$

Overall Rxn $\underline{2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O}$
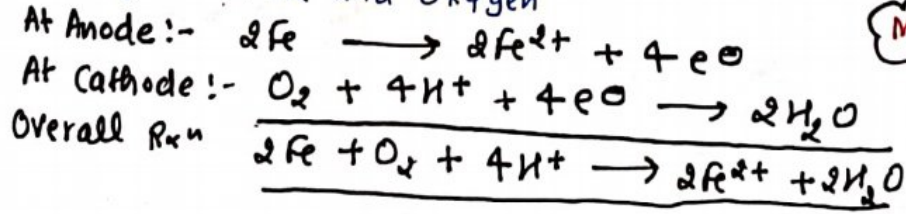
Methods of Prevention
- Barrier Protection
- Sacrificial protection
- Using anti-rust sol.
- Electrical protection

Dry Cell (Leclanche)

Used in Toys, Wall clocks, Remotes, Radios etc.
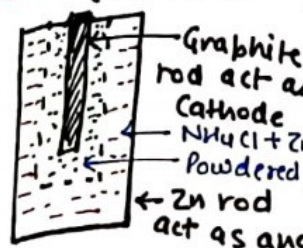
This cell consist of Zn vessel act as anode (oxidation) which is filled with the paste of NH_4Cl and $ZnCl_2$. Graphite rod is placed in middle of cell act as cathode surrounded by powdered MnO_2
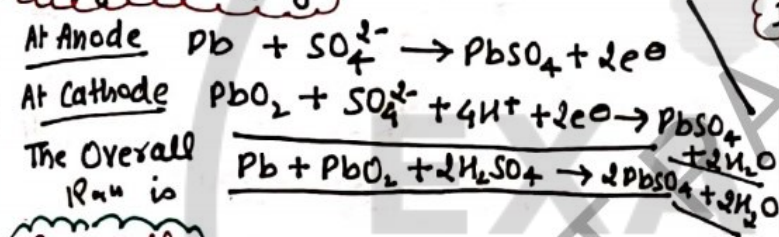
- Graphite rod act as Cathode
- $NH_4Cl + ZnCl_2$
- Powdered MnO_2
- Zn rod act as anode

At Anode: $Zn \longrightarrow Zn^{2+} + 2e^{\ominus}$

At Cathode: $MnO_2 + NH_4^+ + 2e^{\ominus} \longrightarrow MnO(OH) + NH_3$

Overall Rxn: $Zn + MnO_2 + NH_4^+ \longrightarrow Zn^{2+} + MnO(OH) + NH_3$

Mercury Cell ②

This cell consist of a Zn vessel act as anode, and graphite rod act as cathode. Mixture of HgO and KOH act as electrolyte

- Zn vessel as Anode
- Graphite rod as Cathode
- $HgO + KOH$

This cell give the voltage of 1.35 V through its whole life

Use – Toys, hearing aids, watches

At Anode $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^{\ominus}$

At Cathode $HgO + H_2O + 2e^{\ominus} \rightarrow Hg + 2OH^-$

Overall Rxn $Zn + HgO \longrightarrow ZnO + Hg$

Lead Storage Battery

Uses – In inverter, in automobiles etc.

This cell consist of six voltaic cell. In which three are of lead and other three are of lead oxides. lead act as anode, lead oxide act as cathode. Each cell give the voltage of 2V. A 38% sol. of sulphuric acid acts as electrolyte. These voltaic cell are separated by thin fibre Glass sheet

During Discharging

At Anode $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^{\ominus}$

At Cathode $PbO_2 + SO_4^{2-} + 4H^+ + 2e^{\ominus} \rightarrow PbSO_4 + 2H_2O$

The Overall Rxn is $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

During Recharging

At Cathode $PbSO_4 + 2e^{\ominus} \rightarrow Pb + SO_4^{2-}$

At Anode $PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^{\ominus}$

$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

Fuel Cell

- Anode (−)
- Cathode (+)
- aq. KOH or NaOH as electrolyte
- O_2
- H_2
- Porous C-electrodes contain Ni/Pt/Pd as catalyst
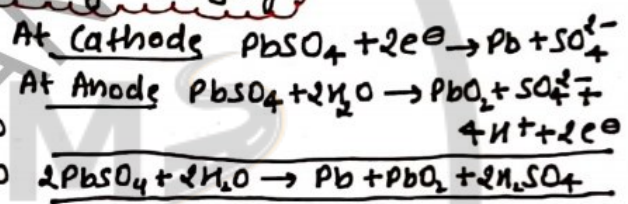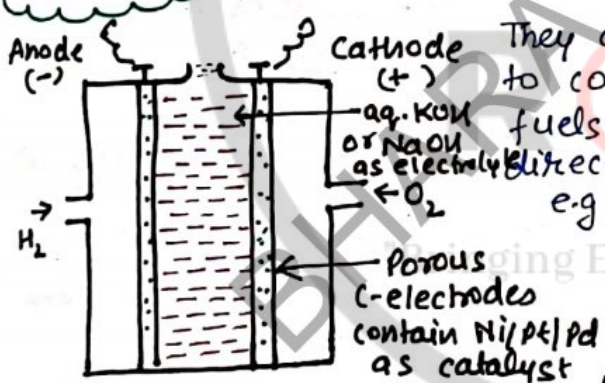
They are galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol directly into electrical energy

e.g H_2-O_2 fuel cell

Hydrogen and oxygen are bubbled through the electrodes into aq. KOH or NaOH.

At Anode

$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^{\ominus}$

At Cathode

$O_2 + 2H_2O + 4e^{\ominus} \longrightarrow 4OH^-$

The Overall Reaction

$2H_2 + O_2 \longrightarrow 2H_2O$
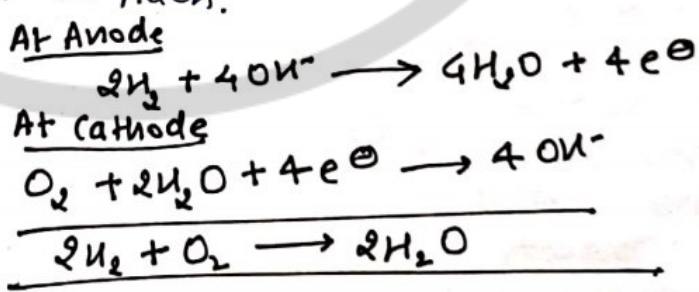
Advantage of fuel cell

– Pollution Free

–

Chemical Kinetics — It is that branch of chemistry which deals with the study of reaction rates and their mechanism

Types of Reaction
1) **Very Fast Rxn** :– Those chemical reaction which takes very fastly e.g ionic Rxn.
2) **Very Slow Rxn** :– which takes very long time e.g formation of coal
3) **Moderate Rxn** :– neither very slow nor very fast e.g Hydrolysis of water

Rate of Rxn — The rate of reaction can be defined as the change in conc. of a reactant or a product in unit time.

$R \rightarrow P$

$$Rate = \frac{-\Delta[R]}{\Delta t} \text{ or } + \frac{\Delta[P]}{\Delta t}$$

Unit of rate $mol\, L^{-1} s^{-1}$ or $atm\, s^{-1}$

Average rate of Rxn It is the appearance of products or disappearance of reactants over a long time interval

$$A + 2B \rightarrow C$$
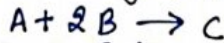
Average Rate :– $-\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t}$

Instantaneous Rate It is the rate of reaction at a particular instant of time

$R \rightarrow P$
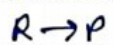
Inst. time = $\frac{-d[R]}{dt} = \frac{+d[P]}{dt}$

N-1 for the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ the rate of formation of NO_2 is 2.8×10^{-3} Ms^{-1}. calculate the rate of disappearance of N_2O_5

Ans: Given,   〔2018〕

$$\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3} Ms^{-1}$$

Acc. to rate law expression,

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4} \times 2.8 \times 10^{-3}$$

$$= 1.4 \times 10^{-3} Ms^{-1}$$

Factors influencing rate of a reaction

Concentration :– Greater the conc. of reactants, faster is the rate of Rxn

Physical State :– Reactions involving gaseous reactants are faster than reactions containing solid and liquid reactants.

Temperature :– The rate of reaction increases with increase of temp. For most of reactions, rate of reaction becomes almost doubles with 10°C rise of temperature

Presence of catalyst :– A catalyst generally increase the speed of reaction

Surface Area of reactant :– for a reaction involving a solid reactant or catalyst, the greater is the surface area, the faster is the reaction.

Presence of light :– photochemical reactions take place in the presence of light only $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

Activation energy :– lower the activation energy faster is the reaction

Rate law Acc. to this law, the rate of reaction is proportional to the product of molar concenteration of reactant and each raise to the power their concenteration term on which rate of reaction actually depends

Consider a general reaction

$$aA + bB \rightarrow cC + dP$$
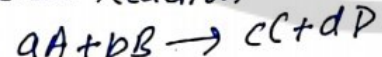
$$Rate = K[A]^x[B]^y \text{ or } -\frac{d[R]}{dt} = K(A)^x[B]^y$$

Order It is the sum of powers on which rate of reaction actually depends acc. to rate law expression.

$$Rate = K[A]^x[B]^y$$

$$Order = x + y$$

Rate constant — rate constant is rate of reaction when concenteration of each reactants becomes unity.

$K = (mol\, L^{-1})\ldots$

Unit of rate constant for different order

〔Zero order〕	$K = (mol\, L^{-1})^{1-0} s^{-1}$
〔First order〕	$K = (mol\, L^{-1})^{1-1} s^{-1}$ or s^{-1}
〔Second order〕	$K = (mol\, L^{-1})^{1-2} s^{-1} = mol^{-1} L^1 s^{-1}$

Molecularity of a Reaction

- It is the total no. of species taking part in a chemical reaction
- It is a theoretical concept
- It is derived from the mechanism of reaction
- It can neither be zero nor fractional. It is always a whole no.
- It is applicable only to elementary reactions

The overall molecularity of a complex reaction has no significance

Order of a Reaction

- It is the sum of the powers of the conc. terms of reacting species in rate law equⁿ
- It is an experimental concept
- It is ~~an ex~~ derived from the rate expression
- It may be zero, fractional or an integer (may range from 0 to 3)
- It is applicable to elementary as well as complex reactions

---

Integrated rate eqⁿ ⟨for first order⟩ :- Those reaction whose rate depends upon one concentration term of reactants.

$R \rightarrow P$
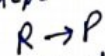
Rate of Rxn $\propto [R]^1$

$$-\frac{d[R]}{dt} = K[R]$$

$$-\frac{d[R]}{[R]} = K dt$$

Integrating both sides

$$-\int \frac{dR}{R} = K \int dt$$

$$\boxed{-\ln[R] = Kt + C} - ①$$

⟨To get value of C⟩
$t=0 , R = R_o$

$$\therefore -\ln R_o = C$$

Put value of C in ①

$$-\ln[R] = Kt - \ln[R_o]$$

$$\ln[R_o] - \ln[R] = Kt$$

$$\boxed{\frac{2.303 \log \frac{R_o}{R}}{K} = t}$$

⟨for Zero Order⟩

whose rate depends upon zero conc. term of reactant

consider a general reaction...

$R \rightarrow P$

Rate of Rxn $\propto [R]^0$

$$-\frac{d[R]}{dt} = K$$

$$-d[R] = K \cdot dt$$

Integrating both sides

$$-\int d[R] = K \int dt$$

$$\boxed{-[R] = Kt + C} - ①$$

⟨To get value of C⟩
$t=0, R=R_o$

$$-[R_o] = C$$

Put value of C in ①

$$-[R] = Kt - [R_o]$$

$$\boxed{\frac{[R_o] - [R]}{K} = t}$$ is denoted by $t_{1/2}$.

⟨Half life Period⟩ It is the time in which half of the reactant reduced. It

for first Order $t = t_{1/2}$ $R = R_o/2$

$$t_{1/2} = \frac{2.303}{K} \log \frac{R_o}{R_o} \times 2$$

$$t_{1/2} = \frac{0.693}{K}$$

For Zero order $t = t_{1/2}$ $R = R_o/2$

$$t_{1/2} = \frac{R_o - \frac{R_o}{2}}{K}$$

$$t_{1/2} = \frac{R_o}{2K}$$

Ⓝ-1 for a reaction $A + B \rightarrow P$, the rate law is given by, |2013|
$r = K[A]^{1/2}[B]^2$. Give order

Anu:
$$order = \frac{1}{2} + 2$$
$$= 2\frac{1}{2}$$

Ⓝ-2 Identify the order for |2011|
(i) $L^{-1} mol \, s^{-1}$ (ii) $L \, mol^{-1} s^{-1}$

Ans: (i) zero
(ii) second

N-3) A first order reaction takes 30 minutes for 20% decomposition. Calculate $t_{1/2}$ ($\log 2 = 0.3010$)

2019

Ans: for a first order reaction, $K = \dfrac{2.303}{t} \log \dfrac{[R_0]}{[R]}$

$$K = \dfrac{2.303}{30} \log \dfrac{100}{100-20} \Rightarrow \dfrac{2.303}{30} \times 0.097 = 7.4 \times 10^{-3}$$

$$t_{1/2} = \dfrac{0.693}{K} = \dfrac{0.693}{7.4 \times 10^{-3}} = 93.65 \text{ min}$$

N-4) A first order reaction takes 20 minutes for 25% decomposition. calculate the time when 75% of the reaction will be completed.
(Given $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$) 2017

Ans: Acc. to 1st order kinetics

$$K = \dfrac{2.303}{t} \log \dfrac{[A]}{[A-t]} \Rightarrow K = \dfrac{2.303}{20 \text{ min}} \log \dfrac{(100)}{(75)} \Rightarrow K = 0.014 \text{ min}^{-1}$$

Similarly for 2nd process

$$K = 0.014 = \dfrac{2.303}{t} \log \dfrac{100}{25} \Rightarrow t = 99 \text{ min}$$

N-5) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction 2017

Ans: for first order reaction, $t = \dfrac{2.303}{K} \log \dfrac{[R_0]}{[R]}$

for 99% completion of reaction,

$$t_{99\%} = \dfrac{2.303}{K} \log \dfrac{100}{1} \quad , \quad t_{90\%} = \dfrac{2.303}{K} \log \dfrac{100}{10}$$

$$\dfrac{t_{99\%}}{t_{90\%}} = \dfrac{\dfrac{2.303}{K} \times 2}{\dfrac{2.303}{K} \times 1} \Rightarrow t_{99\%} = 2 \times t_{90\%}$$

Pseudo First Order R^n: Those reaction which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo first order R^n.

e.g. Acid hydrolysis of ethyl acetate

$$CH_3 COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3 COOH + C_2H_5 OH$$
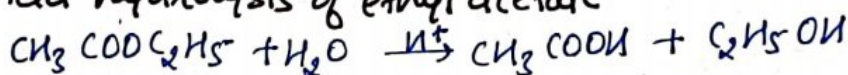
$$Rate = K [CH_3 COOC_2H_5]$$

• Acid catalysed inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\text{Glucose} \quad \text{fructose}$$
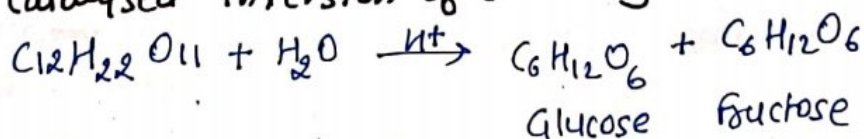
$$Rate = K [C_{12}H_{22}O_{11}]$$

Arrhenius Equation

Equation which give relationship b/w rate constant and temperature

$$K \propto e^{-Ea/RT} \Rightarrow K = Ae^{-Ea/RT}$$

$$\log K = \text{#} \quad \ln K = \ln A \cdot e^{-Ea/RT}$$

$$\ln K = \ln A + \ln e^{-Ea/RT}$$

$$\ln K = \ln A - \frac{Ea}{RT}$$

At temp T_1

$$\ln K_1 = \ln A - \frac{Ea}{RT_1} \quad -\textcircled{1}$$

At temp T_2

$$\ln K_2 = \ln A - \frac{Ea}{RT_2} \quad -\textcircled{2}$$

operating eq. ② − eq.①

$$\ln K_2 - \ln K_1 = \ln A - \frac{Ea}{RT_2} - \ln A + \frac{Ea}{RT_1}$$

$$\boxed{\ln \frac{K_2}{K_1} = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$K \to$ rate constant
$A \to$ frequency factor
$Ea \to$ Activation energy
$T \to$ Temperature

Activation energy The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy (Ea)

Activation energy =
Threshold energy
− Average Kinetic energy of reacting molecules
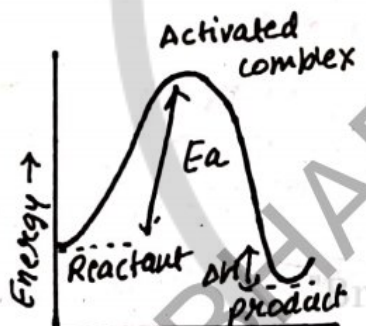
Progress of Rxn
(Exothermic)
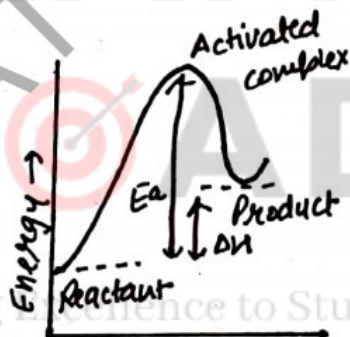
Progress of Rxn
(Endothermic)

Collision theory of Chemical Reactions

- Reaction occurs due to collision of molecules
- All collisions are not effective
- Effective collisions are those collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation

Surface Chemistry :- It deals with phenomena that occur at the surface

Adsorption :- It is the process of accumulation of molecular species at ⑭ the surface rather than in the bulk of a solid or liquid

Adsorbate :- The molecular species or substance, which concentrate at surface

Adsorbent :- The material on the surface of which adsorption takes place

Desorption :- The process of removing an adsorbed substance from surface

Sorption :- The term used when both adsorption and absorption both takes place simultaneously

Adsorption	Absorption
Silica gel in water	$CaCl_2$ in water
- It is a surface phenomenon occurs only at the surface of adsorbent.	- It is a bulk phenomenon occurs throughout the body of the material
- It is rapid in begining than becomes slow	- It occurs at uniform speed

ΔG, ΔH and ΔS all are -ve for adsorption

Physical Adsorption	**Chemical Adsorption**
- Also known as physisorption	- Also known as chemisorption
- low enthalpy of adsorption i.e 20-40 KJ/mol	- High enthalpy of adsorption i.e 80-240 KJ/mol
- It is a reversible process	- It is irreversible process
- It is not specific in nature	- It is highly specific in nature
- With the increase in temperature, physical adsorption decreases	- with the increase in temp. chemical adsorption first increases and then decreases
- No activation energy required	- Activation energy required
- Multimolecular layer are formed	- Unimolecular layer is formed

Factors Affecting Adsorption

• **Surface area of adsorbent :-** greater the surface area, more is adsorption.

• **Nature of adsorbent :-** Greater the strained forces on the surface, more is the ease with which adsorption takes place on the surface. The activated adsorbents have high adsorbing power

• **Nature of gas being adsorbed :-** Easily liquefiable gases like NH_3, HCl, Cl_2, SO_2, CO_2 etc. (whose critical temperature is high) are adsorbed to greater extent.

• **Pressure :-** Adsorption increases with increase in pressure. The effect of pressure is large at low temperature

• **Temperature :-** Adsorption decreases with increase in temperature

Freundlich Adsorption Isotherm

The plot of $\frac{x}{m}$ vs pressure at constant temperature is called freundlich adsorption isotherm

where $x \to$ mass of adsorbate
$m \to$ mass of adsorbent

for low pressure, for high pressure, for ~~high~~ intermediate pressure
$\frac{x}{m} \propto p$, $\frac{x}{m} \propto p^{\circ}$ $\frac{x}{m} \propto p^{1/n}$ $(n > 1)$

$$\frac{x}{m} = kp^{1/n} \qquad \frac{x}{m} = kp^{\circ}$$
$$\frac{x}{m} = kp$$

Pressure → | P_s Saturation Pressure
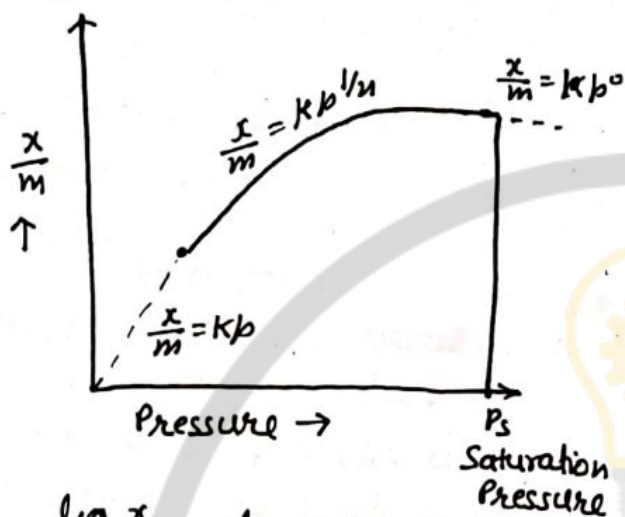
$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Slope $= \frac{1}{n}$
$\log k$
$\log p$
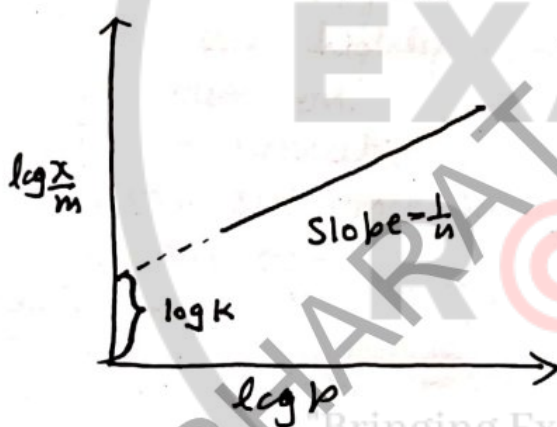
Catalyst
Substance which accelerate the rate of a chemical reaction and themselves remains chemically and quantitatively unchanged after the reaction, are known as catalyst and this phenomena is known as catalysis.

$$N_2 + 3H_2 \xrightleftharpoons{\underset{\text{Catalyst}}{Fe}} 2NH_3$$
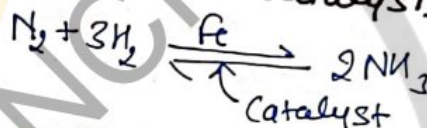
Promoters
The substance that enhance the activity of a catalyst

$$N_2 + 3H_2 \xrightleftharpoons{\underset{\underset{\text{promotes}}{\propto \text{catalytic}}}{\overset{Fe}{Mo}}} 2NH_3$$
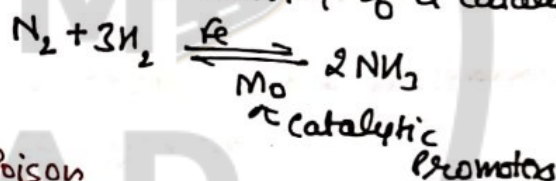
Poison
The substance that decrease the activity of a catalyst.

Activity
It is the capacity of a catalyst to increase the speed of a chemical reaction

Selectivity
It is the ability of a catalyst to direct a chemical reaction and give a particular product.

~~Homogen~~

$$CO + H_2 \xrightarrow{Cu} HCHO$$
$$CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$
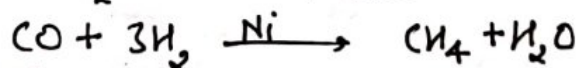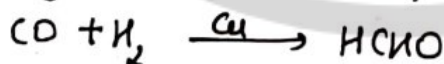
Homogeneous catalysis
The process in which the reactants and catalyst are in same phase

e-g $$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_3$$
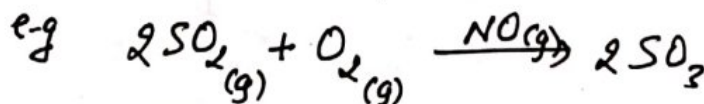
Heterogeneous catalysis

and the catalyst are in different phase The process in which the reactants

e.g $2SO_2 \underset{(g)}{} + O_2 \underset{(g)}{} \xrightarrow{Pt(s)} 2SO_3$
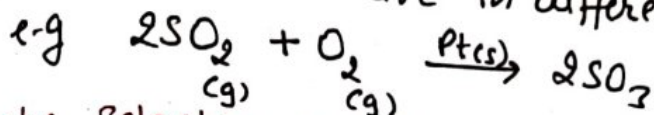
Shape Selective Catalysis

upon the pore str. of The catalytic reaction that depends reactant and product the catalyst and the size of the molecule e.g Zeolite (have honey An important zeolite which is used comb like str.) in petroleum industry is ZSM-5 which directly convert alcohol into gasoline (petrol)

Enzyme

Enzymes are complex nitrogeneous organic compounds. These are biochemical catalyst as numerous reaction that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes.

- They are highly specific in nature
- They are highly efficient
- They are highly active under optimum temp and optimum pH.
- The enzymatic activity is increased in the presence of certain substance, know as co-enzyme
- certain subs

Dispersed Phase	Dispersion Medium	Type of Colloid	Example
Gas	Gas	No Colloid	
gas	liquid	foam	Froth, whipped cream
Gas	solid	Solid Sol	Pumic stone, foam rubber
liquid	Gas	Aerosol	Fog, mist, cloud
liquid	liquid	Emulsion	Milk
liquid	Solid	Gel	cheese, butter
solid	Gas	Aerosol	smoke, dust
Solid	liquid	Sol	Paints, gold sol.
Solid	Solid	Solid Sol	gems, precious stone

Classification of colloids on the basis of interaction b/w dispersed phase and dispersion medium

- Lyophilic colloids
- Lyophobic colloids.

Lyophilic Colloids	Lyophobic colloids
- These are easily formed by direct mixing	- These are formed only by special methods.
- The particles are not easily visible even under ultramicroscope	- The particles are easily detected under ultramicroscope
- These are very stable	- These are unstable and require traces of stabilizers
- They are not easily precipitated by small amount of electrolytes	- These are easily precipitated by small amount of suitable electrolyte
- The particles do not carry any charge	- The particles carry charge and move in a specific direction
- These are reversible in Nature	- These are irreversible in Nature
- They do not show Tyndall effect	- They show Tyndall effect.

On the Basis of types of particles of dispersed phase

1.) Multimolecular Colloids

formed by aggregation of a large no. of atoms or molecules (diameter <1mm) held by weak van der waals forces

Micells

Lyophobic

2.) Macromolecular Colloids

Having Big size molecules. And dispersed phase in colloidal range

lyophilic

Micelles are the cluster or aggregated particles formed by association of colloids in solution

3.) Associated colloids

formed by substance which at low conc. behave as strong electrolyte but at higher conc. exhibit colloidal behaviour due to the formation of aggregates (micelles)

Kraft Temperature

The formation of micelles takes place above a particular temp. called kraft Temp. (T_k)

Critical micellization concentration

The formation of micells takes place above a particular concentration called critical micellization conc. (CMC)

Properties of Colloidal Solution

Colligative Properties

Colloids show colligative properties like relative lowering of vapour pressure, elevation of boiling point etc. and magnitude of colligative properties of colloids is much less than true solutions due to larger size of colloidal particles

Tyndall effect (optical property)

Scattering of light by colloidal particles due to which the path of light beam becomes visible

Brownian movement (Mechanical property)

zig-zag movement of colloidal particles due to the unbalanced bombardment by the molecules of dispersion medium.

Charge on Colloidal Particles

Colloidal particles always carry an electric charge and nature of charge (+ve or -ve) is same on all the particles in a given colloidal solution. The charge is due to preferential adsorption of ions from solution

Positively charged sols

Hydrated metallic oxides e.g $Al_2O_3 \cdot xH_2O$, $Fe_2O_3 \cdot xH_2O$, metal hydroxides $Fe(OH)_3$, $Al(OH)_3$, basic dye stuff like prussian blue, haemoglobin etc.

Negatively charged sols

Metallic particles e.g Cu, Ag, Au, Metal sulphides e.g As_2S_3, CdS, Acidic dyes like eosin, congo red

Electrophoresis (electrical property)
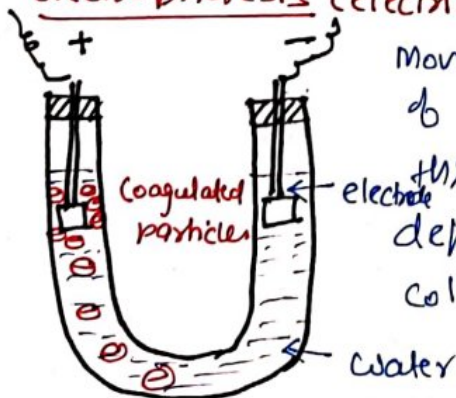
Movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solutions. The direction depends on the type of charge on colloidal particles

Coagulation Precipitation of colloidal solution by induced aggregation of colloidal particles

Lyophobic sols

They can be coagulated by electrophoresis, boiling, persistent dialysis, mixing of oppositely charged sols and addition of electrolytes

Hardy-Schulze Rules

In case of ions electrolytes, the ion carrying charge opposite to that of colloidal particles is effective in causing coagulation and greater the valency of ions causing coagulation, greater the coagulating power

The minimum conc. of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of anion

Lyophilic Sols

They can be coagulated by addition of large amt. of electrolyte.

Emulsion colloids in which both dispersed phase and dispersion medium are in liquid state.

Types of Emulsion → Oil in water → D.P is oil
→ D.M is water   eg. milk, body lotion
Water in Oil → D.P is water
→ D.M is oil   e.g butter, cold cream

Emulsification

Process of making an emulsion

Emulsifying Agent Used to stabilise the emulsion e.g soaps and detergent.

Demulsification

Seperation the two components of an emulsion. Methods used are boiling, freezing, changing pH

General Principles and Processes of Isolation Of Elements

Minerals - Naturally occuring chemical substance in earth crust obtained by mining

Ores The minerals from which metal can be extracted profitably and convenientely

Metallurgy - The scientific and technological process used for the extraction of the metal from its ores is called metallurgy. Three steps:-
(i) concenteration of ores (ii) Extraction of crude metal from concenter-ated ore (iii) Refining.

Gangue - The earthy materials or imburities with which ores are generally associated are called gangue

- All ores are minerals but all minerals are not ores

Metal	Ore	Composition
1.) Aluminium	Bauxite	$Al_2O_3 \cdot xH_2O$
	Kaolinite	$Al_2(OH)_4 \cdot Si_2O_5$
2.) Iron	Haemetite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron Pyrites	FeS_2
3.) Copper	Copper Pyrites	$CuFeS_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
4.) Zinc	Zinc blende	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

Concenteration of ores - Removal of the unwanted materials from the ore is known as concenteration, dressing or benefaction. Some important processes are
(i) Hydraulic washing
(ii) Magnetic Separation
(iii) Froth Floatation Process
(iv) Leaching

Hydraulic Washing

Hydraulic washing is based on the difference in the gravities of the ore and the gangue particles. It is therefore a type of gravity separation. In this process an upward stream of running water is used to wash the powdered ore. The ligther gangue particles washed away and the heavier ores are left behind.

Magnetic Separation

It is based on the difference in the magnetic properties of the gangue and ore particles and is used for magnetite (Fe_3O_4), haemetite (Fe_2O_3), wolframite ($FeWO_4$), chromite ($FeOCr_2O_3$)

Process - The powdered ore containing imburities is dropped on a belt which rotates around a magnetic roller. The magnetic fall nearer to the roller while non-magnetic particles fall farther off.

Non Magnetic Particles   Magnetic Particles

Magnetic roller
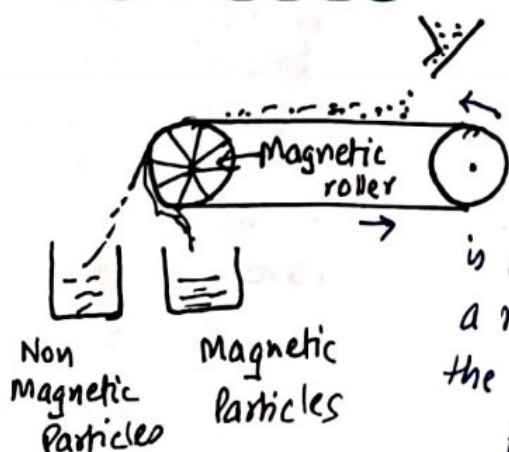
Froth Floatation Process
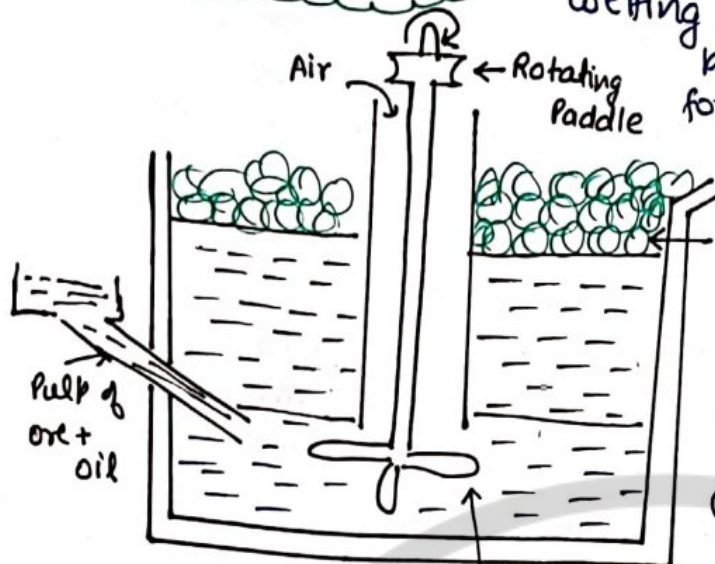
It is based on the difference in the wetting properties of gaugue and ore particles and is mostly used for sulphide ores

Air ← Rotating Paddle

Mineral froth

Pulp of ore + oil

Powdered ore is mixed with pine oil and water and violently agitated with air. Ore particles rise to the surface in the form of froth and impurities remains in water.

Paddle draws in air and stirs the pulp

Depressants are used to separate two sulphide ores for e.g in case of an ore containing ZnS or PbS, the deprassaut used is NaCN. It selectively prevents ZnS from coming to froth but allows PbS to come with the froth.

Leaching

It is based on the difference in chemical properties of gaugue and ore particles and is used for extraction of Au, Ag and pure alumina from bauxite ore.

Baeyer's Process for Al extraction

$$Al_2O_3 \cdot 2H_2O + 2NaOH + H_2O \longrightarrow 2Na[Al(OH)_4]$$

$$2Na[Al(OH)_4] + 2CO_2 \longrightarrow Al_2O_3 \cdot xH_2O + 2NaHCO_3$$

$$Al_2O_3 \cdot xH_2O \xrightarrow{1200°C} Al_2O_3 + x\,H_2O$$
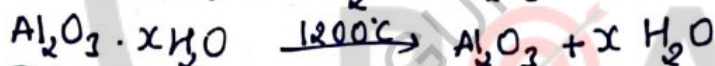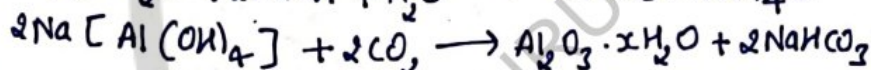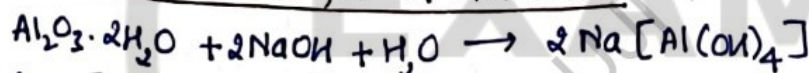
Mac Arthur forest cyanide process for Ag extraction

$$4\,Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

$$2\,Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$
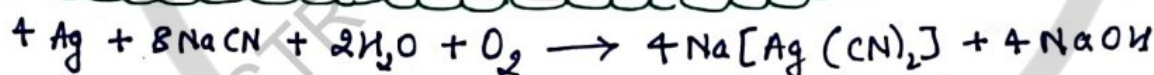
Most abundant metal → Aluminium

Extraction and isolation of metal

Calcination
It is the process of heating the ore (like carbonate and hydrated oxide) strongly below its melting point either in the absence of air or in limited supply of air
→ Carbonate ores are converted into oxide ores

$$ZnCO_2 \longrightarrow ZnO + (O)_2$$
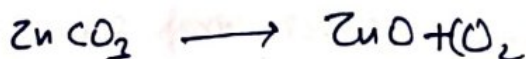
Roasting
It is the process of heating the ore (like sulphide ores) strongly below its melting point in a sufficient supply of air to bring about its oxidation and remove volatile impurities e.g sulphide ores are converted into oxide

$$2\,ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

Reduction or conversion of ores to metal

The ore obtained after calcination or roasting is reduced to metal and choice of reducing agent depends upon the nature of ore

→ Carbon or carbon mono oxide is used for oxides of Fe, Cu, Zn, Mg, Co etc. and the process is called smelting.

→ Electropositive metals like Na, Al, Mg or Hydrogen are used for reduction of ores of Mn, Cr, Ti, Mo, W etc.

→ Water gas is used for Nickel ores

→ Auto reduction process is used for ores of Pb, Hg, Cu etc.

→ Electrolytic reduction is used for higher electropositive metals

→ Hydrometallurgy or displacement method is used for Ag, Au etc.

Refining of Metals

Purification of crude metals by removing the impurities present in it is called refining.

__Liquation__ Used for low melting metals like Sn, Pb, Hg, Bi etc.

__Distillation__ Used for refining low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate

liquation

Metals with low melting point like Sb, Pb are purified by this method. The melting point of metal are lower than those of the impurities. for this purpose, a sloping hearth furnace. This metal is placed at the mouth of the furnace and heated gently. The metal flows down the hearth while impurities are left behind on the hearth

Electrolytic Refining
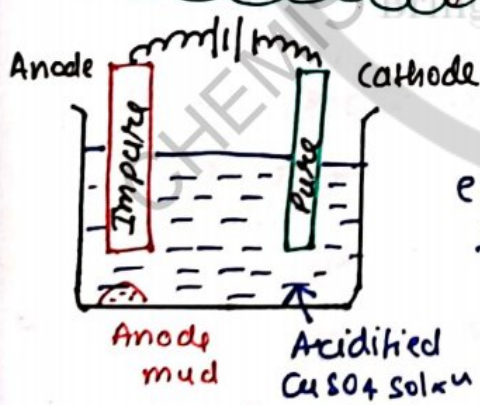
Metals like Cu, Zn, Ag, Au are refined by this method. In this method the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal (more electropositive) remains in the soln and less basic impurities go to anode mud.

copper is refined using an electrolytic method. Anode are of impure copper and pure copper strips are taken as Cathode The electrolyte is acidified solution of copper sulphate. Copper in pure form transfer from Anode to cathode

$$\text{Anode} \qquad Cu \longrightarrow Cu^{2+} + 2e^{\ominus}$$

$$\text{Cathode} \qquad Cu^{2+} + 2e^{\ominus} \longrightarrow Cu.$$
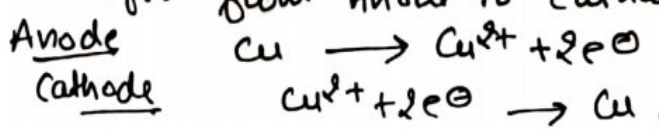
Anode mud contain – antimony, selenium, tellurium, silver, gold ④

Zone Refining

Zone refining method is useful for producing semiconductor and other metals of very high purity e.g germanium, silicon, boron, gallium, indium etc.

metal rod / Molten zone ← induction coil heater moving as shown
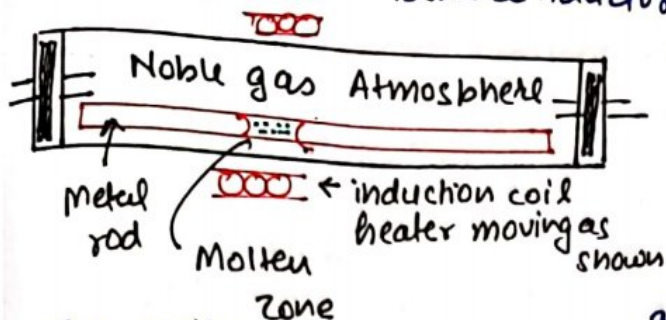
Principle

the impurities are more soluble in melt than in solid. A circular mobile heater is fixed at one end of a rod of the impure metal The molten zone moves along with the heater which is moved forward. As the heater moves forward the pure metal crystallises out of the melt and the impurities pass on into adjacent molten zone at one end, impurities get concencenterated. This end is cut off.

Vapour Phase Refining

The metal is converted into its volatile compound then decomposes to give pure metal.

(i) The metal should form volatile compound with an available reagent

(ii) The volatile compound should be easily decomposable, so that the recovery is easy. Two Types (i) Mond Process (ii) Van Arkel Method.

Mond Process

In this process, nickel is heated is a stream of carbon mono oxide forming a volatile complex nickel tetra carbonyl.

$$Ni + 4CO \xrightarrow{330-350K} Ni(CO)_4 \xrightarrow{450-470} Ni + 4CO$$

Impure Nickel   Nickel tetracarbonyl   Pure Nickel
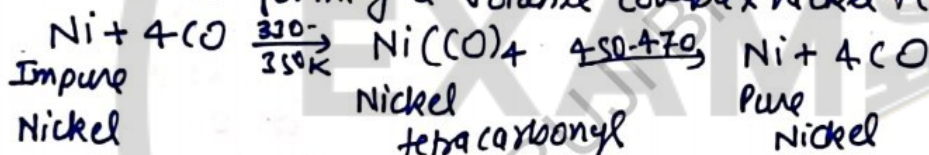
Van-Arkel Method

This method is useful for removing all the oxygen and nitrogen present in the form of impurity in metals like zirconium (Zr) and titanium (Ti)

(rude Zr is heated is an evacuated vessel with iodine volatile zirconium tetra iodide is formed. which is then decomposed by heating on tungsten filament electrically to about 1800 K to give pure zirconium.

$$Zr + 2I_2 \xrightarrow{870K} ZrI_4 \xrightarrow{1800K} Zr + 2I_2$$

Impure zirconium.   Zirconium tetra iodide   Pure zirconium

Chromatography

← Mixture of compound
← Stationary phase

coloured Bands
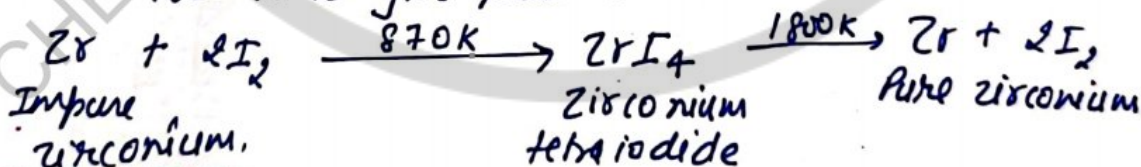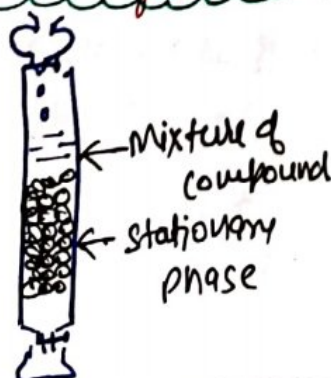
This method is based on the principle that different components of a mixture are differently adsorbed on adsorbent. This mixture is put in liquid or gaseous medium called moving phase which is moved through the adsorbent called stationary phase, Different components are
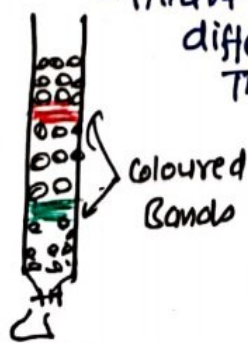
adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvent ⑤ called eluants.

Pig Iron The product obtained from blast furnace is pig iron. It contains about 4% carbon and many impurities in smaller amount (S, P, Si, Mn)

Cast Iron It is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content. (about 3%) and is ~~the~~ extremely hard and brittle.

Wrought iron Also known as malleable iron. It is the purest form of iron. It is prepared from cast iron by oxidising impurities in reverberatory furnace

Extraction of Aluminium ③

① Ore → Bauxite ($Al_2O_3 \cdot xH_2O$)

② Concentration : (leaching)

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Al[Al(OH)_4]$$

$$2Na[Al(OH)_4] + CO_2 \longrightarrow Al_2O_3 \cdot xH_2O + 2NaHCO_3$$

$$Al_2O_3 \cdot xH_2O \xrightarrow{\frac{1470}{K}} Al_2O_3 + xH_2O$$
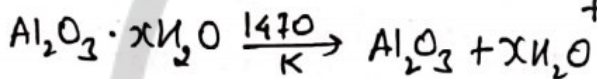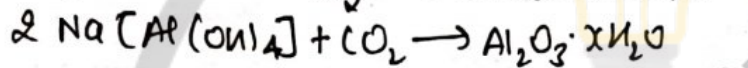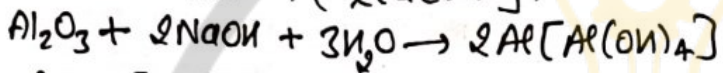
③ Electrolytic Reduction
(Hall and Heroult Process)

In this process a fused mixture of alumina (Al_2O_3), Cryolite (Na_3AlF_6) or Flourspar (CaF_2) is electrolysed using graphite as anode and steel vessel with lining of carbon act as cathode

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

molten aluminium
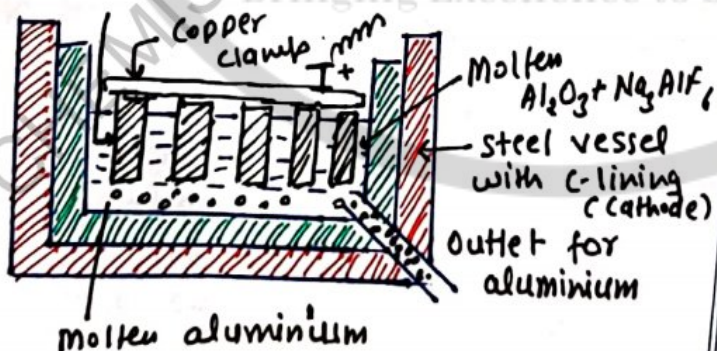
The electrolytic reactions are

cathode: $Al^{3+} + 3e^\ominus \longrightarrow Al$

Anode: $C + O^{2-} \longrightarrow CO + 2e^\ominus$

$C + 2O^{2-} \longrightarrow CO_2 + 2e^\ominus$

⇒ **what is the role of cryolite in the metallurgy of aluminium**

Ans- fused alumina (Al_2O_3) is a bad conductor of electricity cryolite or fluorspar not only make alumina a good conductor of electricity but also reduce the melting point of the mixture to around 1140 K from 2323 K

Extraction of Zn

Ores:
(i) zinc blende : ZnS ✓
(ii) calamine : $ZnCO_3$
(iii) Zincite : ZnO
↓

Concentration:
Froth floatation method
↓

Roasting :
$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$
$$ZnS + 2O_2 \longrightarrow ZnSO_4$$
$$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$$
↓
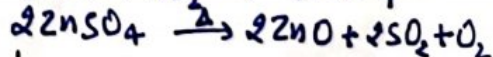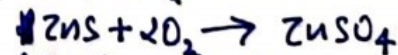
Reduction
$$ZnO + C \longrightarrow Zn + CO$$
↓

Purification
Electrolytic refining, distillation.

▶ **Thermodynamic principles:** Thermodynamics helps in understanding the conditions of temp. and selecting Suitable reducing agent in a metallurgical process.

- Gibbs Helmholtz equation is used to check the feasibility of a reduction process.
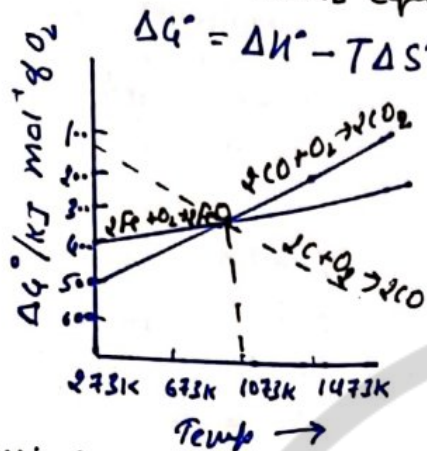
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ , \text{ if } \Delta G^\circ < 0, \text{ the reduction is feasible}$$

- It provides a sound idea about selecting a reducing agent in reduction of oxides
- For a reaction, enthalpy change is fixed but temperature factor can be controlled and it can be the deciding factor for feasibility of that reaction.

Ellingham diagram for formation of feO from Fe, CO from C and CO_2 from CO.

▶ **Coupled reactions:** If reactants and products of two reactions are put together in a system and the net ΔG of two possible reactions is -ve, the overall reaction will take place. These reactions are called coupled reaction
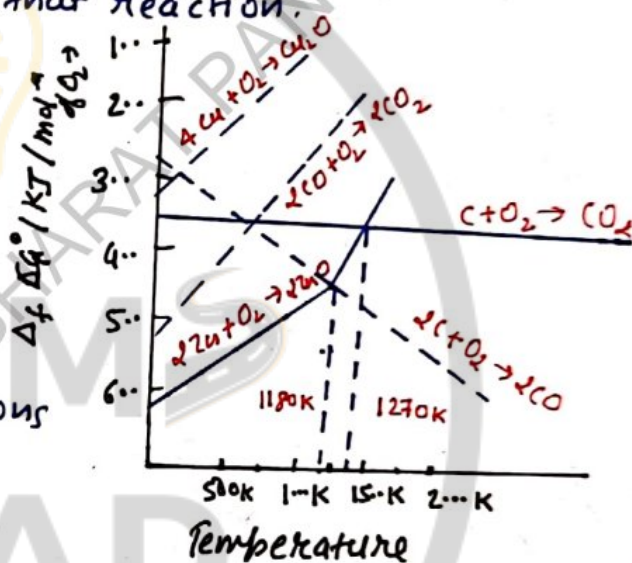
Ellingham diagram showing the formation of Cu_2O from Cu, ZnO from Zn CO from C and CO_2 from C and CO.

Such diagrams helps in predicting the feasibility of thermal reduction of an ore ΔG must be -ve at a given temp for a reaction to be feasible

Electrochemical Principles Electrolysis is used to carry out the reduction of a molten metal salt

- The electrochemical principles of this method can be understood the equation, $\Delta G^\circ = -nFE^\circ$
- More reactive metals have large negative values of the electrode potential so their reduction is difficult
- If the difference of two E° values corresponds to a positive E° and consequently, negative ΔG°, then the less reactive metal will come out of the solution and the more reactive metal will go to the solution.

The p-block Elements

Elements in which the last $e^{\ominus}$ enters in p-orbital are called p-block elements.

Group-16 (oxygen family)

- O — 8 — Oxygen — $2s^2 2p^4$ → gas
- S — 16 — Sulphur — $3s^2 3p^4$ → solid non metal
- Se — 34 — Selenium — $4s^2 4p^4$] Solid, metalloid
- Te — 52 — Tellurium — $5s^2 5p^4$] Solid, metalloid
- Po — 84 — Polonium — $6s^2 6p^4$] radioactive

Also known as chalcogen or ore forming

Atomic Radii Increase down the group

Ionisation enthalpy Decrease down the group

Electronegativity Decrease down the group

Electron gain enthalpy Increase from oxygen to sulphur and then decreases

Melting and Boiling Point Increase down the group upto Te and then decreases

Allotropy All elements show allotropy.

Chemical Properties

Oxidation State stability of -2 oxidation state decreases down the group, stability of +4 oxidation state increases and that of +6 oxidation state decreases down the group due to inert pair effect.

Hydrides

All the elements form stable hydrides of the type H_2M. Their general trends are.

Boiling Point $H_2O > H_2Te > H_2Se > H_2S$

Volatility $H_2S > H_2Se > H_2Te > H_2O$

Bond Angle $H_2O > H_2S > H_2Se > H_2Te$

Acidic Character $H_2O < H_2S < H_2Se < H_2Te$

Reducing Power $H_2Te > H_2Se > H_2S > H_2O$

Halides

All elements form halides of the type EX_6, EX_4 and EX_2

Oxides

Simple Oxides MgO, Al_2O_3 Mixed Oxides Pb_3O_4, Fe_3O_4

Acidic Oxides SO_2, Cl_2O_7, CO_2, N_2O_5 Basic Oxides Na_2O, CaO, BaO

Amphoteric Oxides ~~Al_2O~~ Al_2O_3 Neutral Oxides CO, NO, N_2O

Dioxygen

▶ Preparation

$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$

$2Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$

$2HgO \longrightarrow 2Hg + O_2$

$2PbO_2 \longrightarrow 2PbO + O_2$

$2H_2O_2 \longrightarrow 2H_2O + O_2$
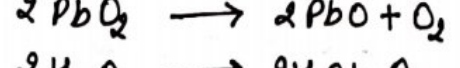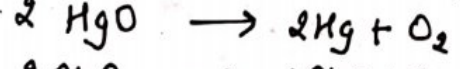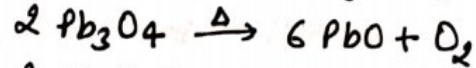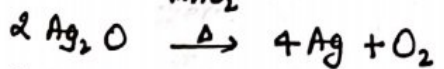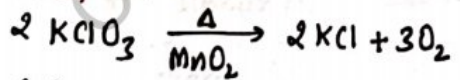
Properties

- Dioxygen is colourless and odourless gas
- Soluble in water and paramagnetic in Nature
- Dioxygen directly reacts with all metals (except noble metals like Au, Pt) non metals (except noble gases)

$2Ca + O_2 \longrightarrow 2CaO$ (Basic Oxide)

$4Al + 3O_2 \longrightarrow 2Al_2O_3$ (Amphoteric Oxide)

$P_4 + 5O_2 \longrightarrow P_4O_{10}$ (Acidic Oxide)

$C + O_2 \longrightarrow CO_2$ (Acidic Oxide)

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2 \text{ (Roasting)}$$
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \text{ (Combustion)}$$
$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3 \text{ (Catalytic Oxi.)}$$
$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O \text{ (Cat. Oxi.)}$$
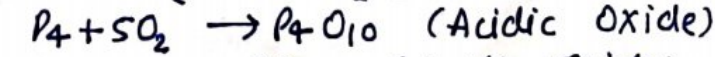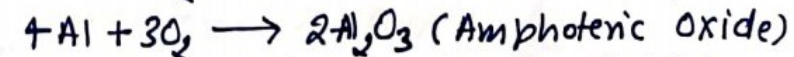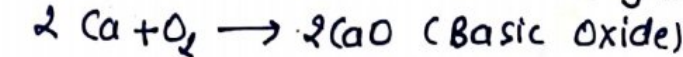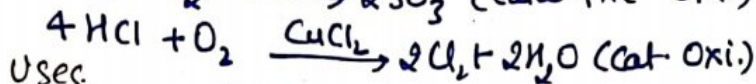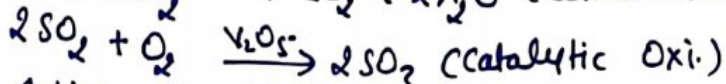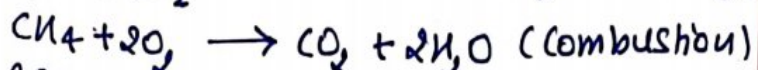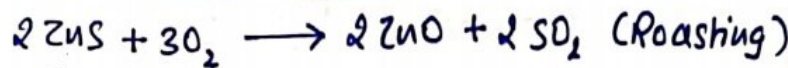
Uses.
- For artificial respiration in hospitals by mountaineers, pilots and divers
- In oxy-hydrogen and oxy-acetylene torches which are used for cutting and welding of metals
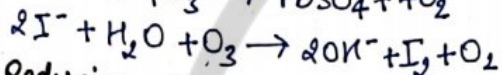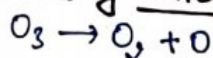- liquid dioxygen is used as rocket fuel.

Ozone (O_3) Preparation $3O_2 \xrightarrow{\text{electric discharge}} 2O_3$
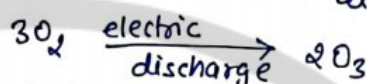
Properties It is a pale blue gas, dark blue liquid and violet black solid.

Oxidising action
$$O_3 \longrightarrow O_2 + O$$
$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$
$$2I^- + H_2O + O_3 \longrightarrow 2OH^- + I_2 + O_2$$

Reducing Action
$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$
$$BaO_2 + O_3 \longrightarrow BaO + 2O_2$$
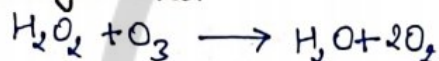
Structure:
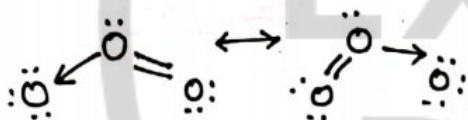
Oxidation state of O is +1 & -1

Uses
- used for bleaching ivory, flour, delicate fabrics etc.
- As germicide and disinfectant for sterilising water
- Manufacture of $KMnO_4$ and artificial silk.

Allotropes of Sulphur
- Rhombic sulphur (α-sulphur) It has S_8 molecules, yellow in colour, m.pt 385.8 K, specific gravity 2.06 g c·m³ Insoluble in water, soluble in CS_2
- Monoclinic sulphur (β-sulphur) It has S_8 molecules, colourless, needle shaped crystals, m.pt 393 K, specific gravity 1.98 g cm⁻³, soluble in CS_2.

Sulphur dioxide (SO_2)

Preparation
(i) $S + O_2 \xrightarrow{\Delta} SO_2$
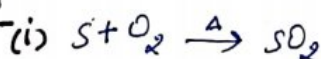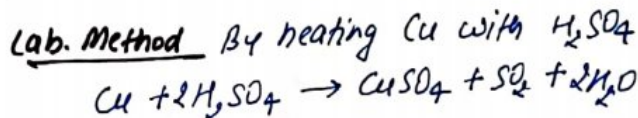
→ **Dioxygen is a gas while sulphur is a solid at room temp.? (2018, 2012)** 8.

Ans: O_2 molecules are held together by weak van der waal forces because of the small size and High E·N of oxygen

Sulphur shows catenation and the molecule is made up of eight atoms (S_8) with strong intermolecular attractive forces. Hence sulphur exist as solid at room temperature.

Ozone is thermodynamically unstable. Give Reason. (D-2019, 2016)

Ans: Ozone is thermodynamically unstable and decomposes into oxygen
$$2O_3 \xrightarrow{\Delta} 3O_2 \quad (\Delta H = -ve)$$
The above conversion is exothermic i.e ΔH is negative. Also, entropy increases i.e ΔS is positive. Thus, ΔG for the decomposition of ozone is negative. Hence, it is thermodynamically unstable
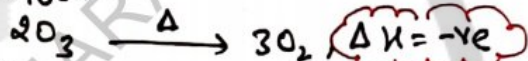
→ **O_3 acts as a powerful oxidising agent**

Ans: Ozone is a powerful oxidising agent because ozone has higher energy content than dioxygen·hence decomposes to give dioxygen and atomic oxygen
$$O_3 \longrightarrow O_2 + O$$
ozone → dioxygen + Atomic oxygen

atomic oxygen thus liberated brings about the oxidation while molecular oxygen set free

→ **Sulphur in vapour form exhibits paramagnetic behaviour**

Ans: At elevated temp. sulphur exist as S_2 molecule which has two unpaired $e^{\ominus}$ in the antibonding π^* orbitals like O_2 hence exhibits paramagnetism
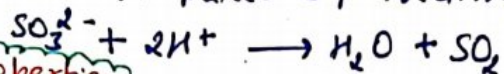
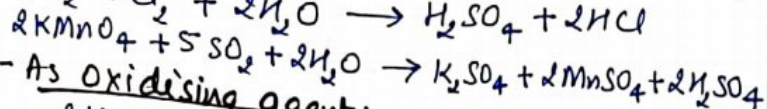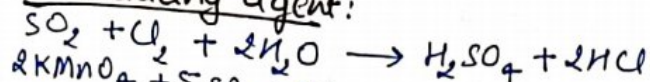→ **Stable allotropic form of sulphur**

Ans: Rhombic Sulphur.

rhombic sulphur $\xrightarrow{370K}$ Monoclinic Sulphur

(ii) **Lab. Method** By heating Cu with H_2SO_4
$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

It is also prepared by treating a sulphite with dil. H_2SO_4. ④

$$SO_3^{2-} + 2H^+ \longrightarrow H_2O + SO_2$$

Properties

- As reducing agent:

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$
$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

- As oxidising agent:

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S\downarrow$$

- **Bleaching Action:** Its bleaching action is temporary due to reduction and is

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$
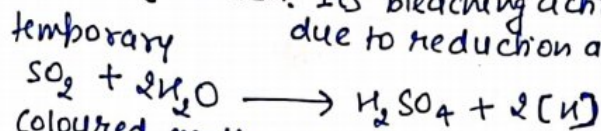
Coloured matter + [H] → colourless matter

Structure: SO_2 is a gas having sp^2 hybridisation and v-shape
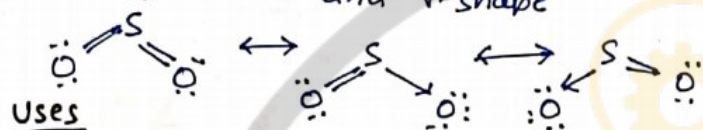
Uses
- In the manufacture of sulphuric acid, sulphite and hydrogen sulphide
- As a disinfectant, fumigant and preservative
- For bleaching delicate articles.

Oxoacids of Sulphur

Sulphurous (+4) Acid H_2SO_3

Sulphuric (+6) Acid H_2SO_4

Peroxodisulphuric Acid (+6) $H_2S_2O_8$

Pyrosulphuric Acid (+6)

Persulphuric Acid H_2SO_5 (+6)

$$Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

Sulphuric Acid H_2SO_4 | Prepared by CONTACT PROCESS.

S → Burner → SO_2 → Dust chamber → Cooling and Drying → Arsenic Purifier → Testing Box

Impure SO_2

$2H_2SO_4 \xleftarrow{H_2O} H_2S_2O_7 \xleftarrow{} $ Absorption Tower $\xleftarrow{SO_3}$ Catalytic Converter $\xleftarrow{}$ Preheater ← Pure SO_2

Conc. H_2SO_4

oleum

Str.

Sulphuric Acid

sulphate ion

Properties
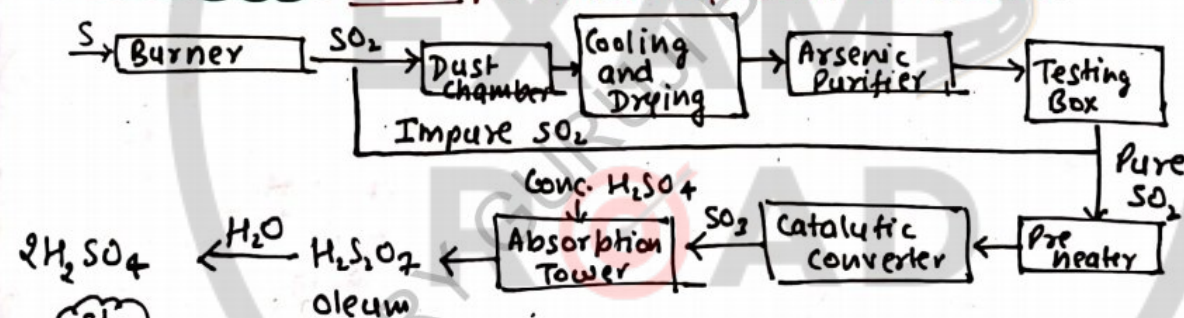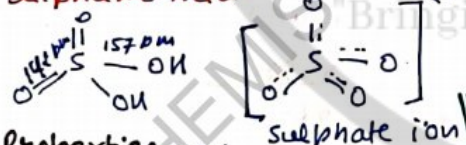
$$H_2SO_4 \begin{cases} \xrightarrow{NaOH} NaHSO_4 + H_2O \\ \xrightarrow{2NaOH} Na_2SO_4 + 2H_2O \\ \xrightarrow{Zn} ZnSO_4 + H_2 \\ \xrightarrow{C_{12}H_{22}O_{11}} 12C + 11H_2O \\ \xrightarrow{S8} SO_2 + H_2O \\ \xrightarrow{Na_2S} Na_2SO_4 + H_2S \\ \xrightarrow{BaCl_2} BaSO_4 + 2HCl \\ \xrightarrow{K_4[Fe(CN)_6]} K_2SO_4 + FeSO_4 \\ + (NH_4)_2SO_4 + CO \uparrow \end{cases}$$
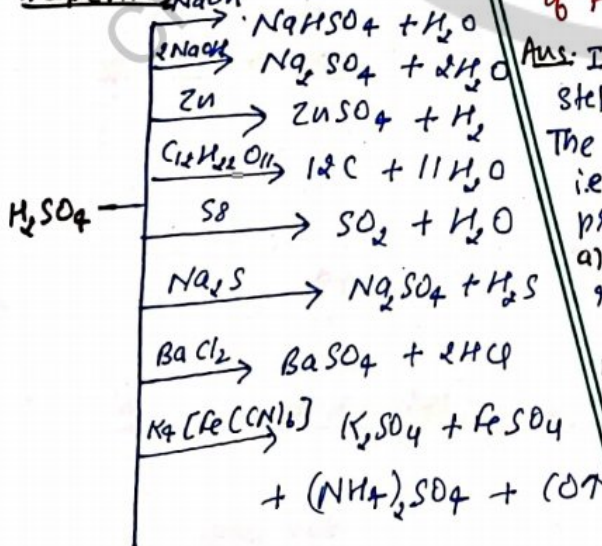
Uses It is used as oxidising agent, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids etc.

⇒ Write the condition to maximise the yield of H_2SO_4 by contact process.

Ans: In contact process, the rate determining step is $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$, $\Delta H° = -196.6$ KJ/mol. The reaction is reversible and exothermic ie ΔH is negative. Thus according to Le-chatelier principle, the condition to maximise the yield are

a) **At lower temperature:-** As heat is evolved in the reaction so, at lower temperature the reaction proceeds more in forward direction.

b) **At high pressure:-** As three moles of gaseous reactants give two moles of gaseous products thus at higher pressure reaction moves in forward direction.

c) **Catalyst** - Presence of catalyst increase the rate of reaction.
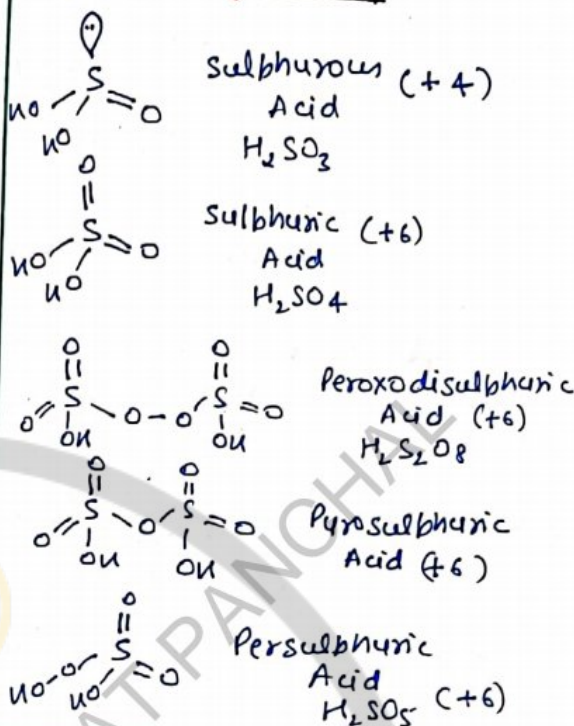
Group 17 elements (HALOGEN FAMILY)

Group 17 elements are collectively called halogen

फिटर	F – Fluorine + 9	$2s^2 2p^5$	$ns^2 np^5$	– Pale Blue Gas
कल	Cl – Chlorine + 17	$3s^2 3p^5$		– Greenish Yellow Gas
बारात	Br – Bromine + 35	$4s^2 4p^5$		– reddish brown liquid
आरजी	I – Iodine + 53	$5s^2 5p^5$		– Purple Solid
अस्टेलियास	At – Astatine + 85	$6s^2 6p^5$		

Atomic radii :- Increase down the group

Ionisation enthalpy :- Very High and decreases down the group.

Electronegativity :- Decreases down the group.

Electron gain enthalpy :- $Cl > F > Br > I$ **Bond energy** $Cl_2 > Br_2 > F_2 > I_2$

m.pt and B.pt :- Increase down the group **Heat of Hydration** $F^- > Cl^- > Br^- > I^-$

Chemical Properties
F shows only −1 oxidation state while other elements show −1, +1, +3, +5 and +7 oxidation state also.

Reactivity $F_2 > Cl_2 > Br_2 > I_2$

Hydrides G-17 elements form Hydrides of the general form HX (HF, HCl, HBr, HI)

Boiling Point : $HF > HI > HBr > HCl$

Melting Point :- $HI > HF > HBr > HCl$

Bond length :- $HI > HBr > HCl > HF$

Bond dissociation enthalpy :- $HF > HCl > HBr > HI$

Acidic Strength :- $HI > HBr > HCl > HF$

Thermal stability :- $HF > HCl > HBr > HI$

Reducing Power :- $HI > HBr > HCl > HF$

Oxides of G-17
Fluorine form two oxides of OF_2 and O_2F_2 called oxygen fluorides, other halogens form oxides in which oxidation state of these halogens range from +1 to +7.
The higher oxides of halogens are more reactive than the lower ores.

→ **F_2 is a stronger oxidising agent than Cl_2** (2019, 2012, 201−)
Ans. fluorine is the strongest oxidising agent as it accept electron easily. It oxidise other halide ions in solution or even in solid phase.

→ **why are halogens coloured.**
Ans. Halogens adsorb radiations in visible region which result in excitation of outer electrons to higher level resulting in different colour (2-1-)

→ **fluorine show only −1 Oxi. State.** fluorine is most electronegative element and it can not exhibit any positive oxidation state. other halogens have vacant d-orbitals so can show +ve oxidation state. i.e +1, +3, +5, +7

Metal Halides
Ionic character: $MF > MCl > MBr > MI$

For metals exhibiting more than one oxidation state, the halides in higher oxidation states will be more covalent than the one in lower Oxi-State

Chlorine Preparation

(i) $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$

(ii) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

(iii) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
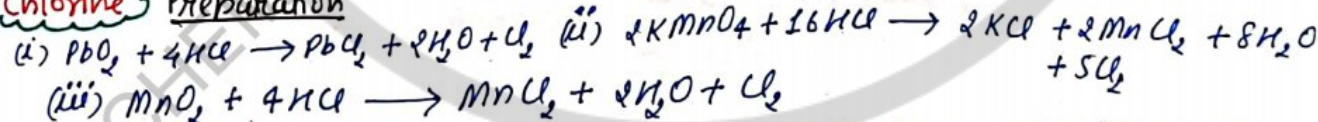
Manufacture : → **Dacron's Process** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ at 723 K

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Electrolytic Process :- By the electrolysis of brine solution

Down's Process :- Obtained as by product during manufacture of sodium by electrolysis of fused NaCl.

Properties It is a yellowish green gas, poisonous in nature, soluble in water Its aqueous solution is known as chlorine water

Bleaching Action and oxidising Property $Cl_2 + H_2O \longrightarrow HOCl + HCl$

$HOCl \longrightarrow HCl + [O]$
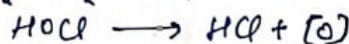
Coloured matter + [O] → colourless matter

The bleaching action of chlorine is permanent and is due to its oxidising nature.

Action of Hydrogen

$$H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{U.V light}} 2HCl$$

Displacement Rxn

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$
$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

Action of NaOH

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$
(cold & dil.)

$$6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$
(hot & conc.)

Addition Reactions

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2 \quad , \quad CO + Cl_2 \longrightarrow COCl_2$$
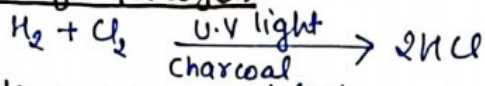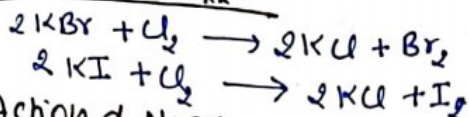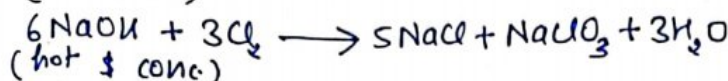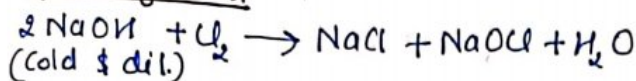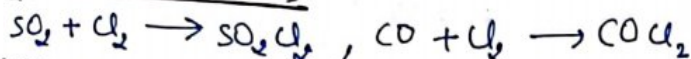
Uses: as a bleaching agent, disinfectant and in the manufacture of $CHCl_3$, CCl_4, DDT, bleaching powder, poisonous gas phosgene ($COCl_2$), tear gas (CCl_3NO_2) and mustard gas ($Cl C_2H_4 S C_2H_4Cl$)

⇒ Name two poisonous gases which can be prepared from Cl_2 gas (2012)

Ans: phosgene (ii) calcium hypochlorite

⇒ How can you prepare Cl_2 from HCl and HCl from Cl_2 (2019)

Ans. $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
$$Cl_2 + H_2S \longrightarrow 2HCl + S$$
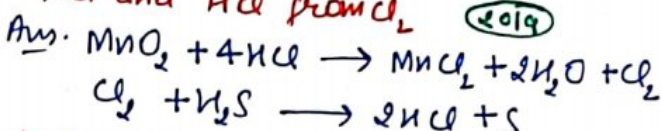
⇒ Bleaching power of Cl_2 is permanent by SO_2 is temporary (2013)

Ans. The bleaching action of Cl_2 is due to oxidation of coloured substances to colourless substances by nascent oxygen. Since, the bleaching action of Cl_2 is due to oxidation and that of SO_2 is due to reduction. Therefore bleaching effect of Cl_2 is permanent while that of SO_2 is temporary

Hydrogen Chloride HCl

Preparation $NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$, $NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$
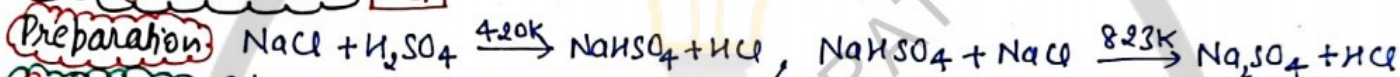
Properties Colourless and pungent smelling gas, easily liquifiable, extremely soluble in water.

$$NH_3 + HCl \longrightarrow NH_4Cl \; ; \; Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$
$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$
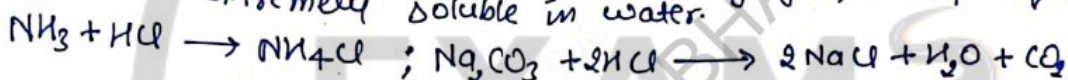
3 parts of conc HCl and 1 part of conc. HNO_3 is used for HNO_3 is used for dissolving noble metals e.g gold, platinum

$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$
$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$
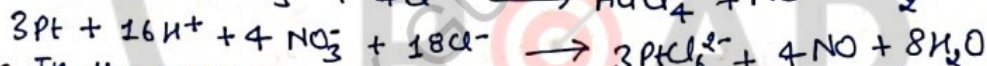
Uses In the manufacture of Cl_2, NH_4Cl and glucose, in medicine and as a laboratory reagent. for extracting glue from bones and purifying bone black.

Oxoacids of Halogens

Halogen	Hypohalous Acid (+1)	Halous Acid (+3)	Halic Acid (+5)	Perhalic Acid(+7)
F	HOF	—	—	—
Cl	HClO	HClO_2	HClO_3	HClO_4
Br	HBrO	—	HBrO_3	HBrO_4
I	HIO	—	HIO_3	HIO_4

(columns to right, arrows pointing down: Electronegativity decreases — Thermal stability decreases — Oxidising power decreases — Acidic strength decreases —)

→ Oxidation Number of Central Atom increases →
  - Thermal stability increases →
  - Covalent character of X–O bond increases →
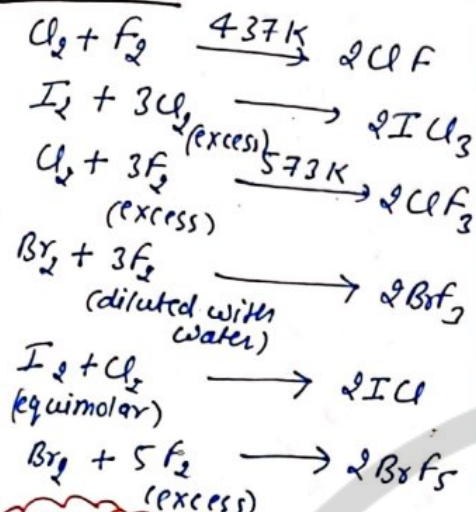 - Oxidising power decreases →
  - Acidity increases →
  - E.N of central atom remains the same →

Interhalogen Compounds

Halogens combine amongst themselves to form a number of interhalogens of the type XX', XX'_3, XX'_5 and XX'_7 where X is a larger size halogen (more electropositive) and X' is smaller size halogen
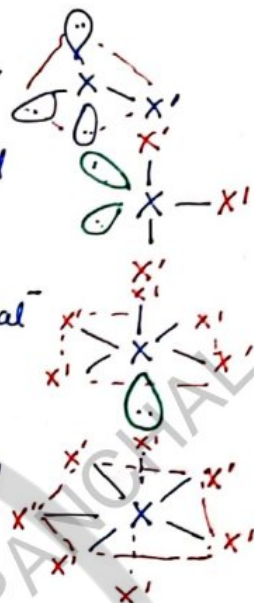
Preparation

$$Cl_2 + F_2 \xrightarrow{437K} 2ClF$$

$$I_2 + 3Cl_{2(excess)} \longrightarrow 2ICl_3$$

$$Cl_2 + 3F_2 \xrightarrow[(excess)]{573K} 2ClF_3$$

$$Br_2 + 3F_2 \xrightarrow[\text{water}]{\text{(diluted with}} 2BrF_3$$

$$I_2 + Cl_2 \xrightarrow{\text{(equimolar)}} 2ICl$$

$$Br_2 + 5F_2 \xrightarrow{\text{(excess)}} 2BrF_5$$

XX' - sp^3 - linear

XX'_3 - sp^3d - T-shaped

XX'_5 - sp^3d^2 - Square pyramidal

XX'_7 - sp^3d^3 - Pentagonal Bipyramidal

Shape of BrF_5

ClF_3

BrF_3
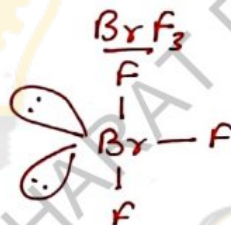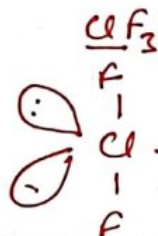
Group-18 Elements (Noble Gases)

These are monoatomic gases and are also known as rare gases or aerogens

General characteristics

हँसता	He	Helium	2	$1s^2$	
नीता	Ne	Neon	10	$2s^2 2p^6$	
अरे	Ar	Argon	18	$3s^2 3p^6$	$ns^2 np^6$
कहीं	Kr	Krypton	36	$4s^2 4p^6$	
चली	Xe	Xenon	54	$5s^2 5p^6$	
रहना	Rn	Radon	86	$6s^2 6p^6$	

Physical State	Atomic Radii	Electron Gain Enthalpy	M.Pt & B.Pt
Gases	Increase down the group	Positive	Very low

Chemical Properties

Noble gases are least reactive due to high ionization enthalpy and more positive electron gain enthalpy.

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$
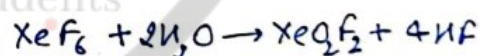
Xenon - fluorine compounds

$$Xe + F_2 \xrightarrow{673K, 1bar} XeF_2$$
(excess)

$$Xe + 2F_2 \xrightarrow{873K, 7bar} XeF_4$$
(1:5 ratio)

$$Xe + 3F_2 \xrightarrow[60-70 bar]{573K} XeF_6$$
(1:20 ratio)

Xenon Oxygen Compounds

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
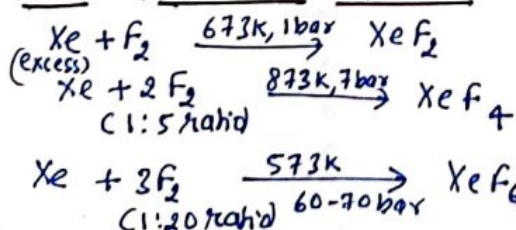
Structure of Compounds of Xenon

XeF_2 (linear) sp^3d

XeF_4 (Square Planar) sp^3d^2

XeO_3 Pyramidal (sp^3)

XeF_6 sp^3d^3 (distorted Octahedral)
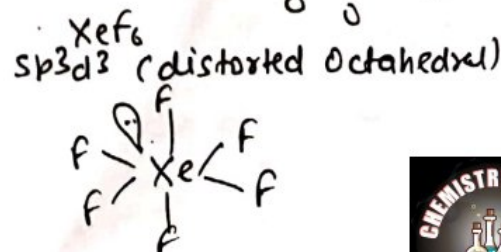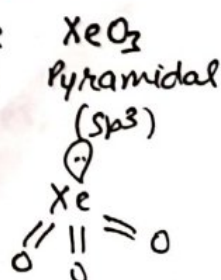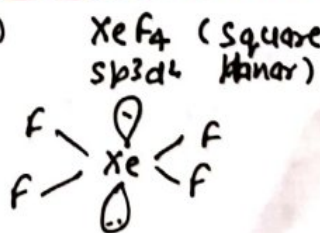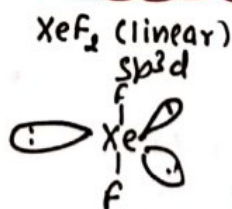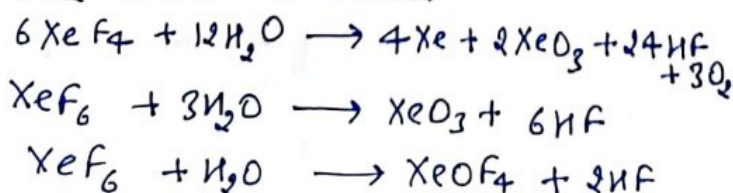
Uses of Helium - To lift weather balloons and air ships
- As breathing mixture - For inflating the tyres of aeroplanes

Neon - for advertising - For filling sodium vapour lamps
- In becon light

Argon - To create an inert atmosphere
- To geiger counters - To date the age of rocks.

Krypton - For runway and approach lights in airports
- In high efficiency miners cap lamps

Xenon : In electric flash bulbs for high speed photography
Krypton and xenon are more efficient than argon in gas filled lamps

Radon :- In the treatment of cancer - In x-ray photography for the detection of flaws in metals and other solids.

=> Complete the following Rxn

$XeF_6 + NaF \longrightarrow Na^+ [XeF_7]^-$

$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$

=> Noble Gases have low Boiling Pt?
Noble gases being mono atomic gases are held together by weak london dispersion forces. therefore they have low boiling point.

what inspired N. Bartlett for carrying out reaction between Xe and PtF_6 ?

Ans. N. Bartlett first prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He then realised that the first ionisation enthalpy of molecular oxygen (1175 KJ/mol) is almost identical with Xe (1170 KJ/mol). He made efforts to prepare same compound with Xe. And was successful in preparing another red compound $Xe^+ PtF_6^-$

The d- and f- block elements

d-block element

Those elements in which last e⊖ enters in d-orbital are called d-block element. These are also known as transition elements.

four series of transition elements.

1st transition series: 3d Series - $_{31}Sc$ - $_{30}Zn$
2nd transition series: 4d Series - $_{39}Y$ - $_{48}Cd$
3rd transition series: 5d series - $_{57}La$ $_{72}Hf$ - $_{80}Hg$
4th transition series: 6d Series - $_{89}Ac$ $_{104}Rf$ - $_{112}Cn$

3d Series

श्रीमान				Elec. Confi.	Oxidation state
अति	Sc - Scandium	21		$3d^1 4s^2$	+3
Very	Ti - Titanium	22		$3d^2 4s^2$	+2, +3, +4
Crazy	V - Vanadium	23		$3d^3 4s^2$	+2, +3, +4, +5
क्रोधी	Cr - Chromium	24	Ar	$3d^5 4s^1$	+1, +2, +3, +4, +5, +6
माताजी	Mn - Manganese	25		$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
को	Fe - Iron	26		$3d^6 4s^2$	+2, +3, +4, +5, +6
नि	Co - Cobalt	27		$3d^7 4s^2$	+2, +3, +4
दुःख	Ni - Nickel	28		$3d^8 4s^2$	+2, +3, +4
से	Cu - Copper	29		$3d^{10} 4s^1$	+1, +2
	Zn - Zinc	30		$3d^{10} 4s^2$	+2

Zn, Cd and Hg are not considered as transition elements because
$3d^{10}, 4d^{10}, 5d^{10}$ they have fully filled d-orbital And can't show most of the properties shown by transition elements.

Metallic character with the exception of Zn, Cd and Hg, all the (147) transition elements are much harder and less volatile. Although hardness and brittleness are associated with covalent bonding b/w metal atoms.

Melting and Boiling Point:- High due to strong metallic bonding

Enthalpies of atomisation:- High due to strong interatomic interactions.

Ionisation enthalpies:- Generally increases from left to right in a series

Oxidation state:- show variable oxidation state due to participation of ns and $(n-1)d$ electrons.

Atomic radii Decrease from left to right but becomes constant when pairing of electron takes place

Complex formation form complex due to high nuclear charge and small size and availability of empty d-orbitals to accept lone pair of electrons donated by ligands.

Coloured compounds:- form coloured compounds due to d-d transitions.

Magnetic Properties:- Transition metal ions and their compounds are paramagnetic due to presence of unpaired $e^{\ominus}$ in the $(n-1)$ d-orbitals and it is calculated by using the formula

$$\mu = \sqrt{n(n+2)}$$ where, n is the no. of unpaired electrons.

Catalytic behaviour Due to variable oxidation states and ability to form complexes

Interstitial compounds Due to empty space in their lattices, small atoms can be easily accommodated

Alloy formation:- Due to similar atomic sizes.

Potassium Dichromate, $K_2Cr_2O_7$

Prepared from ferrochromate $(FeO \cdot Cr_2O_3)$

(i) $4FeO \cdot Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

(ii) $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ (orange)

(iii) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Pot. dichromate is orange red crystalline solid act as oxidising Agent
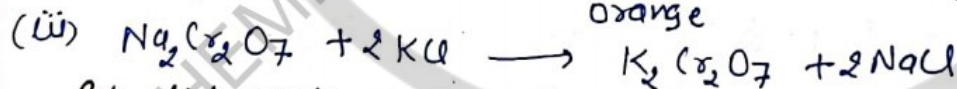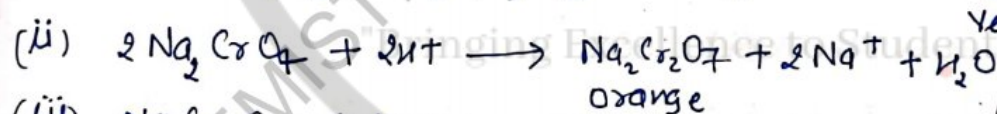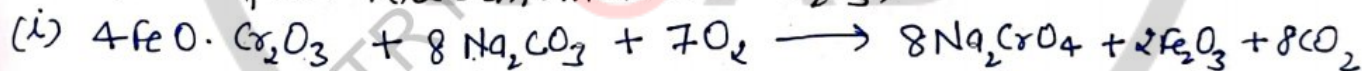
Pot. dichromate can be converted into chromate

$$Cr_2O_7^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CrO_4^{2-}$$
Orange ⇌ Yellow
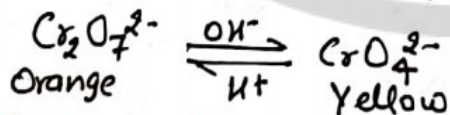
Str. of Dichromate ion and chromate ion

$Cr_2O_7^{2-}$

CrO_4^{2-}

oxidising agent in acid medium →

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

Oxidise

$I^- \rightarrow I_2$
$H_2S \rightarrow S$
$Sn^{2+} \rightarrow Sn^{4+}$
$Fe^{2+} \rightarrow Fe^{3+}$
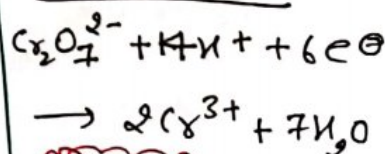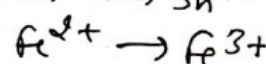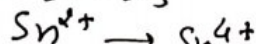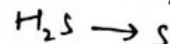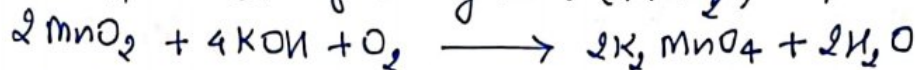
Potassium Permanganate (KMnO4)

Prepared from ore of manganese $(MnO_2) \rightarrow$ Pyrolusite ore

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
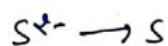
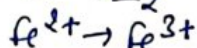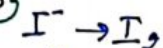$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

It is a deep purple crystalline solid, oxidising agent having m.pt $240°C$

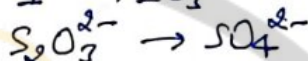**Oxidising agent in acidic medium**

$$MnO_4^- + 8H^+ + 5e^\ominus \longrightarrow Mn^{2+} + 4H_2O$$

Oxidises
- $I^- \rightarrow I_2$
- $Fe^{2+} \rightarrow Fe^{3+}$
- $C_2O_4^{2-} \rightarrow CO_2$
- $S^{2-} \rightarrow S$
- $SO_3^{2-} \rightarrow SO_4^{2-}$
- $NO_2^- \rightarrow NO_3^-$

Oxidising agent in faintly alkaline or neutral medium

$$MnO_4^- + 2H_2O + 3e^\ominus \rightarrow MnO_2 + 4OH^-$$
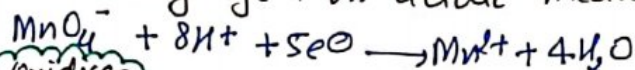
Oxidises
- $I^- \rightarrow IO_3^-$
- $S_2O_3^{2-} \rightarrow SO_4^{2-}$
- $Mn^{2+} \rightarrow MnO_2$
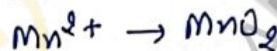
Str. of Permanganate ion (MnO_4^-)

and Permanganate ion (MnO_4^{2-})
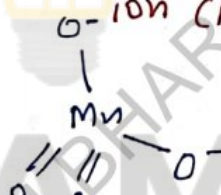
KMnO4 is used as a disinfectant, germicide and Baeyer's Reagent

Volumetric titration involving KMnO4 are carried out only in the presence of dil. H_2SO_4 but not in the presence of HCl or HNO_3 because HCl oxidised to Cl_2 and HNO_3 is itself a strong oxidising agent and partly oxidises the reducing agent. H_2SO_4 does not give any oxygen of its own to oxidise the reducing agent

f-block elements : INNER TRANSITION ELEMENTS

lanthanoids - Last $e^\ominus$ enters in 4f-orbital. Ce (at. 58) to Lu (at.no.71)

Actinoids - last $e^\ominus$ enters in 5f orbital. Thorium (at.no 90.) to Lawrencium (a.n.103)

General electronic config. $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$

lanthanoid Contraction In lanthanoid series, with increasing atomic number there is progressive decrease in atomic/ionic radii (M^{3+}) from La^{3+} to Lu^{3+} OOOOOOOO ○○○.....

Reason Due to addition of new electrons into f-subshell and imperfect shielding of one electron by another in the f-orbitals, there is greater effect of increased nuclear charge than screening effect hence contraction in size.

Consequences

(i) Their separation is different because they have small difference in properties

(ii) 4d and 5d transition series have almost same atomic radii C2r and Hf have similar properties due to same size.

(iii) Basic character of lanthanoids decreases from left to right

Uses of lanthanoids - Used in making mischmetal (16)
and traces of S, C, Ca and Al. It is used to make tracer bullets, shells
and lighter flints
⇒ Difference between lanthanoids and Actinoids

Lanthanoids	Actinoids
• They show +2 and +4 oxidation states in some cases besides +3	• They show higher oxidation state of +4, +5, +6 and +7, besides +3.
• Except promethium, they are non radioactive	• All actinoids are radioactive
• They do not form oxo-cations	• They form oxo-cations like UO_2^{2+}, PuO_2^{2+}, UO_2^+ etc.
• The compounds of lanthanoids are less basic	• Actinoid compounds are more basic
• They have less tendency of complex formation	• They have greater tendency of complex formation.

COORDINATION COMPOUNDS

Those compounds in which the central metal atom is linked to ions
or neutral molecules by co-ordinate bond (donation of lone pair of e⁻)
are called co-ordinate compounds or complex compounds

Types of Complexes: (i) Cationic complex e.g $[Co(NH_3)_6]^{3+}$
(ii) Anionic complex e.g $[Ag(CN)_2]^-$
(iii) Neutral complex e.g $[Ni(CO)_4]$

Double Salt	Complex Compound
(i) They have two simple salts in equimolar ratio	(i) They may or may not have simple salts in equimolar ratio.
(ii) They do not contain co-ordinate bond	(ii) They contain co-ordinate bond.
(iii) Their properties are same as their constituents	(iii) Their properties are different from their constituents.
(iv) They lose their identity in the solution	(iv) They lose their identity in the solution
e.g $FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O \rightarrow$ (Mohr's salt) $Fe^{2+} + 2NH_4^+ + 2SO_4^{2-} + 6H_2O$	e.g $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

$$K_4[Fe(CN)_6]$$

Counter ion
Central metal atom
ligands
Co-ordination sphere
Co-ordination Number
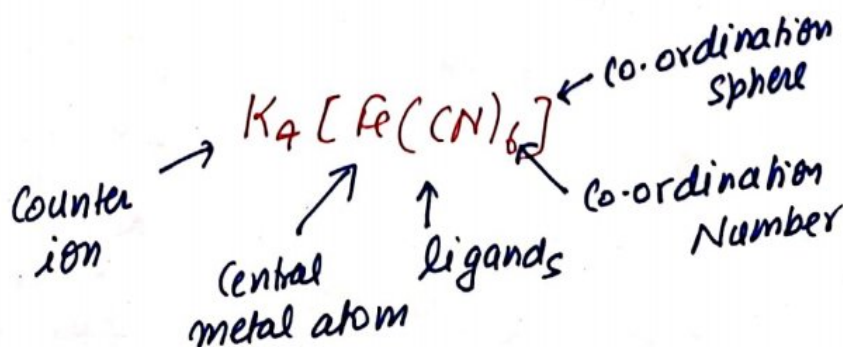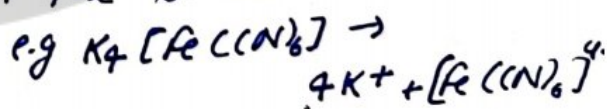
Ligand :- The donor species (atom, molecule or ion) which donate a pair of e⊖ to the metal atom is called ligand.

Denticity The number of donor atoms present in a ligand is called the denticity of ligand.

Monodentate or Unidentate :- ligand has one donor atom eg NH_3, H_2O, Cl^-

Bidentate ligand :- ligands which can donate two lone pair of e⊖ to central metal atom.

e.g   ethylene diamine (en)

$CH_2 - NH_2$
$|$
$CH_2 - NH_2$

oxalato (ox)

$C OO^-$
$|$
$C OO^-$

> **Counter ion** ← The Ionizable group which are written outside the bracket is called counter ion

Hexadentate ligand :- which has six donor atoms

(EDTA $^{4-}$)
ethylene diamine tetra acetate ion

$^-_{H_2}C - \overset{1}{N} <^{CH_2 COO^-}_{CH_2 COO^-}$
$^-_{H_2}C - \overset{2}{N} <^{CH_2 COO^-}_{CH_2 COO^-}$

> **Co-ordination Sphere** The central atom and the ligands are enclosed in square bracket

Ambidentate ligands Those unidentate co-ordination are called ambidentate ligands which have more than one ligand s

$NO_2 \leftrightarrow ONO$, $SCN \leftrightarrow NCS$, $CN \leftrightarrow NC$

Chelate when a bidentate or a polydentate ligand is attached by two or more atoms to the central atom forming a ring, the ligand is called chelating ligand and the complex is called chelate, the effect is called chelate effect

eg $[Pt\, Cl_2(en)]$

$\begin{matrix} Cl \\ \\ Cl \end{matrix} \searrow Pt \nearrow \begin{matrix} \overset{H_2}{N} - CH_2 \\ | \\ \underset{H_2}{N} - CH_2 \end{matrix}$
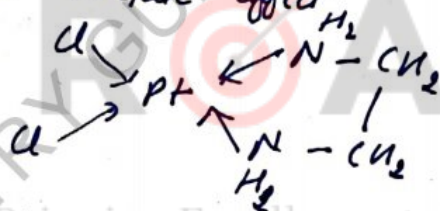
> **Co-ordination Number** Total number of co-ordinate bonds formed with C.M.A by the ligands.

> **Negative ligands**

$F^- \rightarrow$ fluorido
$Cl^- \rightarrow$ chlorido
$Br^- \rightarrow$ Bromido
$I^- \rightarrow$ Iodido
$NO_2^- \rightarrow$ Nitrito – N
$NO_3^- \rightarrow$ Nitrato
$ONO^- \rightarrow$ Nitrito – O
$CN^- \rightarrow$ Cyanido
$SCN^- \rightarrow$ thiocyanato
$NCS^- \rightarrow$ isothiocyanato
$SO_4^{2-} \rightarrow$ sulphato
$O^{2-} \rightarrow$ oxo
$CO_3^{2-} \rightarrow$ Carbonato
$NH_2^- \rightarrow$ amido
$NH^{2-} \rightarrow$ imido

$H^- \rightarrow$ Hydrido
$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \rightarrow$ ox (oxalato)
$OH^- \rightarrow$ Hydroxo
$CH_2 <^{NH_2}_{COO^-} \rightarrow$ Glycinato (gly)

> **Positive ligand**

$NO^+ \rightarrow$ nitrosonium
$NO_2^+ \rightarrow$ nitronium
$NH_2 - NH_3^+ \rightarrow$ hydrazinium

> **Neutral ligands**

$NH_3 \rightarrow$ ammine
$H_2O \rightarrow$ aqua
$NO \rightarrow$ Nitrosyl
$PH_3 \rightarrow$ Phosphine
$CO \rightarrow$ Carbonyl
$SO \rightarrow$ thionyl

$CH_3 NH_2 \rightarrow$ methyl amine
C_5H_5N or $Py \rightarrow$ Pyridine
$(C_6H_5)_3 P \rightarrow$ triphenyl phosphine
$\begin{matrix} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{matrix}$ ethane-1,2-diamine

1.) $K_3[Fe(CN)_6]$ → potassium hexacyano ferrate (III)

2.)

3.) $[Co(NH_3)_6]Cl_3$ → hexa ammine cobalt (III) chloride

4.) $[Pt(NH_3)_2Cl(NO_2)]$ → diammine chlorido nitrito-N-platinum (II)

5.) $K_3[Cr(C_2O_4)_3]$ → potassium tetra hydroxo zincate (II)

6.) $[Ag(NH_3)_2][Ag(CN)_2]$ → diammine silver (I) dicyano argentate (I)

7.) $Hg[Co(SCN)_4]$ → mercury tetra thiocyanato cobaltate (III)

8.) $[Co(NH_3)_5-(CO_3)]Cl$ → pentaammine carbonato cobalt (III) chloride

9.) $K_3[Fe(C_2O_4)_3]$ → potassium trioxalato ferrate (III)

10.) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ → diammine chlorido methanamine platinum (II) chloride

11.) $[CoCl_2(en)_2]Cl$ → dichlorido bis (ethane-1,2-diamine) cobalt (III) chloride

12.) $[Co(en)_3]^{3+}$ → tris (ethane-1,2-diamine) cobalt (III) ion

12.) $[NiCl_4]^{2-}$ → tetra chloridonickelate (II) ion

13.) $[Ni(NH_3)_6]Cl_2$ → hexa ammine nickel (II) chloride

Isomerism Two or more substances having the same molecular formula but different structural or spatial arrangement are called isomers and phenomenon is called isomerism

Structural Isomerism

Ionisation isomerism	Hydrate isomerism	Linkage Isomerism	Co-ordination Isomerism
Compounds which have different ions in solution due to the exchange of ions in coordination sphere and counter ions are called ionisation isomers. e.g $[CoBr(NH_3)_5]SO_4$ $[CoSO_4(NH_3)_5]Br$	Isomers which differ in the no. of water molecules attached to the metal atom or ion as ligand e.g $[Cr(H_2O)_6]Cl_3$ $[Cr(H_2O)_5Cl]Cl_2.H_2O$	When an ambidentate ligand attached to metal through different atoms the the compounds are said to be linkage isomers e.g $[Co(NO_2)(NH_3)_5]Cl$ $[Co(ONO)(NH_3)_5]Cl$	when both +ve and -ve ions of a salt are complex ions and two isomers differ in the distribution of ligands in two complex ions $[Co(NH_3)_6][Cr(CN)_6]$ $[Co(CN)_6][Cr(NH_3)_6]$

Stereo isomerism

Geometrical or cis-trans isomerism

If two identical ligands ocupy adjacent position ⇒ cis

If occupy opposite position ⇒ trans

In Square Planar	In Octahedral
shown by MA_2X_2 $MABX_2$ MA_2XY $MABXY$	shown by MA_4X_2 → cis trans MA_3X_3 If all three similar gp. occupy adjacent position then fac-Isomer

Optical Isomerism

The isomerism arises due to non super imposable mirror images

only in Octahedral complexes with 2 or 3 bidentate ligands

cis (optically active)   trans (optically inactive)

If three similar groups are present around meridian of octahedra then mer-isomer

Valence Bond Theory — It was developed by Pauling

C.N	Type of hyb.	Geometry	Example
4	sp3	Tetrahedral	$[Ni(CO)_4]$ $[ZnCl_4]^{2-}$
	dsp2	Square planar	$[Ni(CN)_4]^{2-}$ $[Cu(NH_3)_4]^{2+}$
5	dsp3	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	sp3d	Square pyramidal	$[SbF_5]^{2-}$
6	d²sp3	Octahedral (Inner)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp3d²	Octahedral (Outer)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$

Inner orbital complex
Involve inner d-orbitals i.e (n-1)d

Low spin complexes

Have less or no unpaired $e^{\ominus}$

eg $[Co(NH_3)_6]^{3+}$

Outer orbital complex
Involve outer d-orbitals i.e nd

High spin complexes

Have large no. of unpaired $e^{\ominus}$

e.g $[MnF_6]^{3-}$, $[CoF_6]^{3-}$

→ low spin complexes are generally diamagnetic and high spin complexes are paramagnetic

→ Paramagnetism $\propto$ No. of unpaired electrons

→ Magnetic moment $= \sqrt{n(n+1)}$ B.M

where n = no. of unpaired $e^{\ominus}$

Give Hybridisation and shape of following

(a) $[Fe(H_2O)_6]^{2+}$

(b) $[Ni(CN)_4]^{2-}$

(c) $[NiCl_4]^{2-}$

(a) Name → hexaaqua iron(II)ion

$Fe^{2+} = (Ar)^{18}$ $3d^6 4s^0$

3d | 4s | 4p

4d

hyb → sp3d²

Geom.→ Octahedral

Mag. → Paramagnetic

(b) → tetracyano nickelate(II)ion

$Ni^{2+} → (Ar)^{18}$ $3d^8 4s^0$

3d | 4s | 4p

CN is a strong ligand which force unpaired $e^{\ominus}$ to become pair

3d | 4s | 4p
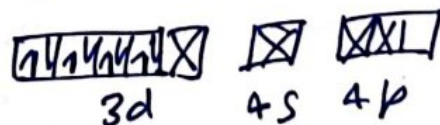
hyb - dsp2

Geo → square planar

Mag → Diamagnetic

(c) → tetra chlorido nickelate(II) ion

$Ni^{2+} → (Ar)^{18}$ $3d^8 4s^0$

3d | 4s | 4p

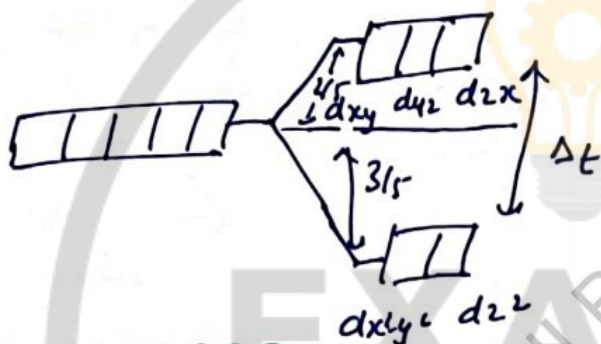hyb → sp3

Geo → tetrahedral

Mag → Paramagnetic

Crystal Field Theory

- Metal ligand bonds are ionic having electrostatic interaction similar to ions in a crystals.
- ligand is treated as point negative charge

### Splitting in Octahedral Complex

degenerate d-orbital

Weak field ligand

$dx^2-y^2 dz^2$ eg

Bary centre

Δ_o

t_{2g}

dxy dyz dzx

degenerate d-orbital

Strong field ligand

dx^2-y^2

$3/5$

$2/5$

Bary centre

Δ_o

dxy dyz dzx
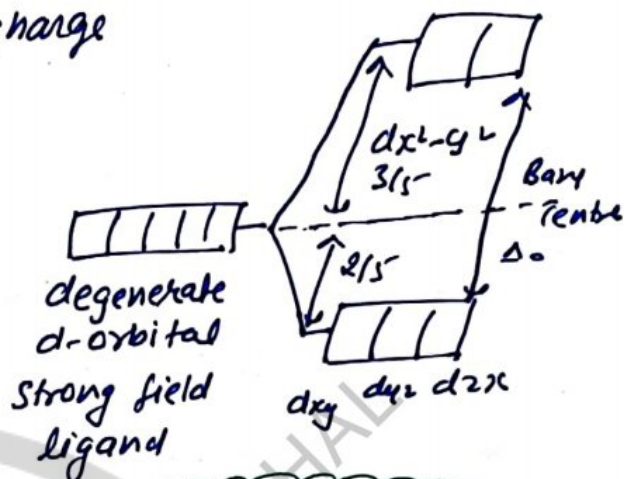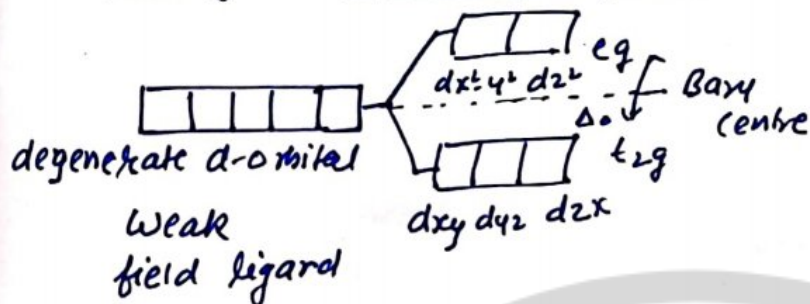
Splitting in tetrahedral Complex

$4/5$

dxy dyz dzx

$3/5$

Δ_t

dx²y² dz²

Crystal field Splitting Energy

The difference of energy b/w the two sets of d-orbitals is called crystal field splitting energy or (crystal field stabilisation energy (CFSE). Represented by Δ_o for Octahedral Δ_t for tetrahedral

$$\Delta_t = \frac{4}{9} \Delta_o$$

Spectrochemical Series

The arrangement of ligands in order of their increasing crystal field splitting energy (CFSE) values is called spectrochemical series as given below.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$
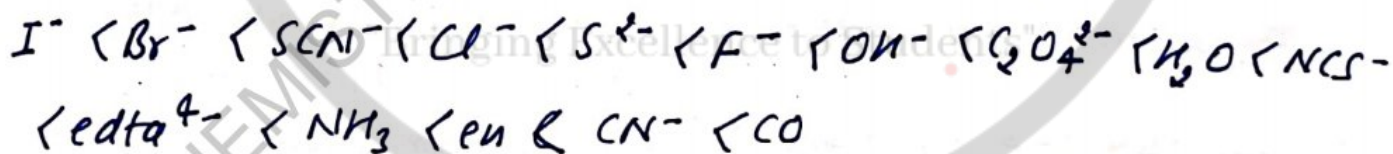
The ligands with small values of CFSE are called weak field ligands whereas those with large value of CFSE are called strong field ligands.

On the Basis of C.F.T write the electronic configuration of d4 in terms of t_{2g} and eg in an octahedral field when

(i) $\Delta_o > P \rightarrow t_{2g}^4 eg^0$

(ii) $\Delta_o < P \rightarrow t_{2g}^3 eg^1$

Bonding in Metal Carbonyls

▷ Metal-carbon bond in metal carbonyls possesses both σ and π characters

▷ Its formation involve the following steps:

- Overlap of filled π_{2p} orbital of CO with suitable empty metal d-orbital resulting in the formation of sigma bond.


Vacant metal orbital   orbital containing lone pair $M \leftarrow C$ σ bond
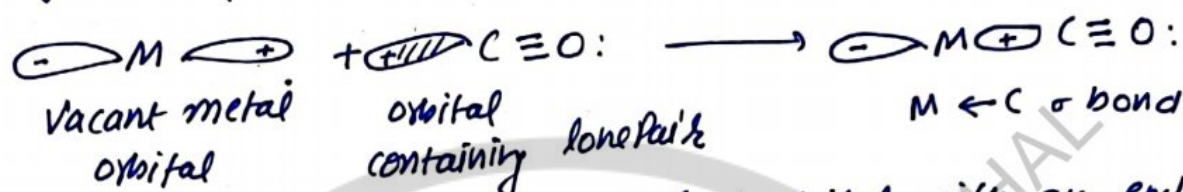
- π-overlap involving filled metal d-orbital with an empty antibonding $\pi^* 2p$ orbital of same CO. This results in formation of $M \rightarrow C$ π bond. This is also called back bonding.

filled metal d-orbital   Empty $\pi^* 2p$ orbital of CO $M \rightarrow C$ π bond
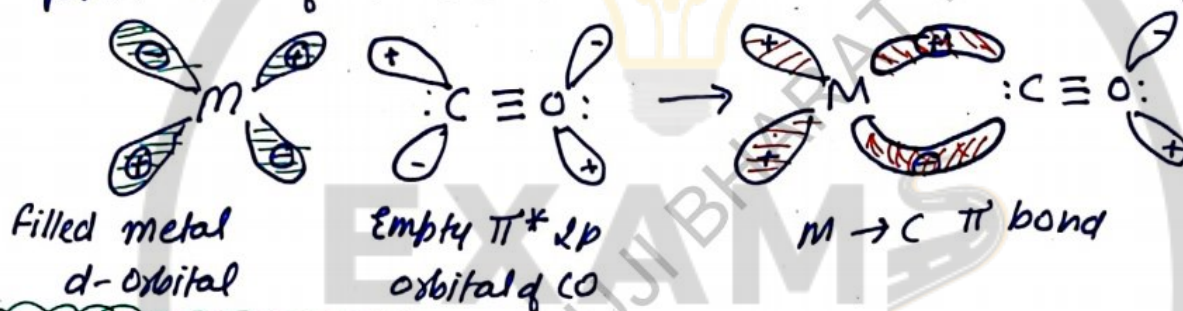
Stability of Complexes

The formation of the complex in a solution is a reversible and exothermic process

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} \qquad K = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$
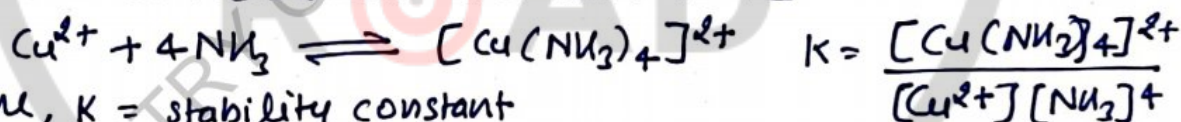
where, K = stability constant

▶ Higher the value of stability constant (K), higher will be the stability of complex

▶ Higher the polarising power of metal ion and basicity of ligand, higher will be the stability of complex.

Application of Co-ordination Compounds

- Co-ordination compounds are of great importance in biological system e.g chlorophyll, haemoglobin, vitamin B_{12} etc. are co-ordinate compounds of Mg, Fe and Co respectively
- Cis-platin is used in Cancer treatment.
- EDTA is often used for treatment of lead poisoning.
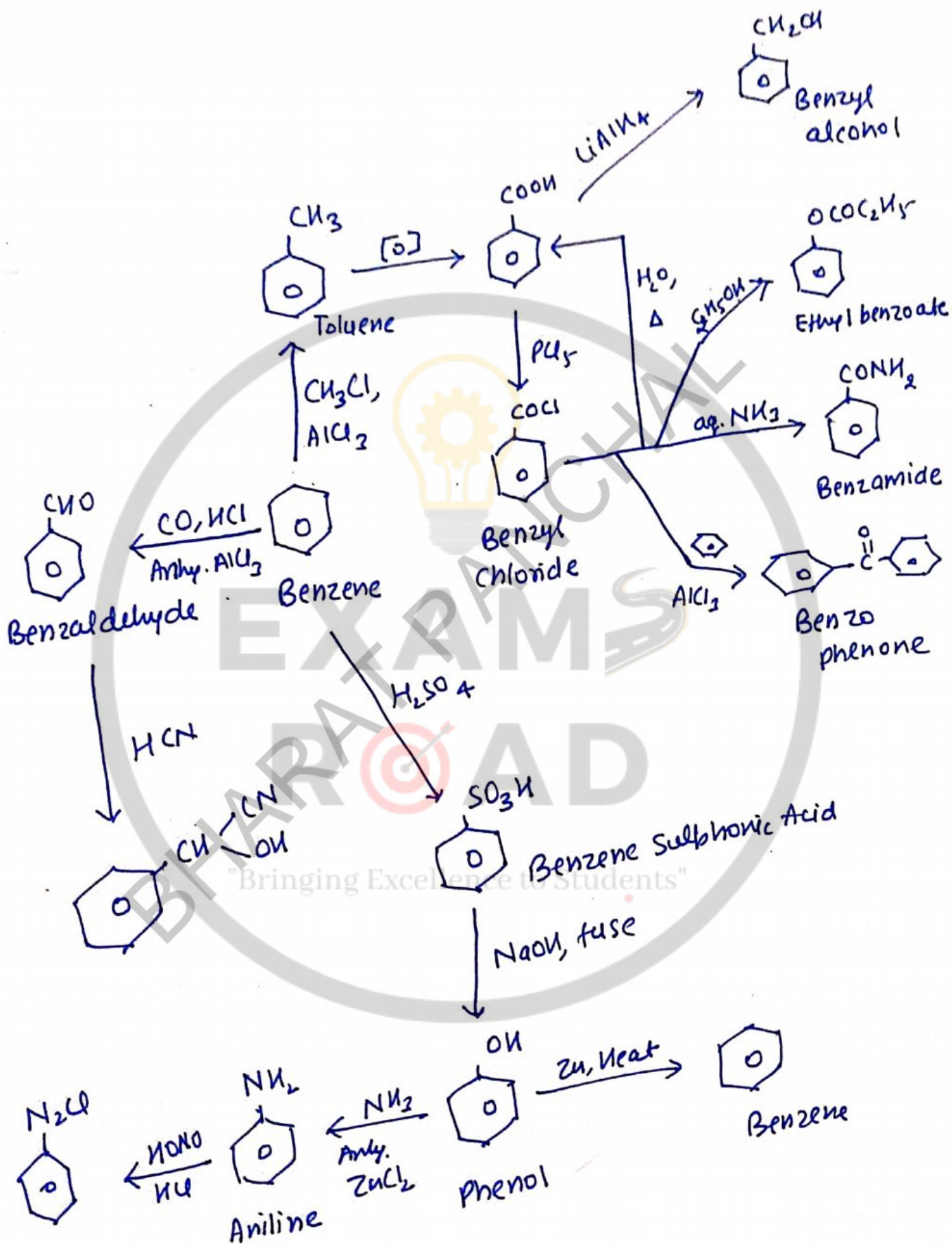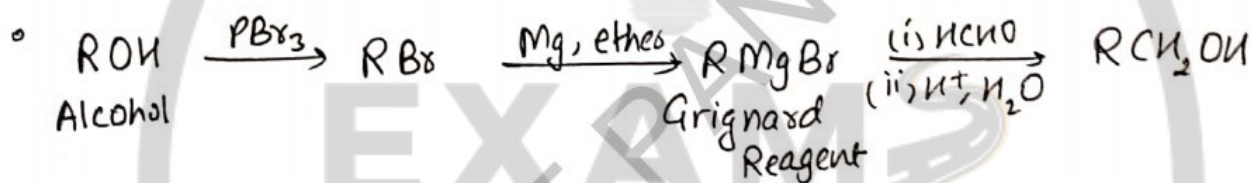- Co-ordination compounds are used as catalyst.

Diazonium Salt

N_2Cl (on benzene ring)

- $\xrightarrow{H_2O, \text{ warm}}$ OH — **Phenol**
- $\xrightarrow[H_2O]{H_3PO_2}$ — **Benzene**
- $\xrightarrow{Cu, HCl}$ Cl — **Chlorobenzene**
- $\xrightarrow{Cu, HBr}$ Br — **Bromobenzene**
- $\xrightarrow{CuCN}$ CN — **Cyanobenzene**
- $\xrightarrow{KI, \Delta}$ I — **Iodobenzene**
- $\xrightarrow[NaNO_2]{HBF_4, \Delta}$ F — **Fluorobenzene**
- $\xrightarrow{KSH}$ SH — **Thiophenol**
- $\xrightarrow[(G = NH_2, OH)]{\text{⬡-G}}$ ⬡-N_2-⬡-G — **Azo dye**

Aromatic Conversions

$\xrightarrow{Sn, HCl}$ from Nitrobenzene NO_2

Nitrobenzene $\xrightarrow[H_2SO_4]{}$ SO_3H **Sulphonic Acid**

Benzene $\xrightarrow[H_2SO_4]{HNO_3,}$ Nitrobenzene NO_2

Sn, HCl $\downarrow$ NH_2 **Aniline**

Benzene $\xrightarrow[Anhy\ AlCl_3]{CH_3COCl}$ $COCH_3$ **Acetophenone** $\xrightarrow[HCl]{Zn, Hg}$ CH_2CH_3 **Ethyl benzene**

Benzene $\xrightarrow{Cl_2, FeCl_3}$ Cl **Chlorobenzene**

Chlorobenzene $\xrightarrow{CH_3Cl, Na}$ CH_3 **Toluene**

Chlorobenzene $\xleftarrow[\text{fittig Re}^n]{2Na}$ ⬡-⬡ **Biphenyl**

$\xrightarrow[Cu_2O, \Delta]{NH_3}$ (to aniline)

⇒ **Road Map #3**

Benzene

Cl_2, $FeCl_3$

Cl (Chlorobenzene)

CH_3Cl, Na →

CH_3 (benzene ring)

← 2Na

(benzene-benzene, biphenyl)

(i) NaOH, 623K
(ii) H⁺, HCl, 300at

OH — **Phenol**

CuCN

CN — **Cyanobenzene**

H^+, H_2O

COOH — **Benzoic Acid**

Cl_2, hv

CH_2Cl — **Benzyl Chloride**

aq. KOH

CH_2OH — **Benzyl alcohol**

[O] →

CHO — **Benzaldehyde**

[O]

COOH

Soda lime → Benzene

[O]

CHO — **Benzaldehyde**

"Bringing Excellence to Students"

Road Map # 4

Phenol reaction road map showing products:

- H_2SO_4, 373 K → $OH-\langle\bigcirc\rangle-SO_3H$ (p-product)
- NaOH → ONa sod. Phenoxide
- $Na_2Cr_2O_7$ / H_2SO_4 → Quinone
- NaOH / CO_2, H^+ → Salicylic Acid (OH, COOH)
- H_2 / Ni, 533 K → Cyclohexanol
- NaOH, $CHCl_3$ / H^+ → Salicyldehyde (OH, CHO)
- Zn / Δ → benzene + ZnO
- $3Br_2$ → tribromophenol + 3 HBr

Left side:

- Br_2 / CS_2 → OH + Br (o and p bromophenol)
- dil. HNO_3 → OH + NO_2 (o and p nitrophenol)
- conc. HNO_3 / conc. H_2SO_4 → Picric Acid (NO_2 substituted)
- CH_3Cl / Anhy $AlCl_3$ → OH, CH_3 (p-Cresol)
- NH_3 / Anhy $ZnCl_2$ → Aniline (NH_2)

Road Map #5

Aliphatic Conversion   Step Up

• $R-H$ $\xrightarrow{Br_2, h\nu}$ $R-Br$ $\xrightarrow[\substack{Wurtz \\ R^n}]{Na, ether}$ $R-R$ Alkane

Alkane

• $R-OH$ $\xrightarrow{P, I_2}$ $R-I$ (Alkyl iodide) $\xrightarrow{KCN}$

$\xrightarrow[Reduction]{Na, (2H_5OH)}$ RCN (Alkyl cyanide)

RCH_2OH $\xleftarrow{HONO}$ RCH_2NH_2 Amine

$\downarrow$ 2H Reduction

$R-CHO$ Aldehyde $\xleftarrow[\substack{Cal.Salt \\ with Cal. \\ formate}]{Heat}$ $R\,COOH$ Carboxylic Acid $\xleftarrow{H^+, H_2O}$ $RCONH_2$ Amide

RCN $\xrightarrow[or\ H_2O_2,\ OH^-]{conc. HCl}$ $RCONH_2$

• ROH Alcohol $\xrightarrow{PBr_3}$ RBr $\xrightarrow{Mg, ether}$ $RMgBr$ Grignard Reagent $\xrightarrow[(ii)\,H^+,\,H_2O]{(i)\,HCHO}$ RCH_2OH

• $R-X + NaC\equiv C-R \longrightarrow R-C\equiv C-R + NaX$

Step Down

$\Rightarrow$ RCH_2NH_2 (Higher Amine) $\xrightarrow{HONO}$ RCH_2OH Alcohol $\xrightarrow{[O]}$ $RCHO$ Aldehyde $\xrightarrow{[O]}$ $R-COOH$ Carboxylic Acid

RNH_2 (lower Amine) $\xuparrow{Br_2, KOH}$ $RCONH_2$ Amide $\xleftarrow{Heat}$ $R\,COONH_4$ Ammonium Salt of Acid $\xleftarrow{NH_3}$

$\rightarrow$ RCH_3 (Higher Alkane) $\xrightarrow{Cl_2}$ RCH_2Cl Alkyl chloride $\xrightarrow{aq\ KOH}$ RCH_2OH

$R-H$ $\xuparrow{NaOH, CaO}$ $RCOONa$ Sod. Salt $\xleftarrow{NaOH}$ $R\,COOH$ Carboxylic Acid $\xleftarrow{[O]}$ $RCHO$ Aldehyde $\xleftarrow{[O] \ Oxidation}$

Aldol Condensation

$$CH_3-\underset{\underset{H}{|}}{C}=O \;+\; H-CH_2\,CHO \;\xrightarrow{NaOH}\; CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH.O$$

$$CH_3-CH=CH-CHO \;\overset{H^+,\,H_2O}{\underset{\Delta}{\longleftarrow}}$$
$$+\,H_2O$$

Crossed aldol condensation

Aldol condensation b/w two different aldehydes is called crossed aldol condensation.

$$CH_3-\overset{O}{\overset{||}{C}}-H \;+\; H-\overset{O}{\overset{||}{C}}-H \;\xrightarrow[NaOH]{dil.}\; HO-CH_2-CH_2-\overset{O}{\overset{||}{C}}-H$$

Balz- Schiemann Rxⁿ

Aromatic primary amine is first diazotised with $NaNO_2$ in presence of HBF_4 (fluoroboric acid) at 273-278 K and the aryl diazonium tetrafluoroborate thus formed is heated to give the corresponding aryl fluoride

Aniline $\xrightarrow[273-278K]{NaNO_2/HBF_4}$ N_2BF_4 $\xrightarrow{\Delta}$ F $+ N_2 + BF_3$

Fluorobenzene
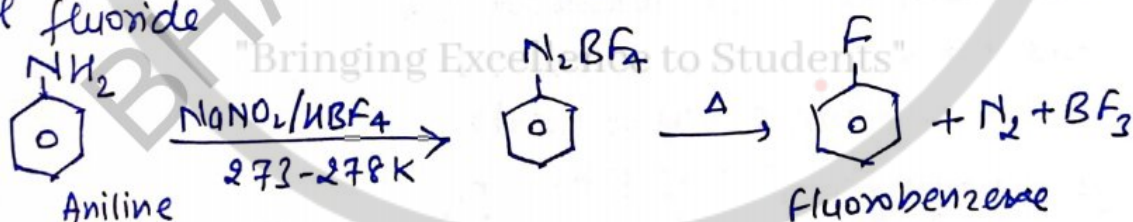
Benzoin Condensation

On heating with an ethanolic soln of KCN, two molecules of aromatic aldehydes undergo condensation to form benzoin.

$$\xrightarrow[\Delta]{Alc.\,KCN}$$ Benzoin.
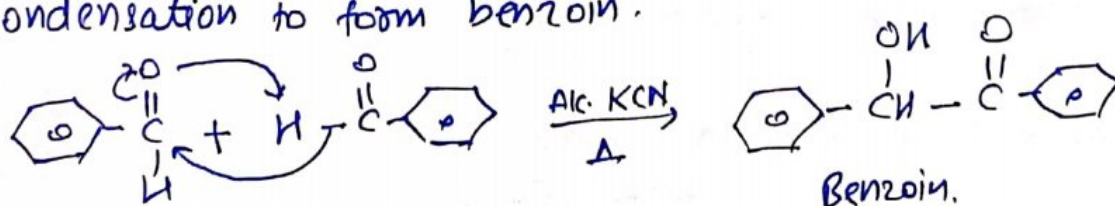
Cannizzaro Reaction

Aldehydes which do not contain an α-hydrogen atom, when treated with conc. alkali solution undergo disproportionation i.e self oxidation-reduction.

$$2H-\overset{O}{\overset{||}{C}}-H + NaOH \longrightarrow CH_3-OH + H-\overset{O}{\overset{||}{C}}-ONa$$

formaldehyde   Methyl alcohol.   Sod. formate

$$2 \langle O \rangle- CHO + NaOH \longrightarrow \langle O \rangle-CH_2OH + \langle O \rangle-COONa$$

Benzaldehyde   Benzyl alcohol   Sod. Benzoate
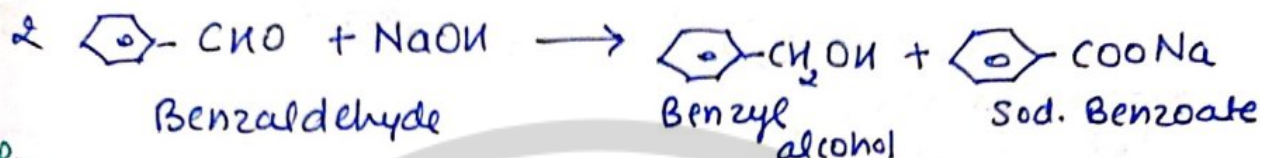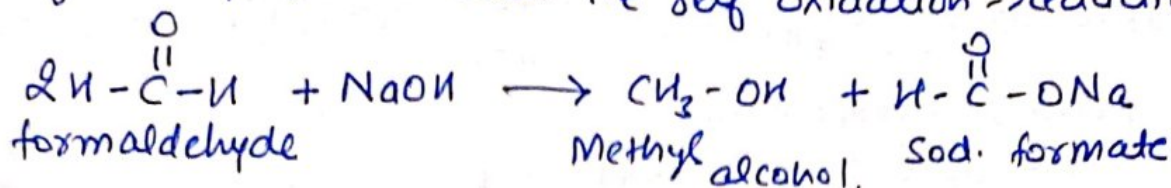
Carbylamine reaction

When a primary amine (aliphatic or aromatic) is warmed with chloroform and alc. KOH, it forms an isocyanide or carbylamine having offensive smell.

$$CH_3 CH_2 NH_2 + CHCl_3 + 3 KOH \text{ (alc)} \overset{\Delta}{\longrightarrow} CH_3 CH_2-N\overset{+}{\equiv}C$$
ethyl isocyanide   + 3KCl + 3H_2O

$$\langle O \rangle-NH_2 + CHCl_3 + 3 KOH \overset{\Delta}{\longrightarrow} \langle O \rangle-N\overset{+}{\equiv}C + 3KCl + 3H_2O$$

Phenyl carbyl amine
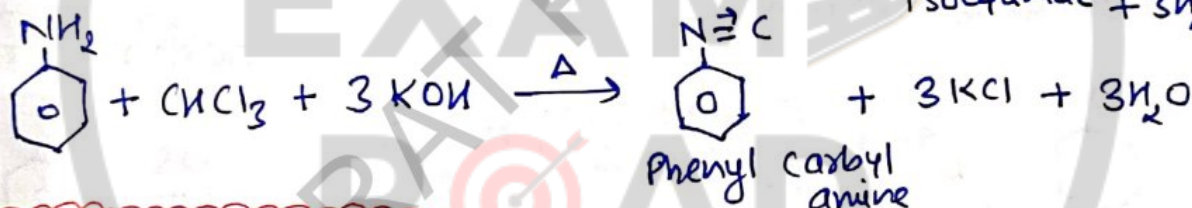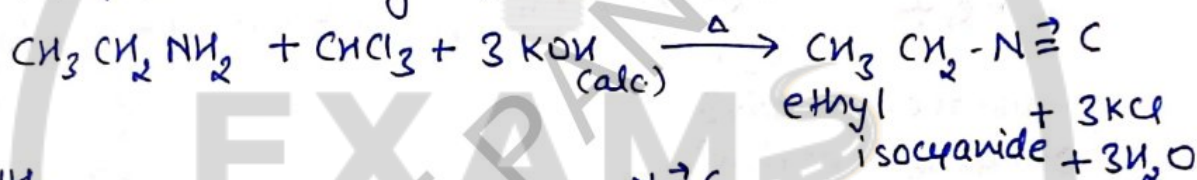
Clemmensen reduction

The reduction of aldehydes and ketones to corresponding hydrocarbons with amalgated zinc and conc. HCl is called clemmensen reduction.

$$CH_3CO CH_3 + 4[H] \xrightarrow[\Delta]{Zn/Hg + Conc.HCl} CH_3 CH_2 CH_3 + H_2O$$

$$\langle O \rangle-COCH_3 + 4[H] \xrightarrow[\Delta]{Zn/Hg + Conc.HCl} \langle O \rangle-CH_2CH_3 + H_2O$$

Ethyl benzene
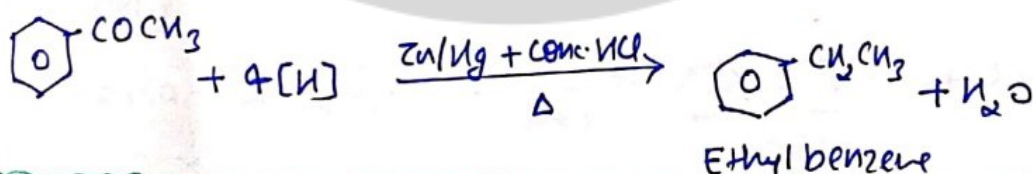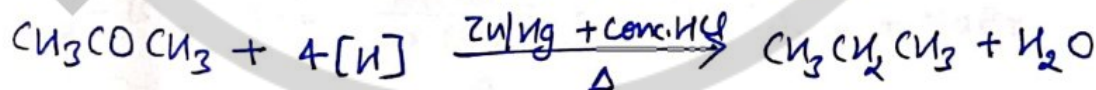
The reduction works better with ketones than aldehydes

Decarboxylation Reaction

The process of removal of a molecule of CO_2 from a carboxylic acid.

$$\langle O \rangle-COOH + 2 NaOH \xrightarrow{CaO, 630K} \langle O \rangle + Na_2CO_3 + H_2O$$
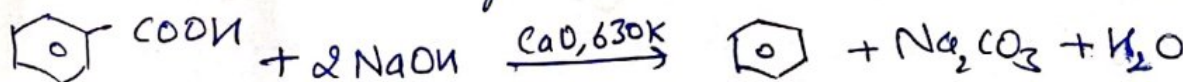
Coupling Reaction

The reaction of diazonium salts with phenol and aromatic amines to form azo compounds

$$\text{Ph-}N_2Cl + \text{Ph-}OH \xrightarrow[\text{(pH 9-10)}]{273-278k, OH^-} \text{Ph-}N_2\text{-Ph-}OH + HCl$$
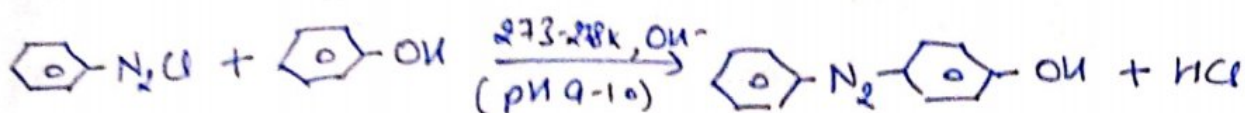
p-Hydroxyazobenzene
(Orange dye)

$$\text{Ph-}N_2Cl + \text{Ph-}NH_2 \xrightarrow[\text{(pH 4-5)}]{273-278k, H^+} \text{Ph-}N_2\text{-Ph-}NH_2$$
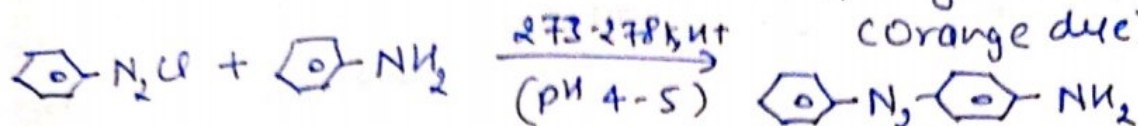
p-Aminoazobenzene
(yellow dye)

Diazotisation Reaction

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$

Nitrous Acid

$$\text{Ph-}NH_2 + HONO + HCl \xrightarrow{273-278k} \text{Ph-}N_2Cl + 2H_2O$$

$$\text{Ph-}NH_2 + HONO + H_2SO_4 \xrightarrow{273-278k} \text{Ph-}N_2HSO_4^- + 2H_2O$$
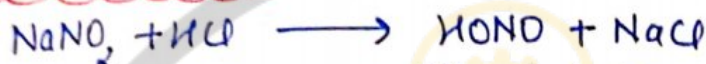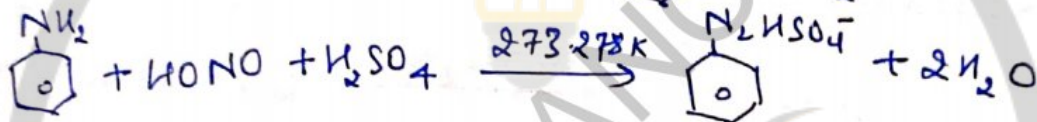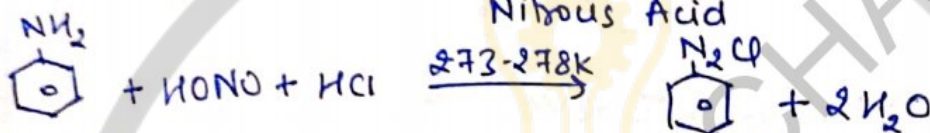
Benzene diazonium hydrogen sulphate
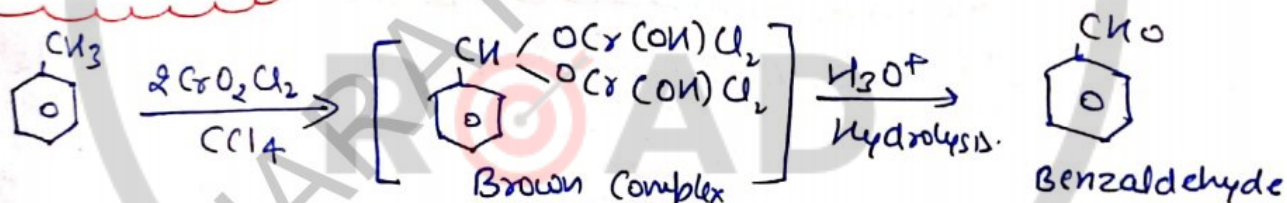
Etard Reaction

$$\text{Ph-}CH_3 \xrightarrow[CCl_4]{2\,CrO_2Cl_2} \left[\text{Ph-}CH \begin{array}{c} OCr(OH)Cl_2 \\ OCr(OH)Cl_2 \end{array} \right] \xrightarrow[\text{Hydrolysis}]{H_3O^+} \text{Ph-}CHO$$

Brown Complex   Benzaldehyde

Finkelstein Reaction

$$CH_3CH_2-Br + NaI \xrightarrow[\text{or Methanol}\atop \Delta]{Acetone} CH_3CH_2-I + NaBr$$

Fittig Reaction

$$\text{Ph-}Cl + 2Na + Cl\text{-Ph} \xrightarrow[\text{ether}]{Dry} \text{Ph-Ph} + 2NaCl$$

Diphenyl

Friedal craft Reaction

(a) Alkylation

$$\text{Ph} + CH_3Cl \xrightarrow[AlCl_3]{Anhy} \text{Ph-}CH_3 + HCl$$

(b) Acylation

$$\text{Ph} + CH_3COCl \xrightarrow[AlCl_3]{Anhy} \text{Ph-}COCH_3 + HCl$$
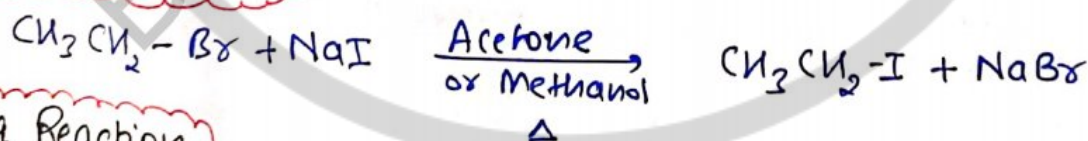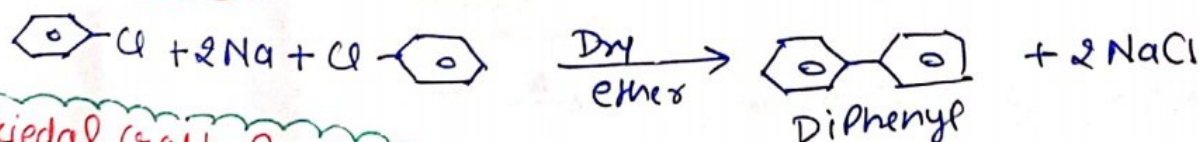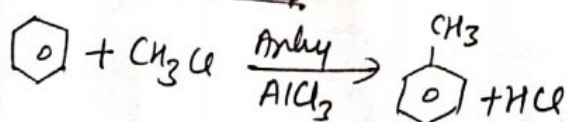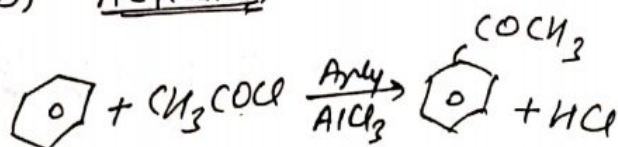
Gabriel phthalimide synthesis

Phthalimide $\xrightarrow[-H_2O]{KOH(alc.)}$ Pot. phthalimide $+ CH_3CH_2I \xrightarrow{-KI}$

N-Ethyl phthalimide $\xrightarrow[\text{Hydrolysis}]{H_2O, H^+}$ $\begin{array}{c} COOH \\ COOH \end{array} + CH_3CH_2NH_2$

Gattermann Reaction

N_2Cl $\xrightarrow{Cu/HCl}$ Cl $+ N_2$

$\xrightarrow{Cu/HBr}$ Br $+ N_2$
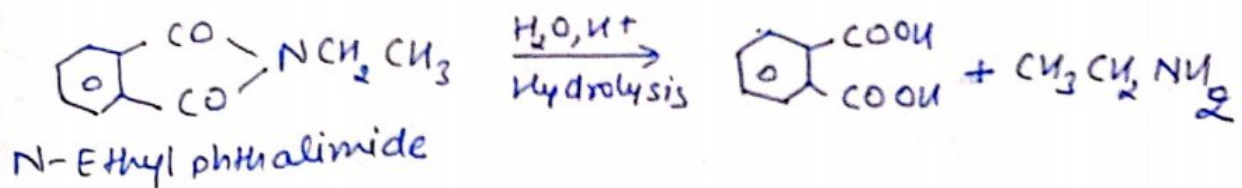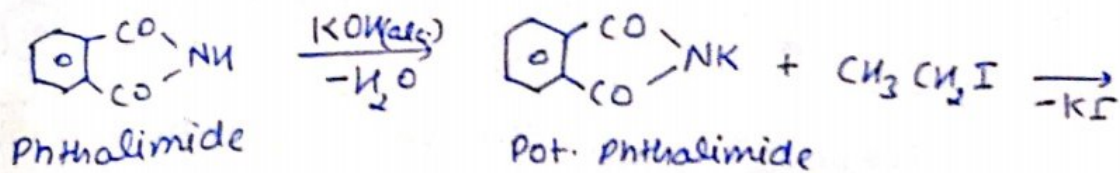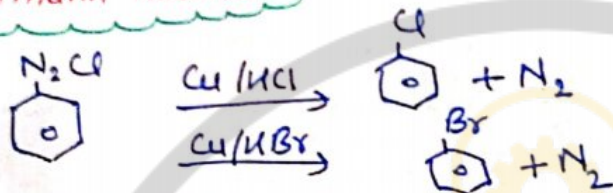
Gattermann Koch Reaction

Most Important for Conversion

$+ CO + HCl \xrightarrow{AlCl_3 + CuCl}$ CHO $+ HCl$

Benzaldehyde
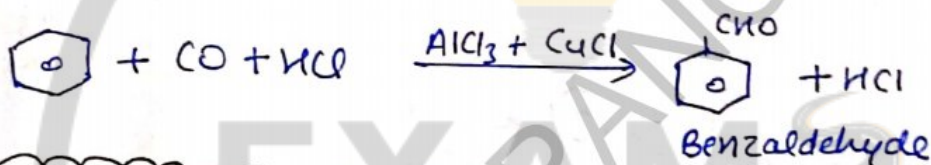
H.V.Z Reaction → Hell Volhard Zelinsky Reaction

$\overset{\alpha}{C}H_3COOH \xrightarrow[-HCl]{Cl_2,P} ClCH_2COOH \xrightarrow[-HCl]{Cl_2,P} Cl_2CHCOOH \xrightarrow[-HCl]{Cl_2,P} Cl_3CCOOH$
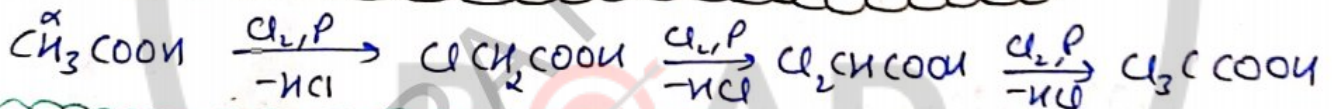
Hofmann Ammonolysis of Alkyl Halides

$H_3N: + R-X \xrightarrow{-HX} R-NH_2 + R-X \xrightarrow{-HX} R-NH-R + R-X$

Ammonia $1°$ amine $2°$ amine

$\downarrow$

$R-N-R$
    $|$
    R $3°$ amine
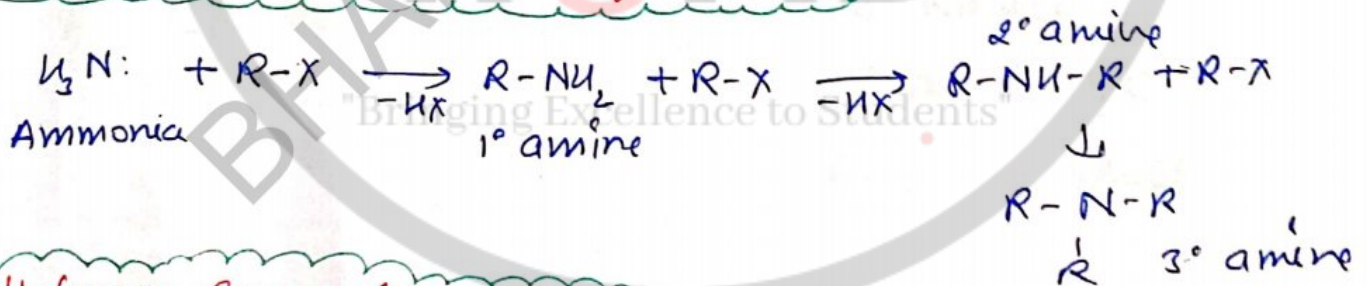
Hofmann Bromamide Reaction

$RCONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} R-NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$

$\langle \rangle - CONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} \langle \rangle - NH_2 + 2KBr + K_2CO_3 + 2H_2O$

Hunsdiecker Reaction

$RCOOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4, 350k} R-Br + CO_2 + AgBr$
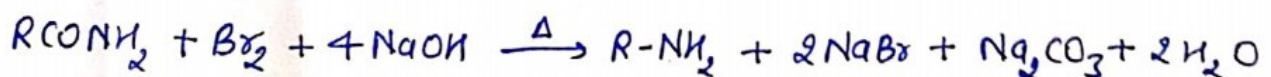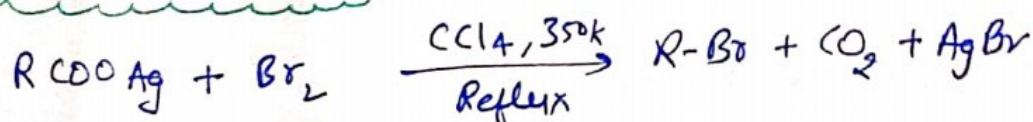
Kolbe Reaction or Kolbe - Schmitt Reaction
Most Important

$$\text{(ONa-phenol)} + CO_2 \xrightarrow[400K]{4.7 \text{ atm}} \text{(OH, COONa)} \xrightarrow[H_2O]{H^+} \text{(OH, COOH)} \quad \text{(Salicylic Acid)}$$
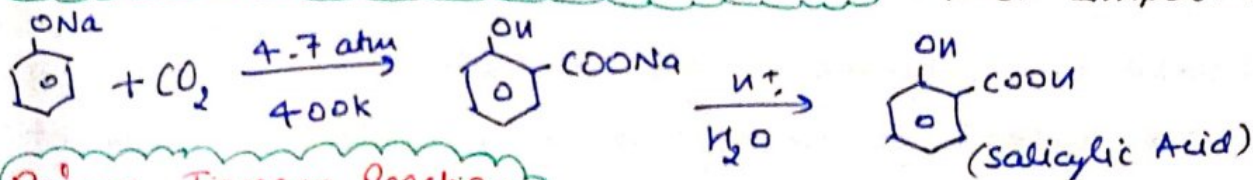
Reimer - Tiemann Reaction
[Most Important]

$$\text{(OH-phenol)} + CHCl_3 \xrightarrow{NaOH} \left[\text{(ONa, CHCl}_2\text{)} \xrightarrow[-2NaCl]{2 NaOH} \text{(ONa, CH(OH)}_2\text{)} \xrightarrow{-H_2O} \right]$$

$$\text{(ONa, CHO)} \xrightarrow[-NaCl]{Dil.HCl} \text{(OH, CHO)} \quad \text{salicylaldehyde}$$
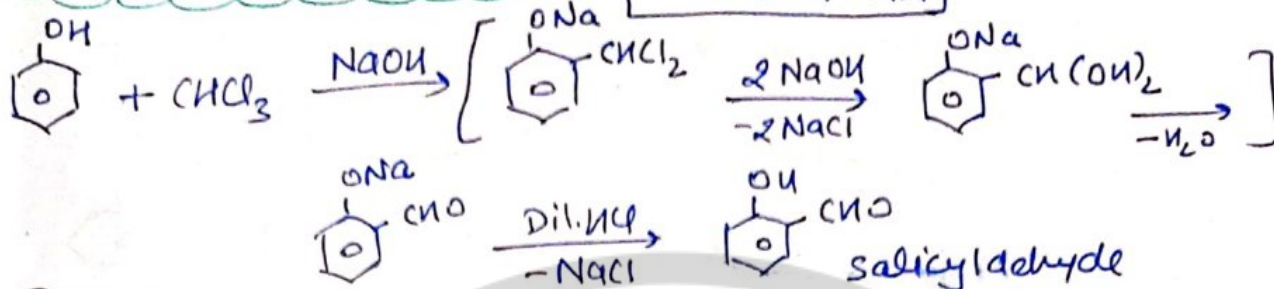
Rosenmund Reduction
[Most Important]

$$R-\overset{O}{\underset{\|}{C}}-Cl + H_2 \xrightarrow[\substack{Boiling \\ Xylene}]{Pd, BaSO_4, S} R-\overset{O}{\underset{\|}{C}}-H + HCl$$

Sandmeyer Reaction

$$N_2Cl\text{-ring} \begin{cases} +HCl & \xrightarrow{Cu Cl} & \text{Cl-ring} + N_2 + Cl^- \\ +HBr & \xrightarrow{Cu Br} & \text{Br-ring} + N_2 + Cl^- \\ +KCN & \xrightarrow{Cu CN} & \text{CN-ring} + N_2 + Cl^- \end{cases}$$

Stephen Reduction

$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2[H]$$

$$R-C\equiv N + 2[H] + HCl \xrightarrow[ether]{Dry} R-CH=NH\cdot HCl$$

$$\downarrow \text{Boiling } H_2O$$

$$R-CH=O + NH_4Cl$$
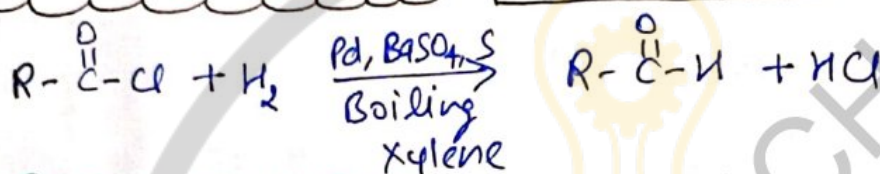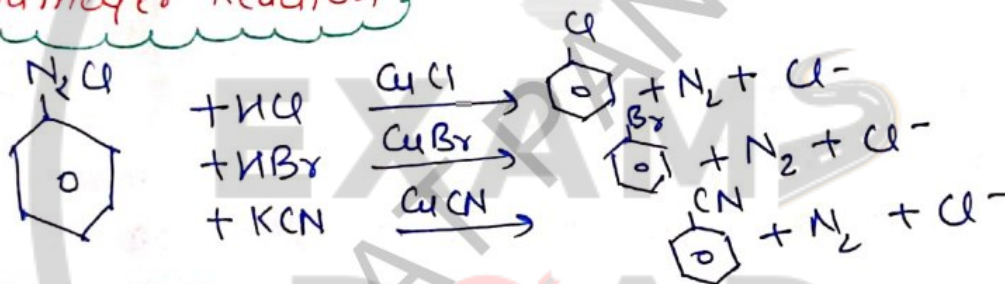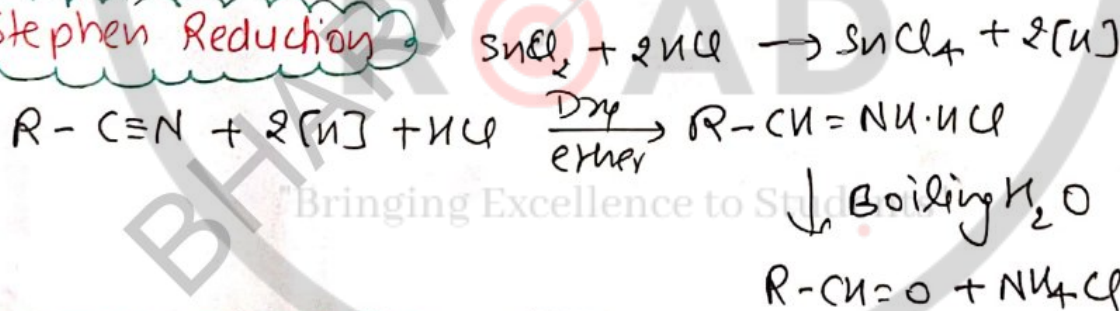
Williamson Synthesis [Imp]

$$R-X + R'-ONa \longrightarrow R-O-R' + NaX$$

$$CH_3I + CH_3CH_2ONa \longrightarrow CH_3-O-CH_2CH_3 + NaI$$

$$\text{(ONa-ring)} + CH_3I \longrightarrow \text{(OCH}_3\text{-ring)} + NaI$$

Best method for the preparation of ether

Wolff - Kishner reduction — Most Important

The reduction of corresponding aldehydes and ketones to the corresponding hydrocarbons by heating them with hydrazine and KOH

$$R-CHO \xrightarrow[glycol]{H_2N-NH_2 ,KOH} R-CH_3 + N_2$$

$$CH_3COCH_3 \xrightarrow{\quad\quad} CH_3 CH_2 CH_3$$

$$\langle O \rangle - COCH_3 \xrightarrow{\quad\quad} \langle O \rangle - CH_2 CH_3$$

Wurtz Reaction

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

$$CH_3-Br + 2Na + Br-CH_3 \xrightarrow{\quad\quad} CH_3-CH_3 + 2NaBr$$
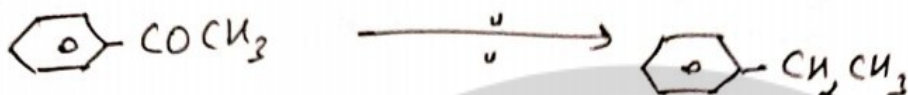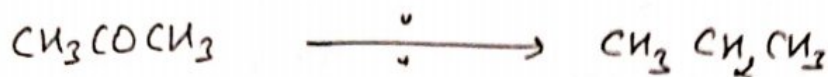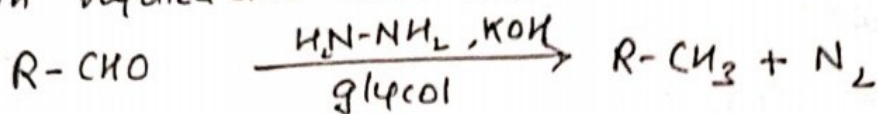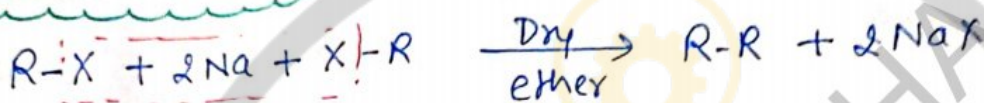
Wurtz-Fittig Reaction

Used to prepare homologous of benzene by warming a mixture of an aryl halide and an alkyl halide with metallic sodium in presence of dry ether

$$\langle O \rangle - Br + 2Na + Br-CH_3 \xrightarrow[\Delta]{Dry\ ether} \langle O \rangle - CH_3 + 2NaBr$$

$$\langle O \rangle - Br + 2Na + Br-CH_2CH_3 \xrightarrow[\Delta]{Dry\ ether} \langle O \rangle - CH_2CH_3 + 2NaBr$$

(+R) Positive Resonane

(-R) Negative Resonance
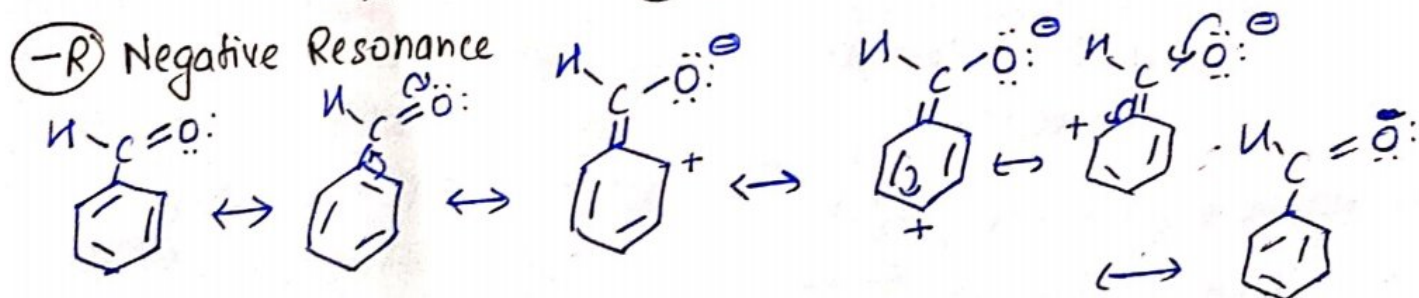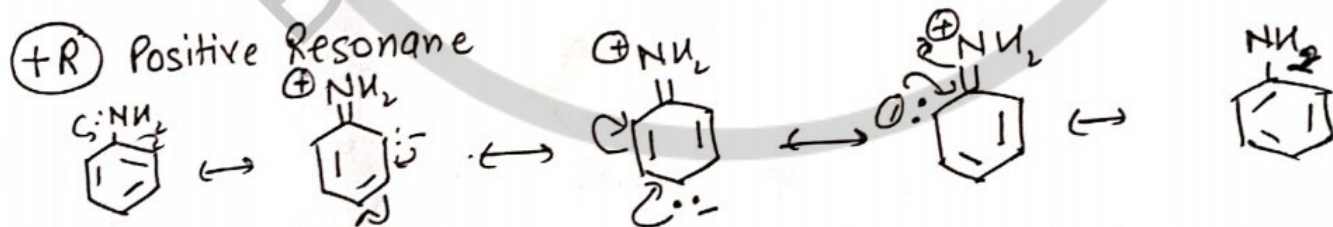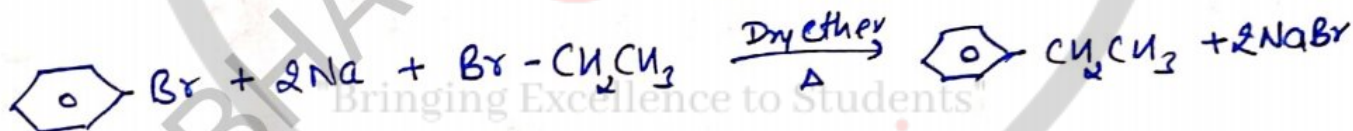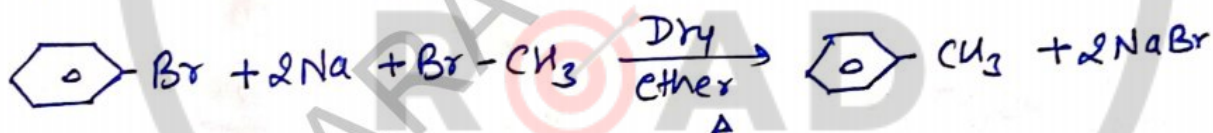
Distinction between pair of Compounds TEST

⇒ How will you distinguish b/w propanol & propanone
$(CH_3CH_2CH_2OH)$ (CH_3COCH_3)

Ans.

IODOFORM TEST

Propanol	Propanone
$CH_3CH_2CH_2OH$ $+ I_2 + NaOH$ $\longrightarrow$ No Reaction	$CH_3COCH_3 + I_2 + NaOH$ $\longrightarrow CHI_3 + CH_3COONa$ Yellow ppt $+ H_2O + NaI$
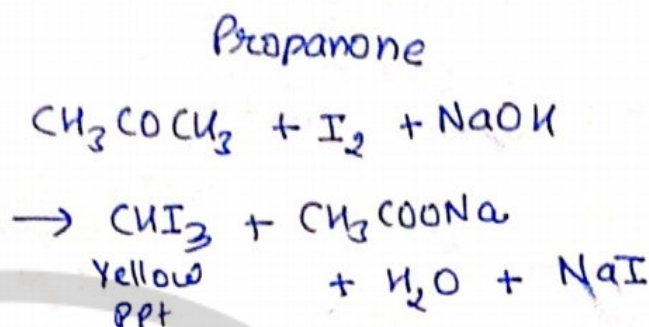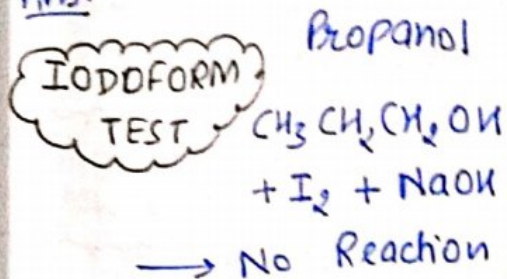
⇒ How will you distinguish b/w ethanol and phenol

Ans.

	Ethanol	Phenol
Litmus Test	Does not give litmus test	Turns blue litmus into red
Iodoform Test	$CH_3CH_2OH + NaOI$ $\longrightarrow CHI_3 + HCOONa +$ (Yellow ppt) $NaI + 2NaOH + H_2O$	OH ⬡ $+ NaOI \longrightarrow$ No yellow ppt of CHI_3
Br₂ water Test		

OH ⬡ $+ 3Br_2 (aq) \longrightarrow$ Br—⬡—Br $+ 3HBr$ Br
2,4,6-Tribromo phenol (white ppt)

$CH_3CH_2OH \xrightarrow[water]{Br_2}$ No white ppt.

दूर का उदाहरण है ज्यादा
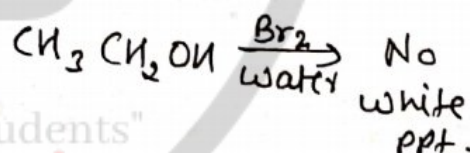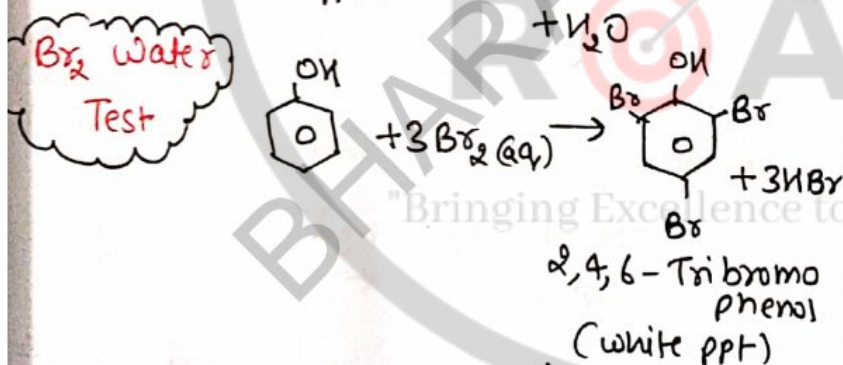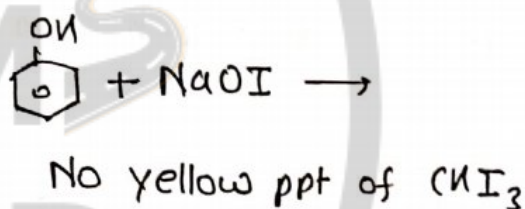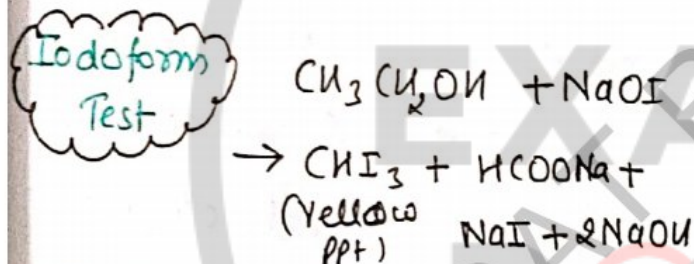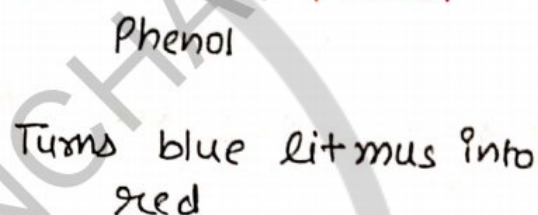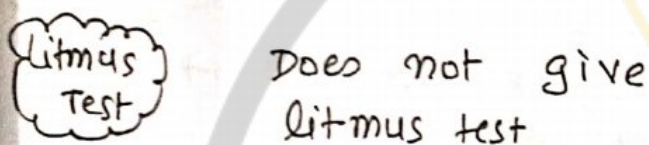
⇒ How will you distinguish b/w ethanal and propanal
(CH_3CHO) (CH_3CH_2CHO)

Iodoform Test

Ethanal	Propanal
$CH_3CHO + 3I_2 + 4NaOH$ $\xrightarrow{Heat} CHI_3 + HCOONa$ $+ 3NaI + 3H_2O$	$CH_3CH_2CHO + I_2 + NaOH$ $\longrightarrow$ No yellow ppt of CHI_3
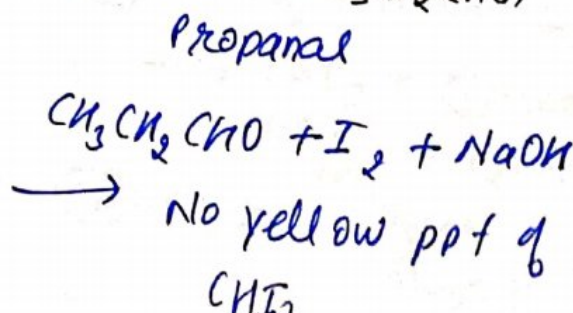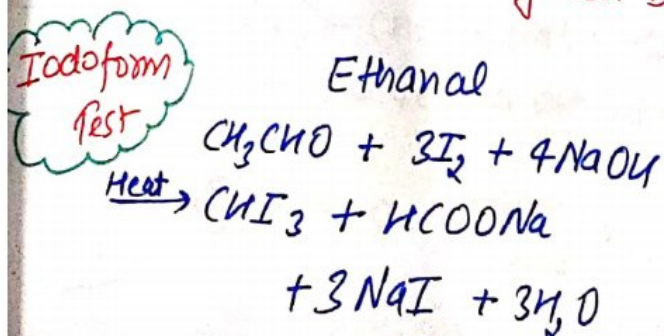
⇒ How will you distinguish b/w Propanal and Propanone
(CH_3CH_2CHO) (CH_3COCH_3)

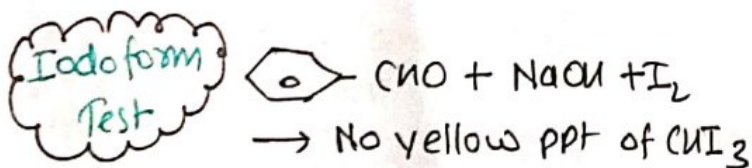|	Propanal	Propanone

Iodoform Test

$CH_3CH_2CHO + I_2 + NaOH$

→ No yellow ppt of CHI_3

$CH_3COCH_3 + I_2 + NaOH$

→ CHI_3 + CH_3COONa
Iodoform   + H_2O + NaI

Tollen's Reagent Test

$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$
          Tollen's Reagent

→ $CH_3CH_2COO^- + 2Ag↓ + 4NH_3 + 2H_2O$
          Silver
          mirror

$CH_3COCH_3 \xrightarrow{\text{Tollen's Reagent}}$

No Silver Mirror

Fehling Solun Test

$CH_3CH_2CHO + 2Cu^{2+} + 5OH^-$
          From Fehling sol.

→ $CH_3CH_2COO^- + Cu_2O + 3H_2O$
          Red ppt.

$CH_3COCH_3 \xrightarrow{\text{Fehling Sol.}}$ No Red ppt

⇒ How will you distinguish b/w Butanal and Butan-2-one

Ans. Same As Above

⇒ Distinguish b/w Pentan-2-one and Pentan-3-one.
   $(CH_3COCH_2CH_2CH_3)$ $(CH_3CH_2COCH_2CH_3)$

Iodoform Test

$CH_3COCH_2CH_2CH_3 + I_2 + NaOH$

→ $CHI_3 + C_3H_7COONa$
   $+ H_2O + NaI$

$CH_3CH_2COCH_2CH_3 + I_2 + NaOH$

→ No yellow ppt of CHI_3
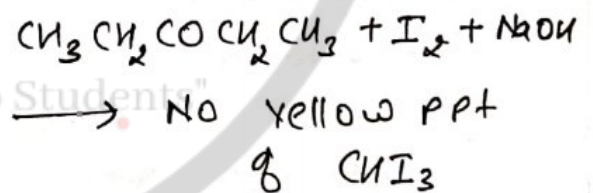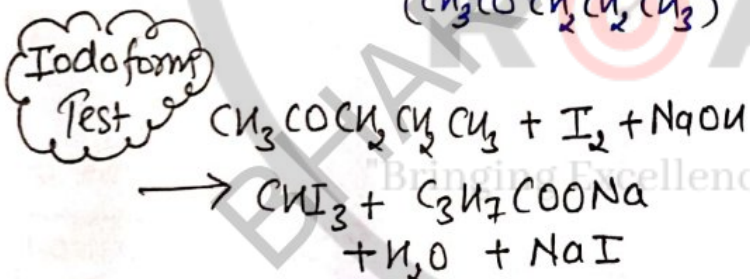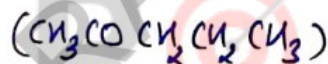
⇒ Distinguish b/w Benzaldehyde and Acetophenone.
   (⬡-CHO)   (⬡-COCH₃)
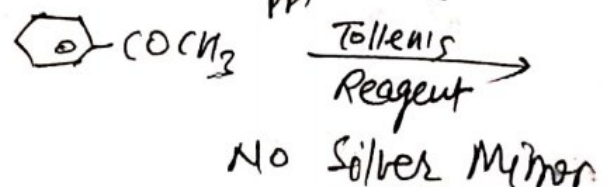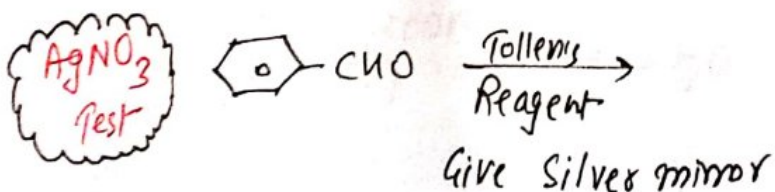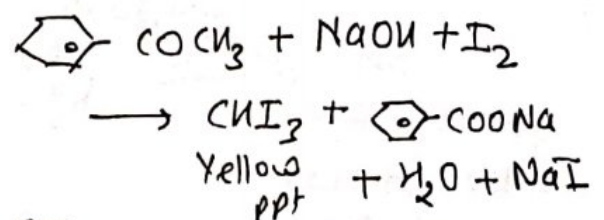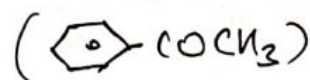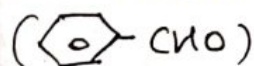
Iodoform Test

⬡-CHO + NaOH + I_2

→ No yellow ppt of CHI_3

⬡-COCH₃ + NaOH + I_2

→ CHI_3 + ⬡-COONa
   Yellow ppt + H_2O + NaI

AgNO₃ Test

⬡-CHO $\xrightarrow{\text{Tollen's Reagent}}$

Give Silver mirror

⬡-COCH₃ $\xrightarrow{\text{Tollen's Reagent}}$

No Silver Mirror

⇒ Acetophenone (⬡–COCH₃) and benzophenone (⬡–CO–⬡)

Iodoform Test

$$⬡–COCH_3 + I_2 + NaOH$$
$$\rightarrow CHI_3 + ⬡–COONa$$
$$+ H_2O + NaI$$

$$⬡–CO–⬡ + I_2 + NaOH$$
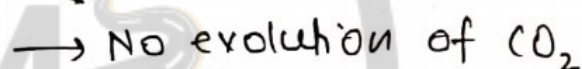$$\rightarrow \text{No yellow ppt of } CHI_3$$
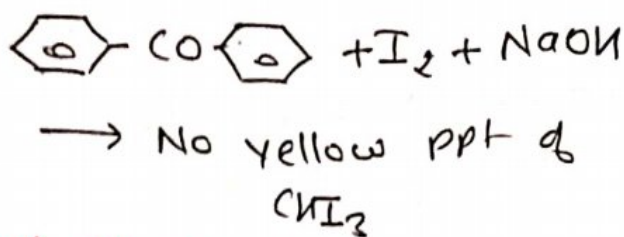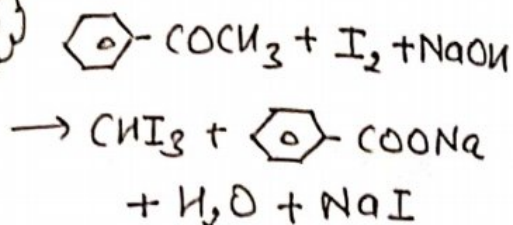
⇒ Methanoic acid or formic acid and ethanoic acid or acetic acid
(HCOOH)   (CH₃COOH)

Tollen's Reagent
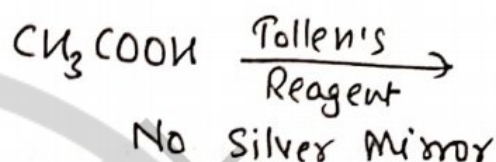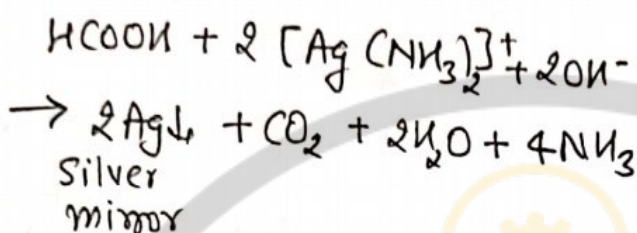
$$HCOOH + 2[Ag(NH_3)_2]^+ + 2OH^-$$
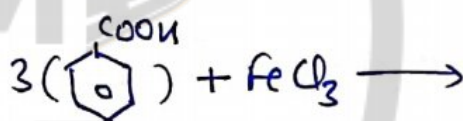$$\rightarrow 2Ag\downarrow + CO_2 + 2H_2O + 4NH_3$$
Silver mirror

$$CH_3COOH \xrightarrow{\text{Tollen's Reagent}}$$
No Silver Mirror

⇒ Benzoic Acid (⬡–COOH) and Phenol (⬡–OH) M.IMP

NaHCO₃ Test

$$\underset{⬡}{COOH} + NaHCO_3 \rightarrow$$
$$⬡–COONa + CO_2\uparrow + H_2O$$

$$\underset{⬡}{OH} + NaHCO_3$$
$$\rightarrow \text{No evolution of } CO_2$$

FeCl₃ Test

$$\underset{⬡}{OH} + FeCl_3 \rightarrow \text{Violet colouration}$$

$$3(\underset{⬡}{COOH}) + FeCl_3 \rightarrow$$
$$(⬡–COO)_3Fe + 3HCl$$
Buff coloured ppt (ferric Benzoate)
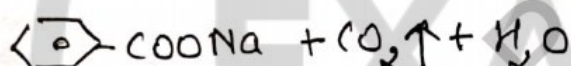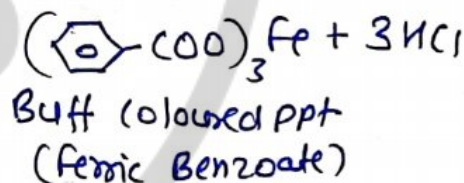
⇒ Benzaldehyde and Benzoic Acid

NaHCO₃ Test
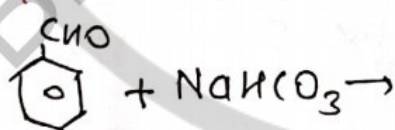
$$\underset{⬡}{CHO} + NaHCO_3 \rightarrow$$
No effervescence due to evolution of CO_2

$$\underset{⬡}{COOH} + NaHCO_3 \rightarrow$$
$$\underset{⬡}{COONa} + CO_2\uparrow + H_2O$$
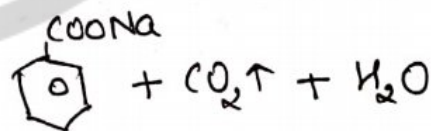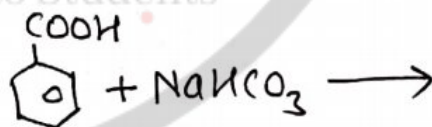
⇒ Benzoic acid and ethyl benzoate

NaHCO₃ Test

$$\underset{⬡}{COOH} + NaHCO_3 \rightarrow$$
$$\underset{⬡}{COONa} + CO_2\uparrow + H_2O$$

$$\underset{⬡}{COOC_2H_5} \xrightarrow{NaHCO_3}$$
No effervescence due to evolutn of CO_2
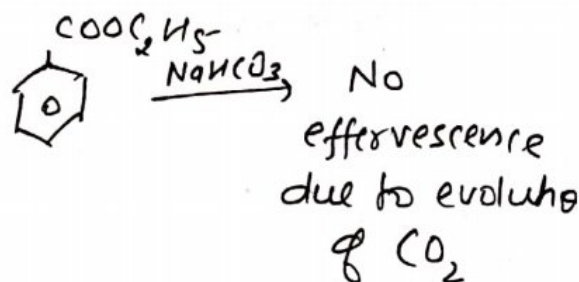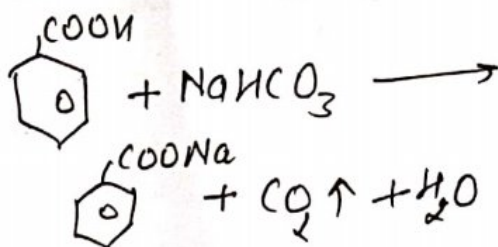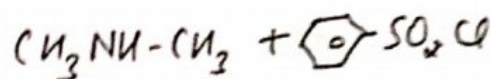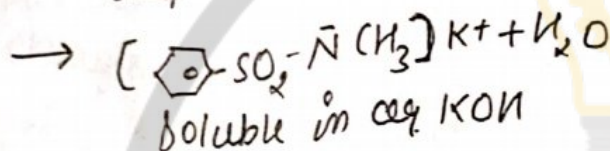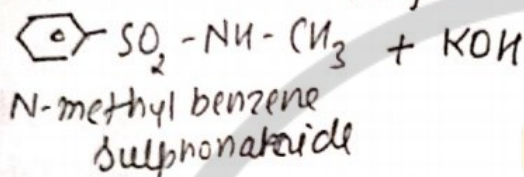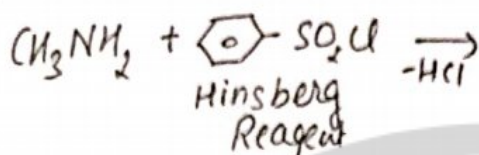
⇒ Methylamine (CH_3NH_2) and dimethylamine (CH_3NHCH_3)
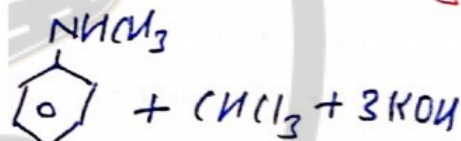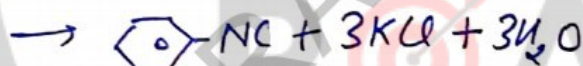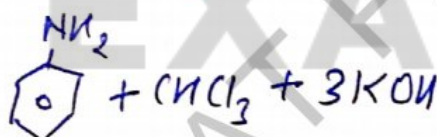
M.Imp   1° amine   2° amine

Carbylamine Test

$CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta}$ $CH_3NHCH_3 + CHCl_3 + 3KOH$

$CH_3NC + 3KCl + 3H_2O$ $\xrightarrow{\Delta}$ No Reaction

Hinsberg Reagent

$CH_3NH_2 + \langle o \rangle-SO_2Cl \xrightarrow[-HCl]{}$ $CH_3NH-CH_3 + \langle o \rangle-SO_2Cl$

Hinsberg Reagent

$\longrightarrow \langle o \rangle-SO_2-N-CH_3$
                 CH_3

$\langle o \rangle-SO_2-NH-CH_3 + KOH$ N,N-Dimethyl benzene
N-methyl benzene   sulphonamide
sulphonamide

$\longrightarrow [\langle o \rangle-SO_2-\bar{N}(CH_3)]K^+ + H_2O$ $\xrightarrow{\text{insoluble in aq. KOH.}}$
soluble in aq. KOH
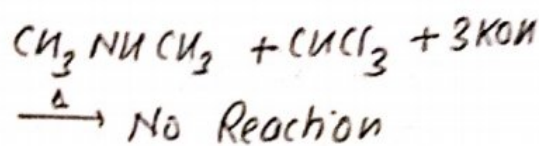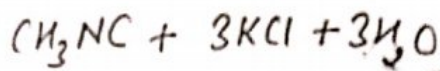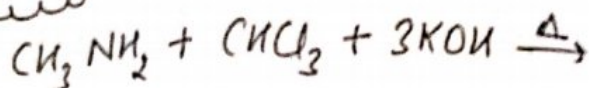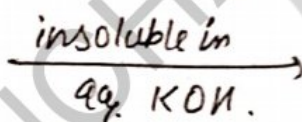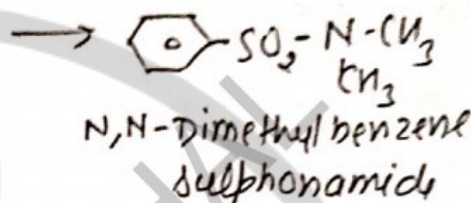
⇒ Aniline ($\langle o \rangle-NH_2$) and N-methyl aniline ($\langle o \rangle-NH-CH_3$)

Carbylamine Test

$\langle o \rangle$–NH_2 + $CHCl_3$ + $3KOH$ $\langle o \rangle$–$NHCH_3$ + $CHCl_3$ + $3KOH$

$\longrightarrow \langle o \rangle-NC + 3KCl + 3H_2O$ $\longrightarrow$ No Rxn

Hinsberg Reagent Test

"Bringing Excellence to Students"

$\langle o \rangle-SO_2Cl + \langle o \rangle-NH_2 \xrightarrow{-HCl}$ $\langle o \rangle-SO_2Cl + \langle o \rangle-NHCH_3$

$\langle o \rangle-SO_2-NH-\langle o \rangle + KOH$ $\xrightarrow{-HCl} \langle o \rangle-SO_2-N-\langle o \rangle$
                                 CH_3

$\longrightarrow [\langle o \rangle-SO_2-\bar{N}-\langle o \rangle]K^+$ Insoluble in
soluble in aq. KOH $+H_2O$ aq. KOH.
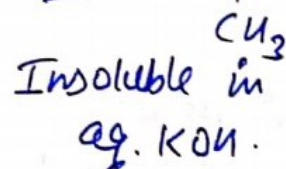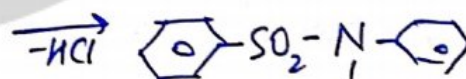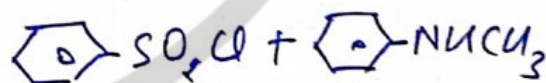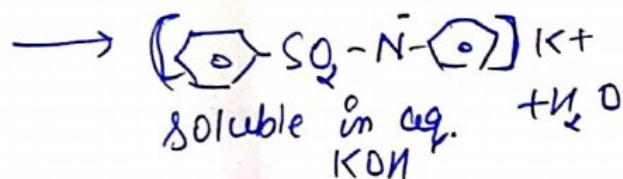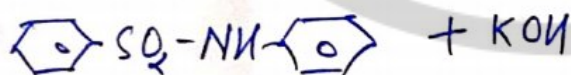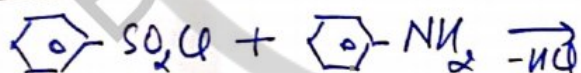
Ques. Related to Physical Properties

- p-dichlorobenzene has higher m.pt than that of ortho or meta isomer

Ans: p-Dichlorobenzene has higher m.pt than those of o- and m-isomers because it is more symmetrical and packing is better in solid form. Hence, it has stronger intermolecular forces of attraction than o- and m-isomers

- Alkyl halides though polar are immiscible with water

Ans: Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H-bond among water molecules is much higher than energy released by water Halide interaction

- Why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

Ans.

Cyclohexyl Chloride — Sp^3
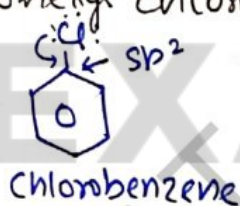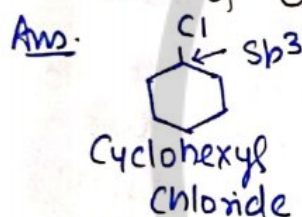
Chlorobenzene — Sp^2

In chlorobenzene C-Cl bond has some double bond character So its bond length is smaller Hence dipole moment is smaller than cyclohexyl chloride which has a longer C-Cl single bond.

Solubility of alcohols

Solubility of alcohols in water is due to their ability to form hydrogen bond with water molecules The solubility decreases with increase in size of alkyl groups and solubility increases with increase in branching and the order is $1° < 2° < 3°$

Boiling Points

The B.Pt of alcohol increases with increase in no. of carbon atoms as van der waal forces increases and the b.pt decreases with increase in branching of carbon chain due to decrease in Van der Waal's forces with decrease in surface area and the order is $1° > 2° > 3°$

Acidity of alcohols (reaction with metals)

$$2ROH + 2Na \longrightarrow 2RONa + H_2$$
Sod. alkoxide
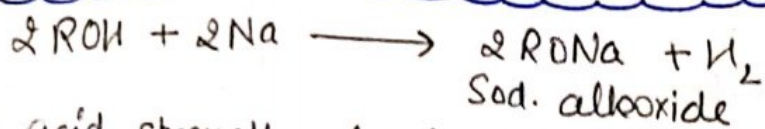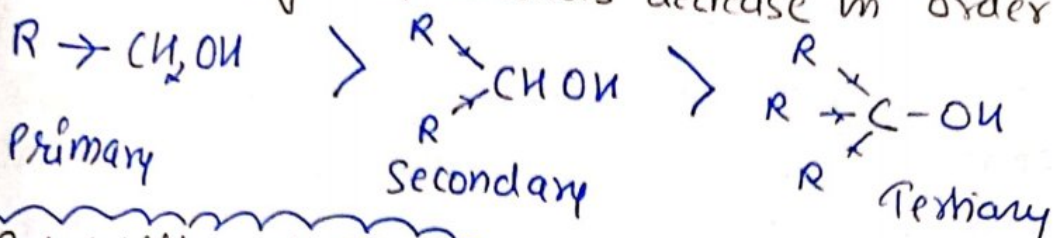
The acid strength of alcohols decrease in order

$$R \rightarrow CH_2OH > \underset{R}{\overset{R}{\diagdown}}CHOH > \underset{R}{\overset{R}{\underset{|}{R \rightarrow C - OH}}}$$

Primary   Secondary   Tertiary

Solubility of Ethers

Ethers are soluble in water to certain extent due to hydrogen bonding.
- Solubility decreases with increase in mol. mass.
- Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene eh.

Boiling Points

Ethers have lower B.Pt than isomeric alcohols due to their inability to form hydrogen bonds and get associated.
- But lower ethers have slightly higher B.Pt than n-alkanes of comparable molecular masses due to dipole-dipole interactions.
- Higher ethers (containing carbon atom more than four) have slightly lower B.Pt than n-alkanes of comparable molecular masses due to weak Van der Waal's forces of attraction.

Solubility of Phenols

like alcohols, phenols are soluble in water due to the formation of hydrogen bonding with water
- Phenols are less soluble than alcohols due to large hydrocarbon (benzene ring) part.
- Phenols are soluble in alcohols, ethers and also in NaOH.

Boiling Point

Much higher than the corresponding aromatic hydrocarbons and haloarenes due to inter molecular Hydrogen Bonding

Boiling Point of Aldehyde & Ketones

The B.Pt of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak dipole dipole interactions

- Their b.pt are lower than those of alcohols of similar molecular masses due to absence of intermolecular H-Bond.

- Among isomeric aldehydes and ketones, ketones have slightly higher B.Pt due to the presence of two e⊖ releasing alkyl group which make carbonyl group more polar.

Solubility of aldehydes and ketones

Lower members of aldehydes and ketones (upto C4) are soluble in water due to H-Bonding b/w polar carbonyl group and water. However, solubility decreases with increase in mol.wt.

- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.

- All carbonyl compounds are fairly soluble in organic solvents.

Solubility of carboxylic Acid

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to formation of hydrogen bonds with water.

- The solubility decreases with increasing no. of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.

- Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.

- Carboxylic acids are soluble in less polar organic solvents like benzene, ether, alcohol, chloroform etc.

Boiling Point Of Carboxylic Acid

Carboxylic acids are higher b.pt than aldehydes, ketones and even alcohols of comparable molecular mass due to more extensive association of their molecules through inter molecular H-Bonding. The H-Bonds are not broken completely even in their vapour phase

Boiling point and solubility of Amines

$1°$ and $2°$ amines have higher B.Pt than other organic compounds due to hydrogen bonding

Primary and secondary amines are soluble in water due to H-Bonding b/w $>NH_2$ and H_2O molecules

Basic Character Of Amines

- Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom.

- Aliphatic amines are stronger bases than ammonia due to $+I$ effect of alkyl groups present in amines

- Aromatic amines are weaker bases than ammonia due to $-I$ effect of aryl group.

- Beside inductive effect there are other effects like steric effect, solvation effect, resonance effect which affect the basic strength of amines.

- In gaseous phase, the order of basicity of amines is
$$3° \text{ amine} > 2° \text{ amine} > 1° \text{ amine} > NH_3$$

- In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also plays an important role. Thus, the order of basicity of amines is
$$(C_2H_5)_2 NH > (C_2H_5)_3 N > C_2H_5 NH_2 > NH_3$$
and $(CH_3)_2 NH > CH_3NH_2 > (CH_3)_3 N > NH_3$
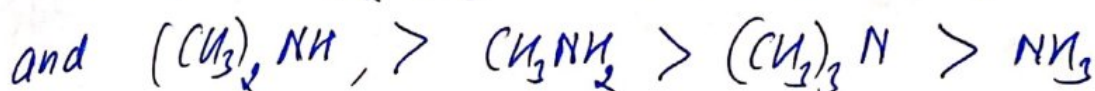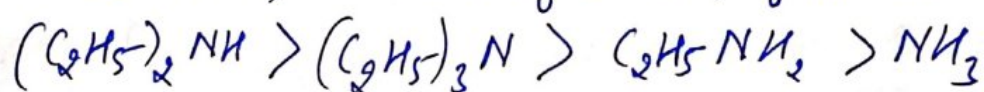
POLYMERS

⇒ Poly olefins

Polymers	Str. of Monomers
- Polythene	$CH_2 = CH_2$ (Ethylene)
- Polypropylene	$CH_3 - CH = CH_2$ (Propylene)
- Teflon (P.T.F.E) Poly Tetra Floro ethene	$CF_2 = CF_2$ (Tetra fluoro ethene)
- Poly Vinyl Chloride (PVC)	$CH_2 = CH$ (chloroethene) $\quad\;\;\mid$ $\quad\;\;Cl$ (Vinyl Chloride)
- Poly Acrylo Nitrile (PAN) (Orlon)	$CH_2 = CH$ Acrylo Nitrile $\quad\;\;\mid$ $\quad\;\;CN$ (Vinyl Cyanide)
- Polystyrene (Styron)	$CH_2 = CH$ (Styrene)
- Poly methyl meth acrylate (PMMA)	$CH_2 = C - COOCH_3$ $\qquad\;\mid$ $\qquad\;CH_3$ Methyl meth acrylate
- Poly mono chloro tri fluoro ethylene (PCTFE)	$Cl - C = CF_2$ (Chloro tri fluoro $\quad\;\;\mid$ ethylene) $\quad\;\;F$
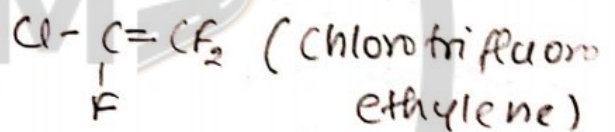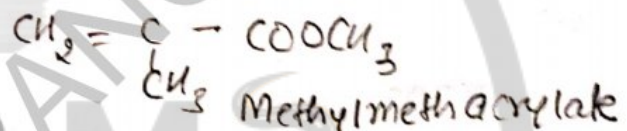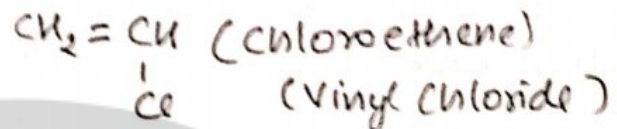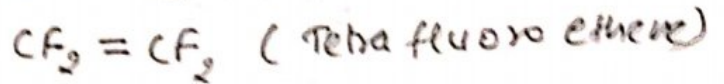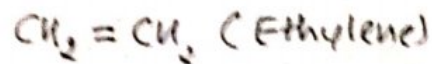
⇒ Polydienes

Natural Rubber (cis -1,4- polyisoprene)	$CH_2 = C - C = CH_2$ $\qquad\;\mid$ $\qquad\;CH_3$ Isoprene (2-Methyl-1,3-butadiene)
Neoprene (Synthetic rubber)	$CH_2 = C - CH = CH_2$ $\qquad\;\mid$ $\qquad\;Cl$ Chloroprene (2-chloro-1,3- butadiene)
Buna-S (SBR) (Styrene Butadiene Rubber)	$CH_2 = CH - CH = CH_2 \; + $ $CH = CH_2$ 1,3- Butadiene Styrene
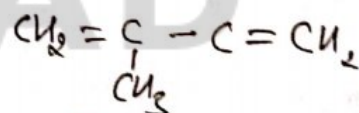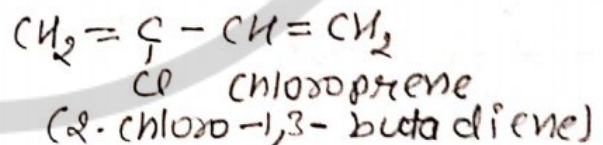
Buna-N (Nitrile Rubber)	$CH_2 = CH - CH = CH_2 \; + \; CH_2 = CH$
	1,3-Butadiene $\mid$
	                             CN
	                       Acrylo Nitrile
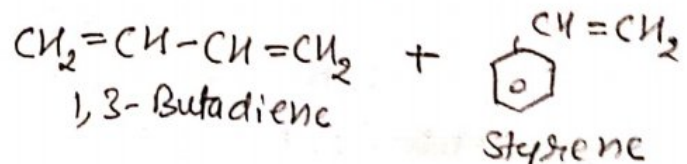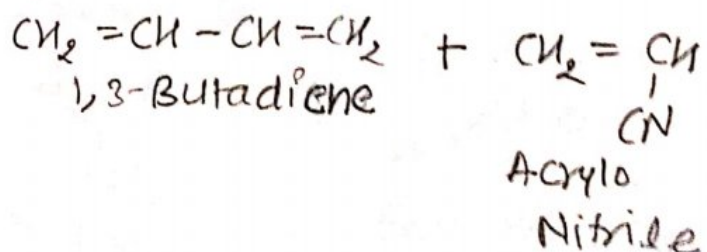
⇒ **Polyamides**

Nylon - 6 (Perlon-L)

Caprolactum

Nylon - 6,6

$HOOC-(CH_2)_4-COOH$ + $H_2N-(CH_2)_6-NH_2$
Adipic Acid   Hexamethylene diamine

Nylon - 6,10

$HOOC-(CH_2)_8-COOH$ + $H_2N-(CH_2)_6-NH_2$
Sebacic Acid   Hexamethylene diamine

Nylon - 2,6

H_2N-CH_2-COOH + $H_2N-(CH_2)_5-COOH$
Glycine   6-Amino hexanoic acid
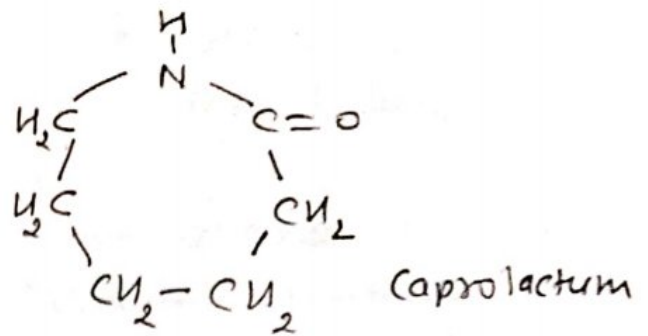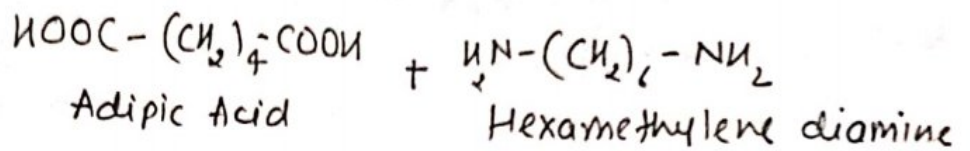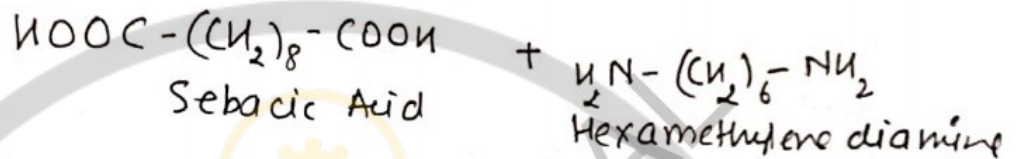
⇒ **Polyesters**

Terylene (Dacron)
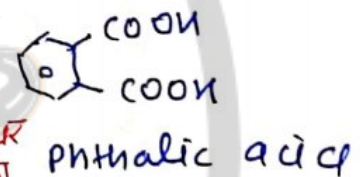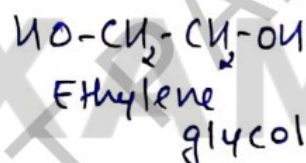
$HO-CH_2-CH_2-OH$
Ethylene glycol

phthalic acid

Glyptal (Alkyd Resin)

$HOCH_2-CH_2OH$
Ethylene glycol

दोनो का उधर से आया

Terephthalic acid

P.H.B.V
(Poly β-hydroxy butyrate-co-β hydroxy valerate)

$CH_3-\overset{OH}{\underset{|}{CH}}-CH_2-COOH$
3-Hydroxybutanoic acid

$CH_3-CH_2-\overset{OH}{\underset{|}{CH}}-CH_2-COOH$
3-Hydroxy pentanoic acid.
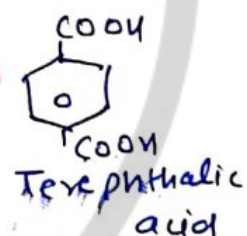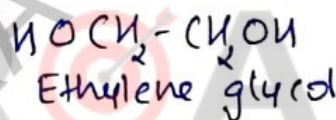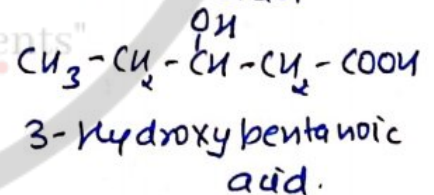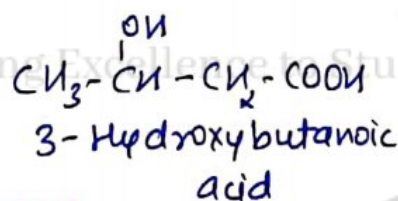
Formaldehyde Resins

Phenol - formaldehyde resin (Bakelite)

Phenol + $HCHO$
      Formaldehyde
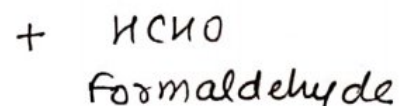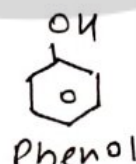
Melamine - formaldehyde resin (Melmac)

Melamine + $\overset{H}{\underset{H}{>}}C=O$
      Formaldehyde
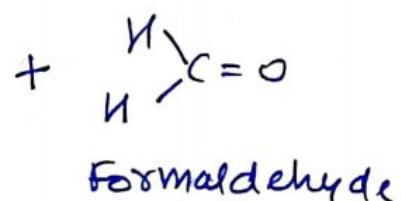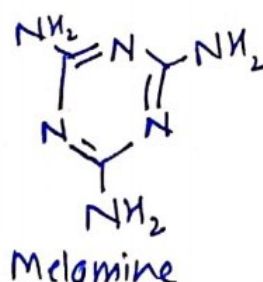
Urea-formaldehyde resin

$$NH_2CONH_2 \quad + \quad HCHO$$
Urea   Formaldehyde

Biodegradable polymers

Aliphatic polyesters are ~~not~~ one of the most important class of biodegradable polymers e.g Nylon-2-Nylon-6, PHBV (Poly β-hydroxybutyrate -co-β-hydroxy valerate

Classification of Polymers

→ Source
- Natural Polymers
- Synthetic Poly.
- Semi-Synthetic Poly.

– Str.
- Linear Poly.
- Branched
- Cross linked

– Forces
- Elastomers
- Fibres
- Thermoplastic
- Thermosetting

– Synthesis
- Addition Polymers
- Condensation Polymers.

▶ **Natural polymers :** These are substances of natural origin and are mainly found in plants and animals, *e.g.,* starch, cellulose, proteins, etc.

▶ **Synthetic polymers :** These polymers are prepared in the laboratories, they are also called *man-made polymers, e.g.,* teflon, terylene, synthetic rubber, etc.

▶ **Semi-synthetic polymers :** They are mostly derived from naturally occurring polymers by chemical modifications, *e.g.,* vulcanised rubber, cellulose nitrate, etc.

▶ **Linear polymers :** In these polymers, the monomers are linked together to form linear chains, *e.g.,* polyethene, polyester, nylon, etc.

▶ **Branched chain polymers :** In these polymers, the monomers are joined to form long chains or branches of different lengths, *e.g.,* glycogen, starch, etc.

▶ **Cross-linked polymers :** In these polymers, the monomer units are cross-linked together to form a three-dimensional network polymers, *e.g.,* bakelite, melamine, etc.

▶ **Elastomers :** These are the polymers having very weak intermolecular forces between the polymer chains. The weak forces permit the polymer to be stretched. Elastomers, thus, possess elastic character, *e.g.,* vulcanised rubber.

▶ **Fibres :** These are the polymers which have strong intermolecular forces between the chains. These are either hydrogen bonds or dipole-dipole interactions, *e.g.,* nylon-6,6.

▶ **Thermoplastics :** These are the polymers in which the intermolecular forces of attraction are intermediate between those of elastomers and fibres. These polymers do not have any cross-links between the chains, they can be easily moulded on heating, *i.e.,* thermoplastics soften on heating and become hard on cooling, *e.g.,* polythene, polystyrene, PVC, etc.

▶ **Thermosetting polymers :** They have extensive cross-links formed between polymer chains on heating. They undergo a permanent change on heating, *e.g.,* bakelite, melamine, etc.

▶ **Addition polymerisation :** A polymer formed by direct addition of repeated monomers without the elimination of by-product molecules is called *addition polymer* and the phenomenon is known as *addition polymerisation, e.g.,* polythene.

▶ **Condensation polymerisation :** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, alcohol, etc. is called *condensation polymer* and the phenomenon is known as *condensation polymerisation, e.g.,* terylene.

⊙ **Types of polymerisation reactions :**

▶ **Addition or chain growth polymerisation :** Depending upon the reactive particles formed, it is of three types :

– **Free radical polymerisation :** It takes place in three steps :

Nucleophilic Substitution Reaction

C-X bond in haloalkanes is polar and halide ion can be replaced by a stronger nucleophile

$$Nu + \overset{\delta+}{\underset{/}{\overset{|}{C}}} - \overset{\delta-}{X} \longrightarrow \overset{|}{\underset{/}{C}} - Nu +$$
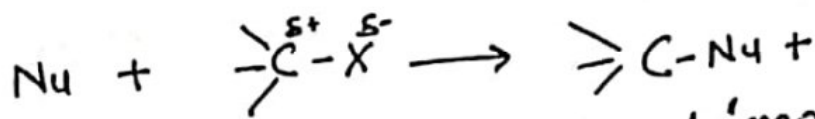
- SN^1 (Substitution Nucleophilic Unimolecular)
- SN^2 (Substitution Nucleophilic Bimolecular)

⇒ **Plane Polarized Light**

when a normal light from a light source (also called diffused light) is passed through nicol prism, then the light is changed into PPL (plane polarised light)

Plane Polarised light

(d)

I optically inactive

(l)
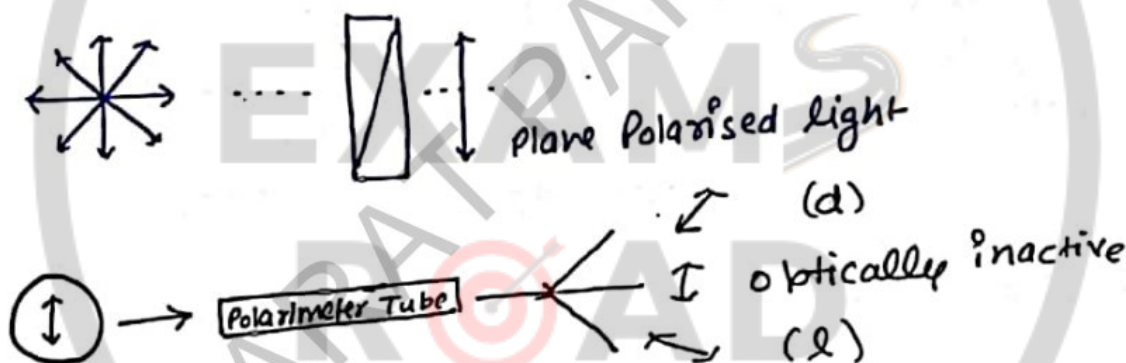
Optically active substance

when this plane polarized light is passed through a solution of an organic compound, then the light may rotate either clockwise or anti clockwise such substance are called optically active substance

dextro rotatory

If plane polarized light is rotated clockwise. It is called dextro rotatory or d or (+)

laevorotatory

If plane polarised light is rotated anti-clockwise It is called laevo-rotatory or l or (-)

⇒ **Stereocentre**

    If all the substituent attached to a carbon are different, then such a carbon is called asymmetric carbon or stereocentre or chiral carbon

- The asymmetry of the molecule is responsible for the optical activity in such organic compounds The asymmetry is also called disymmetry

⇒ **Chirality**

    The carbon which is bonded to four different atoms or group of atoms is called chiral carbon. Such carbon do not have a plane of symmetry. This property of compound is called chirality or dissymmetry

⇒ **Enantiomers**

    The non superimposable mirror images of an organic compound are optically active. And one of them will be dextro rotatory and other will be laevo rotatory. So, such pair of d and l isomers are called enantiomers.

- Essential condition for enantiomerism is disymmetry.

e.g Butan-2-ol has chiral carbon

$$C_2H_5 - \overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}} - CH_3$$
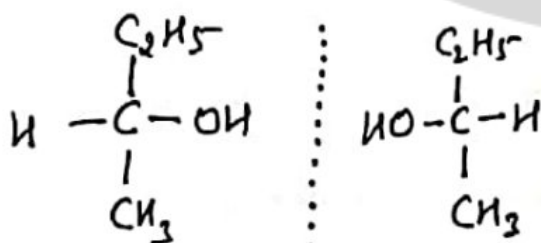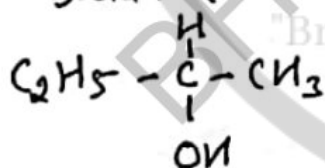
e.g Bromo chloro fluoromethane
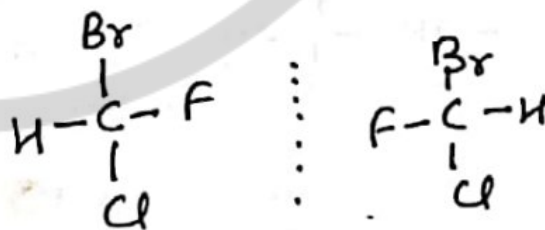
a pair of enantiomers

a pair of enantiomers.

Racemic Mixture

equimolar mixture of d and l substance so that net rotation is zero is called racemic mixture. The process of making a racemic mixture is called racemization. These are represented as prefixes dl or ±

Resolution

The separation of dextro rotatory (d) and laevo rotatory (l) isomers from racemic mixture by suitable method is called resolution

SN² Mechanism

Bimolecular Nucleophilic Substitution Rxn

Order = 2 , molecularity = 2

because the rate of reaction depends upon the conc. of both reactants i.e alkyl halide and Nucleophile

ex: Substitution by hydroxy group.

$$R-X + \underline{OH^-} \longrightarrow R-OH + X^-$$
$$\text{Nucleophile} \qquad\qquad \text{Leaving Group.}$$
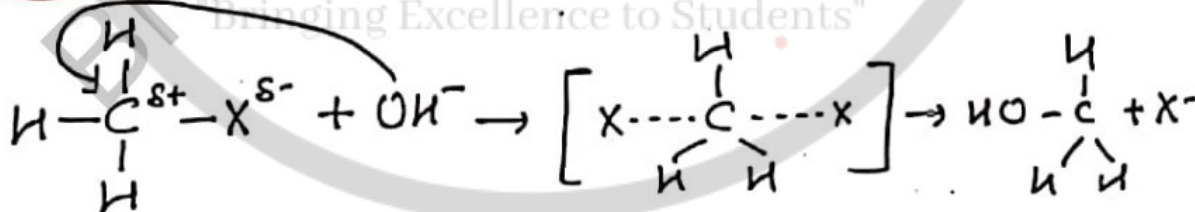
Mechanism

$$\text{Rate of Rxn} = K[CH_3X][OH^-]$$

- In this mechanism, the configuration of alkyl halide gets inverted. This is called inversion of configuration or Walden inversion.

SN1 Mechanism

Unimolecular Nucleophilic Substitution Rxⁿ.

The rate of reaction depends only on the conc.
of 1 reactant i.e alkyl halide

e.g order of reaction = 1
     molecularity of reaction = 1

This reaction takes place in two steps.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-X + OH^- \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + X^-$$
Nucleophile
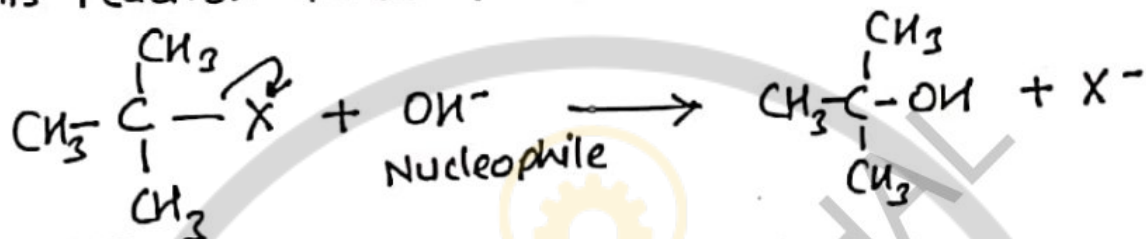
Mechanism

Step-I   Formation of intermediate carbocation

$$\underset{\underset{CH_3}{|}}{\overset{CH_3 \diagup CH_3}{C}}-X \underset{\xleftarrow{\hspace{1cm}}}{\overset{Slow}{\xrightarrow{\hspace{1cm}}}} \overset{CH_3 \diagup CH_3}{\underset{\underset{CH_3}{|}}{C^{\oplus}}} + X^-$$
                                                            Halide ion
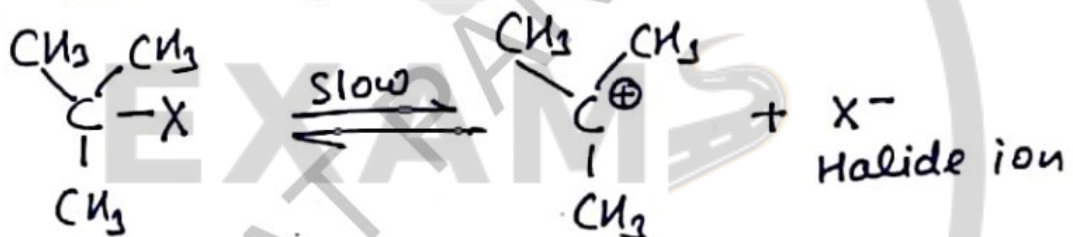
Step-II   Attack of nucleophile on C⁺ may occur
either from front side or from backside

$$\overset{CH_3 \diagdown CH_3}{\underset{\underset{CH_3}{|}}{C^{\oplus}}} + OH^{\ominus} \longrightarrow \underset{\underset{CH_3}{|}}{\overset{CH_3 \diagdown CH_3}{C}}-OH + HO-\underset{\underset{CH_3}{|}}{\overset{CH_3 \diagup CH_3}{C}}$$

                              (50%)   Inversion
                           Retention
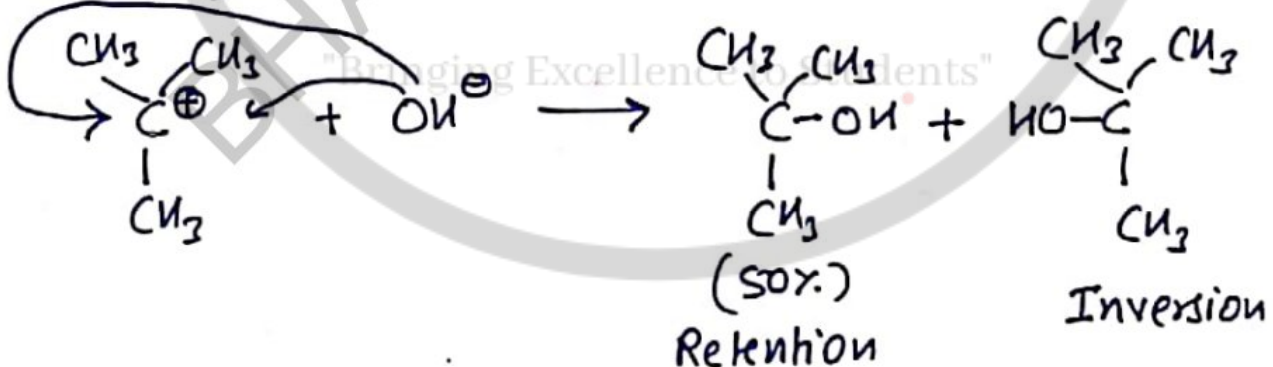
Rate of Rxⁿ = K [(CH₃)₃X]

      Order = 1

order of reactivity of Alkyl Halide

$\boxed{SN2}$

$$CH_3X \; > \; 1° \; > \; 2° \; > \; 3°$$

$$CH_3X \; > \; CH_3CH_2X \; > \; CH_3-\overset{CH_3}{\underset{}{CH}}-X \; > \; CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-X$$

$\longrightarrow$
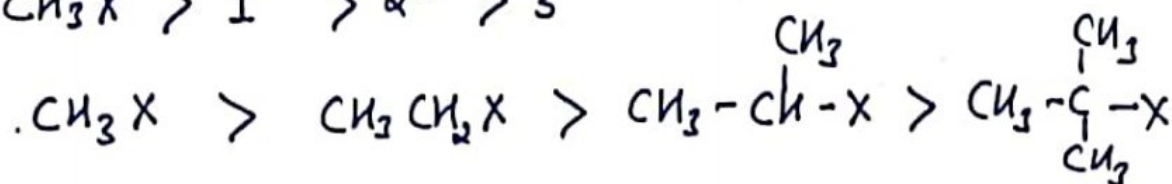
Reactivity decreases for SN2

As stearic hindrance increases and rate of SN2 reaction decreases. It becomes more difficult for a nucleophile to approach C-X carbon due to stearic hindrance

$\boxed{In \; SN1}$

The order of reactivity is

$$3° \; > \; 2° > 1° \; > \; CH_3X$$
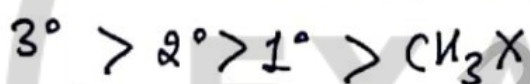
In this, an intermediate c^+ is formed

More is the stability of carbocation is, faster is the substitution reaction. As tertiary carbocation is more stable, So nucleophilic substitution is faster in 3° alkyl halide.

$\Rightarrow$ The allylic and benzylic halides show high reactivity towards SN1 reaction. Although the substitution takes place from 1° carbon. The carbocation. The carbocation thus formed gets stabilized through resonance

$$CH_2= CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2$$
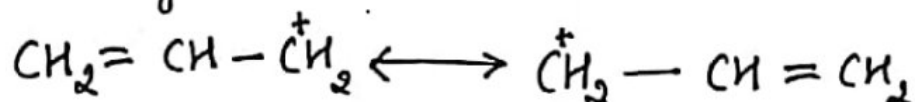
Resonance str. of allylic carbocation
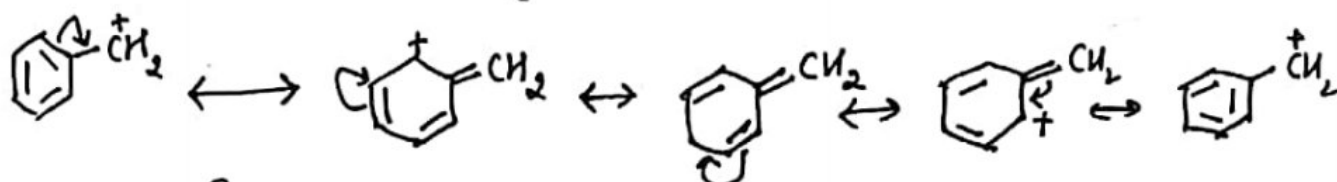
Resonance Str. of Benzylic carbocation

→ For a given alkyl group the reactivity of the halide, R-X follows the same order in both mechanism.

i.e

$$R-I > R-Br > R-Cl > R-F$$

Spectrochemical Aspects

SN2 reaction proceeds with spectrochemical inversion

SN1 reaction proceeds with racemization.

Unimolecular (SN1)

1.) It is first Order Rxn

2.) Generally carried out in polar protic solvents like water, alcohol & acetic acid

3.) Takes place in two steps through Carbocation as the intermediate

4.) Rate of Reaction
$$3° > 2° > 1° > CH_3X$$
Greater the stability of Carbocation, faster will be the reaction.

5.) Tends to proceed with weak nucleophiles
e.g CH_3OH, H_2O, CH_3CH_2OH etc.

6.) Both retention and inversion of configuration takes place

Bimolecular (SN2)

1.) It is second order Rxn

2.) Carried out in polar aprotic solvents like acetone, acetone or DMF or DMSO.

3.) Takes place in one step through transition state.

4.) Rate of Reaction
$$CH_3X > 1° > 2° > 3°$$
Less the steric hindrance in transition state, faster will be the reaction.

5.) Tends to proceed with strong nucleophiles
e.g CH_3O^-, CN^-, OH^-

6.) Inversion of configuration takes place (Walden Inversion)

Dehydration of Alcohol

Removal of water $(-H_2O)$

$$\underset{\underset{(H \quad OH)}{|\quad\quad|}}{-C-C-} \xrightarrow{\text{Conc } H_2SO_4 / \text{Conc } H_3PO_4} \underset{\underset{H \quad\quad H}{|\quad\quad|}}{H-C=C-H}$$

In case of 1° alcohol

$$\underset{\underset{H \quad\quad OH}{|\quad\quad|}}{CH_2-CH_2} \xrightarrow[443K]{\text{Conc. } H_2SO_4} CH_2=CH_2$$

2° alcohol

$$\underset{\underset{OH}{|}}{CH_3-CH-CH_3} \xrightarrow[\substack{or \\ H_3PO_4 (440K)}]{80\% H_2SO_4} CH_3-CH=CH_2$$

3° alcohol

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C-OH}} \xrightarrow[358K]{\substack{20\% H_3PO_4 \\ H_2SO_4}} \underset{}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2}$$
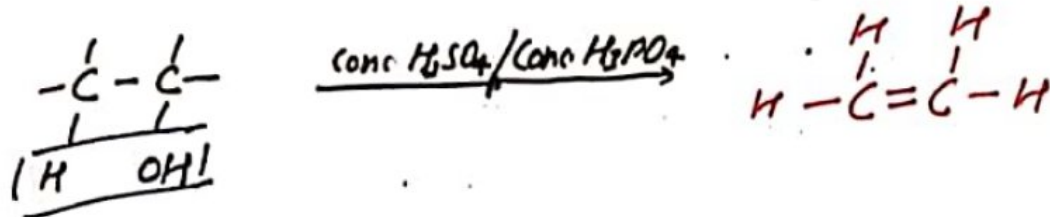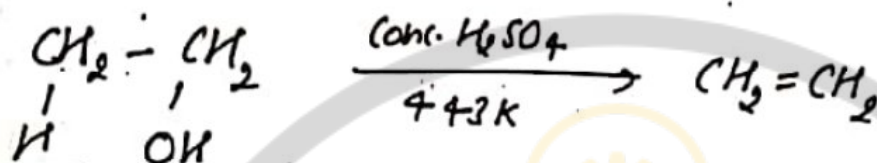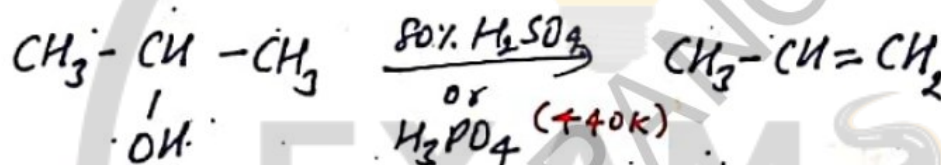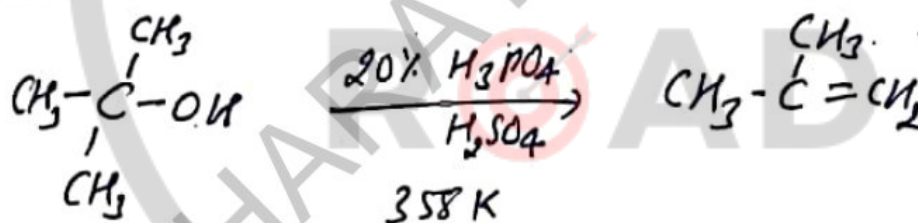
Order of Dehydration   3° > 2° > 1°

Mechanism of Dehydration of alcohol

Step-1

$$\underset{\underset{H}{|}}{CH_2-CH_2-\overset{..}{\underset{..}{O}}-H} \underset{(fast)}{\overset{(H^+)}{\rightleftharpoons}} \underset{\underset{H}{|}}{CH_2-CH_2-\overset{\overset{H}{|}}{\underset{\oplus}{O}}-H} \quad \text{(protonated alcohol)}$$

Step-2

$$\underset{\underset{H}{|}}{CH_2-CH_2-\overset{\overset{H}{|}}{\underset{\oplus}{O}}-H} \underset{RDS}{\overset{Slow}{\rightleftharpoons}} \underset{\underset{H}{|}}{CH_2-\overset{\oplus}{CH_2}+H_2O} \xrightarrow{\text{fast}} CH_2=CH_2+H^+$$
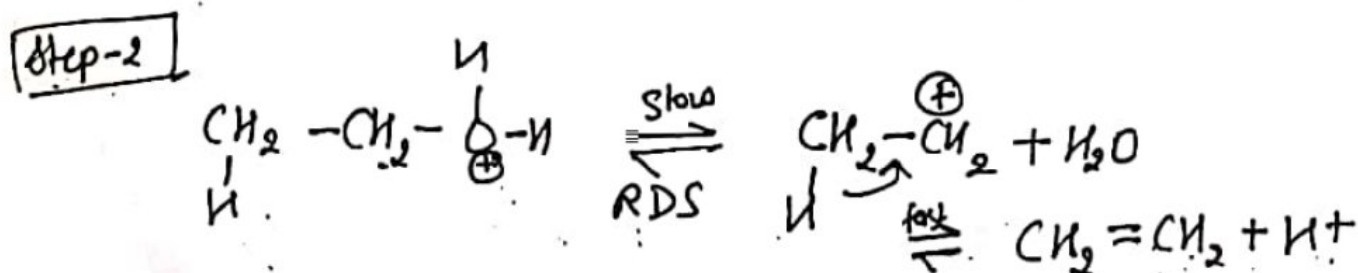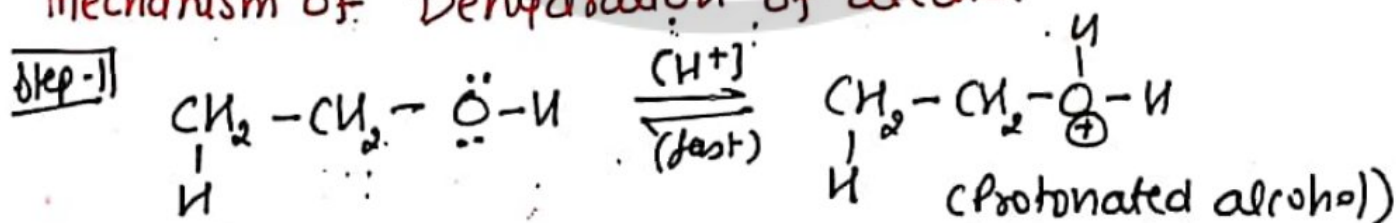
Preparation of Alcohol
(a) from Alkenes

$$\overset{}{\underset{}{>}}C=C\overset{}{\underset{}{<}} \xrightarrow{\text{H-OH}} \overset{}{\underset{}{>}}\underset{\underset{H}{|}}{C}-\underset{\underset{OH}{|}}{C}\overset{}{\underset{}{<}}$$
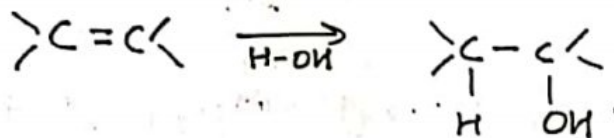
Hydration → Addition of water $\left\{\begin{array}{l}\text{Direct} \rightarrow \text{Acid Catalysed Hydration}\\ \text{Indirect}\end{array}\right.$

Indirect
$\underline{\hphantom{xxxxxxxxxxxxxxxxx}}$

Hydro-Boration   Oxymercuration
Oxidation   Demercuration
(HBO)   (OMDM)
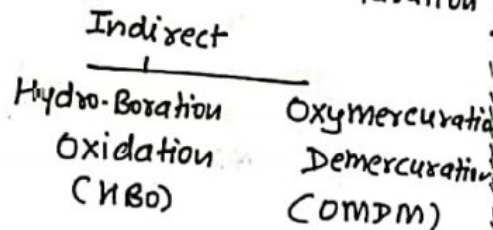
Acid Catalysed Hydration

(a) In Symmetrical Alkenes
(b) In Unsymmetrical Alkenes

(a)
$$CH_2=CH_2 \xrightarrow[\text{(H-OH)}]{H^+, H_2O} \underset{\underset{H}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$$

(b)
$$CH_3-CH=CH_2 \xrightarrow[\text{M.R}]{H^+, H_2O} \underset{\underset{OH}{|}}{CH_3-CH}-\underset{\underset{H}{|}}{CH_2} \quad (2° \text{ Alcohol})$$

Mechanism

$$H^+ + \overset{}{\underset{\underset{H}{|}}{:\overset{..}{O}-H}} \longrightarrow H_3O^{\oplus} \ (\text{Hydronium ion})$$

$$CH_3-CH=CH_2 + H-\underset{\underset{..}{|}}{\overset{\oplus}{O}}\overset{H}{\underset{H}{<}} \left[\begin{array}{l} CH_3-\overset{\oplus}{\underset{2°ct}{CH}}-CH_3 \\ CH_3-CH_2-\overset{\oplus}{\underset{1°ct}{CH_2}} \end{array}\right.$$

---

(6)

$$CH_3-\overset{\oplus}{CH}-CH_3 + :\overset{..}{O}-H \longrightarrow CH_3-\overset{\overset{H+\overset{\oplus}{O}-H}{\underset{..}{|}}}{\underset{|}{CH}}-CH_3$$

$$\longrightarrow \underset{\underset{2° \text{ Alcohol}}{}}{CH_3-\underset{\overset{|}{OH}}{CH}-CH_3} + H_3\overset{+}{O} \ (\text{Hydronium ion})$$

$$\underset{\underset{M.R}{}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H-OH \xrightarrow{H_2SO_4} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{CH_2}$$