

Complete Chemistry in 70 Pages

Coloured Handwritten Notes

**All Chapters
Covered
(Best Short
Notes)**



**Must Watch ChapterWise One Shot
and Previous Year Question For Best
Preparation**

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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 u L	liquid	Sugar Soln
liquid	liquid	L u L	liquid	Alcohol + water
Gas	liquid	G u L	liquid	Aerated drinks
Solid	Solid	S u S	Solid	Alloys
liquid	Solid liquid	L u S	Solid	Hydrated salt
Gas	Solid Gas	G u S	Solid	Rusted iron
Solid	Gas	S u G	Gas	Smoke
liquid	Gas	L u G	Gas	fogg
Gas	Gas	G u G	Gas	Air

Mass Percentage

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

$$\text{Mass \% of A} = \frac{w_A}{w_A+w_B} \times 100$$

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

Volume Percentage

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

$$\text{Vol. \% of B} = \frac{\text{Vol. of B}}{\text{Vol. of Soln}} \times 100$$

| 10% HCl by volume means

| 10 ml HCl in 100 ml solution.

Mass by Volume Percentage

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

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

Mass fraction

$$x_1 = \frac{w_1}{w_1+w_2}, x_2 = \frac{w_2}{w_1+w_2}$$

Parts per million

$$\frac{w_2}{w_1+w_2} \times 10^6$$

Mole Fraction

$$x_1 = \frac{n_1}{n_1+n_2} \quad \text{or} \quad x_2 = \frac{n_2}{n_1+n_2}$$

$$x_1 + x_2 = 1$$

In gases only

$$y_1 = \frac{P_1}{P_1+P_2} \quad \text{or} \quad y_2 = \frac{P_2}{P_1+P_2} \quad | y_1 + y_2 = 1$$

Molarity M

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

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

Unit = Moles
litre

Molality m

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

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

Unit = Moles
kg

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 ($\Delta H > 0$) the solubility increases with rise in temperature

If dissolution process is exothermic ($\Delta H < 0$), 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 ~~incomp.~~
Henry's law and its Application ~~-resible~~

amount of liquid is proportional to its pressure

$$M = k_H p$$

(or)

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

$$P = k_H x$$

k_H is Henry's constant and different ~~gas~~ for different gases at particular temp.

Value of k_H increases with temp

Higher the value of k_H

lower the solubility of gas

Application

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

(2) Difference b/w molarity and molality

Molarity
No. of moles of solute dissolved in one litre solution

$$M = \frac{n_B}{V(\text{in L})}$$

Molality
No. of moles of solute dissolved in one kg solvent

$$m = \frac{n_B}{w_A(\text{kg})}$$

Molarity depends on temperature

Molarity decreases with rise in temperature

Molality is independent of temp.

Molality does not change with temperature

Molarity & Molality of pure water is 55.5

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Raoult's Law It states that partial pressure of a component in solution is directly proportional to its mole fraction in solution. $P_A = P_A^0 \times X_A$ $P_B = P_B^0 \times X_B$ (1)

1) for Volatile Solute

$$\begin{aligned} P_S &= P_A + P_B \\ &= P_A^0 \times X_A + P_B^0 \times X_B \\ &= P_A^0 (1 - X_B) + P_B^0 \times X_B \\ &= P_A^0 - P_A^0 X_B + P_B^0 \times X_B \\ &= P_A^0 + (P_B^0 - P_A^0) X_B \end{aligned}$$

2) for Non-Volatile Solute

$$\begin{aligned} P_S &= P_A \\ P_S &= P_A^0 \times X_A \end{aligned}$$

$$\begin{aligned} \frac{P_S}{P_A^0} &= X_A \\ 1 - \frac{P_S}{P_A^0} &= 1 - X_A \\ \Rightarrow \frac{P_A^0 - P_S}{P_A^0} &= X_B \end{aligned}$$

Relative lowering in v.p.

3) Ideal and Non-ideal Solution

Those solution which obey Raoult's law are called ideal solution.

$$\begin{aligned} P_A &= P_A^0 \times X_A \\ P_B &= P_B^0 \times X_B \end{aligned}$$

$$\Delta V_{mix} = 0$$

$$\Delta H_{mix} = 0$$

Interaction of A-B is same as interaction of A-A and B-B.
e.g. n-hexane + n-heptane

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

$$P_A \neq P_A^0 \times X_A \quad P_B \neq P_B^0 \times X_B$$

$$\Delta V_{mix} \neq 0$$

$$\Delta H_{mix} \neq 0$$

interaction of A-B is not same as interaction of A-A and B-B
e.g. 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

Interaction of A-B is less than interaction of A-A and B-B

$$P_A > P_A^0 \times X_A \quad P_B > P_B^0 \times X_B$$

$$\Delta V_{mix} > 0 \quad \Delta H_{mix} > 0$$

water + methanol
acetone + ethanol

Negative Deviation

Interaction of A-B is High than interaction of A-A and B-B

$$P_A < P_A^0 \times X_A \quad P_B < P_B^0 \times X_B$$

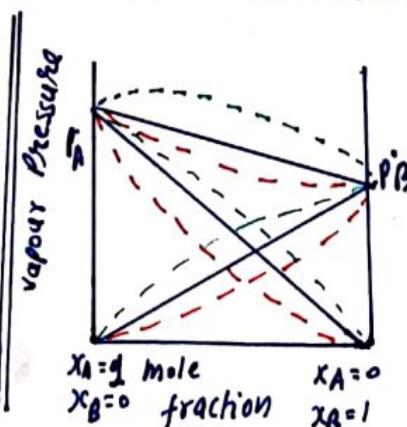
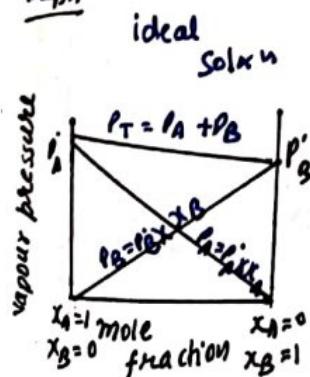
$$\Delta V_{mix} < 0 \quad \Delta H_{mix} < 0$$

- acetone + aniline
- acetone + chloroform

- Min. boiling azeotropes formed by those liquid which show positive deviation from ideal behaviour e.g. $H_2O + C_{10}H_{22}$

- Max. Boiling Azeotropes By those liquid pairs which show negative deviation from ideal behaviour e.g. $HNO_3 + H_2O$

Graph



- negative deviation
- positive deviation
- ideal solution

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

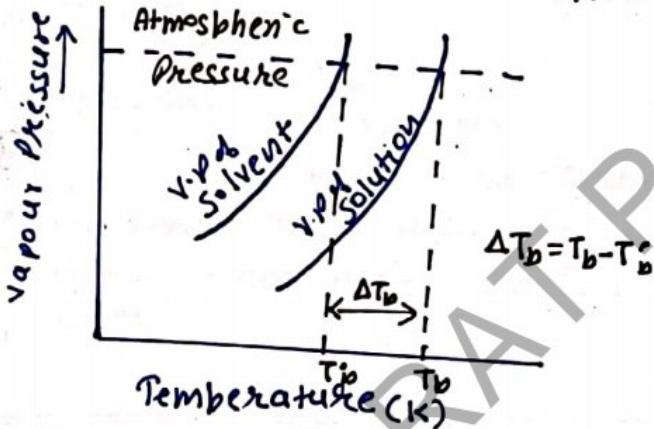
Relative lowering in V.P.

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

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.



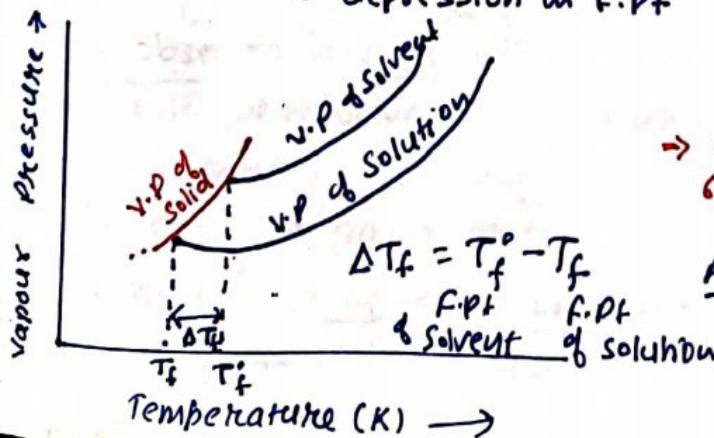
$\Delta T_b \rightarrow$ elevation in B.pt

$T_b \rightarrow$ B.pt of solution

$T_b^* \rightarrow$ B.pt of pure solvent

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 f.pt decrease in f.pt is termed as depression in f.pt



$$\frac{P_A - P_S}{P_A} = X_2 = \frac{n_L}{n_L + n_2}$$

$$P_A - P_S \Rightarrow \text{lowering in V.P.} \quad \frac{P_A - P_S}{P_A} = \text{lowering in V.P.}$$

$$\Delta T_b \propto M$$

$$\Delta T_b = K_b M$$

$$\Delta T_b = K_b \left(\frac{w_B}{M_B} \times \frac{1000}{w_{A(g)}} \right)$$

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_{A(g)}}$$

$K_b \rightarrow$ ebullioscopic constant or molal elevation constant

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)

$$\text{Ans. } \Delta T_b = K_b \times w_B \times 1000 \quad [2010] \quad \begin{matrix} \text{Unit} = \text{KKg mol}^{-1} \\ \text{K/m} \end{matrix}$$

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

$$= 0.019 \text{ K}$$

$$\text{B.pt of solution } \Delta T_b = T_b - T_b^* \quad \Rightarrow 373.019 \text{ K}$$

$$\Delta T_f \propto M$$

$$\Delta T_f = K_f M$$

$$\Delta T_f = K_f \times \frac{w_B}{M_B} \times \frac{1000}{w_{A(g)}} \quad \begin{matrix} K_f = \text{molal} \\ \text{depression} \\ \text{constant} \end{matrix}$$

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_{A(g)}}$$

$$\text{Unit} = \text{KKg mol}^{-1}$$

or
Cryoscopic constant

→ Calculate the f.pt of a solution cont. 60 g of glucose ($M_B = 180 \text{ g mol}^{-1}$) in 150 g water ($K_f = 1.86 \text{ KKg mol}^{-1}$) [2018]

$$\text{Ans. } \Delta T_f = K_f \times w_B \times 1000$$

$$= \frac{1.86 \times 60 \times 1000}{180 \times 150}$$

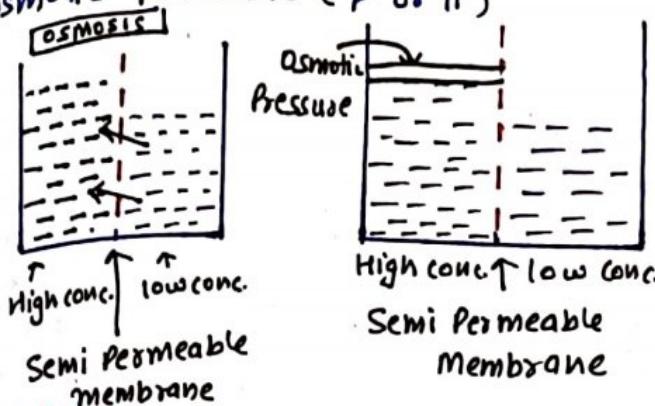
$$T_f = T_f^* - \Delta T_f$$

$$= 273 - 4.8$$

$$= 270.52 \text{ K}$$

Osmosis and Osmotic pressure The movement of solvent molecules from solution through semipermeable membrane is termed as osmosis.

The pressure applied to stop osmosis is called osmotic pressure (Π or π')



(ISOTONIC) Two solutions having same pressure at a given temperature called isotonic solution ($\Pi_A = \Pi_B$)

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 applied on solution side, reverse of osmosis takes place, used in Desalination of water

$$\Pi = C \times R \times T$$

$C \rightarrow$ molar conc.
 $R \rightarrow$ Gas constant
 $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$= \frac{n_B}{V} \times R \times T$$

$T \rightarrow$ Temperature

$$\Pi V = \frac{w_B}{M_B} \times R \times T$$

$$M_B = \frac{w_B \times R \times T}{\Pi \times V}$$

(N-1) Determine the osmotic pressure of a solution prepared by dissolving $2.5 \times 10^{-2} \text{ g}$ of K_2SO_4 in 2 L of water at 25°C . Assuming that it is completely dissociated ($R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

$$M_B = 174 \text{ g mol}^{-1}$$

[D-2013]

Ans. $\Delta T_f = i \cdot K_f \cdot m$

$$= i \cdot \cancel{K_f} \cdot \cancel{174 \text{ g} \times 1000} \cancel{\text{g}} \cancel{\text{mol}^{-1}}$$

$$M_B \times w_B \times 10^3$$

$$\Pi = \frac{w_B}{M_B} \times \frac{R \times T}{V}$$

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

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

Abnormal Molar Mass When the molecular mass of a substance determined 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.

Vant Hoff factor → It is the ratio of experimental value of colligative property to the calculated value of colligative property.

$$i = \frac{\text{observed value of colligative prop.}}{\text{calculated value of collig. Prop.}}$$

$$= \frac{\text{Calculated molar mass}}{\text{Observed molar mass}}$$

$$= \frac{\text{no. of moles after ass. or diss.}}{\text{no. of moles before ass. or diss.}}$$

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

$$\alpha_{\text{diss.}} = \frac{i-1}{n-1} \quad \alpha_{\text{ass.}} = \frac{1-i}{1-n}$$

Vant Hoff & Colligative Property

$$\frac{P_A - P_S}{P_A} = i \times x_B$$

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

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

$$\Pi = i \times C \times R \times T$$

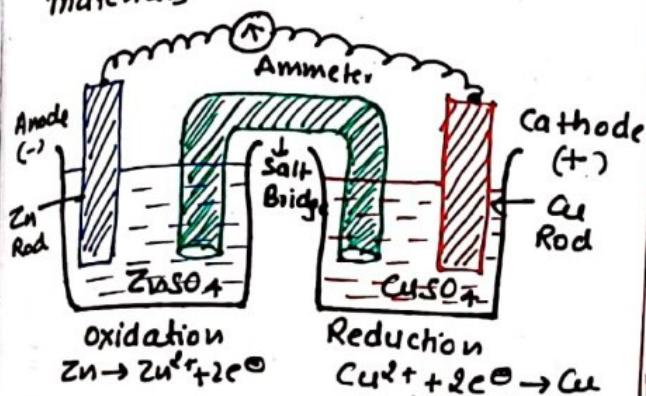
Electrochemistry It is that branch of chemistry in which we are studies about the relationship b/w electrical energy and chemical energy and their interconversion.

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

i) Electrochemical Cell (Galvanic or voltaic)

- It is a device which converts chemical energy into electrical energy
- Redox Reaction is spontaneous
- Two electrolytes are taken

The electrodes taken are of diff. materials



electrical energy is produced

Anode 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

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

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

Application 1) To calculate electrode potential

aA + bB $\xrightarrow{n e^-}$ cX + dY

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[A]^a [B]^b}{[X]^c [Y]^d}$$

2) To calculate equilibrium constant

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$$

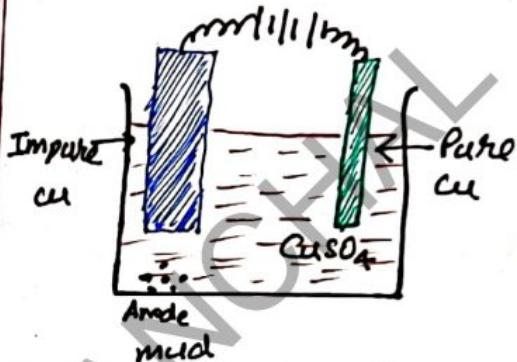
3) Gibbs free Energy and cell potential

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \quad \text{or} \quad \Delta G^{\circ} = -1.303 RT \log K_c$$

Electrolytic cell

It is a device which converts electrical energy into chemical energy.
Redox Rxn is non-spontaneous
only one electrolyte is taken

The electrodes taken may be of the same or different materials



electrical energy is used

Anode is +ve
Cathode is -ve

④ Calculate ΔG° and $\log K_c$ for the following reaction.



$$\text{Given } E_{Cd^{2+}/Cd}^{\circ} = -0.403V$$

$$E_{Zn^{2+}/Zn}^{\circ} = -0.763V$$

$$\text{Ans: } E_{\text{cell}} = E_{\text{Red}}^{\circ} - E_{\text{Oxi}}^{\circ} \\ -0.403 - (-0.763) = 0.36V$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \Rightarrow -2 \times 96500 \times 0.36 \\ = -69480J = -69.48 KJ$$

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

$$= \frac{2 \times 0.36}{0.059} = 12.40$$

$$K_c = \text{anti log}(12.40) = 1.58 \times 10^{12}$$

$$\text{conductance } G \quad \frac{1}{R} = \frac{q}{\rho l} = K \frac{a}{l} \quad \text{Unit} = \Omega^{-1} \text{ or } \text{Siemens}$$

on dilution conductance increased as no. of ions are produced

$$\text{specific Conductance or conductivity } (K) \quad \frac{1}{\rho} \text{ or } G \frac{l}{a} \quad \text{Unit} = \Omega^{-1} \text{ cm}^{-1} \text{ or } \text{S cm}^{-1}$$

on dilution, specific conductance decrease as no. of ions per cm³ decreases

$$\text{Equivalent Conductivity } \Lambda_{eq} \quad K \times V \text{ or } K \times \frac{1000}{N} \quad \text{Unit} = \Omega^{-1} \text{ cm}^2 \text{ or } \text{S cm}^2 \text{ eq}^{-1}$$

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

$$\text{Molar Conductivity } \Lambda_m \quad K \times V \text{ or } K \times \frac{1000}{M} \quad \text{Unit} = \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ or } \text{S cm}^2 \text{ mol}^{-1}$$

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.

$$\text{Ans: Conductivity } (K) = \frac{1}{R} \times A = \frac{1}{200} \times 1 = 5 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$$

$$\text{Molar Conductivity } (\Lambda_m) = K \times 1000 = 5 \times 10^{-3} \times 1000 = 500 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

(N-2) The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length is 50 cm is 5.55 × 10³ ohm. calculate its resistivity, conductivity and molar conductivity [2012]

$$\text{Ans: } a = \pi r^2 = 3.14 \times \left(\frac{1}{2}\right)^2 = \frac{3.14}{4} \text{ cm}^2$$

$$\text{Resistivity, } \rho = R \frac{a}{l} = 5.55 \times 10^3 \text{ ohm} \times \frac{3.14}{4 \times 50} \Rightarrow 86.35 \text{ ohm cm}$$

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

$$\text{And molar conductivity, } \Lambda_m = K \times \frac{1000}{M} = 1.158 \times 10^{-2} \times \frac{1000}{5 \times 10^{-2}} = 231.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

(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 cm⁻¹?

$$\text{Ans: conductivity } (K) = 0.146 \times 10^{-3} \text{ S cm}^{-1} \quad \text{Resistance } (R) = 1500 \Omega$$

$$\text{Cell constant} = \frac{\text{conductivity}}{\text{conductance}}$$

⇒ conductivity × Resistance

$$\Rightarrow K \times R \Rightarrow 0.146 \times 10^{-3} \times 1500 = 0.219 \text{ cm}^{-1}$$

Limiting molar Conductivity when concentration approached 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

$$\Lambda_m AB = \Lambda_m^{\infty} A^+ + \Lambda_m^{\infty} B^-$$

Application of Kohlrausch law

1.) Calculation of molar conductivity of weak electrolyte

$$2.) \Lambda_m \text{ CH}_3\text{COONa} = \Lambda_m^{\infty} \text{CH}_3\text{COO}^- + \Lambda_m^{\infty} \text{Na}^+$$

Calculation of degree of dissociation

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

$$3.) \text{Calculation of dissociation constant } K_c = \frac{c \alpha^2}{1 - \alpha}$$

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

Faraday's first law The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity through the electrolyte $w \propto Q$

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

where, Z is electrochemical equivalent of the substance deposited

$$w = ZQ$$

$$w = ZXIt$$

$$w = \frac{\text{At. Mass}}{n \times 96500} \times ZXIt$$

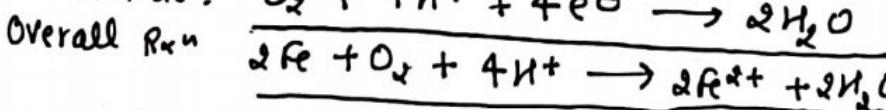
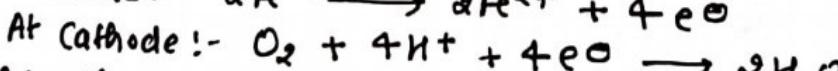
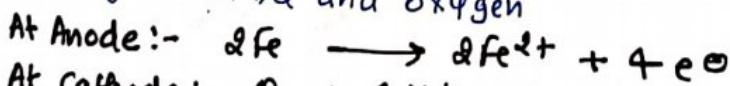
$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

where E is equivalent wt.

- (N-1) How much charge is required for the reduction of 1 mol Zn^{2+} to Zn ? Ans: $Zn^{2+} + 2e^- \rightarrow Zn$ one mole of Zn^{2+} requires 2 moles of e^- [2015]
- $$Q = 2 \times F = 2 \times 96500 = 193000 C$$
- (N-2) Silver is uniformly electrodeposited on a metallic vessel of surface area of 600 $c.m^2$ by passing a current of 0.5 ampere for 2 hours. Calculate the thickness of silver deposited (Given density of silver is $10.5 g/c.m^3$, $M_{Ag} = 108$)
- Ans: electrode reaction $Ag^+ + e^- \rightarrow Ag$
- quantity of electricity passed = Current \times time
 $= 0.5 \times 2 \times 60 \times 60 = 3600 C$
- Thickness of electricity deposit = $108 g / Ag$
- let the thickness of deposit be $x cm$
 $x = \frac{108}{96500} \times 108 = 4.03 g Ag$
- Mass = Volume \times density = Area \times thickness \times density [\because Vol. = area \times thickness]
- $$\therefore 4.03 g = 600 \times x \times 10.5$$
- $$x = 4.26 \times 10^{-4} c.m$$
- (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 $I = 0.5 A$, $t = 2 \text{ hrs}$
 Numbers of e^- = ?
 $= 0.5 \times 2 \times 60 \times 60 = 3600 C$
 $= \frac{3600}{1.6 \times 10^{-19}} = 2.25 \times 10^{22} e^-$
- Total Charge (Q) = $I \times t$
 \therefore No. of e^- = $\frac{\text{Total Charge}}{\text{charge of one } e^-}$

Some Commercial Cells

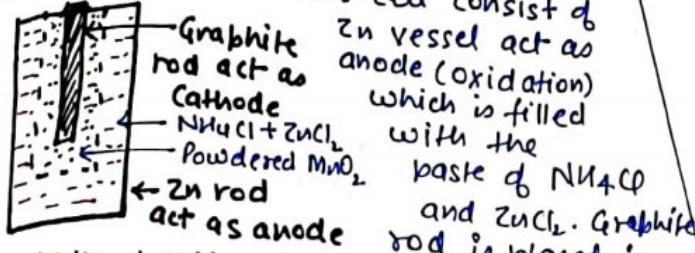
- Primary cells** :- cells once exhausted can not be used again e.g. dry cell, mercury cell
 - Secondary cell** :- Rechargeable cell can be used again and again e.g. lead-storage battery
 - Fuel cell** cell which can convert the energy of combustion of fuels such as H_2 , CO , CH_4 etc. into electrical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



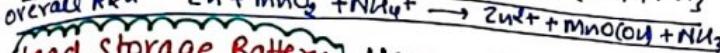
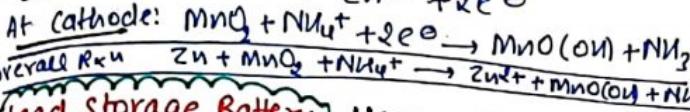
Methods of Prevention

- Barrier Protection
- Sacrificial protection
- Using anti-rust sol.
- Electrical protection

Dry cell (Leclanche) Used in Toys, Wall clocks, Remotes, Radios etc.



middle of cell act as cathode (reduction) surrounded by powdered MnO_2

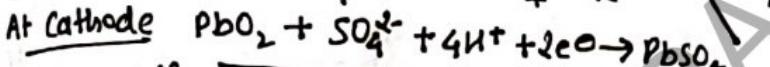
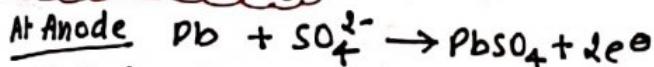


Lead Storage Battery

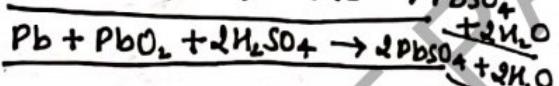
Uses - In inverter, in automobiles etc.



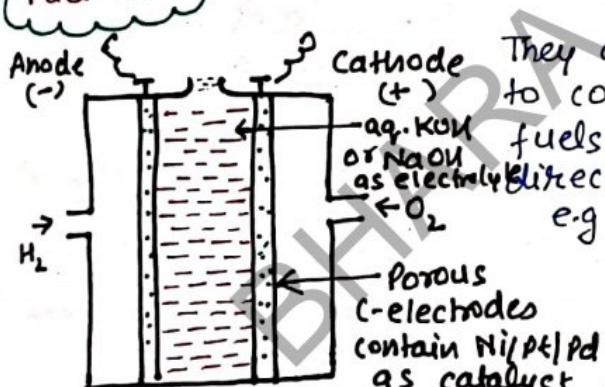
During Discharging



The Overall Rxn is



Fuel cell



Cathode (+) They are galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol directly into electrical energy

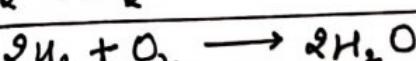
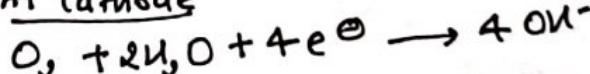
e.g. $H_2 - O_2$ fuel cell

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

At Anode



At Cathode

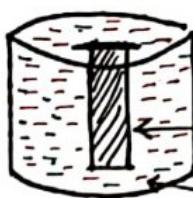


The Overall Reaction

Advantage of fuel cell

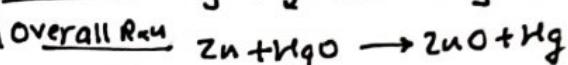
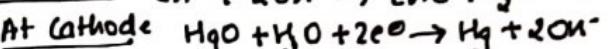
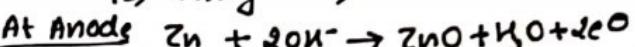
- Pollution free

Mercury cell

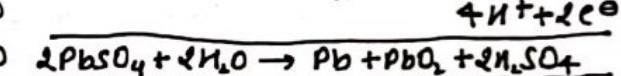
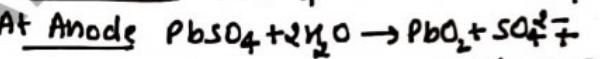


This cell consist of a Zn vessel act as anode, and Graphite rod act as cathode. Mixture of HgO and KOH act as electrolyte

This cell give the voltage of 1.35 V through its whole life
Use - Toys, hearing aids, watches



During Recharging



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

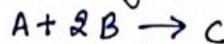
Rate of Rxn



The rate of reaction can be defined as the change in concentration of a reactant or a product in unit time.

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

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



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

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



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

N-1) For the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ the rate of formation of O_2 is $2.8 \times 10^{-3} \text{ M s}^{-1}$. calculate the rate of disappearance of N_2O_5

Ans: Given,

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

Acc. to rate law expression,

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

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

$$= 1.4 \times 10^{-3} \text{ M s}^{-1}$$

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 double with 10°C rise of temperature.

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

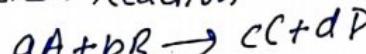
Surface Area of reactant:- For a reaction involving a solid reactant or catalyst, the greater is the surface area, the faster is the reaction.

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 concentration of reactant and each raise to the power their concentration term on which rate of reaction actually depends.

Consider a general reaction



$$\text{Rate} = k[A]^x[B]^y \text{ or } -\frac{d[R]}{dt} = k[A]^x[B]^y$$

Order

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

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

$$\text{Order} = x+y$$

Rate constant

rate constant is rate of reaction when concentration of each reactants becomes unity.

Unit of rate constant

for different order

Zero order $k = (\text{Mol L}^{-1})^{1-0} \text{ s}^{-1}$

First order $k = (\text{Mol L}^{-1})^{1-1} \text{ s}^{-1}$ or s^{-1}

Second order $k = (\text{Mol L}^{-1})^{1-2} \text{ s}^{-1} = \text{Mol}^{-1} \text{ L}^1 \text{ s}^{-1}$

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

- (11)
- It is the sum of the powers of the concentrations of reacting species in rate law eqn
 - It is an experimental concept
 - It is 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 reactions whose rate depends upon one concentration term of reactants.



$$\text{Rate of } R \propto [R]^1$$

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

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

Integrating both sides

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

$$-\ln[R] = Kt + C \quad \text{--- (1)}$$

To get value of C
 $t=0, R=R_0$

$$-\ln R_0 = C$$

Put value of C in (1)

$$-\ln[R] = Kt - \ln[R_0]$$

$$\ln[R_0] - \ln[R] = Kt$$

$$\frac{2.303}{K} \log \frac{R_0}{R} = t$$

for zero Order

whose rate depends upon zero conc. term of reactant
 consider a general reaction...



$$\text{Rate of } R \propto [R]^0$$

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

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

Integrating both sides

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

$$-[R] = Kt + C \quad \text{--- (1)}$$

To get value of C
 $t=0, R=R_0$

$$-[R_0] = C$$

Put value of C in (1)

$$[R] = Kt - [R_0]$$

$$\frac{[R_0] - [R]}{K} = t$$

is denoted by $t_{1/2}$.

For first Order $t = t_{1/2} \quad R = R_0/2$

$$t_{1/2} = \frac{2.303}{K} \log \frac{R_0}{R} \times 2$$

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

(N-1) For a reaction $A+B \rightarrow P$, the rate law is given by, [2013]

$$r = K [A]^{1/2} [B]^2 \text{ Give order}$$

$$\begin{aligned} \text{Ans. Order} &= \frac{1}{2} + 2 \\ &= \frac{5}{2} \end{aligned}$$

for zero order

$$t = t_{1/2} \quad R = R_0/2$$

$$t_{1/2} = R_0 - \frac{R_0}{2}$$

$$t_{1/2} = \frac{R_0}{2K}$$

(N-2) Identify the order for

$$(i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1}$$

[2011]

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 (12)

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

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

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

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

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

Similarly for 2nd process

$$\frac{1}{2} = 0.014 = \frac{2.303}{t} \log \frac{100}{25} \Rightarrow t = 99 \text{ min}$$

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

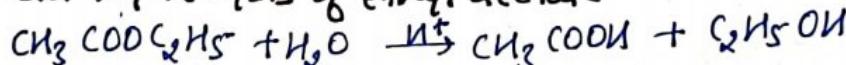
Ans: for first order reaction, 2017
for 99% completion of reaction,

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

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

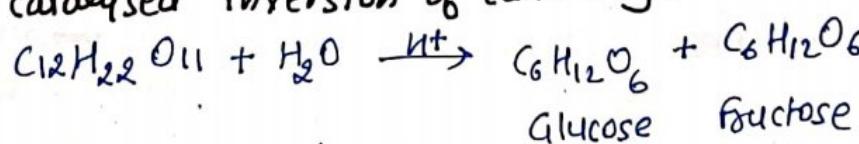
Pseudo First Order Rxn Those reactions which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo first order Rxn.

e.g. Acid hydrolysis of ethyl acetate



$$\text{Rate} = K [\text{CH}_3\text{COOC}_2\text{H}_5]$$

• Acid catalysed inversion of cane sugar



$$\text{Rate} = K [\text{C}_12\text{H}_{22}\text{O}_{11}]$$

Arrhenius Equation

Equation which give relationship b/w rate constant and temperature

$$K \propto e^{-E_a/RT} \Rightarrow K = A e^{-E_a/RT}$$

$$\log K = f \quad \ln K = \ln A \cdot e^{-E_a/RT}$$

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

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

At temp T_1

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \quad \text{--- (1)}$$

At Temp T_2

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \quad \text{--- (2)}$$

operating eq. (2) - eq. (1)

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

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

$K \rightarrow$ rate constant

$A \rightarrow$ frequency factor

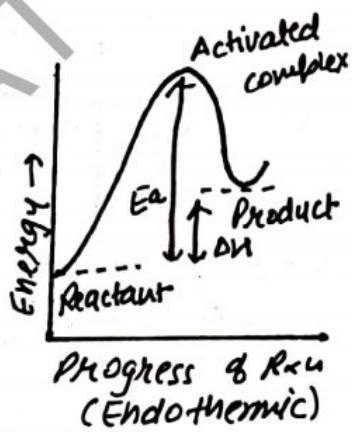
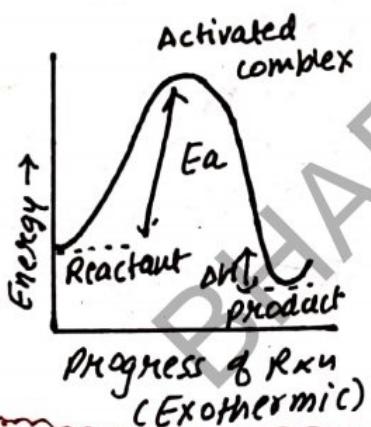
$E_a =$ Activation energy

$T \rightarrow$ Temperature

Activation energy

called activation energy (E_a)

The minimum amount of energy required by reactant molecules to participate in a reaction is



Activation energy =
Threshold energy
- Average Kinetic energy of reacting molecules

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 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



silica gel
in water

- It is a surface phenomenon occurs only at the surface of adsorbent.
- It is rapid in beginning than becomes slow

Δg , ΔH and ΔS all are -ve for adsorption

Physical Adsorption

- Also known as physisorption
- low enthalpy of adsorption i.e $20-40 \text{ kJ/mol}$
- It is a reversible process
- It is not specific in nature
- With the increase in temperature, physical adsorption decreases
- No activation energy required
- Multimolecular layer are formed

Absorption



CaCl_2 in water

- It is a bulk phenomenon occurs throughout the body of the material
- It occurs at uniform speed

Chemical Adsorption

- Also known as chemisorption
- High enthalpy of adsorption i.e $80-240 \text{ kJ/mol}$
- It is irreversible process
- It is highly specific in nature
- With the increase in temp. chemical adsorption first increases and then decreases
- Activation energy required
- 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 , H_2S , 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

freundlich adsorption isotherm

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

where $x \rightarrow$ mass of adsorbate

$m \rightarrow$ mass of adsorbent

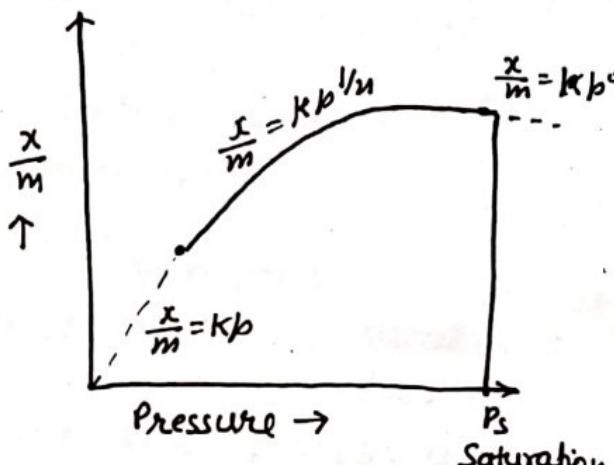
for low pressure

$$\frac{x}{m} \propto p$$

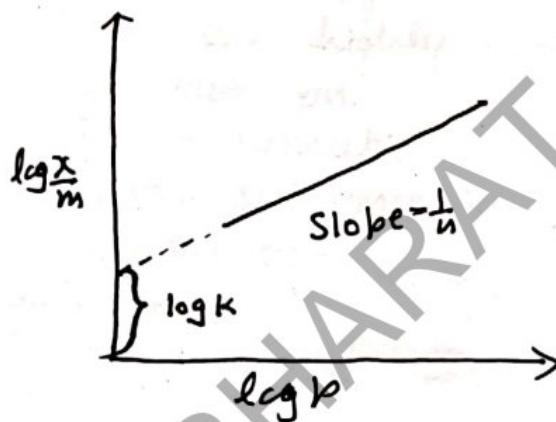
, for high pressure, for intermediate pressure

$$\frac{x}{m} \propto p^n$$

$$\frac{x}{m} \propto p^{1/n} \quad (n > 1)$$



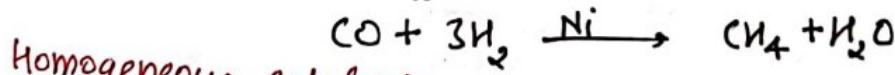
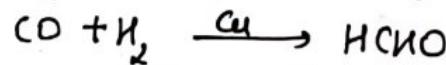
$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$



Selectivity

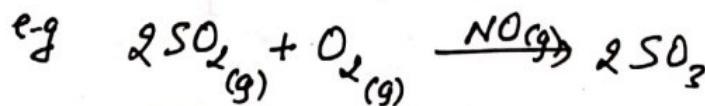
It is the ability of a catalyst to direct a chemical reaction and give a particular product.

Homogen



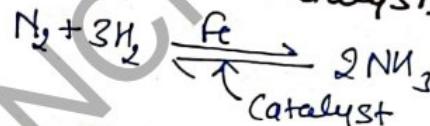
Homogeneous Catalysis

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



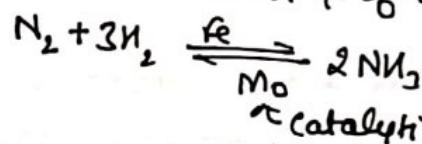
Catalyst

substance which accelerates 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.



Promoters

The substance that enhance the activity of a catalyst



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

Heterogeneous catalysis

(16)

and the catalyst are in different phase
 e.g. $2\text{SO}_2 + \text{O}_2 \xrightarrow[\text{(g)}]{\text{Pt(s)}} 2\text{SO}_3$

Selective Catalysis

upon the pore str. of the catalyst and the size of the reactant and product molecule e.g. zeolite (have honeycomb like str.)

An important zeolite which is used in petroleum industry is ZSM-5 which directly converts alcohol into gasoline (petrol)

Enzyme

Enzymes are complex nitrogenous 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, known as co-enzyme
- Certain subs

Dispersed phase	Dispersion medium	Type of colloid	Example
Gas	Gas	No homo colloid Sol.	Froth, whipped cream
Gas	liquid	foam	Pumice stone, foam rubber
Gas	Solid	Solid Sol	
liquid	Gas	Aerosol	Fog, mist, cloud
liquid	liquid	Emulsion	Milk
liquid	Solid	Gel	Cheese, butter
Solid	Gas	Aerosol	
liquid	liquid	Sol	Smoke, dust
Solid	liquid	Solid Sol	Paints, gold sol.
Solid	Solid		Gems, precious stone

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

- Lyophilic colloids
- Lyophobic colloids.

Lyophilic colloids

- These are easily formed by direct mixing
- The particles are not easily visible even under ultramicroscope
- These are very stable
- They are not easily precipitated by small amount of electrolyte
- The particles do not carry any charge
- These are reversible in Nature
- They do not show Tyndall effect

Lyophobic colloids (12)

- These are formed only by special methods.
- The particles are easily detected under ultramicroscope
- These are unstable and require traces of stabilizers
- These are easily precipitated by small amount of suitable electrolyte
- The particles carry charge and move in a specific direction
- These are irreversible in Nature
- 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 (diameters nm) held by weak van der waals forces

Micells



2.) Macromolecular colloids

Having big size molecules. And dispersed phase in colloidal range

Lyophilic

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)

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

Kraft Temperature

The formation of micelles takes place above a particular temp. called Kraft Temp. (T_K)

Critical micellization concentration

place above a particular concentration called critical micellization conc (CMC)

The formation of micells takes

place above a particular concentration called critical

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

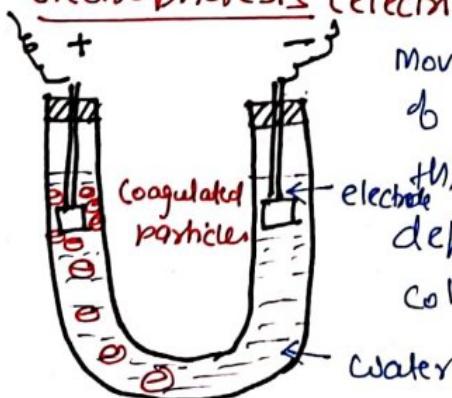
Positively charged sols

Hydrated metallic oxides e.g $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, metal hydroxides $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, basic dye stuff like brussian blue, haemoglobin etc.

Negatively charged sols

Metallic particles e.g Cu, Ag, Au, Metal sulfides 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 two 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 smaller the quantity needed, the higher will be the coagulating power of an ion

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 e.g. 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 detergents.

Demulsification

Separation the two components of an emulsion.

Methods used are boiling, freezing, changing pH

General Principles and Processes of Isolation of Elements

Minerals

Naturally occurring chemical substance in earth crust obtained by mining

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

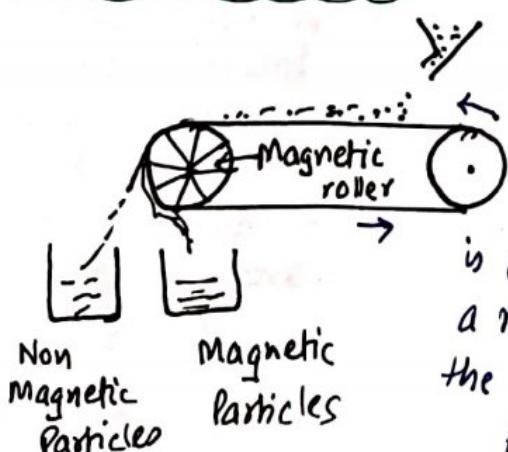
Metallurgy The scientific and technological process used for the extraction of the metal from its ores is called metallurgy. Three steps:-
(i) Concentration of ores (ii) Extraction of crude metal from concentrated ore (iii) Refining.

Metal	Ore	Composition	Gangue
1) Aluminium	Bauxite Kaolinite	$\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ $\text{Al}_2(\text{OH})_4 \cdot \text{Si}_2\text{O}_5$	The earthy materials or impurities with which ores are generally associated are called gangue
2) Iron	Haematite Magnetite Siderite Iron pyrites	Fe_2O_3 Fe_3O_4 FeCO_3 FeS_2	- All ores are minerals but all minerals are not ores
3) Copper	Copper pyrites Malachite Cubrite Copper glance	CuFeS_2 $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ Cu_2O Cu_2S	<u>Concentration of ores</u>
4) Zinc	Zinc blende Calamine Zincite	ZnS ZnCO_3 ZnO	Removal of the unwanted materials from the ore is known as concentration, dressing or benefaction. Some important processes are

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 lighter gangue particles washed away and the heavier ones are left behind.

Magnetic Separation

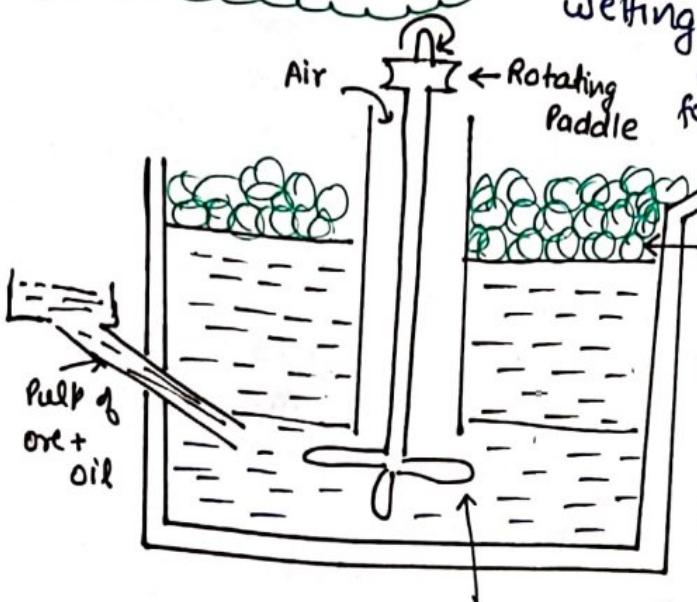


It is based on the difference in the magnetic properties of the gangue and ore particles and is used for magnetite (Fe_3O_4), haemite (Fe_2O_3), wolframite (FeWO_4), chromite ($\text{FeO}(\text{Cr}_2\text{O}_3)$)

The powdered ore containing impurities is dropped on a belt which rotates around a magnetic roller. The magnetic pull causes the magnetic particles to fall closer to the roller while non-magnetic particles fall farther off.

Froth Flotation Process

It is based on the difference in the wetting properties of gangue and ore particles and is mostly used for sulphide ores.



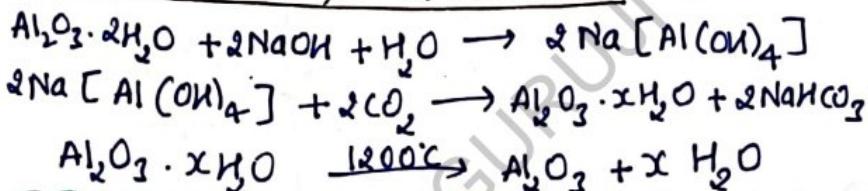
Powdered ore is mixed with pine oil and water and violently agitated with air. Ore particles rise to the surface in the form of froth and impurities remains in water.

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

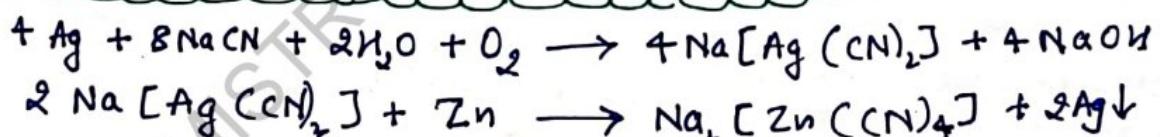
Leaching

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

Baeyer's Process for Al extraction



Mac Arthur Forest Cyanide process for Ag extraction



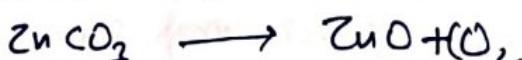
Most abundant metal \rightarrow Aluminium

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.

\rightarrow Carbonate ores are converted into oxide ores



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



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.

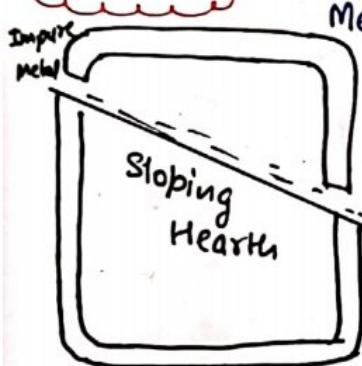
- Carbon or carbon mono oxide is used for oxides of Fe, Cu, Zn, Mg, Co etc. and the process is called smelting.
- Electropositive metals like Na, Al, Mg or Hydrogen are used for reduction of ores of Mn, Cr, Ti, Mo, W etc.
- Water gas is used for Nickel ores
- Auto reduction process is used for ores of Pb, Hg, Cu etc.
- Electrolytic reduction is used for higher electropositive metals.

Refining of Metals

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

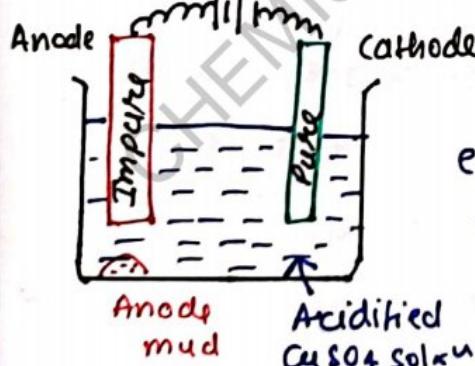
Liquation Used for low melting metals like Sb, Pb, Hg, Bi etc.

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



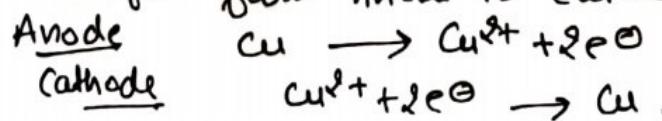
Metals with low melting point like Sb, Pb are purified by this method. The melting point of metal are lower than those of the impurities. For this purpose, a sloping hearth furnace. This metal is placed at the mouth of the furnace and heated gently. The metal flows down the hearth while impurities are 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 electro positive) remains in the solution and less basic impurities go to anode mud.

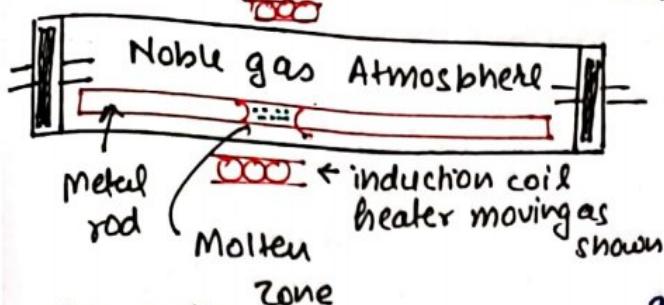
Copper is refined using an electrolytic method. Anode are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate. Copper in pure form transfer from anode to cathode.



Anode mud contains - antimony, selenium, tellurium, silver, gold etc.

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.



The molten zone moves along with the heater which is moved forward. As the heater moves forward the pure metal crystallises zone at one end, impurities get concentrated. This end is cut off.

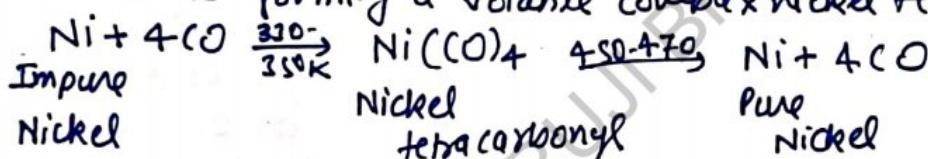
Vapour Phase Refining

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

- The metal should form volatile compound with an available reagent
- The volatile compound should be easily decomposable, so that the recovery is easy. Two Types (i) Mond Process

Mond Process

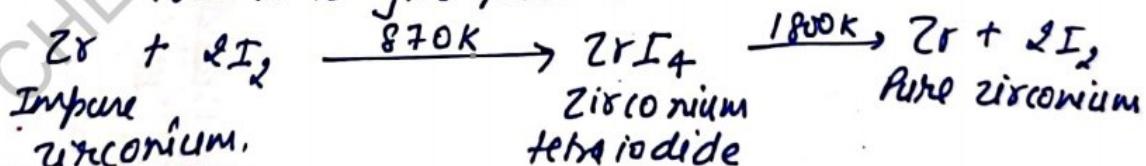
In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex nickel tetracarbonyl.



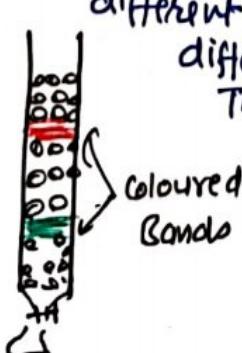
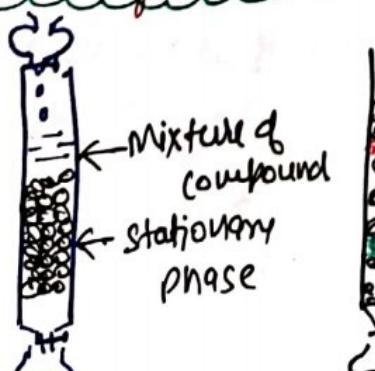
Van Arkel Method

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 in an evacuated vessel with iodine. Volatile zirconium tetr碘ide is formed. Which is then decomposed by heating on tungsten filament electrically to about 1800 K to give pure zirconium.)



Chromatography



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 (e.g.) 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).

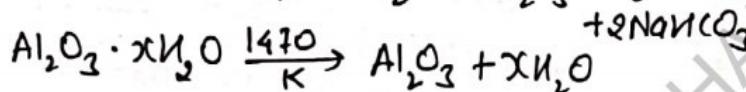
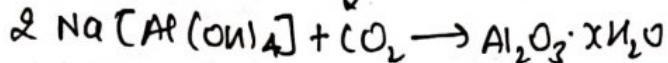
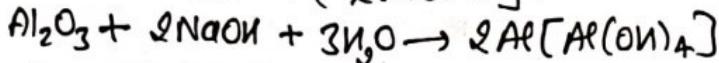
Cast Iron It is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

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

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

(2) Concentration : (leaching)



(3)

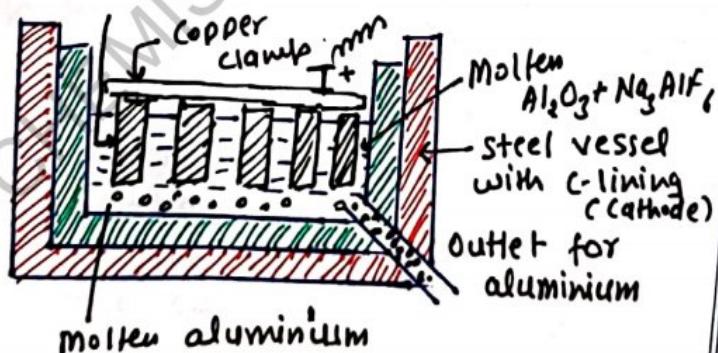
⇒ What is the role of cryolite in the metallurgy of aluminium?

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.

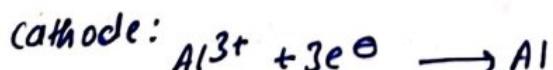
③ Electrolytic Reduction

(Hall and Heroult Process)

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



The electrolytic reactions are:



Extraction of Zn

Ores:

(i) zinc blende: ZnS ✓

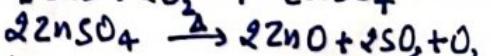
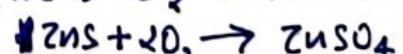
(ii) calamine: $ZnCO_3$

(iii) Zincite: ZnO

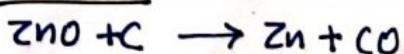
Concentration:

Froth floatation method

Roasting:



Reduction:



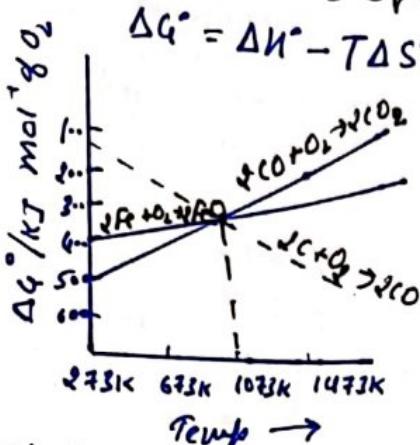
Purification:

Electrolytic refining, distillation.

Thermodynamic and electrochemical principles of extraction

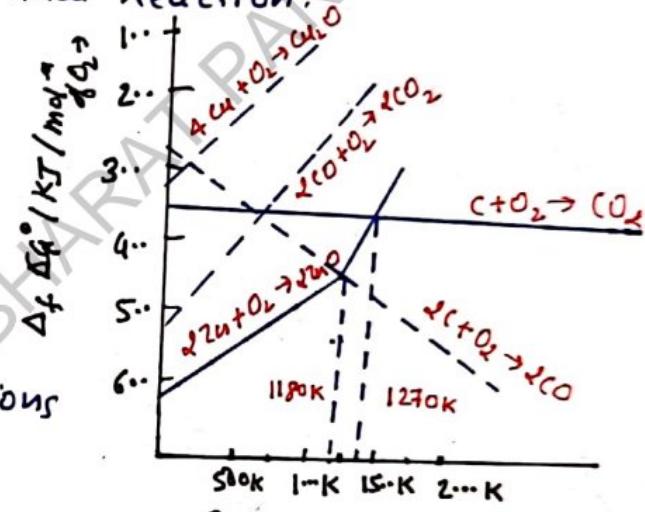
► Thermodynamic principles: Thermodynamics help in understanding the conditions of temp. and selecting suitable reducing agent in a metallurgical process.

- Gibbs Helmholtz equation is used to check the feasibility of a reduction process.



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 CO .

Such diagrams help in predicting the feasibility 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 through 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 electron enters a p-orbital are called p-block elements.

(7)

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 - $5s^2 5p^4$] 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_2O_4

Acidic Oxides SO_3 , Cl_2O_7 , CO_2 , N_2O_5

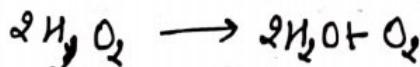
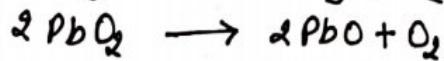
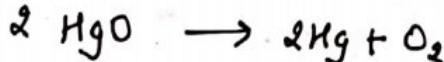
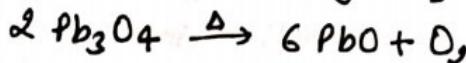
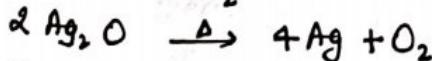
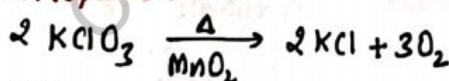
Basic Oxides Na_2O , CaO , BaO

Amphoteric Oxides ~~Al_2O_3~~ Al_2O_3

Neutral Oxides CO , NO , N_2O

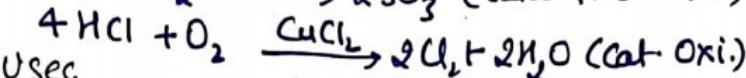
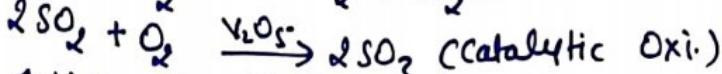
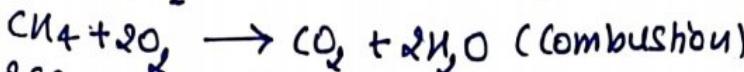
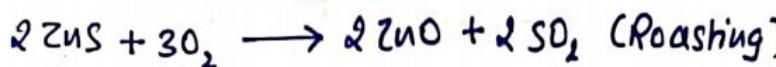
Dioxygen

Preparation



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)
- Dioxygen directly reacts with all 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)



Uses:

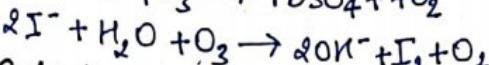
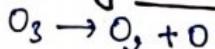
- For artificial respiration in hospitals by mountaineers, pilots and divers
- In Oxy-hydrogen and Oxy-acetylene torches which are used for cutting and welding of metals
- Liquid dioxygen is used as rocket fuel

Ozone (O_3) Preparation

Properties

It is a pale blue gas, dark blue liquid and violet black solid.

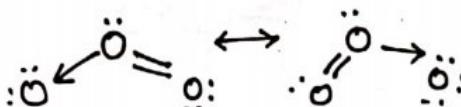
Oxidising action



Reducing Action



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 gills

Allotropes of Sulphur

Rhomboic sulphur (α -sulphur) It has S_8 molecules, yellow in colour, m.pt 385.8 K, specific gravity 2.06 g/cm³. 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/cm³, soluble in CS_2 .

S_8

Rhomboic sulphur

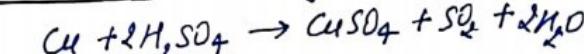
$\xrightarrow{370\text{K}}$ Monoclinic Sulphur

Sulphur dioxide (SO_2) Preparation

Preparation



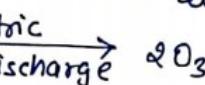
(ii) Lab. Method By heating Cu with H_2SO_4



Dioxygen is a gas while sulphur is a solid at room temp? (2018, 2012) (8)

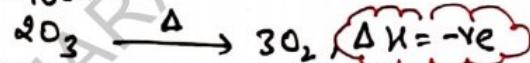
Ans: O_2 molecules are held together by weak van der waal forces because of the small size and high E.N of oxygen

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



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.

$\Rightarrow \text{O}_3$ 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 $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$ Atomic ozone diatomic oxygen atomic oxygen thus liberated brings about the oxidation while molecular oxygen set free

\Rightarrow Sulphur in vapour form exhibits paramagnetic behaviour

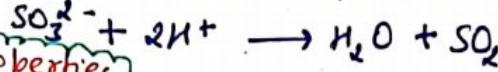
Ans: At elevated temp. sulphur exists as S_2 molecule which has two unpaired e^- in the antibonding π^* orbitals like O_2 hence exhibits paramagnetism

\Rightarrow Stable allotropic form of sulphur

Ans: Rhombic Sulphur.

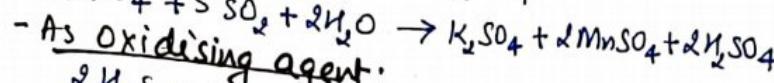
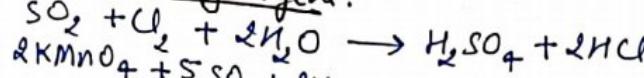
It is also prepared by treating a sulphite with dil. H_2SO_4

(4)

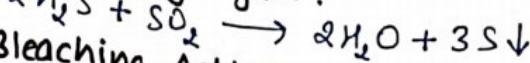


Properties

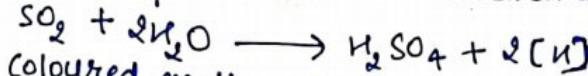
- As reducing agent:



- As oxidising agent:

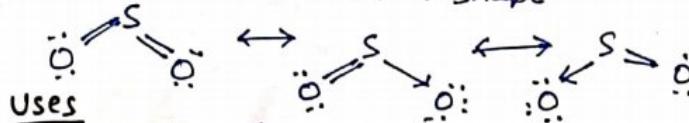


- Bleaching Action: Its bleaching action is temporary due to reduction and is



Coloured matter + [H] → colourless matter

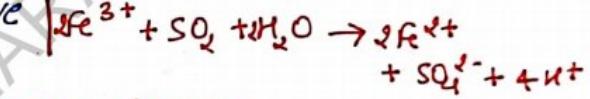
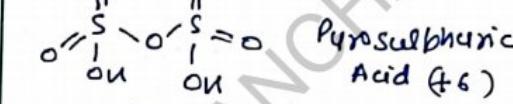
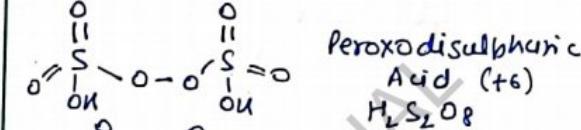
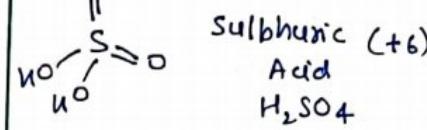
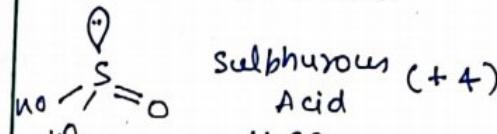
Structure: SO_2 is a gas having sp^2 hybridisation and V-shape



Uses

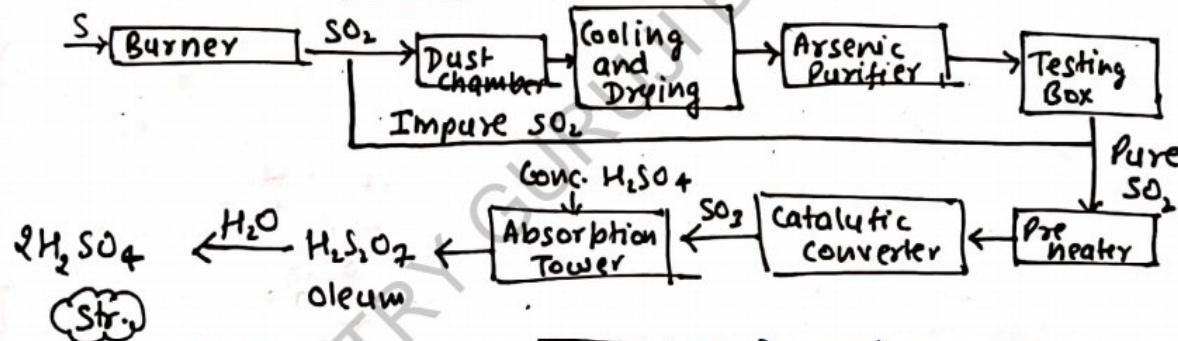
- In the manufacture of sulphuric acid, sulphite and hydrogen sulphide
- As a disinfectant, fumigant and preservative
- For bleaching delicate articles.

Oxoacids of sulphur

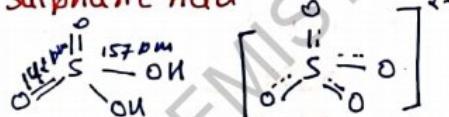


Sulphuric Acid

H_2SO_4 | Prepared by CONTACT PROCESS.



Sulphuric Acid



Properties

- $NaOH \rightarrow NaHSO_4 + H_2O$
- $Zn \rightarrow ZnSO_4 + H_2$
- $C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$
- $S_8 \rightarrow SO_2 + H_2O$
- $Na_2S \rightarrow Na_2SO_4 + H_2S$
- $BaCl_2 \rightarrow BaSO_4 + 2HCl$
- $K_4[Fe(CN)_6] \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO_2$

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 $2SO_2 + O_2 \xrightleftharpoons{V_2O_5} 2SO_3$, $\Delta H^\circ = -196.6 \text{ kJ/mol}$. The reaction is reversible and exothermic i.e. 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)

10

Group 17 elements are collectively called halogens

F	Fluorine	9	$2s^2 2p^5$	$n s^2 n p^5$	Pale Blue Gas
Cl	Chlorine	17	$3s^2 3p^5$		Greenish Yellow Gas
Br	Bromine	35	$4s^2 4p^5$		reddish brown liquid
I	Iodine	53	$5s^2 5p^5$		
At	Astatine	85	$6s^2 6p^5$		Purple Solid

Atomic radii :- Increase down the group

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

Electronegativity :- Decreases down the group.

Electron gain enthalpy :- $\text{Cl} > \text{F} > \text{Br} > \text{I}$ Bond energy $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

M.Pt and B.Pt :- Increase down the group Heat of hydration $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

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

Reactivity :- $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Hydrides :- G-17 elements form hydrides of

Boiling Point :- The general form HX ($\text{HF}, \text{HCl}, \text{HBr}, \text{HI}$)

Melting Point :- $\text{HI} > \text{HF} > \text{HBr} > \text{HCl}$

Bond length :- $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

Bond dissociation enthalpy :- $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

Acidic strength :- $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

Thermal stability :- $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

Reducing Power :- $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

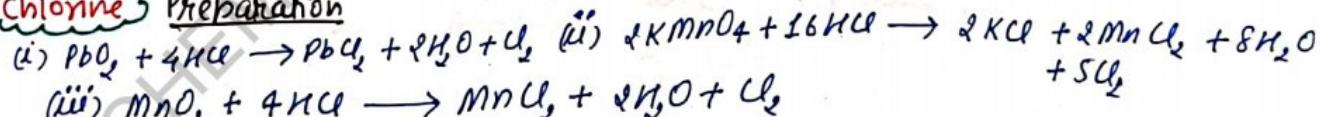
Oxides of G-17 :- Fluorine form two oxides of OF_2 and O_2F_2 called oxygen fluorides, other halogens form oxides in which oxidation state of these halogens range from +1 to +7.

The higher oxides of halogens are more reactive than the lower ones.

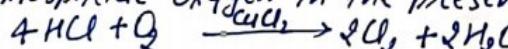
Metal Halides :- Ionic character: $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$

for metals exhibiting more than one oxidation state, the halides in higher oxidation states will be more covalent than the one in lower O.K.I. state

Chlorine Preparation



Manufacture :- \rightarrow Dalton's Process by oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of CuCl_2 at 723 K



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

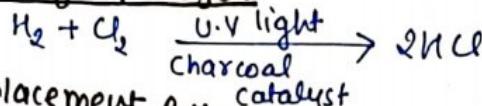
Bleaching Action and Oxidising Property $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$



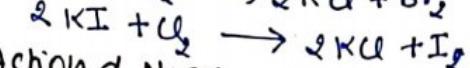
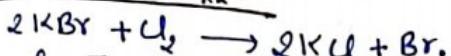
Coloured matter + $[\text{O}] \rightarrow$ colourless matter

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

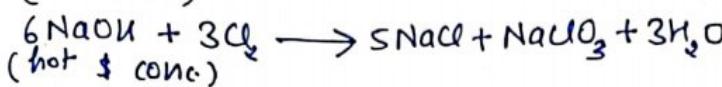
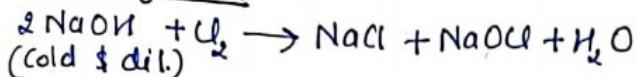
Action of Hydrogen



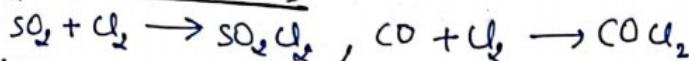
Displacement Rxn



Action of NaOH



Addition Reactions

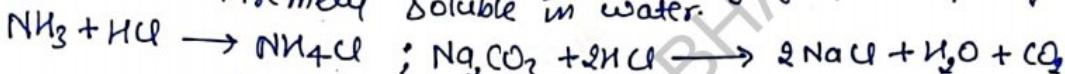


Uses: as a bleaching agent, disinfectants and in the manufacture of CCl_3 , CCl_4 , DDT, bleaching powder, poisonous gas phosgene ($COCl_2$), tear gas (CCl_3NO_2) and mustard gas ($Cl_2S_2N_2Cl_2$)

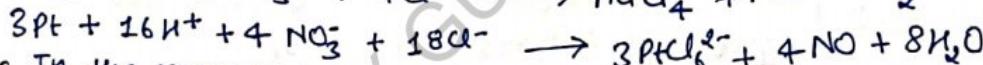
Hydrogen Chloride HCl

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.



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



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

Polyhalous Acid (+1)

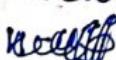
F



Cl



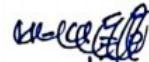
Br



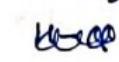
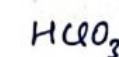
I



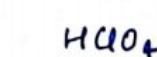
Halous Acid (+3)



Halic Acid (+5)



Perhalic Acid (+7)



→ Oxidation Number of central atom increases →

→ thermal stability increases →

→ covalent character of X-O bond increases →

→ oxidising power decreases →

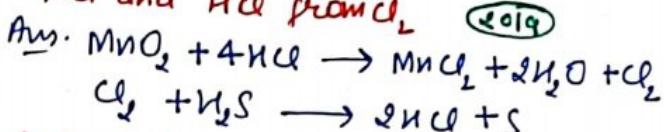
→ Acidity increases →

→ E.N. of central atom remains the same →

⇒ 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 H_2O 11



⇒ Bleaching power of Cl_2 is permanent by SO_2 is temporary

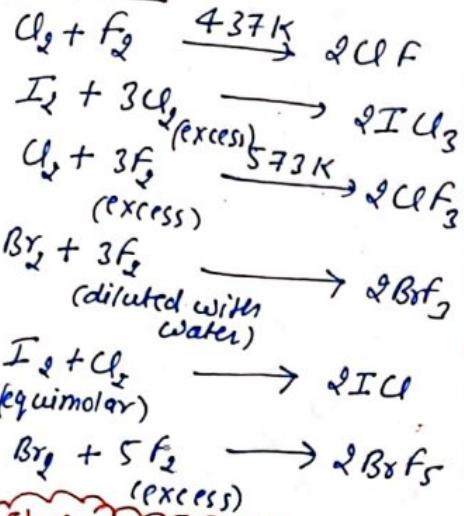
Ans: The bleaching action of Cl_2 is due to oxidation of coloured substances to colourless substances by nascent oxygen. Since, the bleaching action of Cl_2 is due to oxidation and that of SO_2 is due to reduction. Therefore bleaching effect of Cl_2 is permanent while that of SO_2 is temporary

Electronegativity decreases →
 Thermal stability decreases →
 Oxidising power decreases →
 Acidic strength decreases →

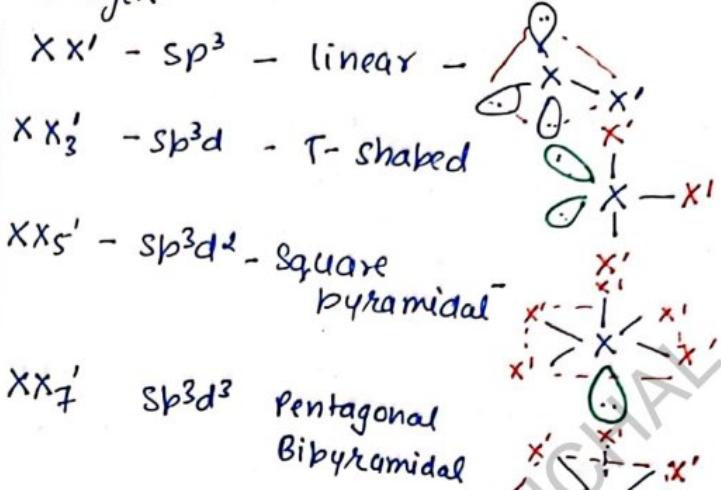
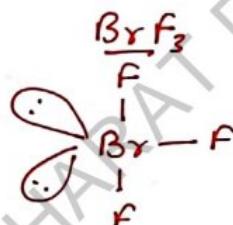
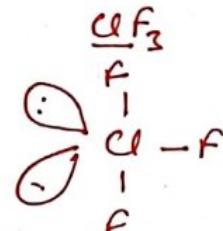
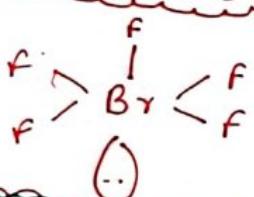
↓
 ↓
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Interhalogen Compounds Halogens combine amongst themselves to form a number of interhalogens of the type XX' , XX'_3 , XX'_5 and XX'_7 where X is a larger size halogen (more electropositive) and X' is smaller size halogen (less electropositive)

Preparation



Shape



Group-18 Elements (Noble Gases)

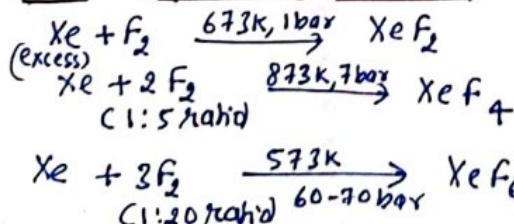
These are monoatomic gases and are also known as rare gases or aerogens

General Characteristics

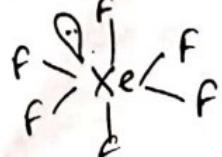
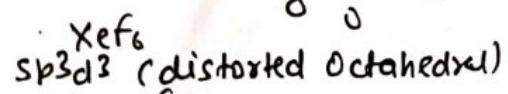
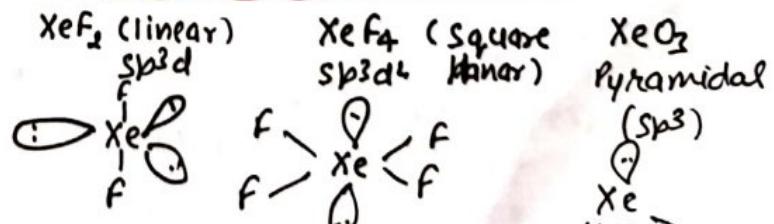
Element	Symbol	Name	Atomic Number	Electron Configuration	Physical State	Atomic Radii	Electron Gain Enthalpy	M.Pt				
He	He	Helium	2	1s ²	Gases	Increase down the group	Positive	Very low				
Ne	Ne	Neon	10	1s ² 2s ² 2p ⁶								
Ar	Ar	Argon	18	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶								
Kr	Kr	Krypton	36	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 4p ⁶								
Xe	Xe	Xenon	54	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 4p ⁶ 5s ² 5p ⁶								
Rn	Rn	Radon	86	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 4p ⁶ 5s ² 5p ⁶ 6s ² 6p ⁶								

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

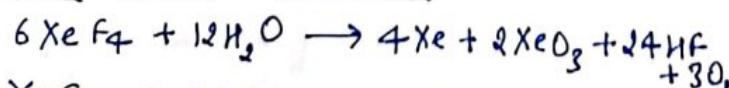
Xenon - Fluorine Compounds



Structure of Compounds of Xenon



Xenon Oxygen Compounds



Uses of Helium - To lift weather balloons and air ships
 As breathing mixture - for inflating the tyres of aeroplanes (189)

Neon - for advertising - for filling sodium vapour lamps

Argon - To create In becon light

- To create an inert atmosphere

Krypton - for geiger counters - To date the age of rocks.

- In runway and approach lights in airports

Xenon : In high efficiency miners cap lamps

Krypton flash bulbs for high speed photography

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

\Rightarrow Complete the following Rxn



\Rightarrow Noble gases have low Boiling Pt?

Noble gases being monoatomic 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 elements

Those elements in which last e^o enters in d-orbital are 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

2f1	Sc - Scandium	21	Elec. Conf.	Oxidation state
2f1	Ti - Titanium	22	$3d^1 4s^2$	+3
Very	V - Vanadium	23	$3d^2 4s^2$	+2, +3, +4
Crazy	Cr - Chromium	24	$3d^3 4s^2$	+2, +3, +4, +5
Boff	Mn - Manganese	25	$3d^5 4s^1$	+1, +2, +3, +4, +5, +6
Unreal	Fe - Iron	26	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Oil	Co - Cobalt	27	$3d^6 4s^2$	+2, +3, +4, +5, +6
of	Ni - Nickel	28	$3d^7 4s^2$	+2, +3, +4
of 2	Cu - Copper	29	$3d^8 4s^2$	+2, +3, +4
Ca	Zn - Zinc	30	$3d^{10} 4s^1$	+1, +2

Ar

$3d^{10} 4s^2$
 $+2$

Zn , Cd and Hg are not considered as transition elements because they have fully filled d-orbital and can't show most of the properties shown by transition element.

Metallic character with the exception of Zn, Cd and Hg, all the (14) 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 n_s and $(n-1)d$ electrons.

Atomic radii Decrease from left to right but becomes constant when 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.

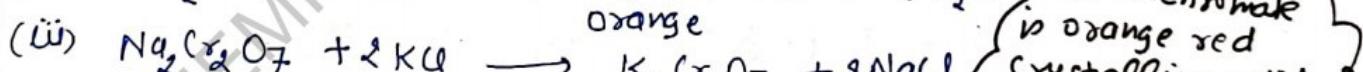
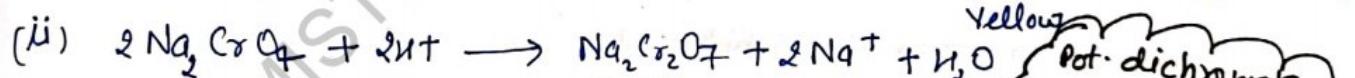
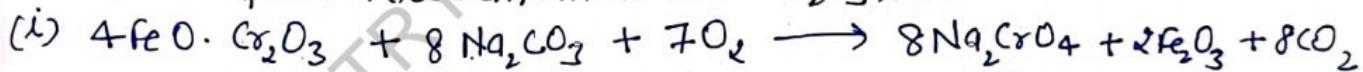
Catalytic behaviour Due to variable oxidation states and ability to form complexes

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

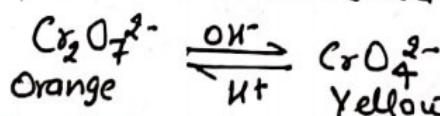
Alloy formation :- Due to similar atomic sizes.

Potassium Dichromate, $K_2Cr_2O_7$

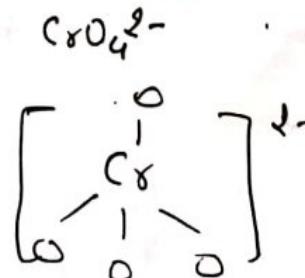
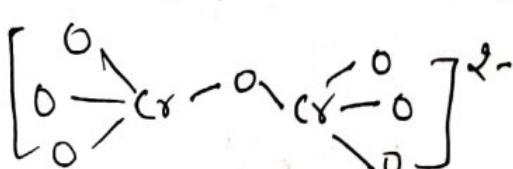
Prepared from Ferrochromate ($FeO \cdot Cr_2O_3$)



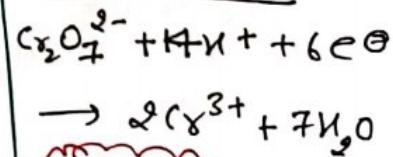
Pot. dichromate can be converted into chromate



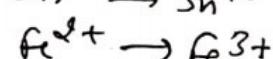
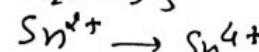
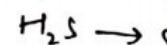
Str. of Dichromate ion and chromate ion



Oxidising agent in acid medium \rightarrow



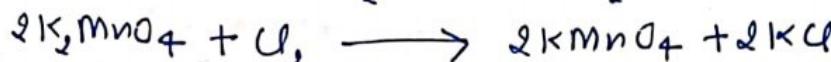
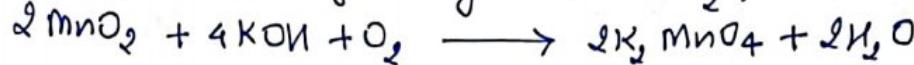
Oxidise



Potassium Permanganate ($KMnO_4$)

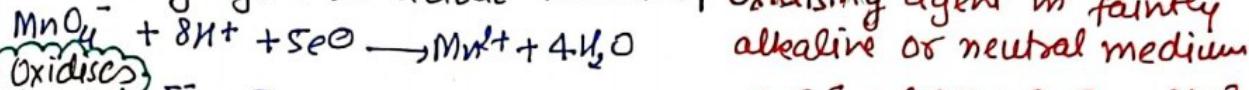
(15.1)

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



It is a deep purple crystalline solid, Oxidising agent having m.pt $240^\circ C$

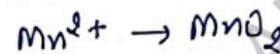
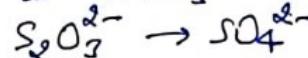
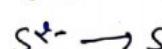
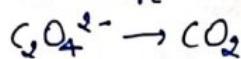
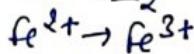
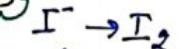
Oxidising agent in acidic medium | Oxidising agent in faintly



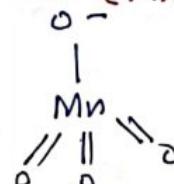
alkaline or neutral medium



(Oxidises)



Str. of Permanganate ion (MnO_4^-)



and ~~Permanganate~~ O^- -ion (MnO_4^{2-})



$KMnO_4$ is used as
disinfectant,
germicide
and Baeyer's
Reagent

Volumetric titrations involving $KMnO_4$ 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^- enters in $4f$ -orbital. Ce (at.no. 58) to Lu (at.no. 71)

Actinoids - last e^- enters in $5f$ orbital. Thorium (at.no. 90) to

General electronic config. $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ Lawrencium (a.n. 103)

Lanthanoid contraction In lanthanoid series, with increasing atomic number there is progressive decrease in atomic/ionic radii (r^{3+}) from La^{3+} to Lu^{3+}

Reason Due to addition of new electrons into f -subshell and imperfect shielding by 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

Cr and Hf have similar properties due to same size.

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

User of Lanthanoids - Used in making misch metal
 and traces of S, C, Ca and Al. It is used to make tracer bullets, shells
 \Rightarrow Difference between lanthanoids and actinoids

(16)

- They show +2 and +4 oxidation states in some cases besides +3.
 - Except promethium, they are non radioactive.
 - They do not form oxo-cations.
 - The compounds of lanthanoids are less basic.
 - They have less tendency of complex formation.
- | Lanthanoids | Actinoids |
|-------------|---|
| | • They show higher oxidation state of +4, +5, +6 and +7, besides +3. |
| | • All actinoids are radioactive. |
| | • They form oxo-cations like UO_2^{2+} , PuO_2^{2+} , UO_3^{+} etc. |
| | • Actinoid compounds are more basic. |
| | • 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 eg) are called co-ordinate compounds or complex compounds.

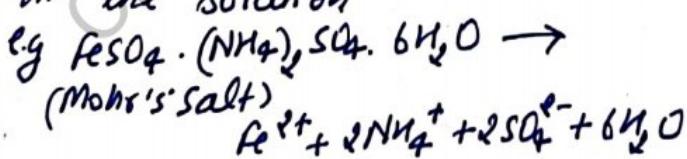
Types of Complexes: (i) cationic complex e.g. $[Co(NH_3)_6]^{3+}$

(ii) Anionic complex e.g. $[Ag(CN)_4]^-$

(iii) Neutral complex e.g. $[Ni(CO)_4]$

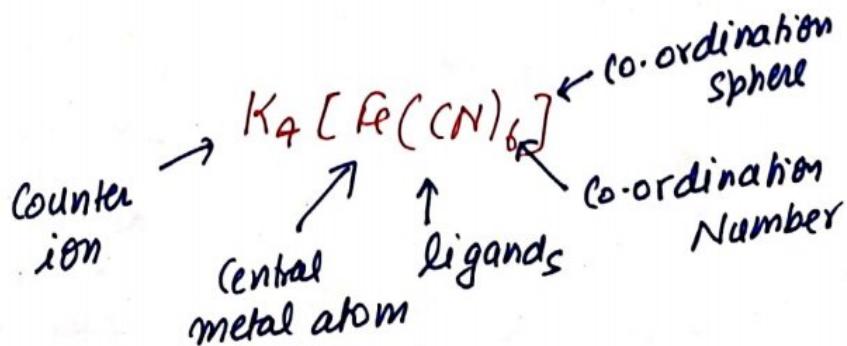
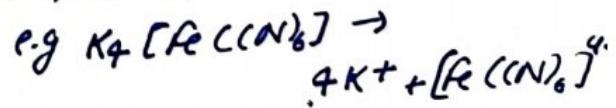
Double Salt

- (i) They have two simple salts in equimolar ratio.
- (ii) They do not contain co-ordinate bond.
- (iii) Their properties are same as their constituents.
- (iv) They lose their identity in the solution.



Complex Compound

- (i) They may or may not have simple salts in equimolar ratio.
- (ii) They contain co-ordinate bond.
- (iii) Their properties are different from their constituents.
- (iv) They lose their identity in the solution.

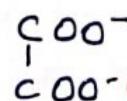
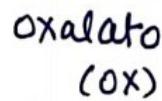
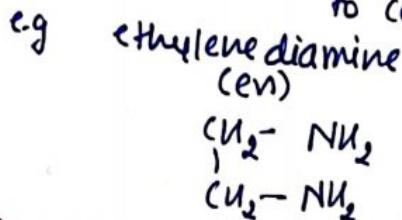


Ligand:- The donor species (atom, molecule or ion) which donate a pair of e^- to the metal atom is called ligand. (17)

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

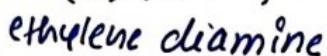
Monodentate or Unidentate:- Ligand has one donor atom eg NH_3 , H_2O , Cl^-

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

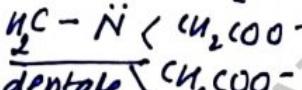
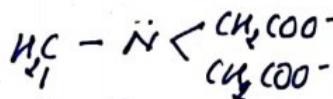


Counterion The ionizable group which are written outside the bracket is called counterion

Hexadentate ligand:- which has six donor atoms



Ambidentate ligands Those unidentate



Co-ordination sphere

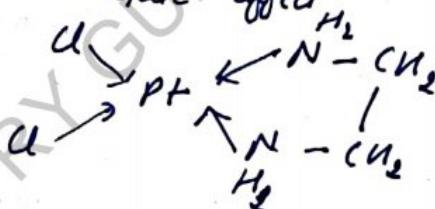
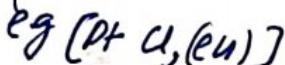
The central atom and the ligands are enclosed in square bracket

Co-ordination are called ambidentate ligands which have more than one ligands



Chelate

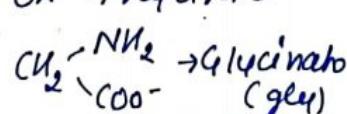
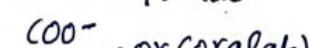
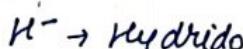
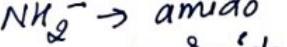
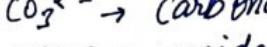
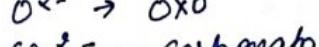
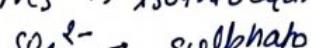
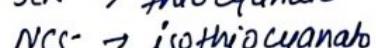
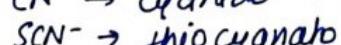
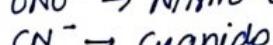
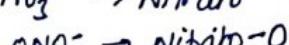
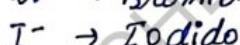
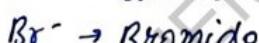
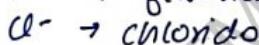
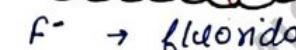
when a bidentate or a polydentate ligand is attached by two or more atoms to the central atom forming a ring, the ligand is called chelating ligand and the complex is called chelate, the effect is called chelate effect



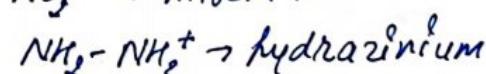
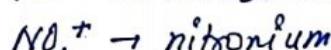
Co-ordination Number

Total number of co-ordinate bonds formed with C.M.A by the ligands

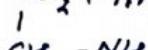
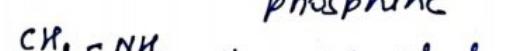
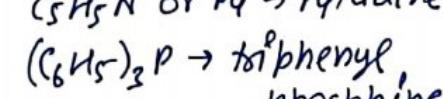
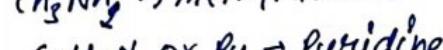
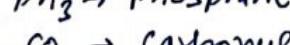
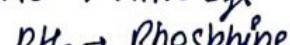
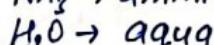
Negative ligands



Positive ligands



Neutral ligands



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

2.) $[Co(NH_3)_6]Cl_3 \rightarrow$ hexa ammine cobalt (III) chloride

3.) $[Pt(NH_3)_4Cl(NO_3)] \rightarrow$ diammine chlorido nitrito - N - platinum (II)

4.) $K_3[Cr(O_4)_3] \rightarrow$ potassium tetra hydroxo zincate (II)

5.) $[Ag(NH_3)_2]^+ [Ag(CN)_4]^- \rightarrow$ diammine silver (I) dicyano argentate (I)

6.) $Hg[Co(SCN)_4] \rightarrow$ mercury tetra thiocyanato cobaltate (III)

7.) $[Co(NH_3)_5CO_3]Cl \rightarrow$ bentaammine carbonato cobalt (III) chloride

8.) $K_3[Fe(O_4)_3] \rightarrow$ potassium trioxalato ferrate (III)

9.) $[Pt(NH_3)_2Cl(NH_3CH_3)]Cl \rightarrow$ diammine chlorido methanamine platinum (II) chloride

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

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

12.) $[NiCl_4]^{2-} \rightarrow$ tetrachloronickelate (II) ion

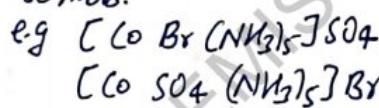
13.) $[Ni(NH_3)_6]Cl_3 \rightarrow$ hexa ammine nickel (III) chloride

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

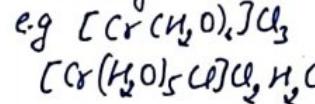
Ionisation isomerism

Compounds which give different ions in solution due to the exchange of ions in coordination sphere and counter ions are called ionisation isomers.



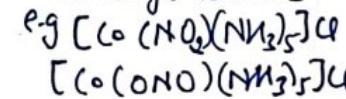
Hydrate isomerism

Isomers which differ in the no. of water molecules attached to the metal atom or ion as ligand



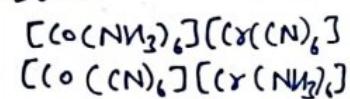
Linkage Isomerism

when an ambidentate ligand attached to metal through different atoms the the compounds are said to be linkage isomers



Co-ordination Isomerism

when both +ve and -ve ions of a salt are complex ions and two isomers differ in the distribution of ligands in two complexes



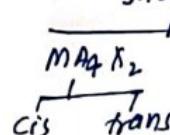
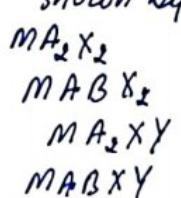
Stereo isomerism

Geometrical or cis-trans isomerism

If two identical ligands occupy adjacent position \Rightarrow cis

If occupy opposite position \Rightarrow trans

In Square planar shown by



In Octahedral shown by

If all three similar gr. occupy adjacent position
then fac-isomer

Optical Isomerism
The isomerism arises due to non superimposable 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

(19)

It was developed by Pauling

C.N	Type of hyb.	Geometry
4	sp^3	Tetrahedral
	$d\;sp^2$	Square planar
5	$d\;sp^3$	Trigonal bipyramidal
6	sb^3d	Square pyramidal
	d^2sp^3	Octahedral (Inner)
	sp^3d^2	Octahedral (Outer)

Inner orbital complex

Involves inner d-orbitals i.e. $(n-1)d$

Low spin complexes

Have less or no unpaired e \ominus

e.g. $[Co(NH_3)_6]^{3+}$

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

→ Paramagnetism & 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) $[Ni(CN)_4]^{2-}$

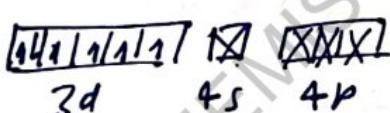
(c) $[NiCl_4]^{2-}$

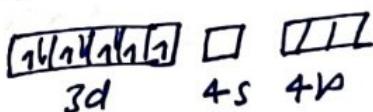
Name → hexaaqua iron(II) ion \Rightarrow tetracyano nickelate(II) ion

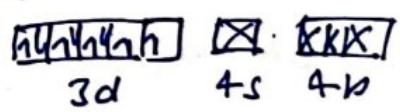
${}_{\text{ff}} Fe^{2+} = (\text{Ar})^{18} 3d^6 4s^0$

${}_{\text{ff}} Ni^{2+} = (\text{Ar})^{18} 3d^8 4s^0$

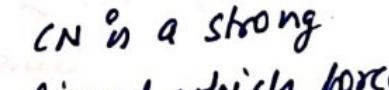
\Rightarrow tetra chlorido nickelate(II) ion
 ${}_{\text{ff}} Ni^{2+} = (\text{Ar})^{18} 3d^8 4s^0$

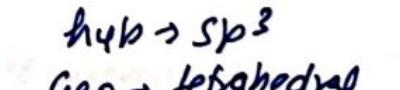


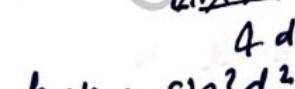


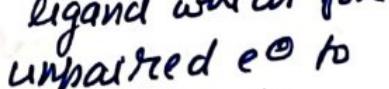


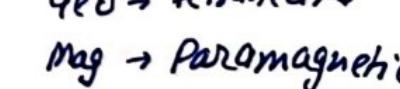




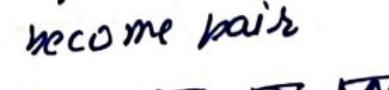








hyb \rightarrow sp^3d^2





Geom. \rightarrow Octahedral



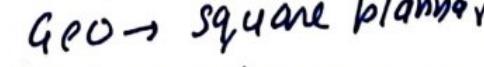


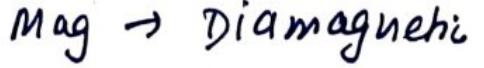
Mag. \rightarrow Paramagnetic











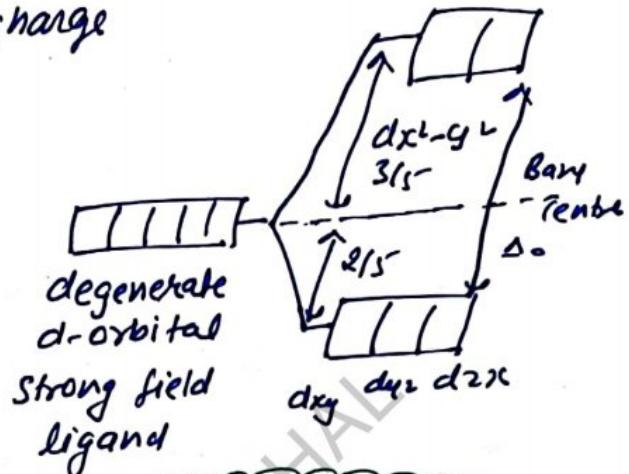
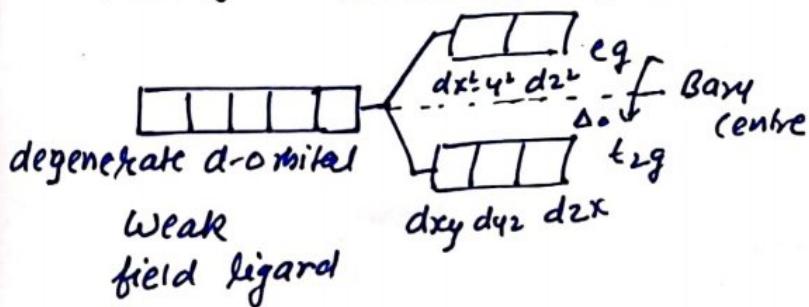




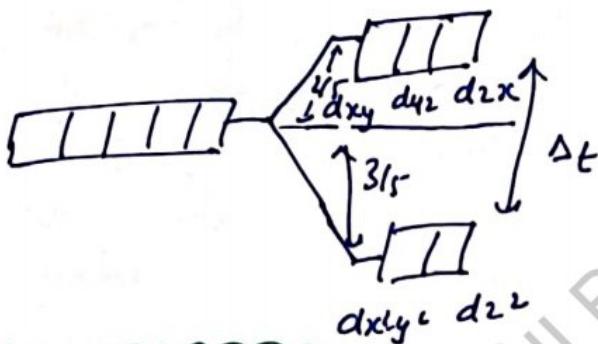
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Crystal field Theory

- 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



splitting in Tetrahedral complex



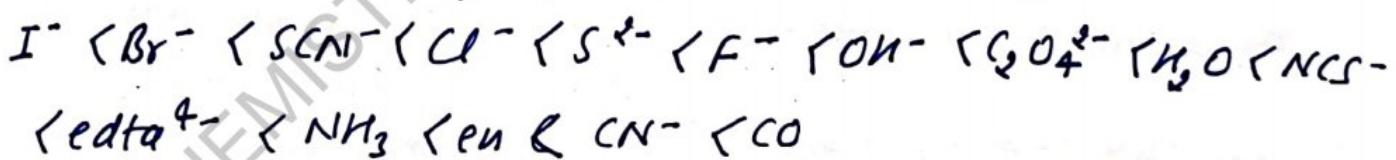
Crystal field Splitting Energy

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.



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 e_g in an octahedral field when

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

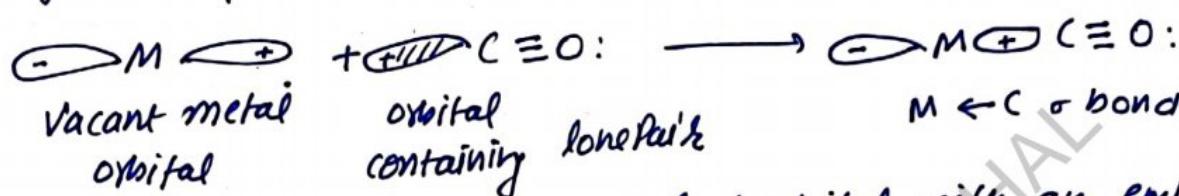
$$(ii) \Delta_o < P \rightarrow t_{2g}^3 e_g^1$$

Bonding in Metal Carbonyls

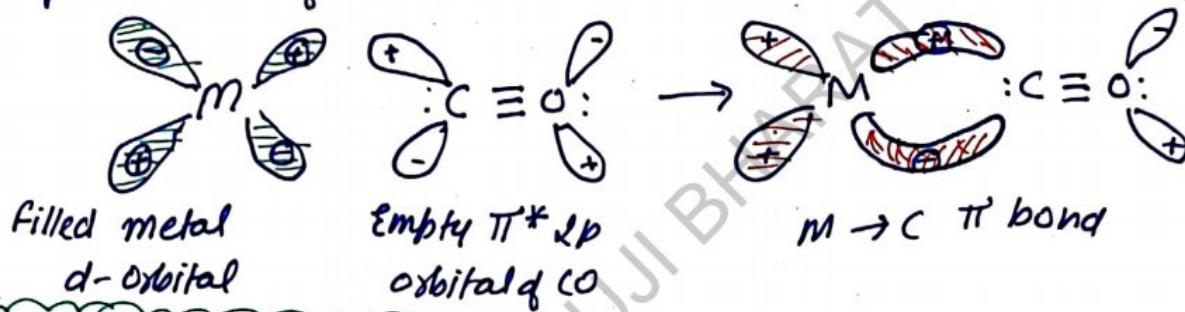
21.

- 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.

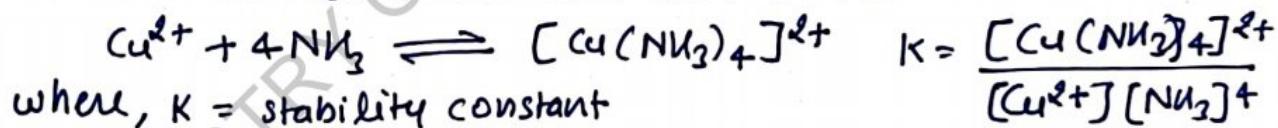


- π -overlap involving filled metal d-orbital with an empty antibonding π^*_{2p} orbital of same CO. This results in formation of $\text{M} \rightarrow \text{C} \pi$ bond. This is also called back bonding.



Stability of Complexes

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

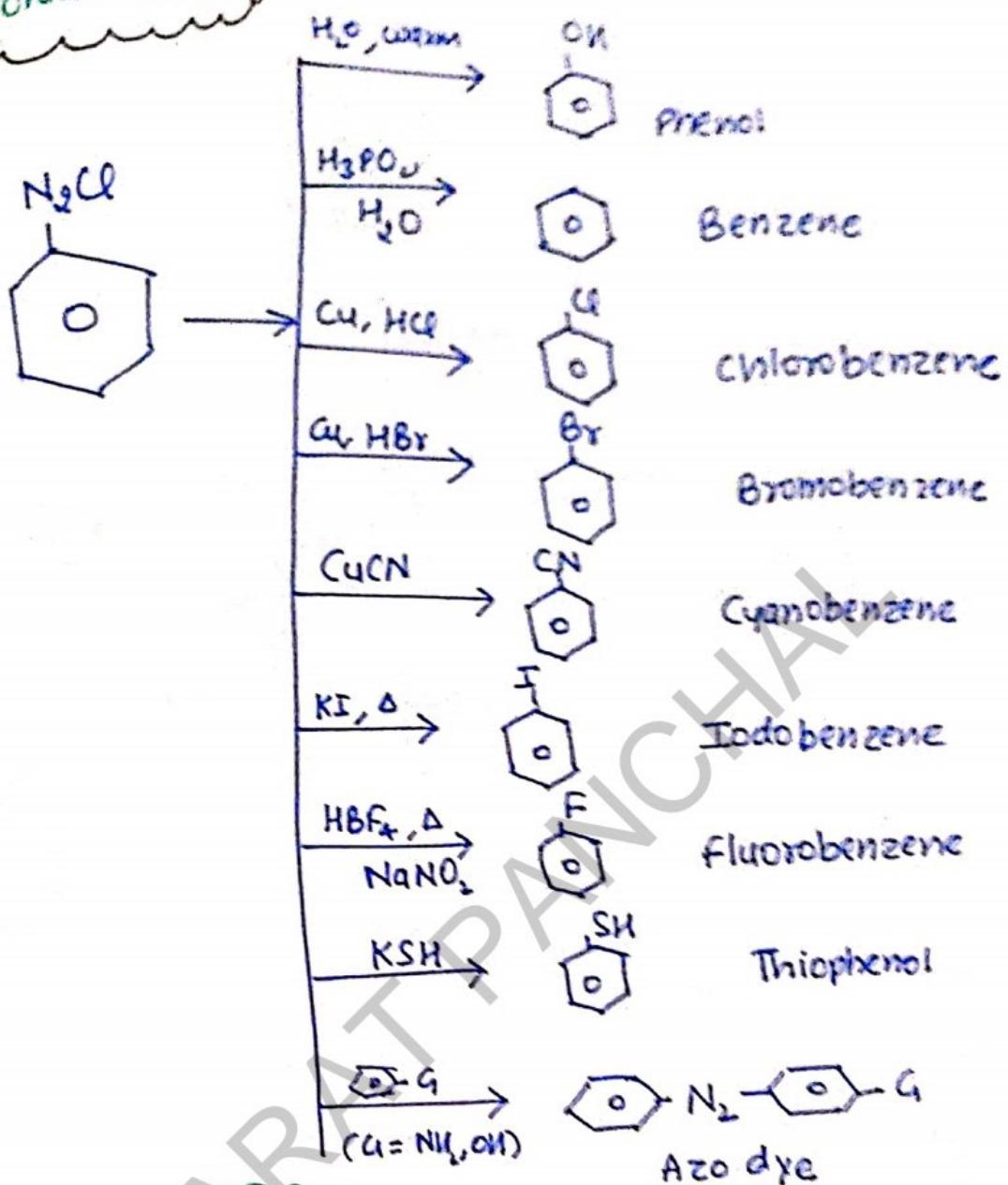


- Higher the value of stability constant (K), higher will be the stability of complex
- Higher the polarising power of metal ion and basicity of ligand, higher will be the stability of complex.

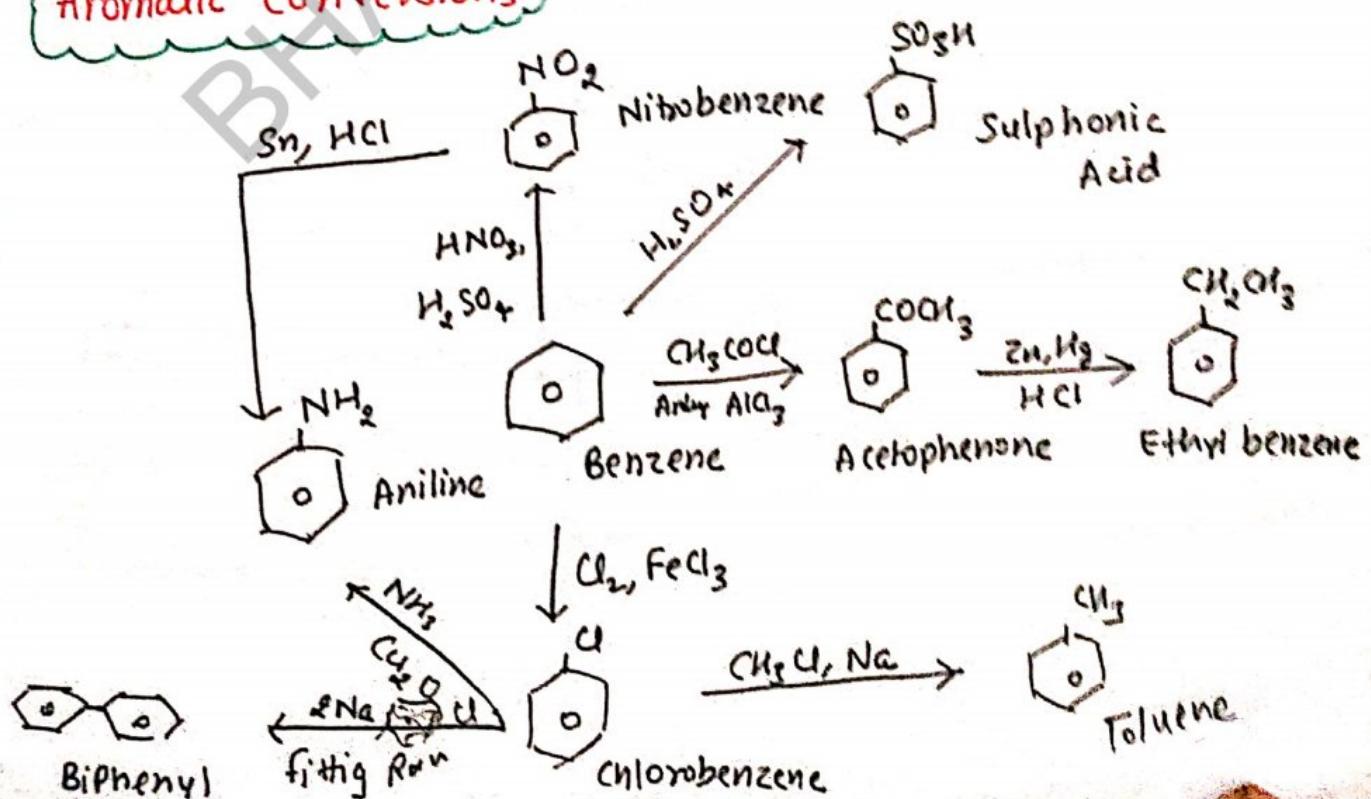
Application of Co-ordination Compounds

- Co-ordination compounds are of great importance in biological system e.g chlorophyll, haemoglobin, Vitamin B₁₂ 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.

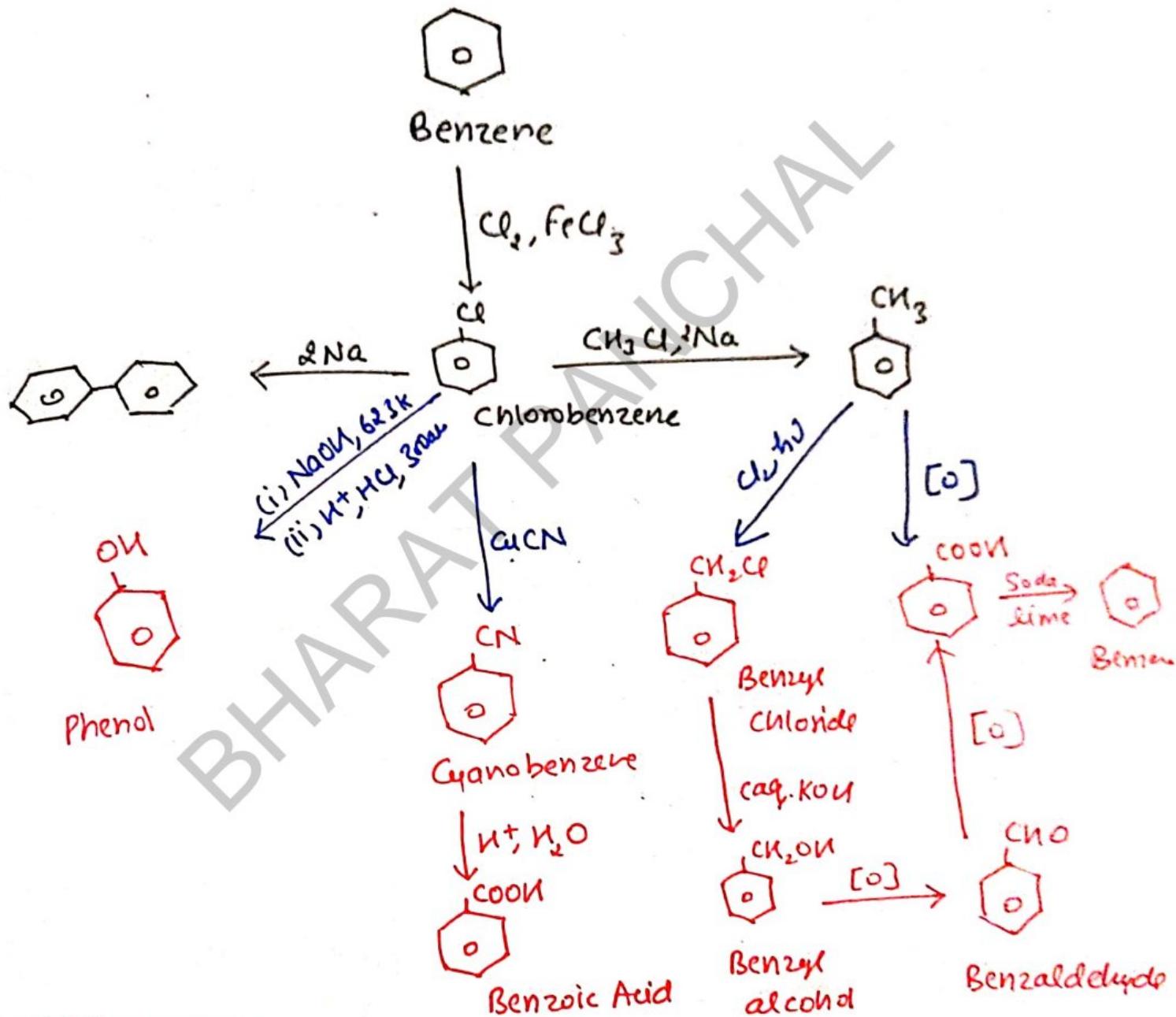
Diazonium Salt



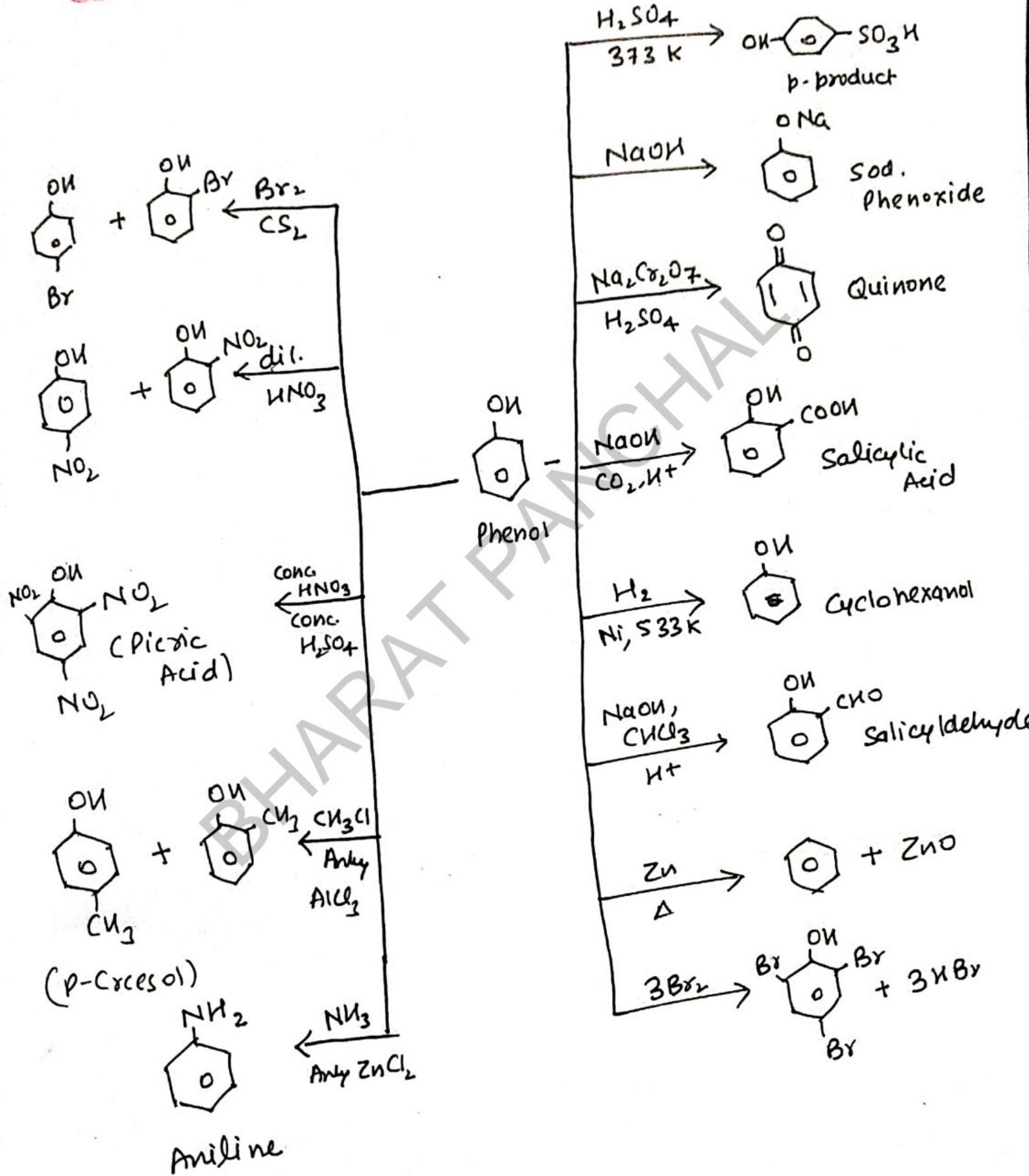
Aromatic Conversions



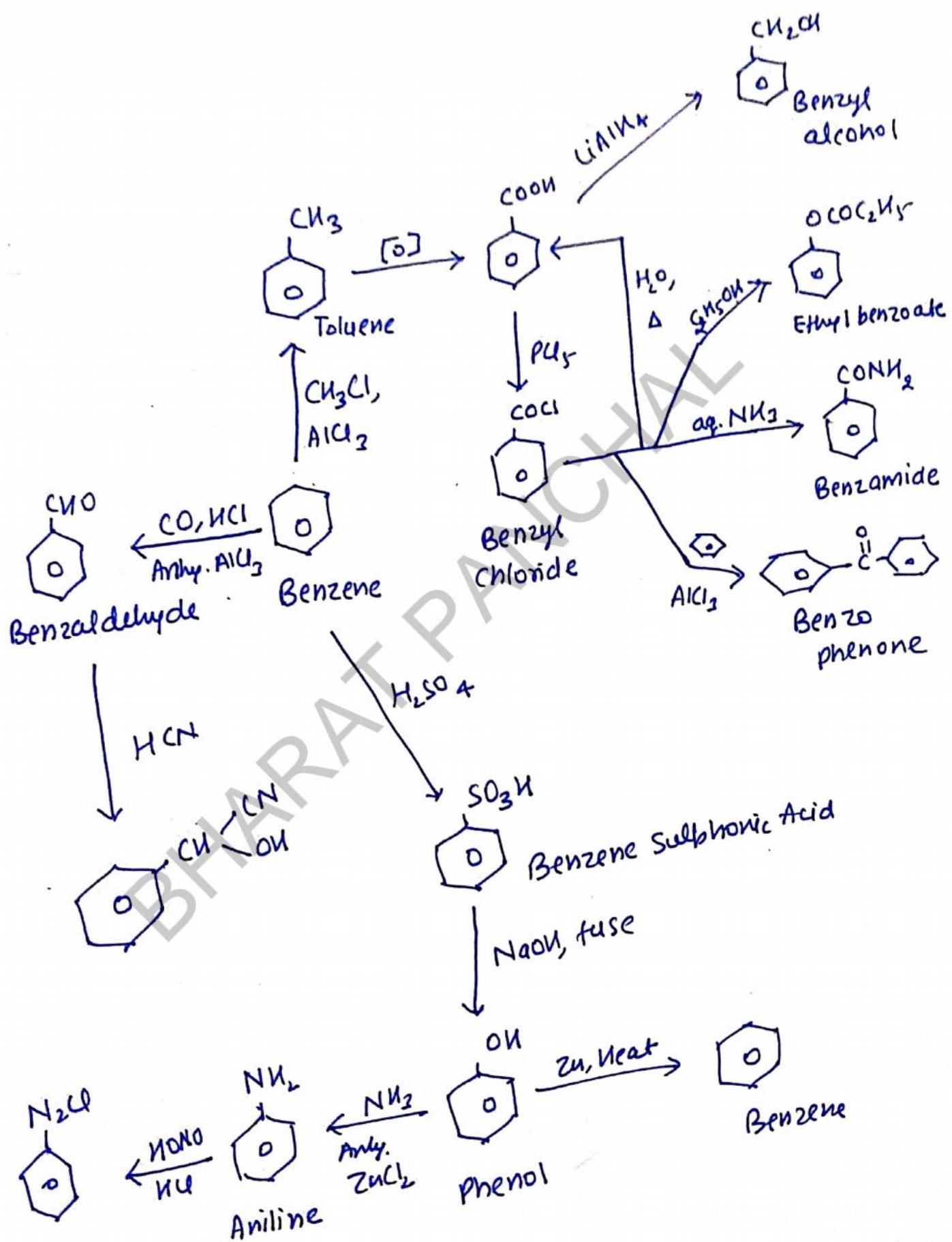
⇒ Road Map #3



Road Map # 4

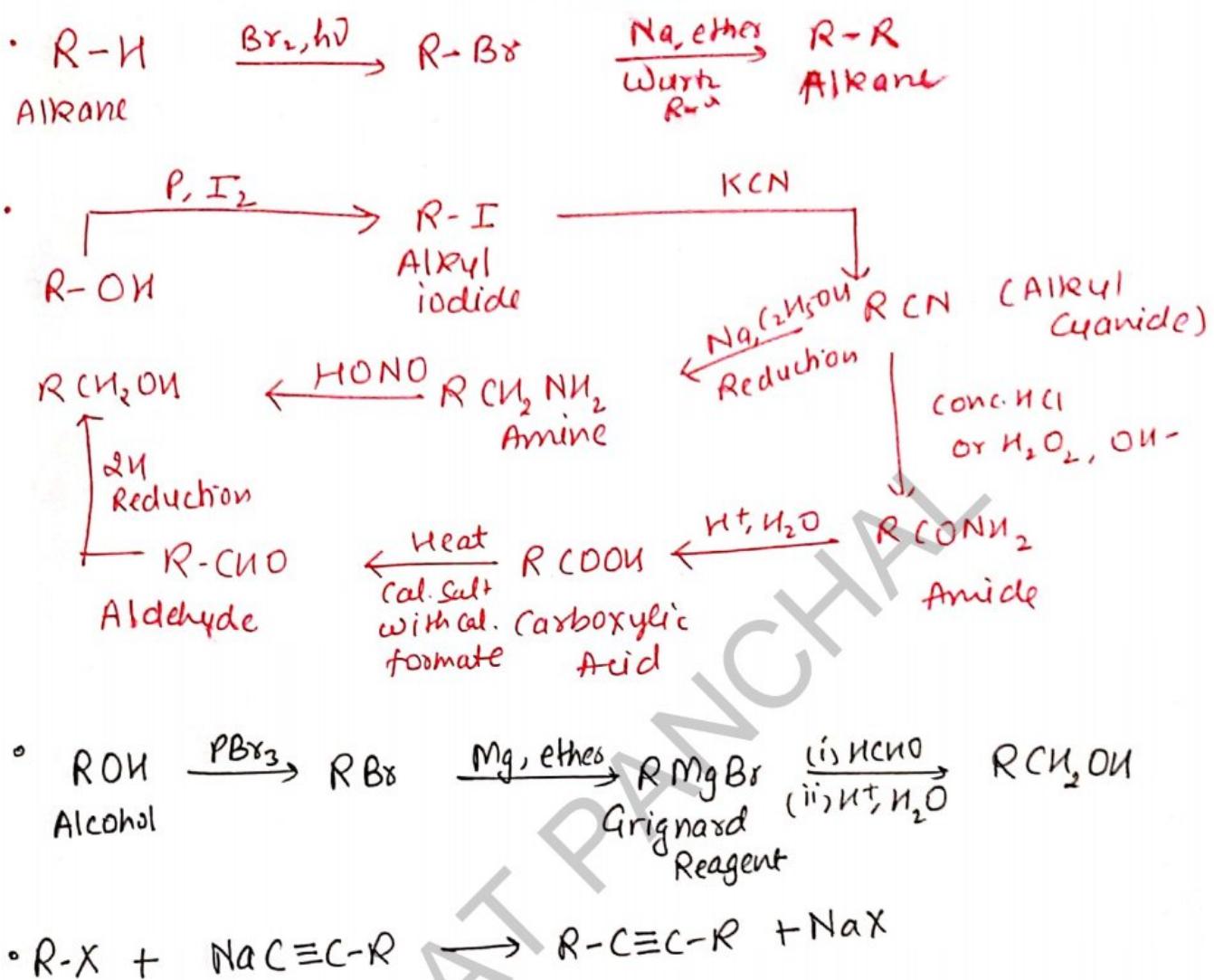


Road Map #5

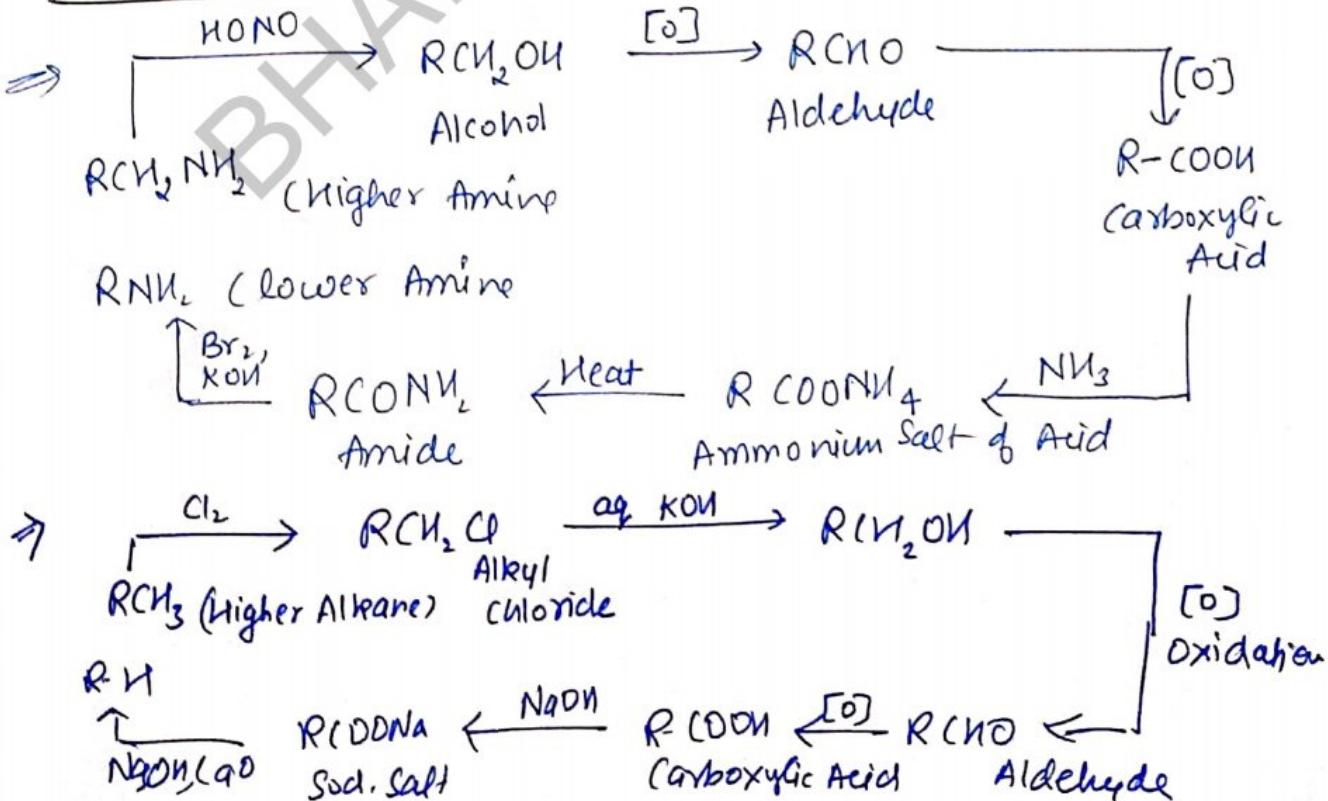


Aliphatic Conversion

Step Up

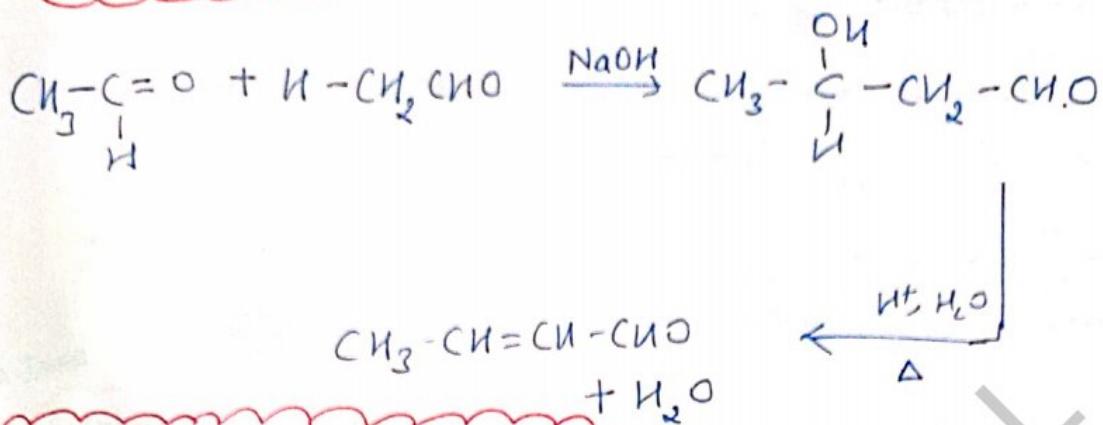


Step Down



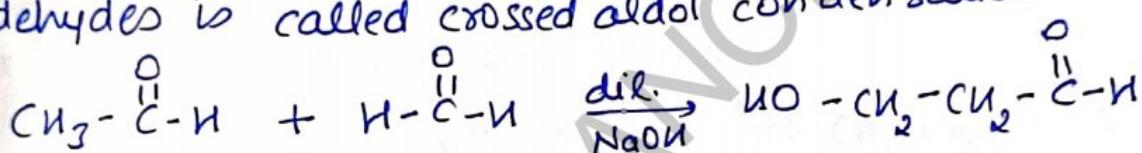
Name Reaction

Aldol condensation



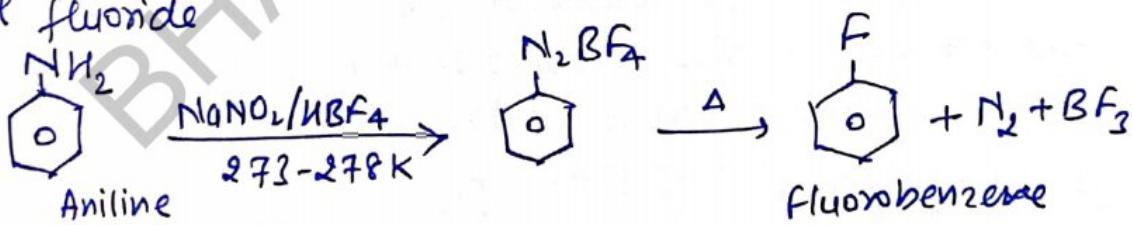
Crossed aldol condensation

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



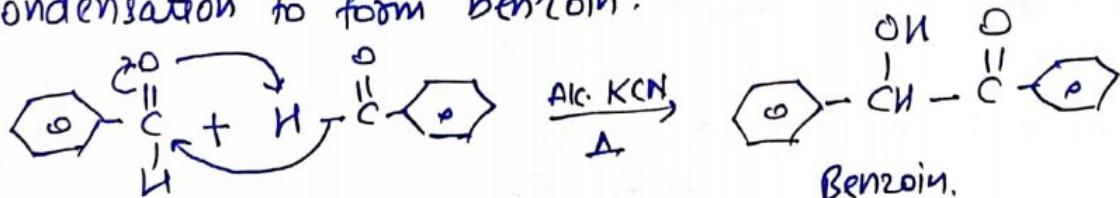
Baeyer-Schiemann Rxn

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



Benzoin condensation

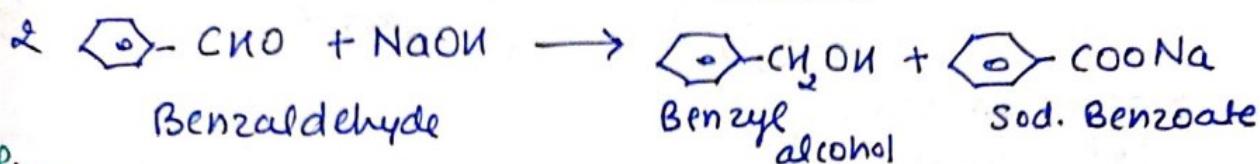
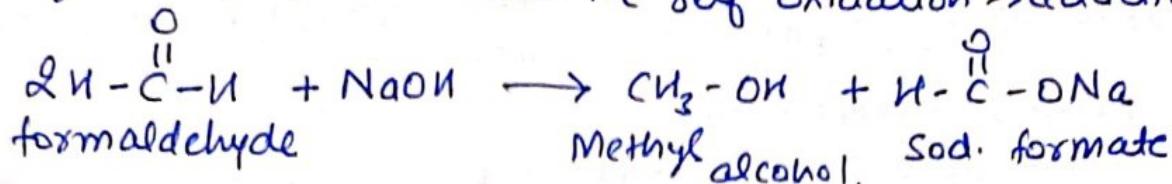
On heating with an ethanolic soln of KCN , two molecules of aromatic aldehydes undergo condensation to form benzoin.



M.IMP.

Cannizzaro Reaction

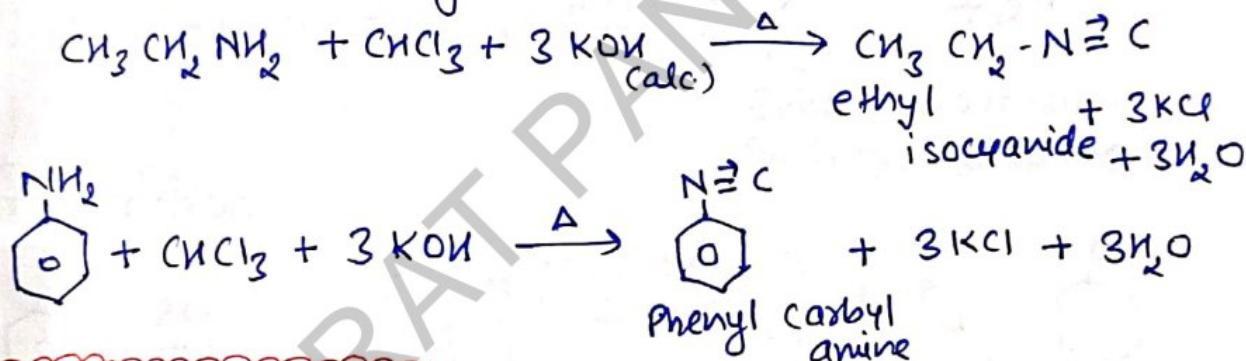
α -hydrogen atoms, when treated with conc. alkali solution undergo disproportionation i.e self oxidation-reduction.



M.Imp.

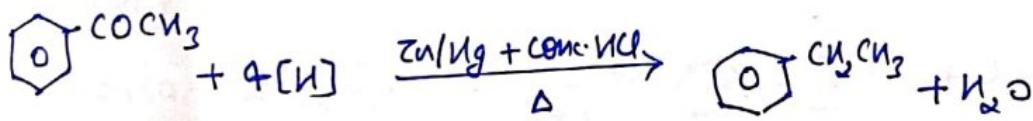
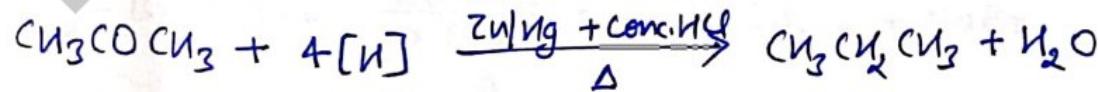
Carbylamine reaction

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



Clemmensen Reduction

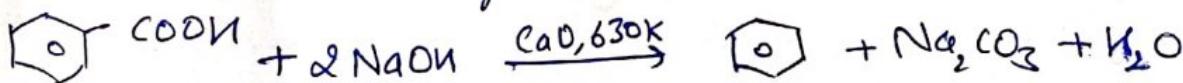
Clemmensen Reduction: The reduction of aldehydes and ketones to corresponding hydrocarbons with amalgated zinc and conc. HCl is called clemmensen reduction.



The reduction works better with ketones than aldehydes

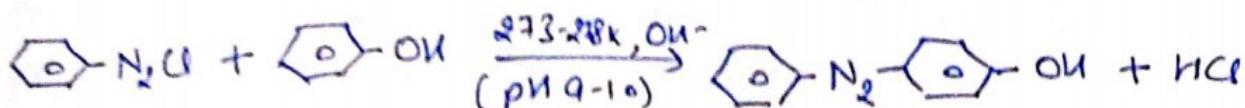
Decarboxylation Reaction

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

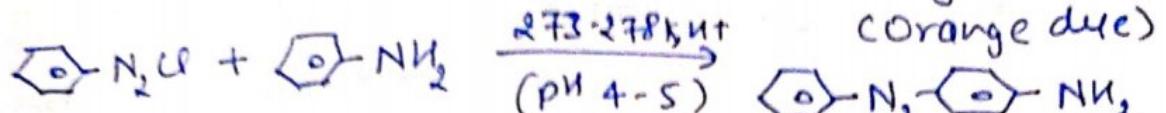


Coupling Reaction

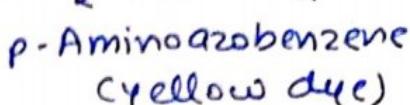
The reaction of diazonium salts with phenol and aromatic amines to form azo compounds



p-Hydroxyazobenzene

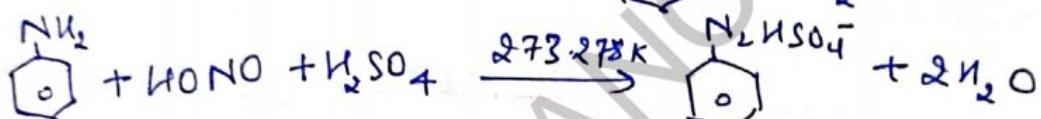
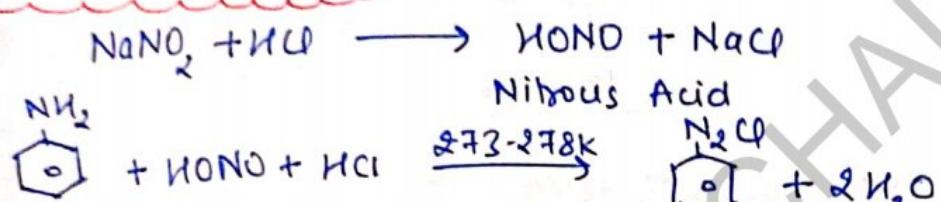


(Orange dye)



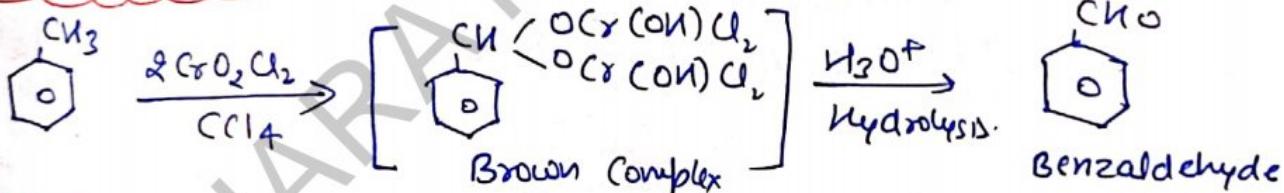
p-Aminoazobenzene
(Yellow dye)

Diazotisation Reaction

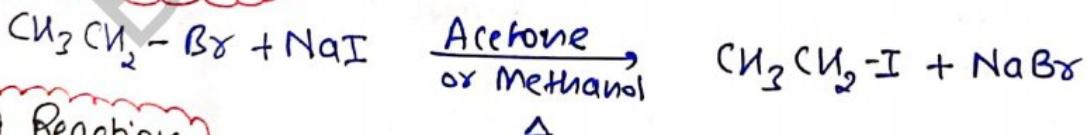


Benzene diazonium
hydrogen sulphate

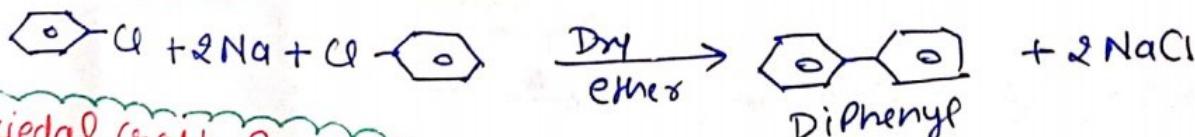
Friedel-Crafts Reaction



Finkelstein Reaction

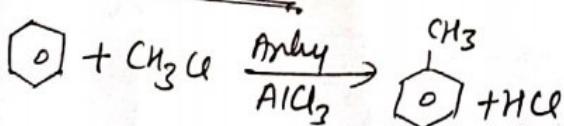


Fittig Reaction

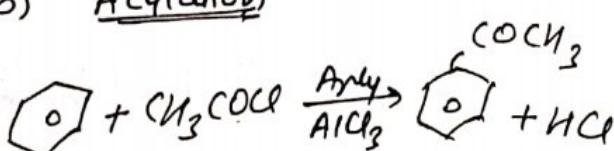


Friedel-Crafts Reaction

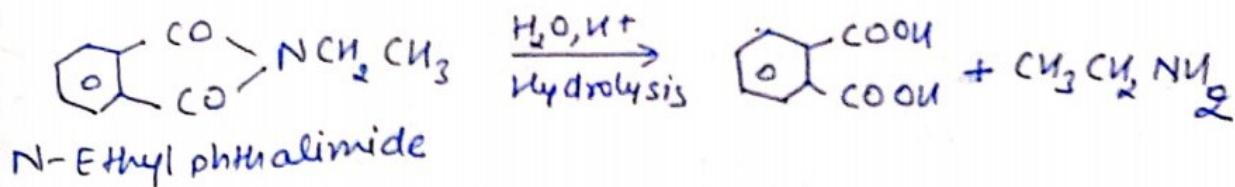
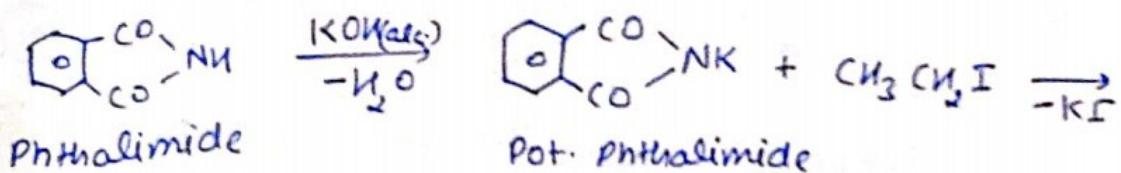
(a) Alkylation



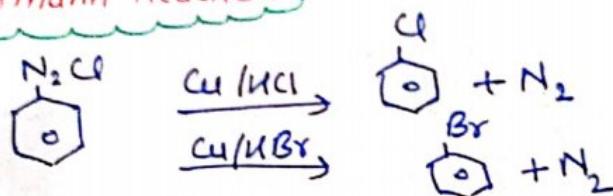
(b) Acylation



Gabriel phthalimide synthesis

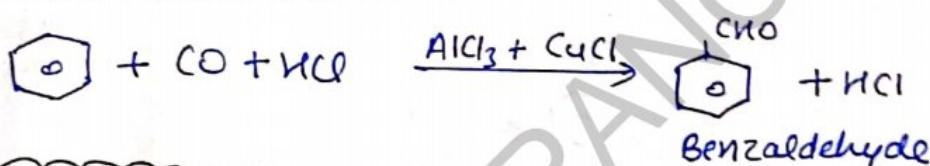


Gattermann Reaction

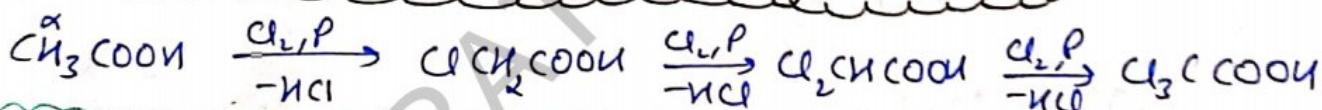


Gattermann Koch Reaction

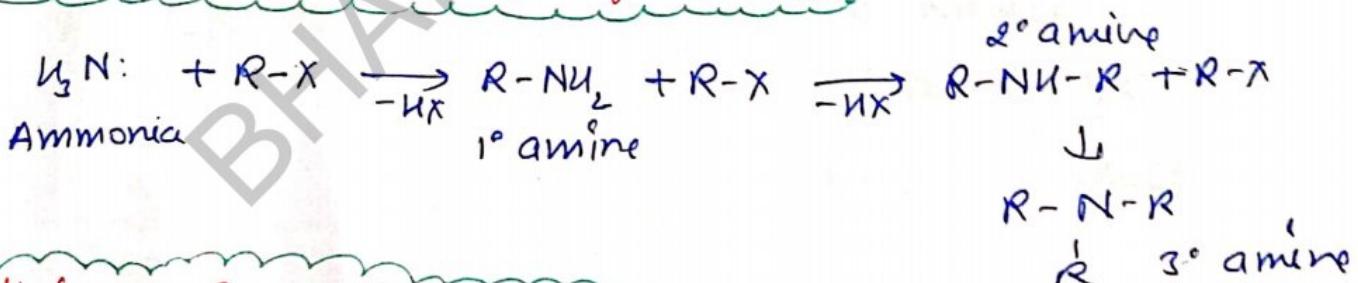
Most Important for conversion



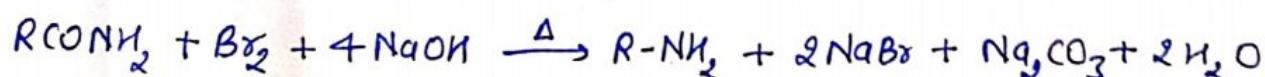
H.V.Z Reaction \rightarrow Hell Volhard Zelinsky Reaction



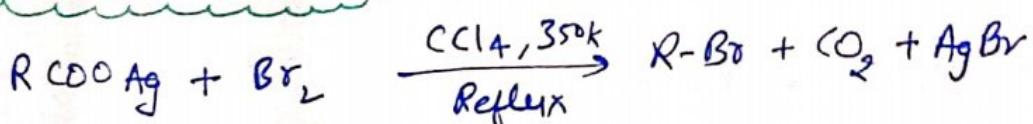
Hofmann Ammonolysis of Alkyl Halides



Hofmann Bromamide Reaction

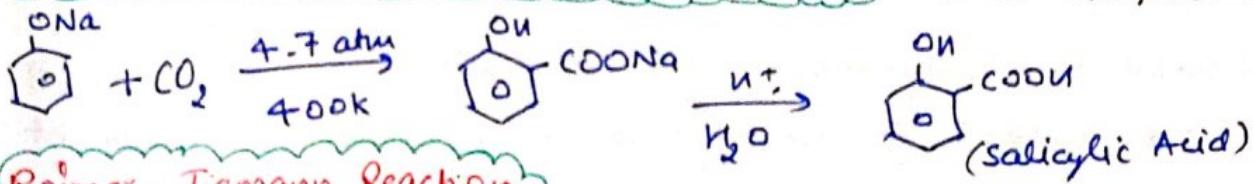


Hunsdiecker Reaction



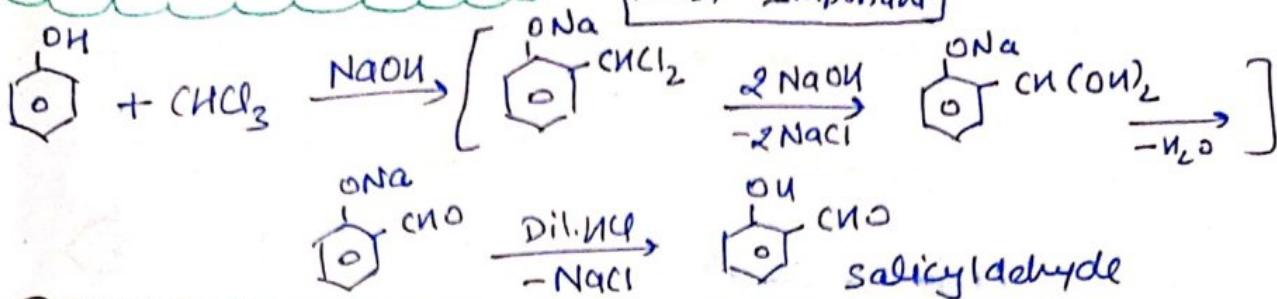
Kolbe Reaction or Kolbe-Schmitt Reaction

Most Important



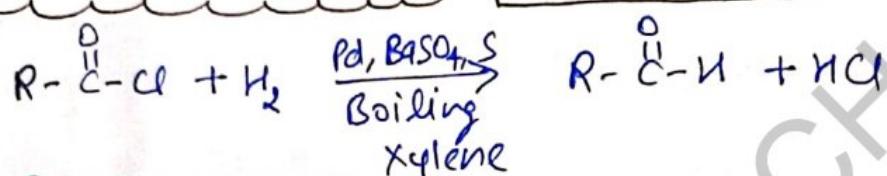
Reimer-Tiemann Reaction

[Most Important]

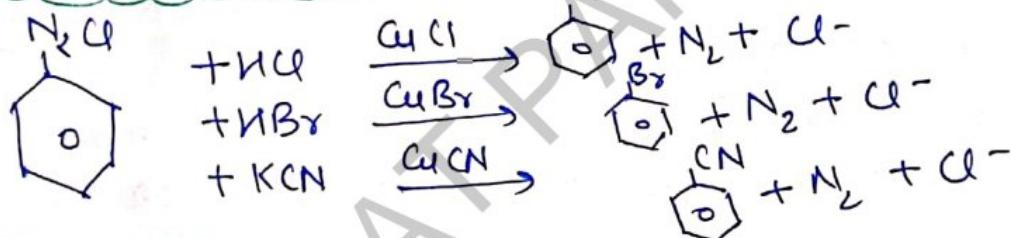


Rosenmund Reduction

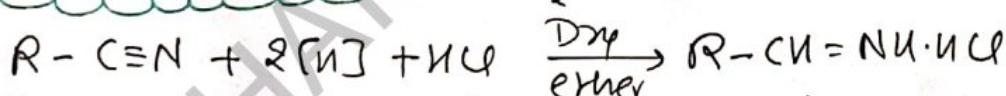
[Most Important]



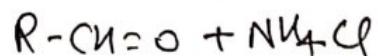
Sandmeyer Reaction



Stephen Reduction

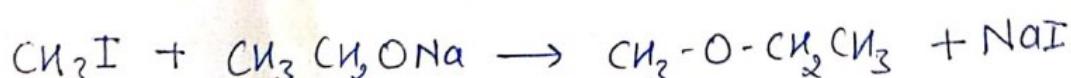


↓ Boiling H_2O



Williamson Synthesis

[Imp]

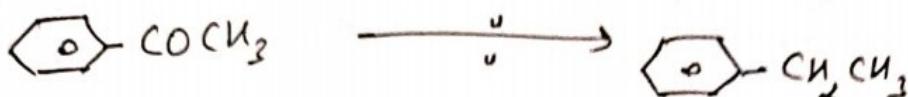
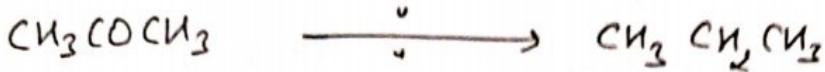
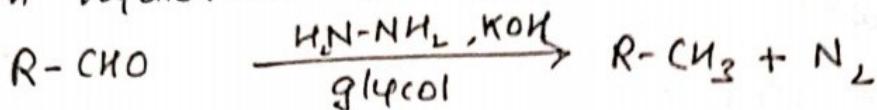


Best method for the preparation
of ethers

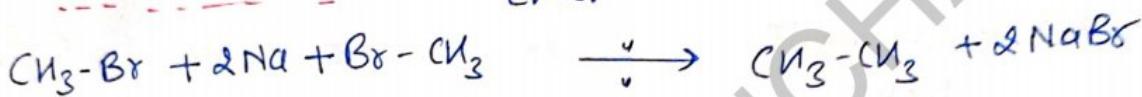
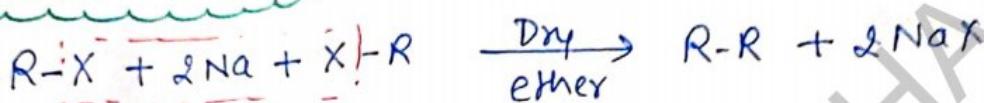
Wolff - Kishner reduction

Most Important

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

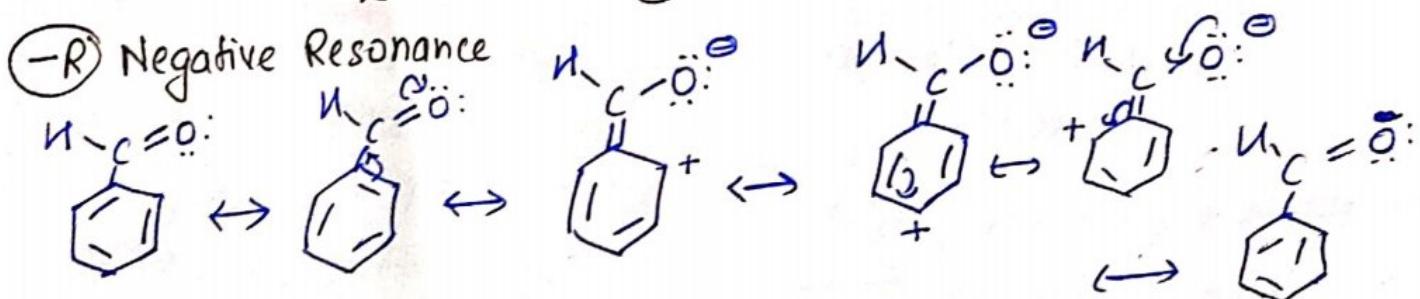
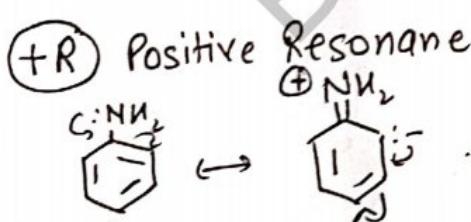
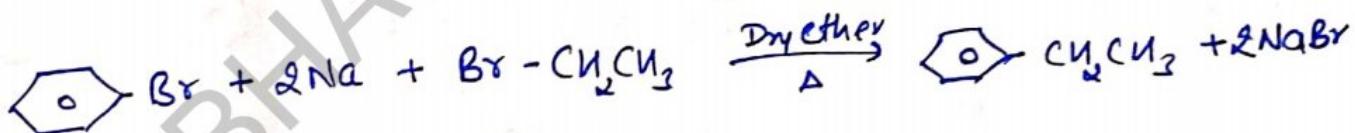
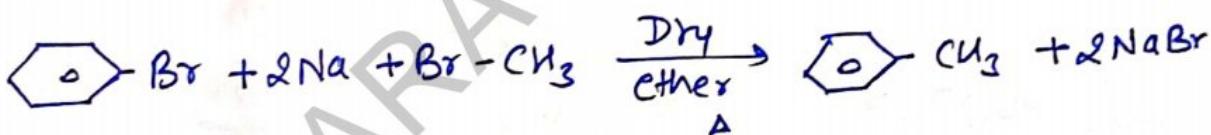


Wurtz Reaction



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



Distinction between pair of Compounds

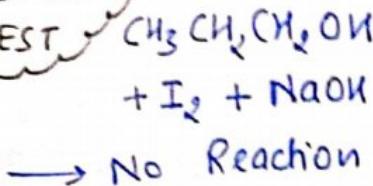
TEST

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

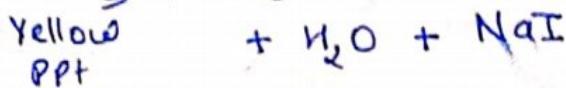
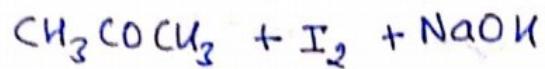
Ans.

IODOFORM
TEST

Propanol



Propanone



⇒ How will you distinguish b/w ethanol and phenol

Ans.

Ethanol

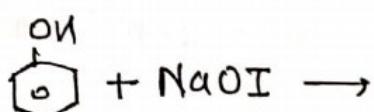
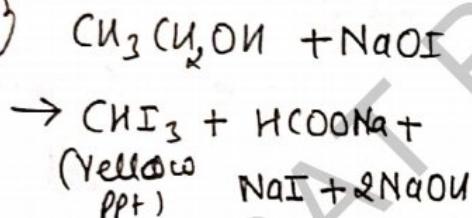
Litmus
Test

Does not give
litmus test

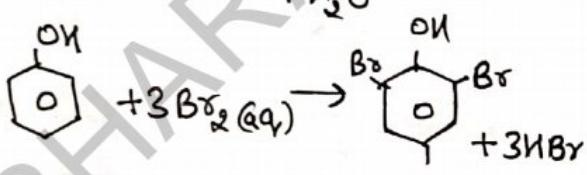
Phenol

Turns blue litmus into
red

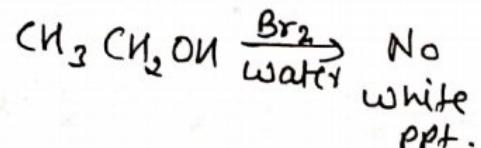
Iodoform
Test



B₂O₅ Water
Test



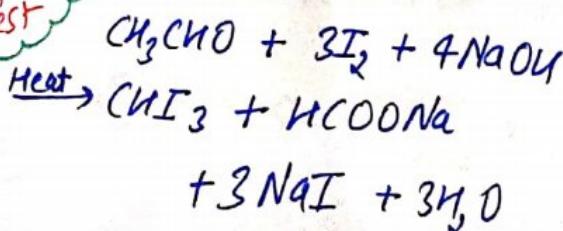
$\alpha, 4, 6$ -Tribromo
phenol
(white ppt)



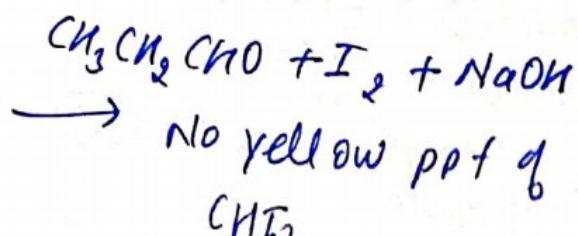
⇒ How will you distinguish b/w ethanal and propanal

Iodoform
Test

Ethanal



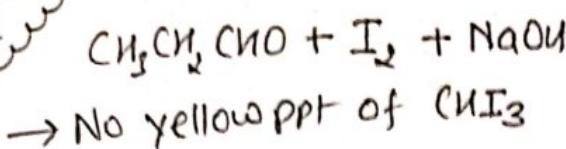
Propanal



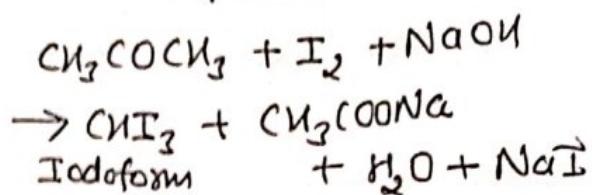
⇒ How will you distinguish b/w Propanal and Propanone
 (CH₃CH₂CHO) (CH₃COCH₃)

(Iodoform)
 Test

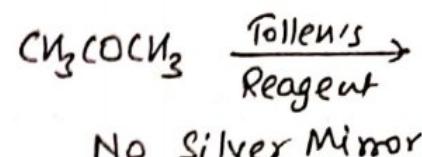
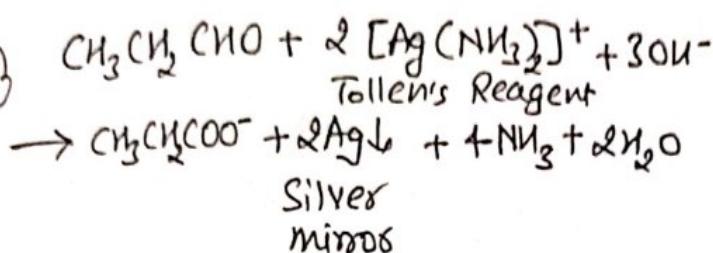
Propanal



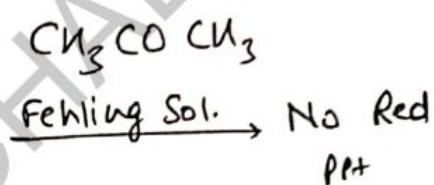
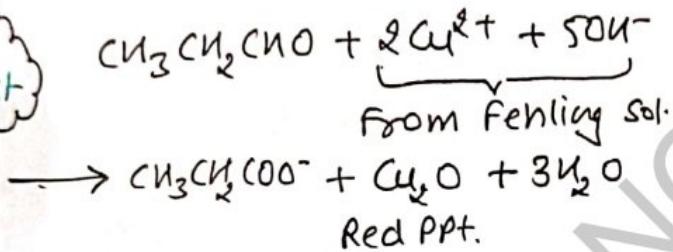
Propanone



Tollen's Reagent Test



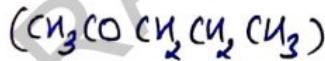
Fehling Soln test



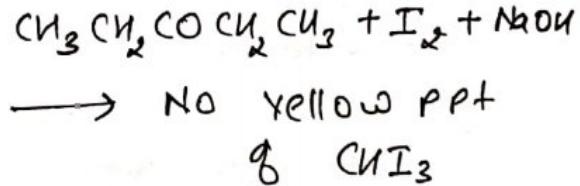
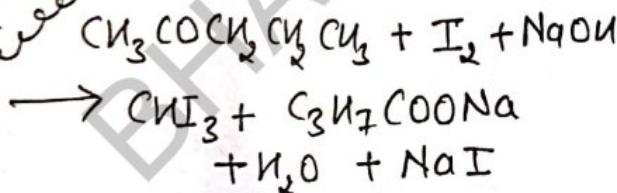
⇒ How will you distinguish b/w Butanal and Butan-2-one

Ans: Same As Above

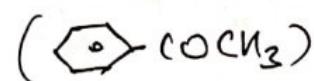
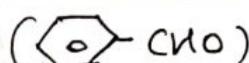
⇒ Distinguish b/w Pentan-2-one and Pentan-3-one.



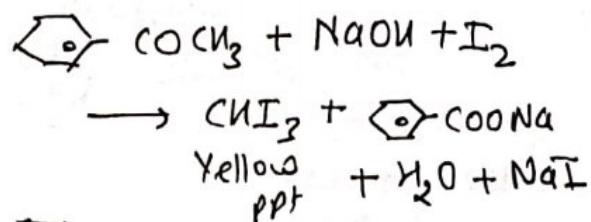
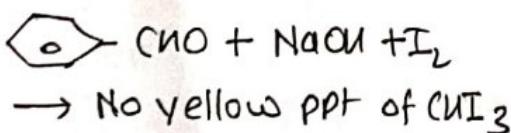
Iodoform
 Test



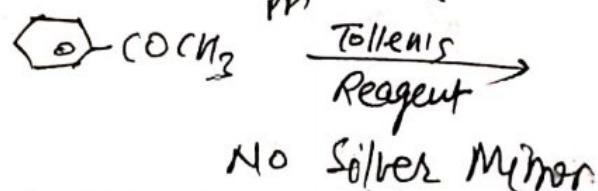
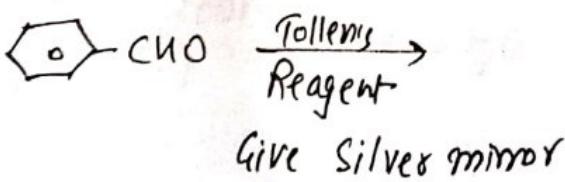
⇒ Distinguish b/w Benzaldehyde and Acetophenone.



Iodoform
 Test

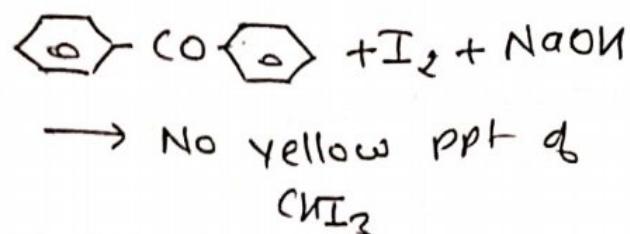
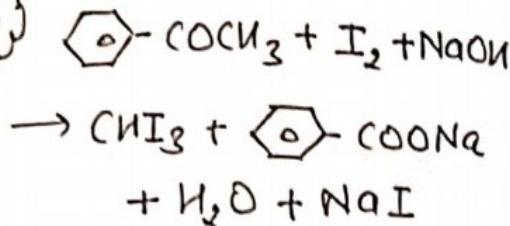


AgNO₃
 Test



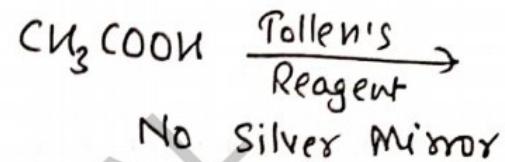
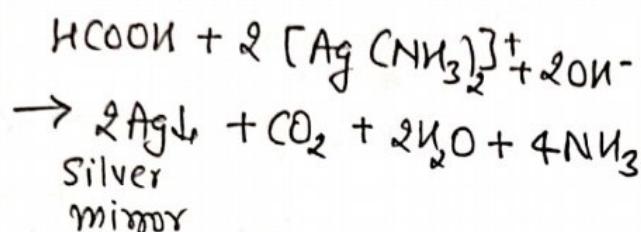
⇒ Acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) and benzo phenone ($\text{C}_6\text{H}_5\text{CO}_2$)

Iodoform Test



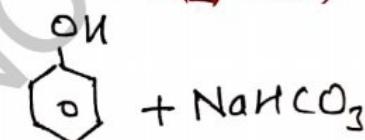
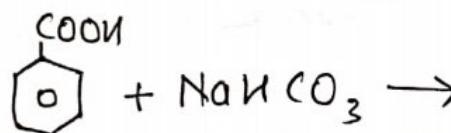
⇒ Methanoic acid or formic acid and ethanoic acid or acetic acid (HCOOH) (CH_3COOH)

Tollen's Reagent



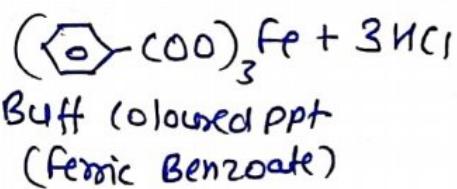
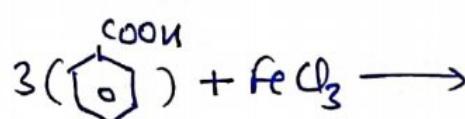
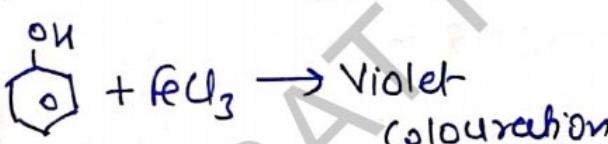
⇒ Benzoic Acid ($\text{C}_6\text{H}_5\text{COOH}$) and Phenol ($\text{C}_6\text{H}_5\text{OH}$) M.IMP

NaHCO_3 Test



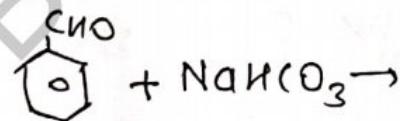
→ No evolution of CO_2

FeCl_3 Test

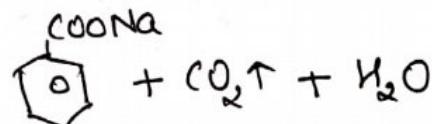
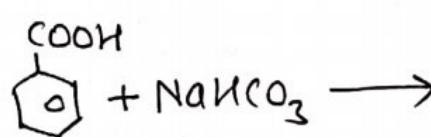


⇒ Benzaldehyde and Benzoic Acid

NaHCO_3 Test

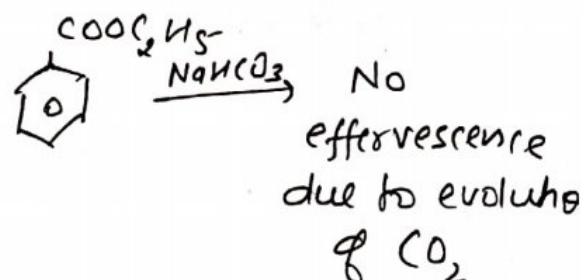
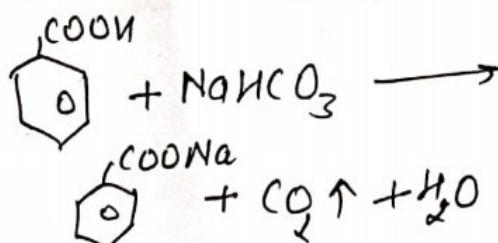


No effervescence due to evolution of CO_2



⇒ Benzoic acid and ethyl benzoate

NaHCO_3 Test



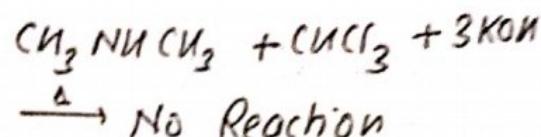
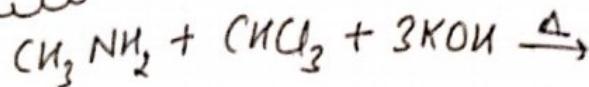
\Rightarrow Methylamine (CH_3NH_2) and dimethylamine (CH_3NHC_2)

M.Imp

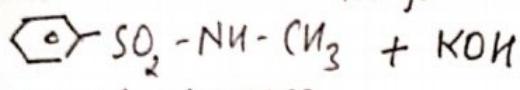
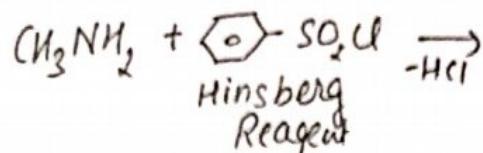
1° amine

2° amine

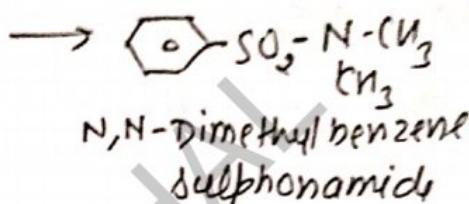
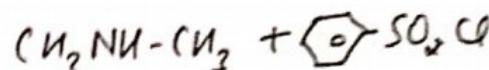
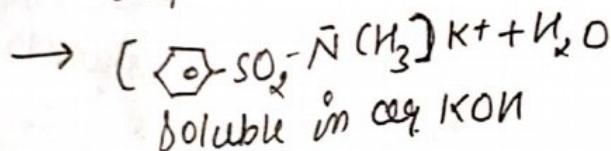
(Carbylamine)
Test



(Hinsberg)
Reagent



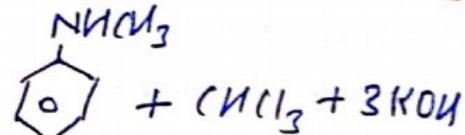
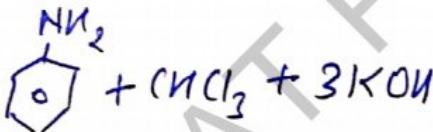
N-methyl benzene
sulphonate



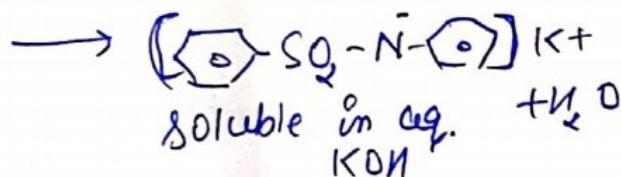
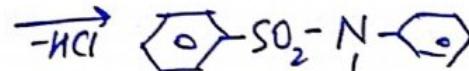
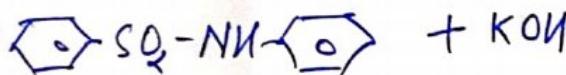
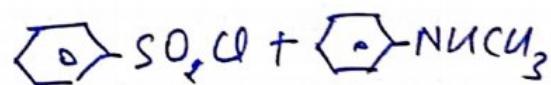
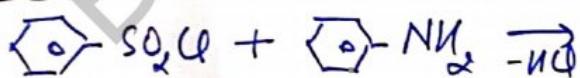
insoluble in
aq. KOH.

\Rightarrow Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) and N-methyl aniline ($\text{C}_6\text{H}_5\text{NHCH}_3$)

(Carbylamine)
Test



(Hinsberg)
Reagent



Insoluble in
aq. KOH.

Ques. Related to Physical Properties

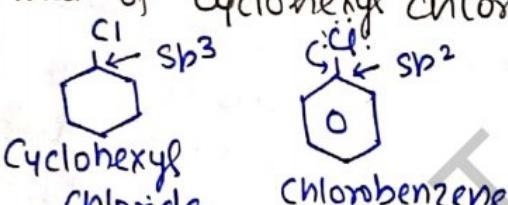
- P-dichlorobenzene has higher m.pt than that of ortho or meta isomer

Ans.: ~~p-Dichlorobenzene~~ 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.:

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.

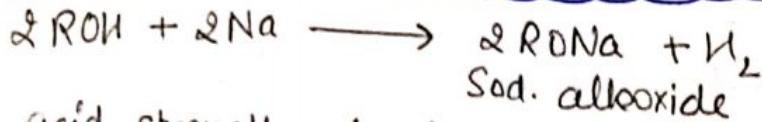
Solubility of alcohols

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 alcohols and solubility increases with increase in branching and the order is $1^\circ < 2^\circ < 3^\circ$.

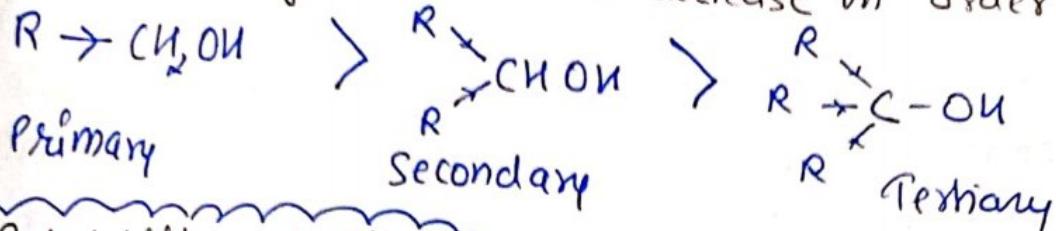
Boiling Points

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 $1^\circ > 2^\circ > 3^\circ$

Acidity of alcohols (reaction with metals)



The acid strength of alcohols decrease in order



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 etc.

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 intermolecular hydrogen bonding

Boiling Point of Aldehydes & 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 (4) 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 intermolecular 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
 $3^{\circ} \text{ amine} > 2^{\circ} \text{ amine} > 1^{\circ} \text{ amine} > \text{NH}_3$
- 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
 $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
and $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$

POLYMERS

⇒ Polyolefins

Polymers

- Polythene
- Polypropylene
- Teflon (P.T.F.E)
- Poly Tetra Fluoro ethene
- Poly Vinyl Chloride (PVC)
- Poly Acrylic Nitrile (PAN) (Orlon)
- Polystyrene (Styron)
- Polymethyl meth acrylate (PMMA)
- Poly mono chloro trifluor ethylene (PCTFE)

⇒ Polydienes

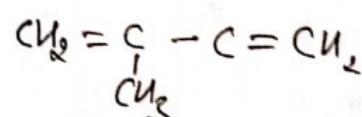
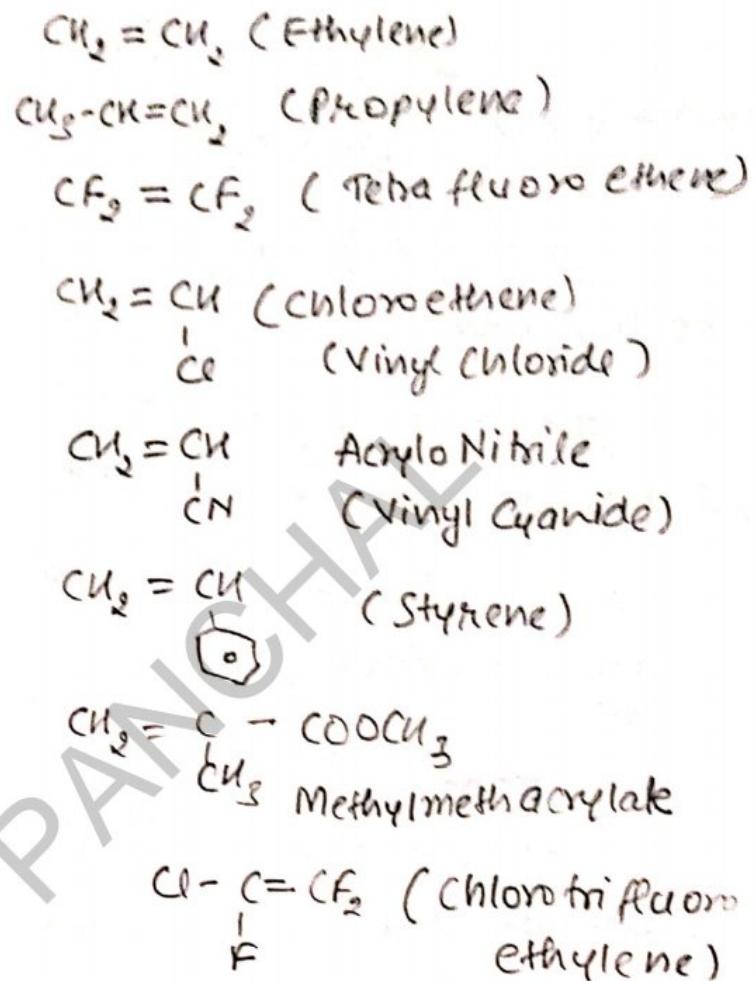
Natural Rubber
(cis -1,4-polyisoprene)

Neoprene
(Synthetic rubber)

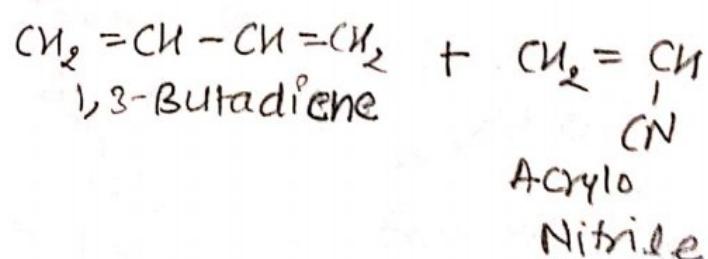
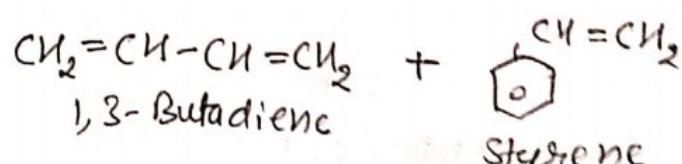
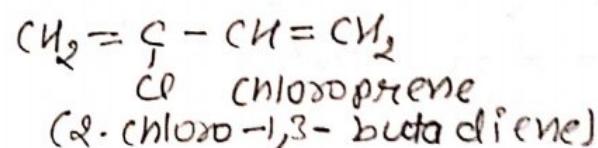
Buna-S (SBR)
(Styrene Butadiene Rubber)

Buna-N
(Nitrile Rubber)

Str. of Monomers

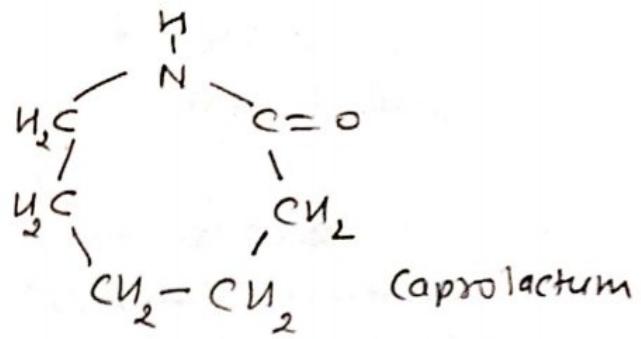


Isoprene
(α -Methyl-1,3-butadiene)

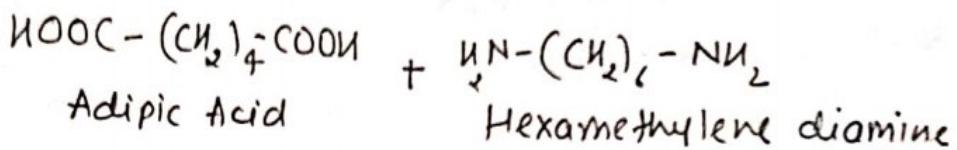


⇒ Polyamides

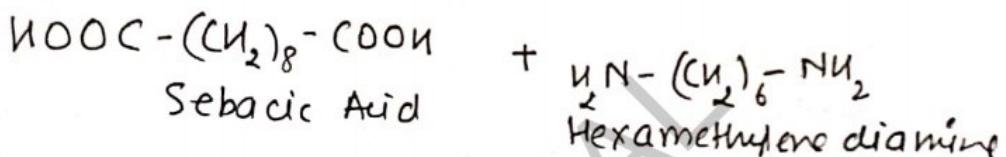
Nylon - 6 (Perlon - L)



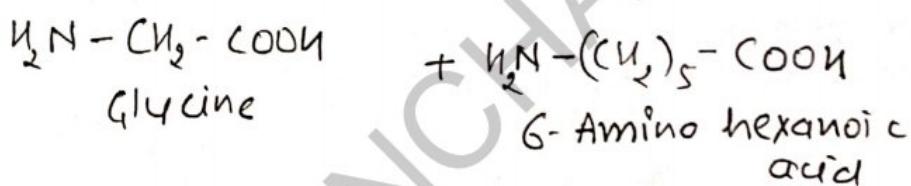
Nylon - 6, 6



Nylon - 6, 10

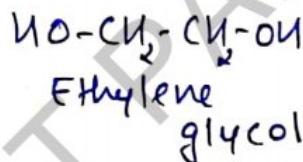


Nylon - 2, 6

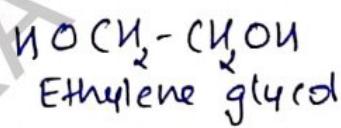


⇒ Polyesters

Terylene (Dacron)

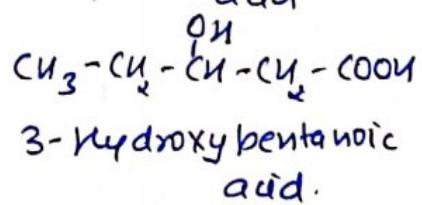
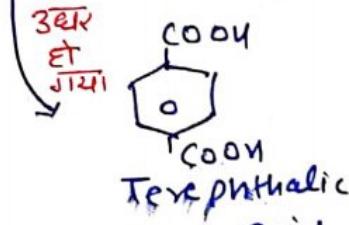
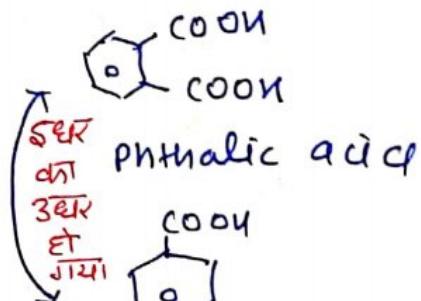
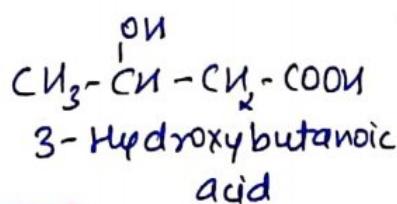


Glyptal (Alkyd resin)



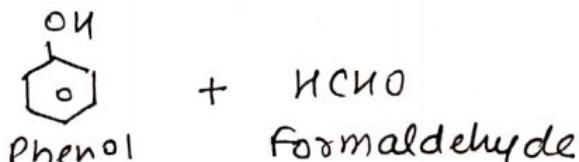
P.H.B.V

(Poly β-hydroxy butyrate - co - β hydroxy valerate)

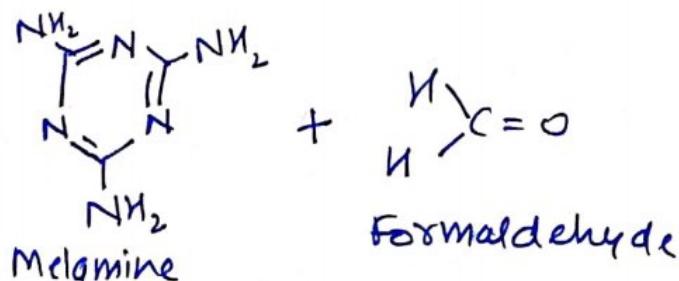


Formaldehyde Resins

Phenol - formaldehyde resin (Bakelite)



Melamine - formaldehyde resin (Melmac)



Urea-formaldehyde
resin



Urea

Formaldehyde

Biodegradable polymers

Aliphatic polyesters are one of the most important class of biodegradable polymers
e.g. Nylon-2-Nylon-6, PIBV (Poly β -hydroxybutyrate -co- β -hydroxy valerate)

Classification of Polymers

→ Source

- Natural Polymers
 - Str.
 - Linear Poly.
 - Branched
 - Cross linked
- Synthetic Poly.
- Semi-Synthetic Poly.

- 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.

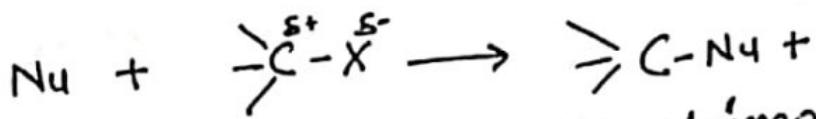
► **Condensation polymerisation** : A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, alcohol, etc. is called *condensation polymer* and the phenomenon is known as *condensation polymerisation*, e.g., terylene.

► **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

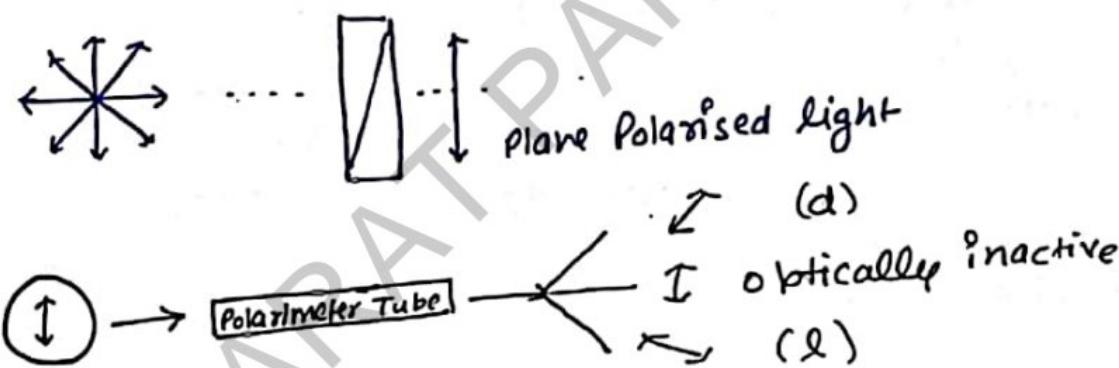
C-X bond in haloalkanes is polar and halide ion can be replaced by a stronger nucleophile



- S_{N}^1 C Substitution Nucleophilic Unimolecular
- S_{N}^2 C 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)



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 laevorotatory 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.

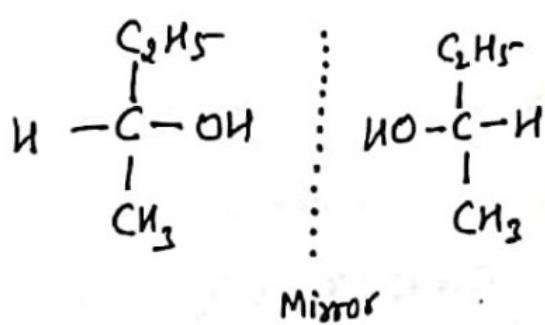
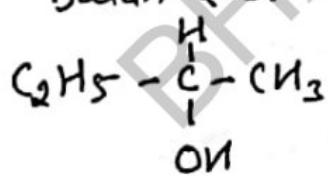
- The asymmetry of the molecule is responsible for the optical activity in such organic compounds. The asymmetry is also called dissymmetry.

⇒ **Chirality** The carbon which is bonded to four different atoms or groups 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.

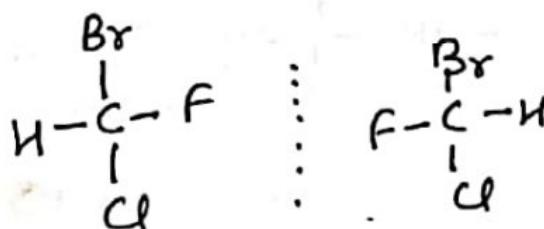
- Essential condition for enantiomerism is dissymmetry.

e.g. Butan-2-ol has chiral carbon



a pair of enantiomers

e.g. Bromochlorofluoromethane



mirror

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 \pm

Resolution

The separation of dextro rotatory (d) and laevo rotatory (l) isomers from racemic mixture by suitable method is called resolution

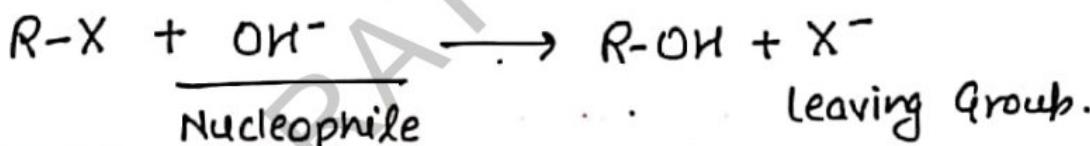
S_N^2 Mechanism

Bimolecular Nucleophilic Substitution Rxn

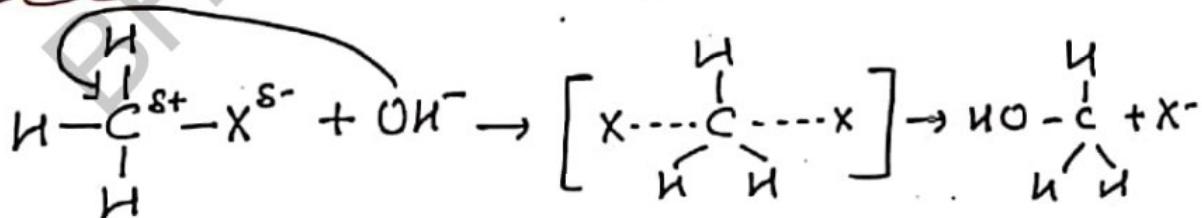
Order = 2, molecularity = 2

because the rate of reaction depends upon the conc. of both reactants i.e. alkyl halide and Nucleophile

ex: Substitution by hydroxyl 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.

S_N^1 Mechanism

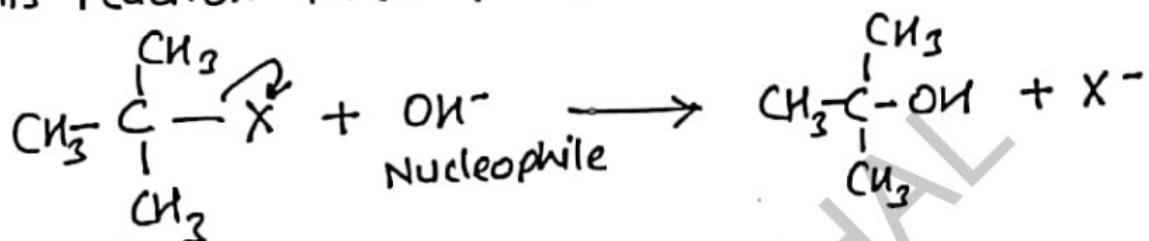
Unimolecular Nucleophilic Substitution Rxn.

The rate of reaction depends only on the conc. of reactant i.e. alkyl halide

e.g. order of reaction = 1

molecularity of reaction = 1

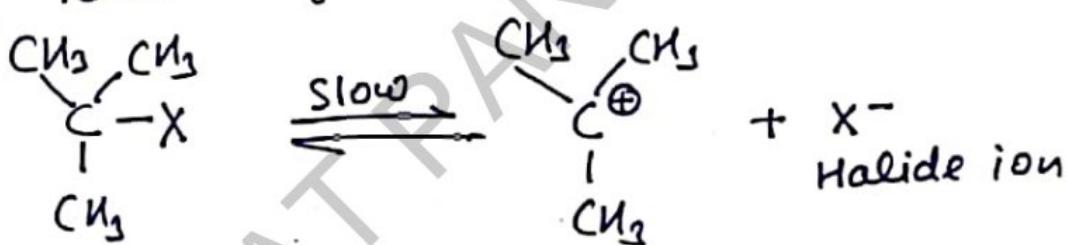
This reaction takes place in two steps.



Mechanism

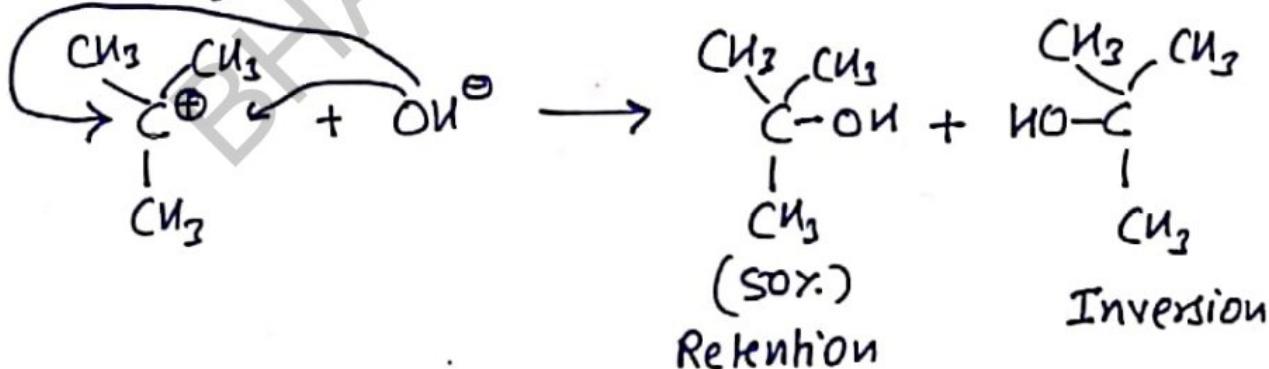
Step-I

Formation of intermediate carbocation



Step-II

Attack of nucleophile on C^+ may occur either from front side or from backside

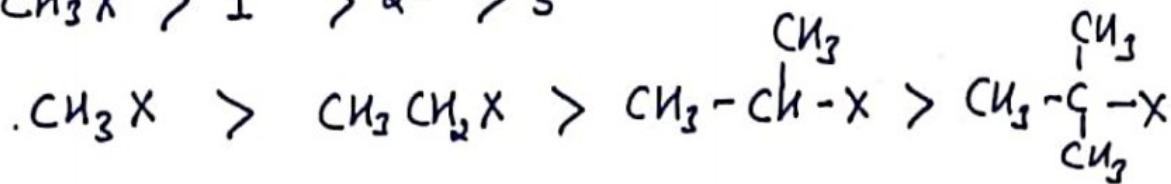
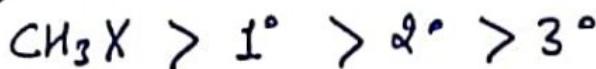


$$\text{Rate of Rxn} = K [(\text{CH}_3)_3\text{X}]$$

Order = 1

Order of reactivity of Alkyl Halide

S_N^2

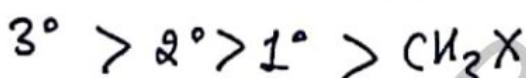


Reactivity decreases for S_N^2

As steric hindrance increases and rate of S_N^2 reaction decreases. It becomes more difficult for a nucleophile to approach C-X carbon due to steric hindrance

In S_N^1

The order of reactivity is



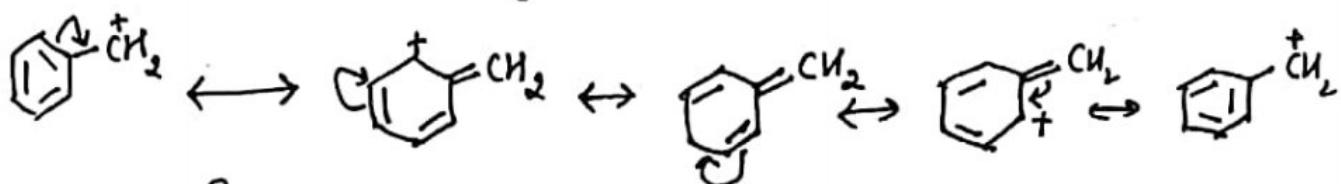
In this, an intermediate c+ is formed

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.

→ The allylic and benzylic halides show high reactivity towards S_N^1 reaction. Although the substitution takes place from 1° carbon. The carbocation. The carbocation thus formed gets stabilized through resonance



Resonance str. of allylic carbocation



Resonance str. of Benzylic carbocation

→ For a given alkyl group the reactivity of the halides, R-X follows the same order in both mechanism.

i.e



Spectrochemical Aspects

S_N^2 reaction proceeds with spectrochemical inversion

S_N^1 reaction proceeds with racemization.

Unimolecular (S_N^1)

- 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



Greater the stability of carbocation, faster will be the reaction.

- 5.) Tends to proceed with weak nucleophiles e.g. CH_3OH , H_2O , CH_3CN , CH_3COON^- etc.
- 6.) Both retention and inversion of configuration takes place

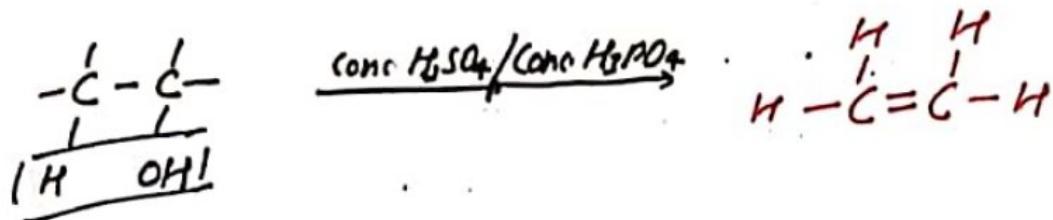
Bimolecular (S_N^2)

- 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
 $CH_3X > 1^\circ > 2^\circ > 3^\circ$
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)

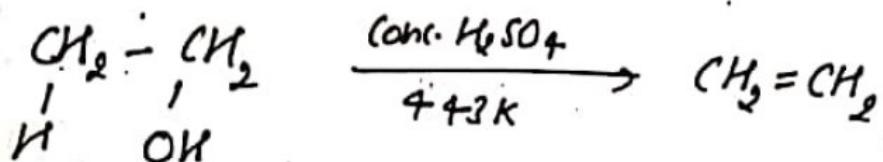
Dehydration of Alcohol

(15)

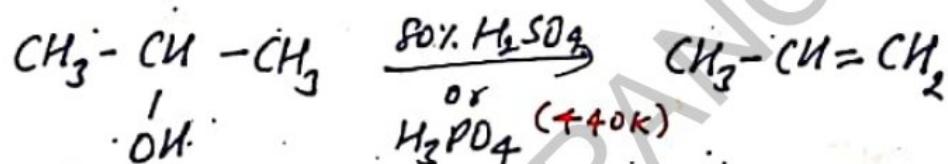
Removal of water ($-H_2O$)



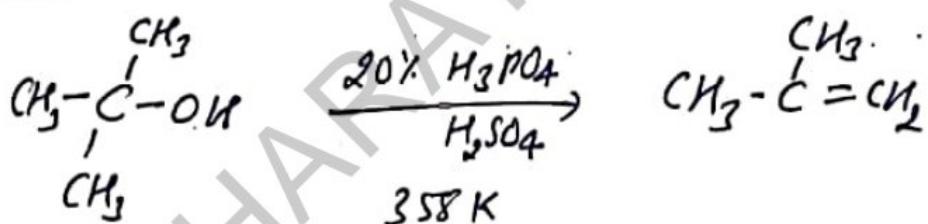
In case of 1° alcohol



2° alcohol

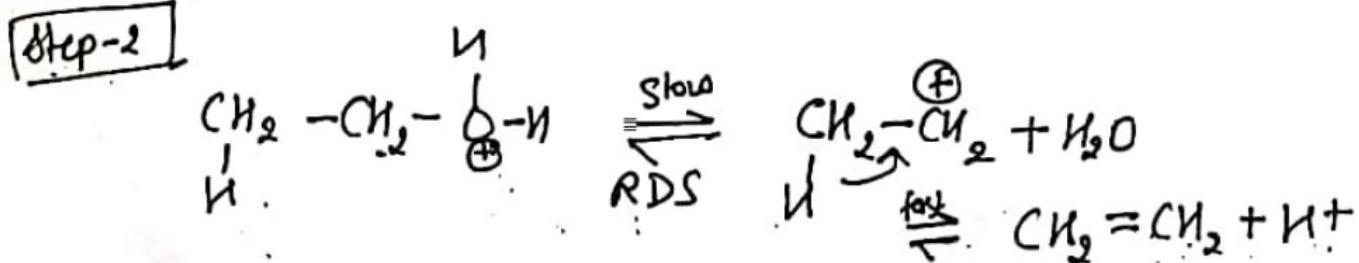
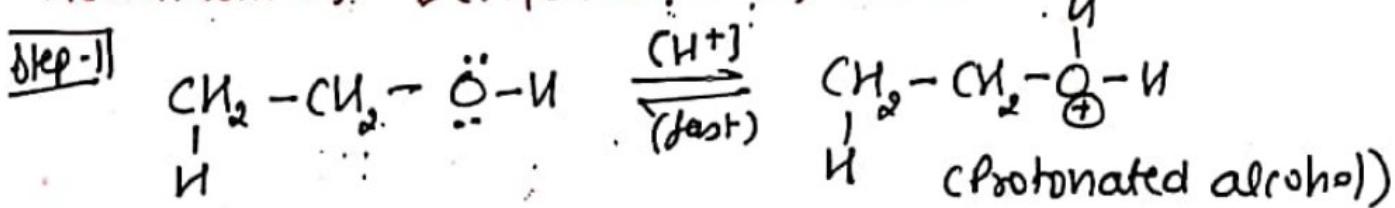


3° alcohol

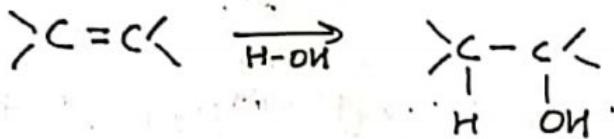


Order of Dehydration $3^\circ > 2^\circ > 1^\circ$

Mechanism of Dehydration of alcohol



Preparation of Alcohol (a) from Alkenes



Hydration \rightarrow Addition of Water \leftarrow Direct Acid Catalysed Hydration

Indirect

Hydro-Boration

Oxidation

(NIBO)

Oxymercuration

Demercuration

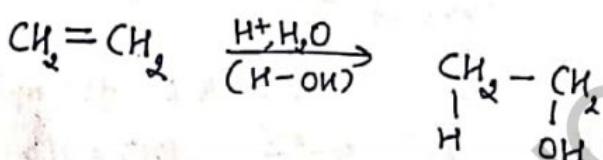
(COMDM)

Acid Catalysed Hydration

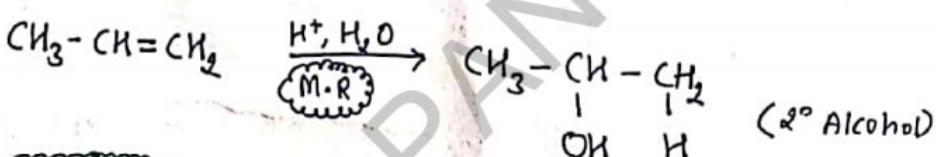
(a) In Symmetrical Alkenes

(b) In Unsymmetrical Alkenes

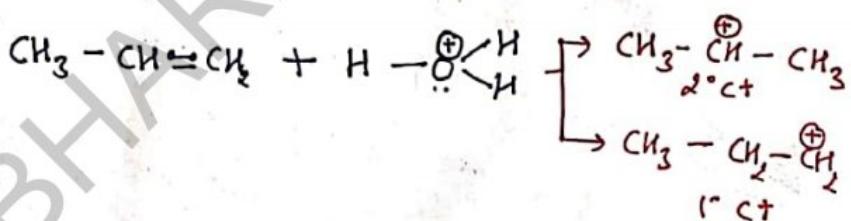
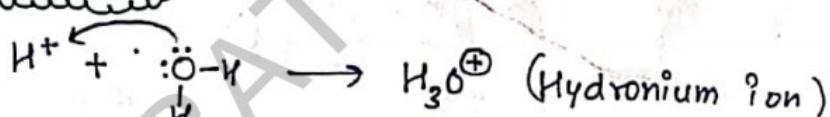
(a)



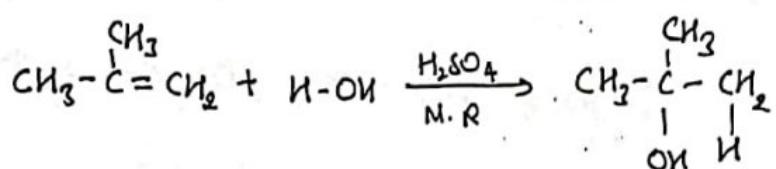
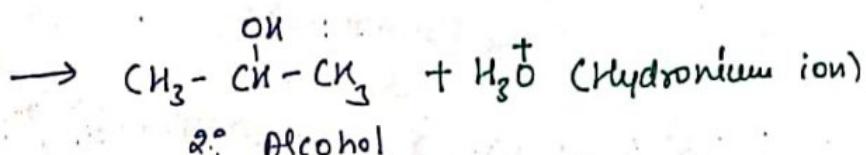
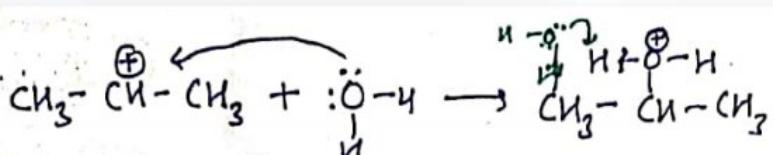
(b)



Mechanism



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