- [x] INTRODUCTION
- [x] CONCENTERATION OF SOLUTION
- [x] SOLUBILITY AND HENRY LAW
- [x] ROULT'S LAW
- [x] IDEAL AND NON IDEAL SOL^N
- [x] AZEOTROPES
- [x] COLLIGATIVE PROPERTIES
- [x] RELATIVE LOWERING OF V.P
- [x] ELEVATION IN B.Pt
- [x] DEPRESSION IN F.Pt
- [x] OSMOTIC PRESSURE
- [x] ABNORMAL MOLECULAR MASS
- [x] VAN'T HOFF FACTOR

SOLUTION

it is a homogeneous mixture of two or more than two substances.

SOLUTE present in less amount

SOLVENT present in large amount.

e.g. sugar solution → water (solvent) + sugar (solute)

BINARY SOLUTION

Prepared by two components.

> Brass → Cu + Zn , German Silver → Cu + Zn + Ni , Bronze → Cu + Sn

Table 2.1: Types of Solutions

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

DILUTE SOLUTE ~ very small quantity of solute

CONCENTERATED SOLUTION ~ very large quantity of solute

CONCENTERATION OF SOLUTION

Mass Percentage (w/w)

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

$$\text{mass \% of A} = \frac{\text{Mass of A}}{\text{Mass of solution}} \times 100$$

Volume Percentage (V/V) :-

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

$$\text{Volume \% of A} = \frac{\text{Vol. of A}}{\text{Vol. of solution}} \times 100$$

Mass by Volume Percentage (w/v) :-

mass of a component to the per 100 parts volume of solution.

Parts Per million (ppm) :-

$$\frac{\text{no. of parts of the component}}{\text{Total no. of all components of soln}} \times 10^6$$

MOLE FRACTION (X)

no. of moles of a component to the total no. of moles of solution.

$$\chi_A = \frac{n_A}{n_A + n_B} \qquad \chi_B = \frac{n_B}{n_A + n_B}$$

$$\text{Mole fraction of a component} = \frac{\text{no. of moles of component}}{\text{Total no. of moles of solution}}$$

- mole fraction is a unitless quantity.
- mole fraction of solution is always 1.

MOLARITY :-

number of moles of solute dissolved in one litre ($1\,dm^3$) of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

Unit = Moles/litre or M or Molar

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

$w_B \rightarrow$ Mass of solute
$M_B \rightarrow$ Molar Mass of solute
$V(ml) \rightarrow$ Volume in mL.

- temperature dependent i.e molarity decreases with increase in temp.

Dilution Law, $M_1V_1 = M_2V_2$

Molarity for mixed solution, $M = \frac{M_1V_1 + M_2V_2}{V_1+V_2}$

Molality (m) number of moles of solute per kg of the solvent.

Molality = $\frac{\text{no. of moles of solute}}{\text{Mass of solvent in Kilogram}}$

Unit = moles/kg

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

$W_B \rightarrow$ mass of solute
$M_B \rightarrow$ Molar Mass of solute
$W_A(g) \rightarrow$ Mass of solvent in g

→ Molality is independent of temperature.

→ When solvent used in water, 1 M solution is more concenterated than 1 molal solution.

SOLUBILITY The maximum amount of solute that can be dissolved in 100 g solvent at a given temperature is termed as its solubility at that temperature.

- **FACTORS AFFECTING SOLUBILITY OF G In L**

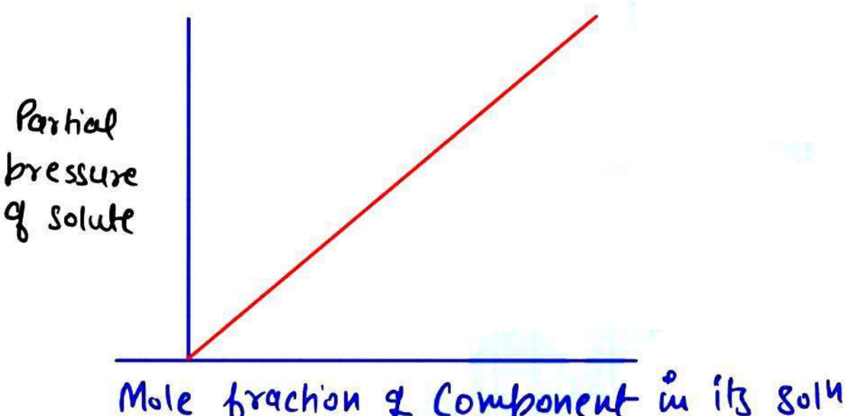
- **Nature of Gas** – The gases which can be easily liquified, are more soluble in common solvents.
- **Nature of the solvent** – The gases which are capable of forming ions in aqueous solutions are much more soluble in water than in other solvent.
- **Temperature** – The solubility of gases in liquid decreases with increase of temperature.
- **Pressure** – The solubility of a gases increase with increase in pressure.

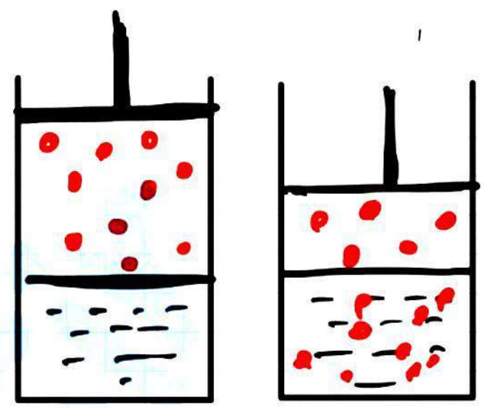
HENRY'S LAW :

"the partial pressure (p) of the gas in vapour phase is proportional to the mole fraction (χ) of the gas in the solution."

$$p = K_H \chi$$

↳ Higher the value of K_H at given pressure, the lower is the solubility of the gas in the liquid
The value of K_H decreases with increase in the temp. Thus, aquatic species are more comfortable in cold water rather than warm water.



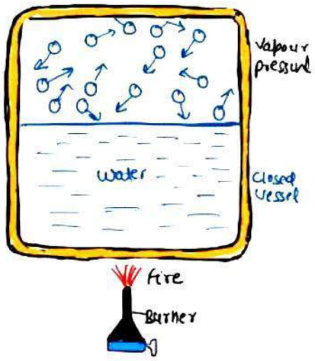


Applications :

in manufacture of soft drinks and soda water, CO_2 is passed at high pressure to increase its solubility.

- To minimise the painful effects (bends) accompanying the decompression of deep sea divers, O_2 diluted with less soluble He gas is used as breathing gas.
- At High altitudes, the partial pressure of O_2 is less than that at the ground level. This leads to low concenteration of O_2 in the blood of climbers which cause "anoxia"

Vapour Pressure



Pressure formed by the vapour of the liquid over the surface of the liquid.
Vapour pressure is the pressure caused by the evaporation of liquid

Intermolecular Force

the vapour pressure will be lower when the intermolecular forces are relatively strong since the rate of evaporation is lower.

$$\text{Vapour Pressure} \propto \frac{1}{\text{intermolecular force of Attraction}}$$

Temperature

As the temperature of the liquid increses the kinetic energy associated with the liquid also increases. and due to this increase in kinetic energy the escaping tendency of molecule increases and hence v.p increases.

$$\text{Vapour Pressure} \propto \text{Temperature}$$

Concenteration of Solute

The presence of solute in the liquid will decrease the vapour pressure.

Raoult's Law

mole fraction of the solute component in a solution is directly proportional to its partial pressure

$$p \propto x \qquad p_A \propto x_A$$

$$\hookrightarrow p_A = p_A^{\circ} \cdot x_A$$

partial Vapour pressure of a component is equal to the Vapour pressure of that component in pure state multiplied by mole fraction of that component.

$p_A \propto x_A$ $\qquad$ $p_B \propto x_B$

$p_A = p_A^{\circ} \times x_A$ $\qquad$ $p_B = p_B^{\circ} \times x_B$

Acc. to Dalton's law of partial pressure, the total pressure the solution in a container

$$p_{Total} = p_A + p_B$$
$$= p_A^{\circ} \cdot x_A + p_B^{\circ} \cdot x_B$$

$\because x_A + x_B = 1$

$$P_{Total} = p_A^{\circ} + (p_B^{\circ} - p_A^{\circ}) x_B$$

Raoult's law for Vapour Pressure of Solid - Liquid Solution

The decrease in V.P of solvent depends on the quantity of non-volatile solute present in the solution irrespective of its nature

$$P_T = P_A + \cancel{P_B}$$
$$P_T = P_A^{\circ} \times x_A$$

ROULT'S LAW AS A SPECIAL CASE OF HENRY'S LAW ⇒

Acc. to Raoult's $\qquad$ Acc. to Henry

$P_1 = P_1^{\circ} \cdot x_1$ $\qquad$ $P = K_H x$

if we compare the eqn for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component of gas is directly proportional to its mole fraction in solution. Only the proportionality constant K_H differs from p_1°. Thus, law becomes a special case of Henry's law in which K_H becomes equal to p_1°.

IDEAL SOLUTION

- solution must obey Raoult's law
  $$p_A = p_A^\circ \chi_A$$
  $$p_B = p_B^\circ \chi_B$$
- Solute - Solvent (A-B) interaction is almost similar to the interaction of A-A and B-B
- $\Delta V_{mix} = 0$ (No expansion or contraction on mixing)
- $\Delta H_{mix} = 0$ (No energy evolved or absorbed)

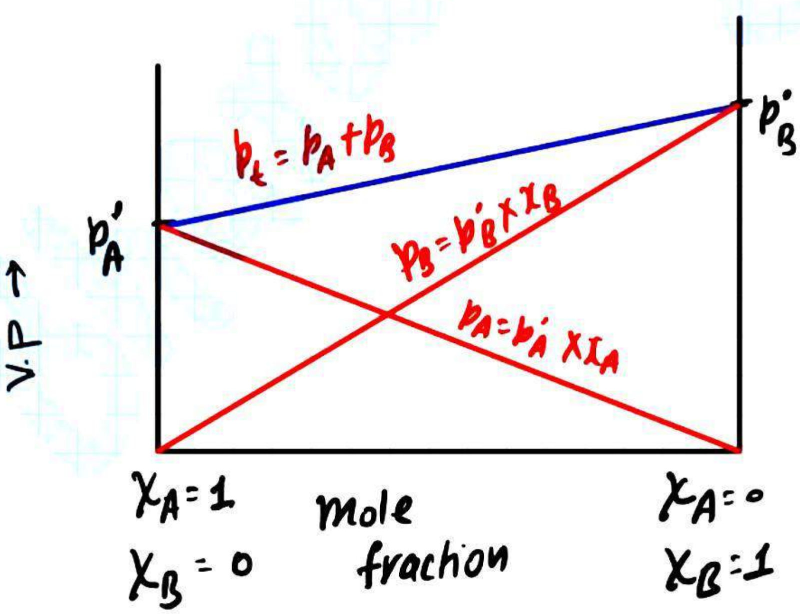
⇨ e.g benzene + toluene
n-hexane + n-heptane
chlorobenzene + bromobenzene

NON-IDEAL SOLUTION

- Solution doesn't obey Raoult's law
  $$p_A \neq p_A^\circ \cdot \chi_A$$
  $$p_B \neq p_B^\circ \chi_B$$
- Solute-Solvent (A-B) interaction is not similar to the interaction of A-A and B-B.
- $\Delta V_{mix} \neq 0$
- $\Delta H_{mix} \neq 0$

⇨ eg ethanol + water
CS_2 + acetone
$CHCl_3 + CH_3COCH_3$
$CHCl_3 + C_6H_6$

GRAPH OF IDEAL SOLUTION



POSITIVE DEVIATION

- A-B interaction is weaker than interaction of A-A and B-B
- observed vapour pressure are greater than V.P calculated by Raoult's law

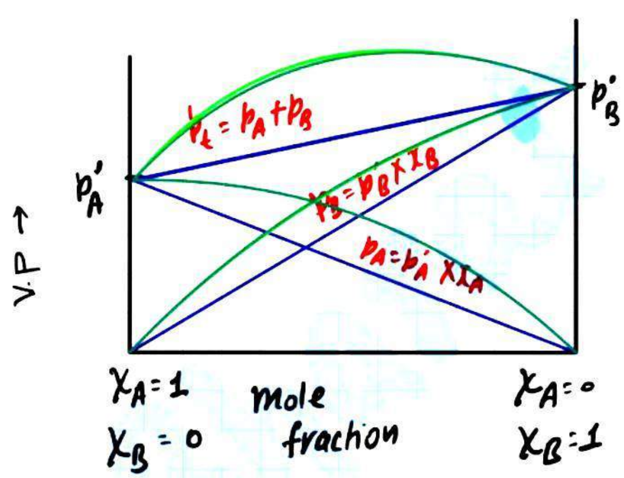
$p_A > p_A^\circ \cdot \chi_A$

$p_B > p_B^\circ \cdot \chi_B$

$\Delta H_{mix} > 0$

$\Delta V_{mix} > 0$

- Form minimum boiling azeotropes



● +ve deviation

Ethanol + water

CS_2 + Acetone

$CCl_4 + C_6H_6$

CCl_4 + Toluene

ethanol + Cyclohexane

$CCl_4 + CHCl_3$

NEGATIVE DEVIATION

- A-B interaction is stronger than interaction of A-A and B-B
- observed vapour pressure are lower than V.P calculated by Raoult's law

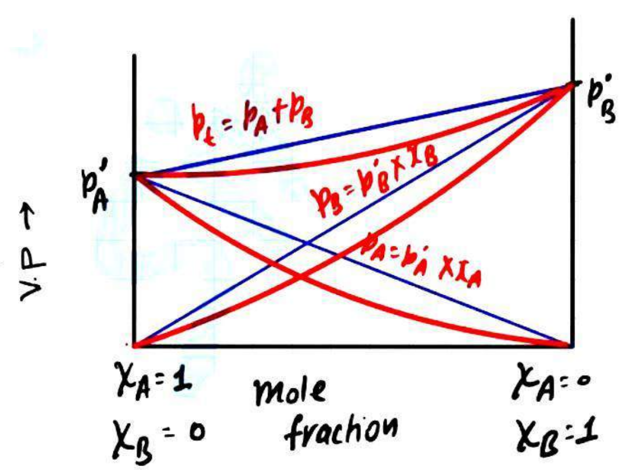
$p_A < p_A^\circ \cdot \chi_A$

$p_B < p_B^\circ \cdot \chi_B$

$\Delta H_{mix} < 0$

$\Delta V_{mix} < 0$

- Form maximum boiling azeotropes



● -ve deviation.

$CHCl_3 + CH_3COCH_3$

$CHCl_3 + C_6H_6$

$H_2O + HCl$

$H_2O + HNO_3$

methanol + acetic acid.

AZEOTROPIC MIXTURE

A mixture of two liquids which boils at a particular temperature like a pure liquid and distils over in the same composition, formed by non-ideal solution.

MAX. BOILING AZEOTROPES

formed by those liquid pairs which show negative deviation

- B.pt higher than either of the components.

e.g $H_2O_{(20.22\%)} + HCl_{(79.78\%)}$

MIN. BOILING AZEOTROPES

formed by those liquid pairs which show positive deviation.

- B.pt lower than either of the components

e.g $C_2H_5OH_{(95.57\%)} + H_2O_{(4.43\%)}$

COLLIGATIVE PROPERTY

Those property which depends upon no. of moles of solute or amount of solute, doesn't depends upon nature of solute or solvent

→ Relative lowering of Vapour pressure

→ Elevation in boiling point

→ Depression in freezing point

→ Osmotic Pressure

RELATIVE LOWERING IN VAPOUR PRESSURE

when a non volatile solute is added to solvent, vapour pressure of solvent decreases.

$$\frac{p_A^\circ - p_s}{p_A^\circ} = \chi_B$$

χ_B → mole fraction of solute

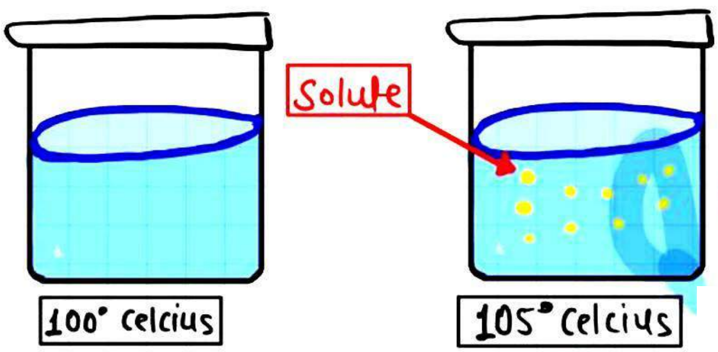
$\frac{p_A^\circ - p_s}{p_A^\circ}$ → relative lowering in V.P for dilute solution $n_B <<< n_A$

$$\frac{p_A^\circ - p_s}{p_A^\circ} = \frac{n_B}{n_A}$$

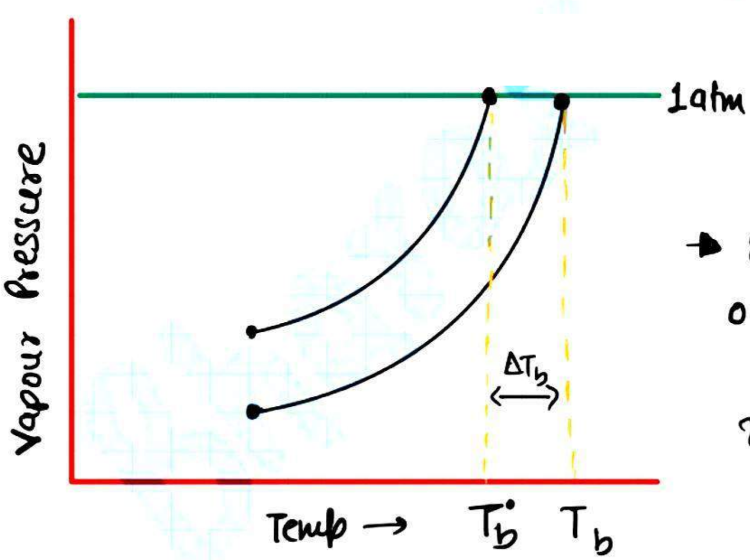
$$\frac{p_A^\circ - p_s}{p_A^\circ} = \frac{w_B}{M_B} \times \frac{M_A}{w_A} \Rightarrow M_B = \frac{w_B}{w_A} \times M_A \times \frac{p_A^\circ}{p_A^\circ - p_s}$$

ELEVATION IN BOILING POINT

Boiling point of a liquid is the temp. at which its vapour pressure becomes equal to the atmospheric pressure



Boiling point elevation is the increase in the boiling point of a Solvent due to the presence of non-volatile Solute.



$\Delta T_b = T_b - T_b^\circ$

- ΔT_b → elevation in B.pt
- T_b → B.pt of Solution
- T_b° → B.pt of pure solvent

→ Experimentally it has been observed that elevation in b.pt is proportional to molal conc.

$\Delta T_b \propto m$

$\Delta T_b = K_b m$

K_b → ebullioscopic constant / molal elevation constant

Unit of K_b = K kg mol⁻¹

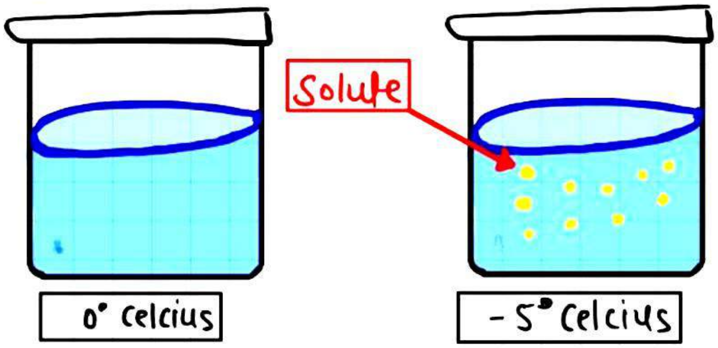
$$\Delta T_b = K_b m = K_b \times \frac{w_B}{M_B} \times \frac{1000}{w_{A(g)}}$$

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

where
- M_B → Molar mass of solute
- $w_{A(g)}$ → Mass of Solvent in g
- w_B → Mass of Solute

DEPRESSION IN FREEZING POINT

Freezing point of a liquid is the temp at which vapour pressure of of the solvent in its liquid and solid phase becomes equal.



Freezing point depression is the decrease in the freezing point of a solvent due to the presence of non-volatile solute particles.

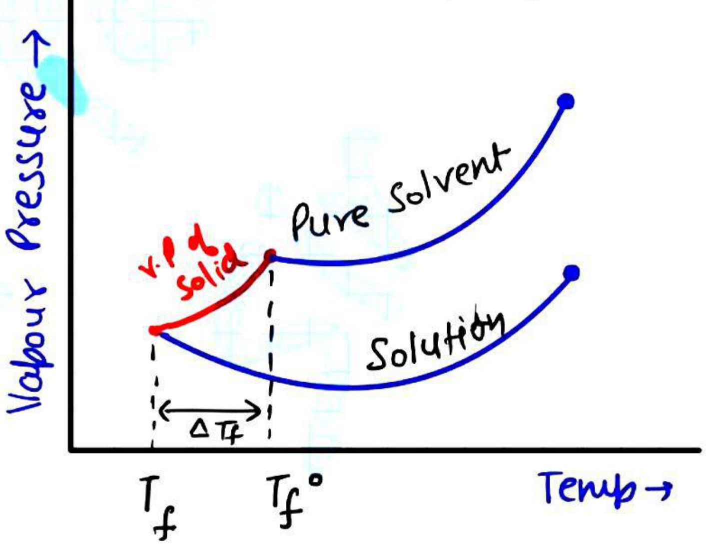
Experimentally it has been observed depression in f.pt is directly proportional to molal conc.

$\Delta T_f \propto m$

$\Delta T_f = K_f m$

K_f → cryoscopic constant / molal depression constant

$$\Delta T_f = T_f^{\circ} - T_f$$



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

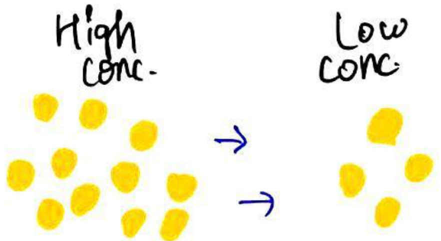
$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A(g)}$$

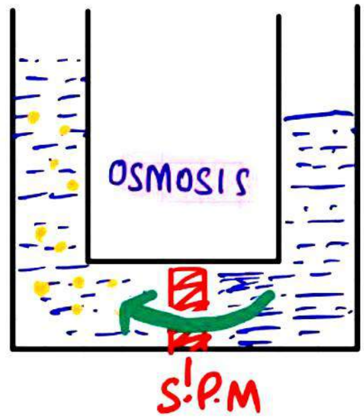
Eg: ethylene glycol is usually added to water in radiator to lower its freezing point. It is called antifreeze solution.

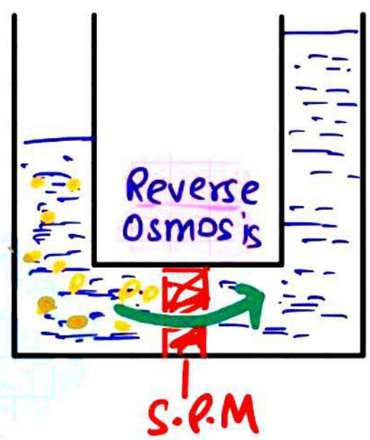
Eg: common salt (NaCl) and anhydrous $CaCl_2$ are used to clear snow on the roads because they depress the f.pt of water

OSMOSIS and OSMOTIC PRESSURE

Diffusion







OSMOSIS

it is the phenomenon of spontaneous flow of solvent molecules through a semi permeable membrane from pure solvent solution to concenterated solution.

SEMI PERMEABLE MEMBRANE

membrane, which allow only solvent molecules to pass through.

→ NATURAL
animal bladder, cell membrane

→ ARTIFICIAL
$Cu_2[Fe(CN)_6]$, which doesn't work in non-aqueous solution as it dissolves in them.

OSMOTIC PRESSURE:

Pressure applied on solution to stop osmosis, is called osmotic pressure. It is denoted by P or π.

Osmotic Pressure $(\pi) \propto T$ —(1)

$\pi \propto C$ —(2)

From (1) & (2)

$\pi = R \times C \times T$

Ⓡ → Gas Constant

$$\pi = R \times T \times \frac{W_B}{M_B} \times \frac{1000}{V(ml)}$$

$$\pi = \frac{R \times T \times d}{M_B}$$

$$M_B = \frac{R \times T \times W_B \times 1000}{\pi \times V(ml)}$$

ISOTONIC SOL^N Two solutions having same osmotic pressure
eg 0.91% solution of pure NaCl is isotonic with human RBC's
They have same molar concenteration

HYPERTONIC
Having high osmotic pressure $(\pi_A > \pi_B)$

HYPOTONIC
Having low Osmotic pressure

EXOSMOSIS
It is outward flow of water or solvent from a cell through semi-permeable membrane

ENDOSMOSIS
It is inward flow of water or solvent from a cell through semi permeable membrane.

ABNORMAL MOLECULAR MASS

In some cases, observed colligative properties deviate from their normal calculated values due to association or dissociation of molecules

$$\text{Colligative Property} \propto \frac{1}{M_B}$$

Higher values observed in case of association e.g benzene
Lower values observed in case of dissociation e.g KCl

VAN'T HOFF FACTOR (i)

ratio of observed value of colligative property to the calculated value of colligative property.

$$i = \frac{\text{Observed Colligative Property}}{\text{Calculated colligative Property}}$$

or $$i = \frac{\text{normal molecular mass}}{\text{observed molecular mass}}$$

or $$i = \frac{\text{no. of particles after association or dissociation}}{\text{number of particles initially}}$$

Colligative Property and Van't Hoff factor

$\Delta T_b = i K_b m$

$\Delta T_f = i K_f m$

$\pi = i\, CRT$

$\frac{P_A^\circ - P_s}{P_A^\circ} = i x_B$

i for strong electrolyte like

$KCl = 2$, $NaCl = 2$, $MgSO_4 = 2$

$K_2SO_4 = 3$, $Al_2(SO_4)_3 = 5$

Degree of Dissociation (α) and Van't Hoff factor (i)

if one molecule of a substance gets dissociated into n particles and α is the degree of dissociation then

	$A \longrightarrow$	np
initially	1 mol	0
At eq.	$1-\alpha$	$n\alpha$

Total no. of moles at equilibrium $= 1-\alpha+n\alpha$

$$i = \frac{1-\alpha+n\alpha}{1}$$

$$\boxed{\alpha = \frac{i-1}{n-1}}$$

Degree of Association (α) and Van't Hoff factor (i)

If n molecules of a substance A associate to form A_n and α is the degree of association, then

	$nA \longrightarrow$	A_n
initially	1 mol	0
At equilibrium	$1-\alpha$	$\frac{\alpha}{n}$

Total no. of moles at equili $= 1-\alpha+\frac{\alpha}{n}$

$$i = \frac{1-\alpha+\frac{\alpha}{n}}{1}$$

$$\alpha = \frac{i-1}{\frac{1}{n}-1}$$

$\boxed{i=1}$ no association or dissociation

$\boxed{i>1}$ particles undergoes dissociation

$\boxed{i<1}$ particles undergoes association

ELECTRO CHEMISTRY

ELECTRO CHEMISTRY

- Electro-chemical Cell
- Electro-lysis
- Chemical Conduction

ElectroChemical Cell A device which can convert chemical energy into electrical energy.

When a metal rod is placed in contact with its solution there may be two cases possible —

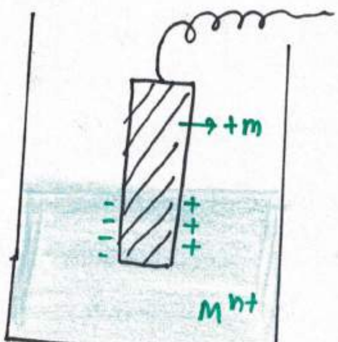
Solution Pressure	Osmatic Pressure
Electro-nation	De-electronation

Osmatic Pressure

for some metals, the atom from neutral rod will move into solution in form of ions leaving behind the electron on the the rod. This tendency is called solution pressure.

In solution, concentration of $[M^{+n}]$ will increase. On the rod negative charge will increase. This process will take place till short time and some time sufficient negative charge will develop on the rod.

Example — Zn rod is placed in contact with $ZnSO_4$ soluth. Because of change sepration three will be potential difference b/w metal rod and ite solution which is called **electrode potential** and the metal rod in contact with its salt solution is called **electrode**. [anode]



$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne$

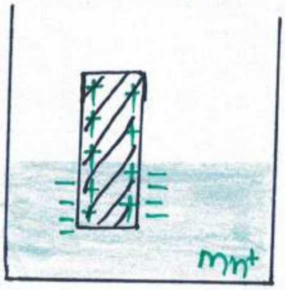
For anode

- Osmatic pressure > solution press.
- Always oxidation will occure at anode $M \longrightarrow M^{n+} + ne$
- Anode is used as source of solution.
- Solution polarity will be negative

Solution Pressure

Tendency of metal ion to get deposited on the rod.

- This type of electrode is called **Cathod**.



For Cathode

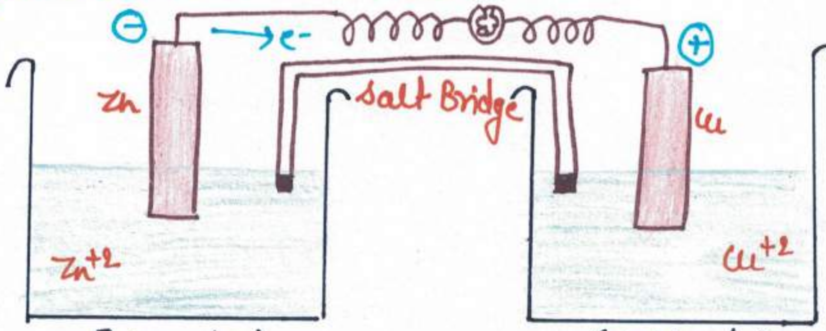
- Solution pressure > Osmatic Press.
- Always reduction will occure at Cathode $M + ne \longrightarrow M$
- $[M]^{+n}$ concn will decrease.
- solution polarity will be negative

Ex:- Cu metal.

- for electrodes if we have osmatic pressure equal to solution pressure, then electrode is called **Inert or null electrode**. Ex:- Platinum electrode

Direction of e^- ⟶ anode to cathode
Direction of current ⟶ Cathode to anode

Construction of electrochemical Cell :-



[Anode)　　　　　　(Cathode)

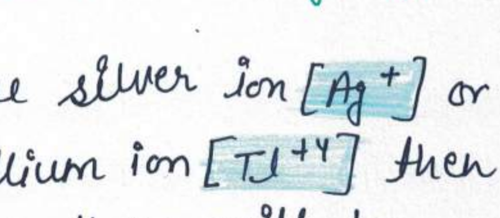
LOAN
- Anode ⇒ L ⇒ Left
- O ⇒ oxidatn
- A ⇒ Anode
- N ⇒ Negative

Salt Bridge — A 'U'-shaped glass tube is fitted with a paste of any electrode [generally KCl] with agar. agar solution and dried.

1. It will form net like structure or porous structure. through Which ion can move.
2. Electrolyte to be used in salt bridge should be such as that its cation speed will be equal to speed of anion i.e Molarity of cation is equal to molarity of Anion.
3. If in any compartment there are silver ion [Ag^{+}] or murcurous ion [Hg_2^{+} Hg^{+2}] or thallium ion [Tl^{+4}] then KCl should not be used. otherwise there will be precipitation of $AgCl$, Hg_2Cl_2, $HgCl_2$ $TlCl$ respectively on opening of salt bridge and salt bridge will stop working.
4. In the case KNO_3 and NH_4NO_3 are used (sped are diff. but we have to use because of no other option) salt bridge complete the Internal circuit of the cell as well as maintain neutrility.

Construction of electro-chemical cell

$Zn/Zn^{+2}//Cu^{+2}/Cu$



Anode　　Salt Bridge　　Cathode

NOTE Always ion must be on the side of salt Bridge.

NOTE

Cell reaction:– $M \longrightarrow M^{n+} + ne \Longrightarrow$ [Anode]

$ne + N^{+n} \longrightarrow N \Longrightarrow$ [Cathode]

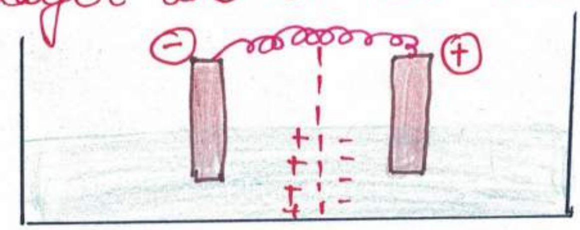
$M_{(s)} + M^{+n}_{(aq.)} \longrightarrow M^{+n}_{(aq.)} + M_{(s)}$

$$Q_c = \frac{[M]^{n+}}{[N]^{+n}}$$

In the reaction, M^{+n} keeps on increasing as it is at anode & N^{+n} keeps on decreaseing as it is at Cathode

Genrally Q_c keeps on (↑)ing.

If we will not use salt bridge then there will be a liquid liquid junction potential due to formation of electrical layer and it will decrease potential of Ecell.



Potential of all → $E_{anode} + E_{cathode}$

$Zn \longrightarrow Zn^{+2} + 2e \rightarrow$ Anode $\rightarrow E_{oxi}$

$2e + Zn^{+2} \longrightarrow Zn \longrightarrow$ Cathode $\rightarrow E_{red}$

$E_{oxi} = -E_{red}$

Notation → $E_{oxi} = E_{Zn|Zn^{+2}}$
$E_{red} = E_{Zn^{+2}|Zn}$

$E_{cell} = (E_{oxi})_{anode} + (E_{red})_{cathod}$
$= (E_{red})_{cathode} - (E_{red})_{Anode}$

Standered condition → It is one atmosphere pressure, Temprature in 25°C and concⁿ of ion is considered 1 molar.

At Standered condition ⇒ $E^\circ_{oxi} = -E^\circ_{red}$

$E^\circ_{cell} = (E^\circ_{oxi})_{anode} - (E^\circ_{red})_{cathode}$

$E^\circ_{cell} = (E^\circ_{red})_{cathod} - (E^\circ_{red})_{Anode}$ standered potential of cell.

Example

$E^\circ_{Zn^{+2}/Zn} = -0.76V$; $E^\circ_{Cu^{+2}/Cu} = 0.34V$

$E^\circ_{cell} = 0.34 - (-0.76) = 1.1V$

Example $E^{0}_{Zn|Zn^{+2}} = 0.76$; $E^{0}_{Cu|Cu^{+2}} = -0.34V$

$E^{0}_{cell} = 0.76 + 0.34 = 1.1V$

Example $E^{0}_{Zn|Zn^{+2}} = 0.76V$; $E^{0}_{Cu|Cu^{+2}} = 0.34V$

$E^{0}_{cell} = 0.76 + 0.34 = 1.1V$

Example $E^{0}_{Cu|Cu^{+2}} = -0.34V$; $E^{0}_{Zn^{+2}|Zn} = -0.76V$

$E^{0}_{cell} = 0.76 + 0.34 = 1.1V$

Standered Hydrogen electrode

Anode ; $H_2 \longrightarrow 2H^+ + 2e$ at anode ; $Pt_{(s)}|H_2|H^+||$

Cathode ; $2H^+ + 2e \longrightarrow H_2$ at cathode ; $||H^+|H_2|Pt_{(s)}$

$E_{H_2|H^+} \longrightarrow 0$ $E_{H^+/H_2} = 0$

concept $E^{0}_{Fe^{+2}|Fe} = 0.41V$; $E_{Ag^+|Ag} = 0.85V$

Fe should be used as anode & Ag should be used as cathode. $E^{0}_{Li^+|Li} = -3.05V \longrightarrow$ best reducing agent (to be used as anode)

$E^{0}_{F_2|F^\ominus} = 2.87V \longrightarrow$ best oxidising agent (to be used as cathode)

In electrode potential series $E^{0}_{Li^+|Li} = -3.05V$; $E^{0}_{F_2|F} = 2.87V$

If we want to make feasible reaction then;

$\Delta G < 0$ free energy $G = -nFE$

n = no. of e^- in half cell rxn.
F = charge on faraday.
e = electrode Potential.

$1F = 6.023 \times 10^{23} \times 1.6 \times 10^{-19} C$
$= 9.638 \times 10^4 = 96368 C$ $\simeq 96500 C$

for feasible $\Delta G < 0$; so for any feasible reaction $E > 0$

E $\longrightarrow$ Inetensive property $\longrightarrow$ independent of mass.

$\Delta G \longrightarrow$ Extensive Property $\longrightarrow$ dependent on Mass.

Quesⁿ $E^\circ_{Cu^{+2}/Cu} = 0.34$; $E_{Li^+/Li} = -3.05\,V$; $E_{Cu^{+2}/Cu} = -0.74\,V$

$E^\circ_{Ag^+/Ag} = 0.85\,V$, find the reaction is feasible or not?

$3Ag + Cu \longrightarrow 3Ag^+ + Cu$

Solⁿ $E^\circ = (E_{anode})_{oxi} + (E_{cathode})_{red.}$

$-0.85 - 0.74 < 0$

Not feasible

Solutⁿ $2Li + Cu^{+2} \longrightarrow 2Li + Cu$

$\Rightarrow 3.05 + 0.34 > 0$

feasible

Solⁿ $Cu + 2HCl \longrightarrow ?$

$Cu + 2HCl \longrightarrow Cu^{+2} + H_2$

$E^\circ = -0.34 + 0 < 0$

Not feasible

solutⁿ $Li + HCl \longrightarrow ?$

$Li + 2HCl \longrightarrow Li^+ + H_2$

$E^\circ = 3.05 - 0 > 0$

feasible

NOTE If metal will react with acid, then it will envolve hydrogen gas if metal is present above Hydrogen in electrode potential series.

- As the electrode potential of electrode will decrease Its reducing nature will decrease.
- As the reduction potential of electrode will increase Its reducing nature will decrease.

Reduction Potential Order

Li K Ba Sr Ca Na Mg Al Zn Cr Fe Cd Co Ni Sn

लिक बसरका नाम गाल थिंकफी कुडकोनी Sn Pb H कुहंग

PbH Cu Hg Ag Pt Au

आग परायु

$F_2 > Cl_2 > Br_2 > I_2$

Nernst Equation

$$\Delta G = \Delta G^\circ + RT\ln Q$$

where ΔG = free energy of electrode
ΔG° = free energy at standered cond'
Q = reaction quotient.

$$\Delta G = -nFE$$

$\Rightarrow -nFE = -nFE^\circ + RT\ln Q$

$\Rightarrow -nF(E^\circ - E) = RT\ln Q$

$\Rightarrow (E^\circ - E) = \dfrac{-RT\ln Q}{nF}$

$\Rightarrow E = E^\circ - \dfrac{RT\ln Q}{nF}$

This equation can be used for cell potential as well as for electrode potential.

$$\frac{RT\ln Q}{nF} = \frac{8.314 \times 298}{2.303 \times n}\log_{10} Q = \frac{0.0591}{n}\log_{10} Q$$

$$E = E^\circ - \frac{0.0591}{n}\log_{10} Q$$ → Nernst Equation

Example $Zn|Zn^{+2}||Cu^{+2}|Cu$

$Zn_{(s)} \rightarrow Zn^{+2} + 2e^-$

$2e^- + Cu^{+2}_{(aq)} \rightarrow Cu_{(s)}$

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

$$Q = \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$E_{cell} = 1.1 - \frac{0.0591}{n}\log\frac{[Zn^{+2}]}{[Cu^{+2}]}$$

When $\dfrac{0.0591}{n}\log\dfrac{[Zn^{+2}]}{[Cu^{+2}]}$ is equal to 1.1, the cell will will stop working.

E_{cell} can't be zero or negative $E_{cell} \nleq 0$

If we get $E_{cell} = 0$ in calculation, then it means reaction is not complete; it is at equillibrium $Q_c = K_c$

$\Delta G = \Delta G^\circ + RT\ln K \quad \because \Delta G = 0$

$\Delta G^\circ = -RT\ln K$

$\ln K = \dfrac{-\Delta G^\circ}{RT}$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{+nFE^\circ}{RT}}$$

CONCENTRTON CELL

When anode and cathode are of same metal electrode It is called concentration cell.

The value of $E^\circ_{cell} = 0$ because $E^\circ_{cell} = E_{cathode} + E_{anode} = 0$

Example Ag | Ag^+ (xm) || Ag^+ (ym) / Ag

$Ag \rightarrow Ag^+ + e^-$

$Ag^+ + e^- \rightarrow Ag$

$Ag^+ + Ag \rightarrow Ag^+ + Ag$
(anode) (cathode)

↳ $Q = \dfrac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$

↳ $E_{cell} = 0 - \dfrac{0.0591}{n} \log \dfrac{[Ag^+]}{[Ag^+]}$ ⇒ $-\dfrac{0.0591}{n} \log \dfrac{x}{y} = E_{cell}$

Quest Calculate E°_{cell} for the cell made of electrodes.

$E^\circ_{Ag|Ag^+} = -0.80V$ $E^\circ_{MnO_4^-/Mn^{+2}} = 1.51V$

Ans. $E^\circ_{cell} = (E^\circ_{oxi}) + (E^\circ_{red})$ ⇒ $-0.80 + 1.51$

Cathode = MnO_4^- ⇒ **0.71V**

Anode = Ag

Quest Check wheather following cell is feasible or not?

$Ag_{(s)} | Ag^+_{(aq.)} || Cu^{+2}_{(aq)} | Cu_{(s)}$
($-0.84V$) ($0.34V$)

$2Ag \rightarrow 2Ag^+ + 2e^-$

$Cu^{+2} + 2e^- \rightarrow Cu$

$2Ag + Cu^{+2} \rightarrow 2Ag^+ + Cu$

Ans. $E^\circ_{cell} = -.84 + 0.34$

$= -0.50V$ Not feasible

Calculation of SRP → We will calculate SRP of an electrod from SRP of other electrode

SRP - Standered reduction Potential

Ex: $E^0_{Cu^{+2}|Cu} = 0.337$ $E^0_{Cu^{+2}/Cu^+} = 0.153V$ $E^0_{Cu^+|Cu} = ?$

$Cu^{+2} + 2e \longrightarrow Cu$ $\Delta G_1 = -2FE^0_1$

$Cu^{+2} + 2e \longrightarrow Cu^+$ $\Delta G_2 = -FE^0_2$

$Cu^+ + e \longrightarrow Cu$ $\Delta G_3 = -FE_3$

$\Delta G_3 = G_1 - G_2$

$-E^0 = -2 \times 0.337 + 0.153$

$E^0 = 2 \times 0.337 - 0.153$

$E^0 = 0.674 - 0.154$

$0.521V$

Example Calculate $E^0_{MnO_4^-|MnO_2}$; $E^0_{MnO_4^-|Mn^{+2}} = 1.51V$

$E_{MnO_2|Mn^{+2}} = 1.23V$

$MnO_4^- + 5e \longrightarrow Mn^{+2}$ $\Delta G_1 = -5FE_1$

$MnO_2 + 2e \longrightarrow Mn^{+2}$ $\Delta G_2 = -2FE_2$

$MnO_4 + 3e \longrightarrow MnO_2$ $\Delta G_3 = -3FE_3$

$\Delta G_3 = \Delta G_1 + \Delta G_2$

$-3FE^0_3 = +2FE_2 - 5FE_1$

$3E_3 = -2 \times 1.23 + 5 \times 1.51$

$3E^0 = -2.46 + 7.55$

$E_3 = 1.69V$

ΔG^0 is an extensive property while E^0 is an intensive. Therefore we can add and subtract according ΔG Equation.

Example Predict whether the following equation will take place or not ?

$Cu_{(s)} + 2H_{(aq.)} \longrightarrow Cu^{+2}_{(aq)} + H_{2(g)}$ $E^0_{Cu^{+2}/Cu} = 0.34$

$E_{H^+/H_2} = 0$

$E^0_{cell} = (E^0_{anode}) + (E^0_{cath.})$ $\Rightarrow -0.34 + 0$

$\Rightarrow -0.34$ Not feasible

Example Predict feasibility of reaction

$E^0_{Fe^{+3}/Fe^{+2}} = 0.77V$ $E_{I_2/I^\ominus} = 0.54V$

$2Fe^{+3} + 2I \longrightarrow 2Fe^{+3} + I_2$

$E^0_{cell} = 0.77 - 0.54$

$= 0.23V$

does not depends on the stoichiometric cofficient.

Ques In which of the following solution oxidising power of $KMnO_4$ will be greater.

[A] 0.01 M H_2SO_4 sol [B] 0.001 M H_2SO_4 soln.

In both cases concn of species are equal.

Ans. $E_a = E^\circ - \frac{0.0591}{5} \log \frac{[Mn^{+2}]}{[MnO_4^-][H^+]^8}$

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

$E_a = E^\circ + \frac{0.0591}{5} \times 8 \log [H^+]$

$(E_{RP})_a = E^\circ + \frac{0.0591}{5} 8 \log(2 \times 10^{-2})$

$(E_{RP})_a = E^\circ + \frac{0.0591}{5} \times 8 \times -2 \times 0.3010$

$= E^\circ - \frac{0.0591 \times 8 \times 1.7}{5}$

$(E_{RP})_b = E^\circ - \frac{0.0591 \times 8 \times 2.7}{5}$

$\log(2 \times 10^{-2})$
$-2 \times \log 2$
-2×0.3010

$(E_{RP})_a > (E_{RP})_b$

oxidising power of a > b

Ques Calculate $E_{Cu^{+2}/Cu}$ at pH = 14. Given that K_{sp} of $Cu(OH)_2 = 10^{-19}$ and $E_{Cu^{+2}/Cu} = 0.34$ at 298 K.

Ans. pH = 14 $[H^+] = 10^{-14}$; $[OH] = 1$; $Cu^{+2} = 10^{-19}$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{1}{Cu^{+2}}$ $Cu^{+2} + 2e^- \longrightarrow Cu$

$E_{cell} = 0.34 - \frac{0.0591}{2} \log \frac{1}{10^{-19}} \Rightarrow 0.34 - 0.0295 \times 19$

$= -0.22V$

Ques for concn cell ; $E_{cell} = 0.029$ V at 298 K Calculate n = ?

$X_{(s)} | X^{n+}_{aq} \left(\frac{1}{20} M\right) || X^{n+}_{(aq)} \left(\frac{1}{2} M\right) | X_{(s)}$

$X \longrightarrow X^{n+} + e^-$

$X^{n+} + e^- \longrightarrow X$

$X^{n+} + Y \longrightarrow X^{n+} + X$

Ans. $0.029 = E^\circ - \frac{0.0591}{n} \log\left(\frac{1}{10}\right)$

$0.029 = E^\circ + \frac{0.0591}{n}$ $E^\circ_{cell} = 0$

$n = \frac{0.0591}{0.029} = 2$ Ans

Quest A Hydrogen electrode is immersed in a solution $p^H = 0$ (HCl). By How much will the the reduction potential change if an equivalent amount of NaOH is added to this solution so that solution become neutral. ($P_{H_2} = 1$ atm)

Ans. $p^H = 0$ $p^{OH} = 14$ $[OH^-] = 10^{-14}$ $[H^+]_i = 1$ intial

finally $[H^+] = 10^{-7}$

$$2H^+ + 2e^- \longrightarrow H_2$$

$$(E_{cell})_i = 0 - \frac{0.0591}{2} \times 0 = 0$$

$$Q = \frac{[H_2]}{[H^+]^2} \Rightarrow (E_{cell})_f = 0 - \frac{0.0591}{2} \times \log \frac{[H_2]}{[H^+]^2}$$

$$= \frac{-0.0591}{2} \times \log 10^{14}$$

$$= \boxed{0.4137}$$

$$E_{change} = E^0_{final} - E_{initial} = \boxed{0.4137\ V}$$

Quest E_{cell} of $Pt_{(s)} | H_2 | HCOOH || CH_3COOH | H_2 | Pt(s)$; Calculate $E^0_{cell} = ?$
(1atm, Ka_1, Ka_2)

Ans.

$$H_2 \longrightarrow 2H^+ + 2e^- \text{ (anode)}$$

$$2H^+ + 2e^- \longrightarrow H_2 \text{ (cathode)}$$

$$\underset{(C_1 - x)}{HCOOH} \longrightarrow \underset{x}{HCOO^-} + \underset{x}{H^+}$$

$$\Rightarrow E_{cell} = 0 - \frac{0.0591}{2} \log \frac{1 \times (\sqrt{C_1 Ka_1})^2}{1 \times (\sqrt{C_2 Ka_2})^2}$$

$$\Rightarrow E_{cell} = \frac{-0.0591}{2} \log \frac{C_1 Ka_1}{C_2 Ka_2}$$

$$\boxed{E_{cell} = \frac{0.0591}{2} \log \frac{C_2 Ka_2}{C_1 Ka_1}}$$

Ques Calculate E_{cell} for $Pt | H_{2(g)} | 1N\ KOH | \frac{N}{10} HCl | H_{2}(g) | Pt(s) |$
($\alpha = 75\%$, $\alpha = 90\%$)

Soln

$$\underset{1-x}{KOH} \longrightarrow \underset{x}{K^+} + \underset{x}{OH^-}$$

$x = 0.75$ $[OH^-] = 0.75$

$[H^+] = 1.3 \times 10^{-14}$

$$\underset{\frac{1}{10}-x}{HCl} \longrightarrow \underset{x}{H^+} + \underset{x}{Cl^-}$$

$x = 0.09$

$x = 9 \times 10^{-2}$

$$E_{cell} = 0 - \frac{0.0591}{2} \log \left[\frac{(\frac{4}{3} \times 10^{-14})^2}{(9 \times 10^{-2})^2} \right] \Rightarrow -\frac{0.0591}{2} \times 2 \log \left[\frac{4}{7} \times 10^{-12} \right]$$

$$\Rightarrow -0.0591 \left[\log \frac{4}{27} - 12 \right] \Rightarrow 12.48 \times 0.0591 \Rightarrow \boxed{0.737V}$$

Ques. At 298 K, the equillibrium constant for reaction $Zn + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{+2}$ is 10^9. If $E^\circ_{Zn^{+2}/(Zn+4NH_3)} = -1.03V$ then value of $E_{Zn/Zn^{+2}} = ?$

Ans.

$$10^9 = \frac{[Zn(NH_3)_4]^{+2}}{[Zn^{+2}]}$$

$$Zn \longrightarrow Zn^{+2} + 2e^- = -2FE^\circ$$

$$Zn^{+2} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{+2} = 1.09V$$

$$E = E^\circ - \frac{0.0591}{2} \log 10^9$$

$$E = 1.03 - \frac{0.06}{2} \times 9$$

$$E = 0.76$$

$\Delta G = \Delta G^\circ + RT \ln Q$ At equlibrium $\Delta G = 0$

$$0 = \Delta G^\circ + RT \ln Q$$

$$-2FE^\circ + 8.31 \times 298 \times 9$$

$$E^\circ = \frac{74.79 \times 298}{2 \times 96500} =$$

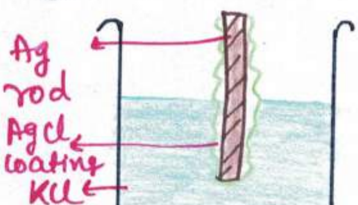
$$E = 0.77V$$

Type of electrodes

Metal-Metal soluble salt electrode → Metal rod dipped in its own solution $Ag|AgNO_3$, $Cu|CuSO_4$.

Gas-electrode → $Pt|H_2|H^+$ ⇝ Hydrogen electrode

Metal-Metal Insoluble salt electrode → In this half cell a metal coated with its insoluble salt in contact with a solution containing the anion of Insoluble salt.



This electrode can be used as cathode or anode, the solution have $Cl^\ominus$ ion that will give priciptation of AgCl.

At anode ⇐

$$Ag \longrightarrow Ag^+ + e^-$$

$$Ag^+ + Cl^- \longrightarrow AgCl$$

$$Ag_{(s)} + Cl^-_{(aq.)} \longrightarrow AgCl + e^-$$

$Ag_{(s)}/AgCl_{(s)}/Cl^\ominus ||$

at cathode

$$Ag^+ + e^- \longrightarrow Ag$$

$$AgCl \longrightarrow Ag^+ + Cl^-$$

$$AgCl_{(s)} + e \longrightarrow Ag_{(s)} + Cl^-_{(aq.)}$$

$|| Cl^\ominus / AgCl_{(s)} / Ag_{(s)}$

Quest. 1 Calculate Ksp of AgI with the help of following cell.

$Ag | AgI_{(s)} | KI || AgNO_3 | Ag_{(s)}$

0.05   0.05 $E_{cell} = 0.7884$ V at 298K.

Ans.

$Ag \longrightarrow Ag^+ + e^-$

$Ag^+ + e^- \longrightarrow Ag$

$Ag + Ag^+ \quad Ag + Ag^+$

$E_{cell} = 0.7884 \quad E^o_{cell} = 0$

$Ag^+_c = 0.05$ M

$[Ag^+][I^-] = K_{sp}$

$[Ag^+] \times 0.05 = K_{sp}$

$[Ag^+]_a = \frac{K_{sp}}{0.05}$

$\Rightarrow E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{Ag^+_a}{Ag^+_c}$

$\Rightarrow 0.7884 = 0 - \frac{0.0591}{1} \log \frac{K_{sp}}{[25 \times 10^{-4}]}$

$\Rightarrow -\frac{0.7884}{0.06} = \log \frac{K_{sp}}{25 \times 10^{-4}} \Rightarrow \log \frac{K_{sp}}{25 \times 10^{-4}} = 1.3$

$\Rightarrow K_{sp} = 25 \times 10^{-4} \times 10^{-13} \Rightarrow$ **$K_{sp} = 2.5 \times 10^{-16}$**

To find Ksp of Ag|AgCl insoluble salt electrode use;

$$E^o_{Cl/AgCl/Ag} = E^o_{Ag/Ag} + 0.059 \log [K_{sp}(AgCl)]$$

Ques 2 A graph is plotted b/w Ecell and $\log \frac{[Zn^{+2}]}{[Cu^{+2}]}$ the curve was linear with interact on cell axis equal to 1.1 V. Calculate Ecell for $Zn | Zn^{+2} || Cu^{+2} | Cu$

0.1   0.01 M

Ans

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

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

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

$Zn^{+2} = 0.1 = 10^{-1}$

$Cu^{+2} = 0.01 = 10^{-2}$

$\Rightarrow E_{cell} = 1.1 - \frac{0.0591}{2} \log \frac{[10^{-1}]}{[10^{-2}]} \Rightarrow 1.1 - \frac{0.0591}{2}$

$\Rightarrow 1.1 - 0.029 \Rightarrow$ **1.07 V**

Quest A standered reduction potential of copper and silver are 0.34 V and 0.8 V. A galvanic cell is constructed using Cu and Ag. Determine anode and cathode of cell, E^o_{cell}, cell potential when concn of Cu^{+2} and Ag^+ are 3×10^{-2} M and 1.73×10^{-3} M.

Ans. Ag ⟶ Cathode
Cu ⟶ Anode

$Cu \longrightarrow Cu^{+2} + 2e^-$
$2Ag^+ + 2e^- \longrightarrow 2Ag$

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

$E^\circ_{cell} = 0.8 - 0.34 = \boxed{0.46}$

$E = 0.46 - \frac{0.0591}{2} \log \frac{3\times10^{-2}}{3\times10^{-6}} = 0.46 - \frac{0.0591}{2} \times 4$

$= 0.46 - 0.1182 = \boxed{0.34}$

Ques. The Emf of all $Pt_{(s)} | H_2 | HOCN || Ag^+ | Ag_{(s)}$ is 0.982 V. Calculate K_a for HOCN (1atm, 1.3×10^{-3}, 0.8M) if E°_{red} of electrode = 0.8 V.

Ans. $HOCN \longrightarrow H^+ + OCN^-$
$1.3\times10^{-3} - x \quad x \quad x$

$H_2 \longrightarrow 2H^+ + 2e^-$
$2Ag^+ + 2e^- \longrightarrow 2Ag$

$2Ag^+ + H_2 \longrightarrow 2H^+ + 2Ag$

$\frac{x^2}{1.3\times10^{-3} - x} = K_a$

↳ $x^2 = K_a \times 1.3\times10^{-3} - K_a x$ ↳ $x^2 + xK_a - 1.3\times10^{-3} K_a = 0$

↳ $K_a = \frac{x^2}{1.3\times10^{-3} - x}$ ↳ $0.982 = 0.8 - \frac{0.0591}{2} \log \frac{[H^+]^2}{[Ag^+]^2 H_2}$

↳ $\frac{-0.364}{0.064} = \log \frac{[H^+]^2}{Ag^+}$ ↳ $\frac{[H^+]^2}{[Ag^+]^2} = 10^{-6}$

↳ $[H^+]^2 = 10^{-6} \times 64\times10^{-2}$ ↳ $[H^+] = 8\times10^{-4}$

↳ $K_a = \frac{64\times10^{-8}}{1.3\times10^{-3} - 8\times10^{-4}} = \frac{64\times10^{-8}}{5\times10^{-4}} = \boxed{1.28\times10^{-3} = K_a}$

THERMODYNAMICS OF CELL

$G = H - T\Delta S$ — (i)
$H = U + PV$ — (ii)
$dQ = dU + PdV$ (iii)
$dS = \frac{dQ}{T}$ (iv)

↳ $dG = dH - TdS - SdT$
↳ $dH = \underbrace{dU + PdV}_{dQ} + VdP$
↳ $dH = dQ + VdP$
↳ $dG = dQ + VdP - TdS - SdT$

$$dG = T\,dS + V\,dP - T\,dS - S\,dT$$

$$dG = V\,dP - S\,dT$$

at constant P $(dP = 0)$ $= dG = -S\,dT$

$$S = -\frac{dG}{dT} \qquad \Delta S = -\frac{d\Delta G}{dT}$$

$$\Delta H = \Delta G + T\Delta S$$

$$\Delta H = -nFE_{cell} + nFT\frac{dE_{cell}}{dt}$$

$$\Delta S = nF\frac{dE_{cell}}{dt}$$

$\dfrac{dE_{cell}}{dt} \Rightarrow$ Temprature Cofficient

Remember only —
$\Delta S = nF\left[\dfrac{dE_{cell}}{dT}\right]$
$\Delta G = nFE$ By using we can find —
$\Delta H = \Delta G + T\Delta S$
$\Delta C_p = nFTd^2$

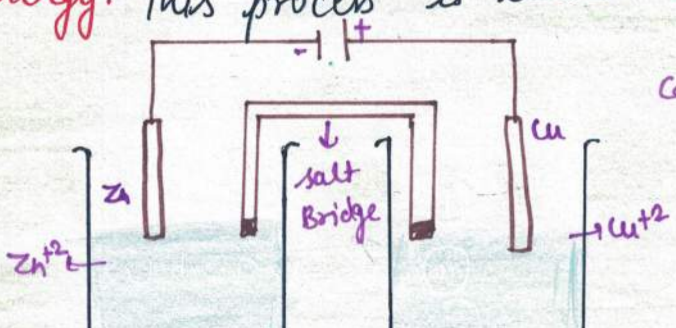
HEAT CAPACITY

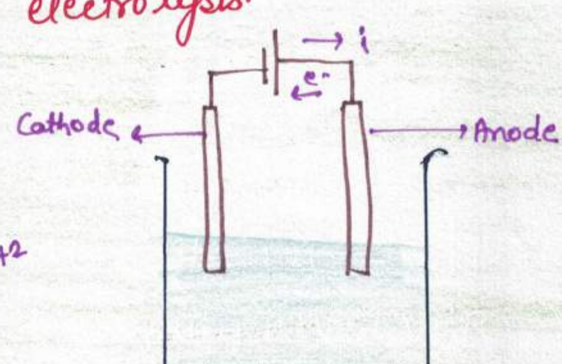
$$C_p = \frac{d(\Delta H)}{dT} \qquad C_p = \frac{TnF\,dE}{dT^2}$$

Enthaphy $\Delta H = \Delta G + T\Delta S = -nFE + TnF\left(\dfrac{dE}{dT}\right)_P$

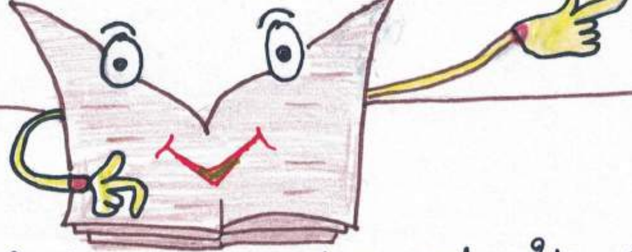
ELECTROLYSIS

It is reverse process of elecro-chemical cell. If we will apply external potential that is more than potential of electrochemical cell. then process will reverse and electrical energy will be converted into chemical energy. This process is called electrolysis.





electrolysis is process of decomposition of an electrolytes.



on passing electrical current through its aqueous solution in its molten state. The cell used for this process is called electrolysis cell. In this anode will be electrode connected with positive terminal of battery and cathode will be electrode connected with negative terminal of the battery.

- During electrolysis, cation will be attracted towards cathode and will get neutrilised after accepting e^- from cathode.
- Anions will be attracted towards anode and will get neutrilised after releasing extra charge

At cathode :- $A^+ + e^- \longrightarrow A$

At anode :- $B^- \longrightarrow B + e$

- In case two or more type of potential (positive and negative) ions +nt in solution during electrolysis, certain ions are discharged and librated at the electrode in preference to other.

Oxidation and reduction of water

Reduction :—

$H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH$

oxidation :—

$H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

- In general such competition, the ion which are stronger oxidising agent is discharged first at cathode (high reduction potential)

Order of Decomposit^n ▸ Similarly ion which is stronger reducing agent will get deposit first at anode [low reduction potential]

$Li^+, K^+, Na^+, mg^+, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}$

Increasing order of Decomposition →

Increasing order of deposition :- SO_4^{-2}, NO_3^-, OH^- Cl^-, Br^-, I

Electrolysis of molten $PbBr_2$

$PbBr_2 \longrightarrow Pb^{+2} + 2Br^-$

At Anode:- $Pb^{+2} + 2e^- \longrightarrow Pb_{(s)}$

at Cathode:- $2Br^- \longrightarrow Br_2 + 2e^-$

$$Pb^{+2} + 2Br^- \longrightarrow Pb_{(s)} + Br_{2(g)}$$

Electrolysis of NaCl (molten

$NaCl \rightarrow Na^+ + Cl^-$

$2Na^+ + 2e^- \longrightarrow 2Na_{(s)}$

$2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$

$$2Na^+ + 2Cl^- \quad 2Na + Cl_{2(g)}$$

Electrolysis of NaCl & $PbBr_2$

At anode :- $2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$

At cathode :- $Pb^{+2} + 2e^- \longrightarrow Pb_{(s)}$

$$Pb^{+2} + 2Cl^- \longrightarrow Pb_{(s)} + Cl_{2(g)}$$

Electrolysis of aq. NaBr

$H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Cathode = (Na^+, H_2O) ✓

$(H_2O_{R.P} > Na^+_{R.P})$

Anode ⇒ Br^-, H_2O

$(H_2O_{R.P}) > (Br^-_{R.P})$

Electrolysis of aq. $CuSO_4$

(Cu^{+2}, H_2O) ⇓ cathode

(SO_4^{-2}, H_2O) ⇓ anode

At anode:- $Cu^{+2} + 2e^- \longrightarrow Cu$

At cathode:- $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

NOTE

- During electrolysis of aquous solution of electrolyte same time water will involve in electrode reaction rather than ion derived from solute

At anode :- $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ $E^\circ_{red} = -1.23V$

At cathode :- $2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$ $E^\circ_{red} = 0.83V$

- In electrolysis of aquous NaCl oxidation of H_2O at anode is not kinetically favoured (as activation energy of oxidation of H_2O is high) because of Over potential
- on electrolysis of aq. NaCl, the solution becom Basic

Faraday Law

The weight or amount of any substance during electrolysis will be propostional to amount of charge passed during electrolysis.

Mathematically, $W \propto Q$ $W = ZQ$ $[Q = i \times t)$

$$W = Zit$$

where z is proportionality constant. Z = electrochemical equivalent.

$i = \frac{dq}{dt} \Rightarrow dq = i\,dt$

$$Q = \int i\,dt$$

Faraday's Second Law

On applying same charge in different electrodes, then amount of deposited metal or substance will be proportional to its equivalent weight

for this we should connect the electrode in series as they should have charge

When 1 mole of charge applied.

$Na + e^- \longrightarrow Na$ Na formed = 1 mole $(M = 23g)$

$Cu^{+2} + 2e^- \longrightarrow Cu$ Cu formed = 1/2 mole $(M = 63.5/2)$

$Al^{+3} + 3e^- \longrightarrow Al$ Al formed = $\frac{1}{3}$ mole $(M = 27/3)$

$$\text{Eq. Wt} = \frac{\text{Molar Mass}}{\text{n-factor}}$$

$W_1 = Z_1 \times F$

$E_1 = Z_1 \times F$

$Z_1 = \frac{E_1}{96500}$

$W_2 = Z_2 \times F$

$E_2 = Z_2 \times F$

$Z_2 = \frac{E_2}{96500}$

In this example with one mole e^- charge we are getting 23g Na, 31.7g Cu, 9gm Al i.e equivalent mass of each metal.

$$Z = \frac{E}{96500}$$

According to Faraday's Ist Law $W = ZQ$

for two electrodes on applying 1 faraday charg i.e 96500

We get the equation derived before i.e

$$Z = \frac{E}{96500} \qquad W = Zit \qquad W = \frac{Eit}{96500}$$

Question How many colomb of charge required for following reactions:-

(i) $Cu^{+2} \longrightarrow Cu$ (1 mol) (2.) $MnO_4^- \longrightarrow Mn^{+2}$

(1) $Cu^{+2} + 2e^- \longrightarrow Cu$

2 mole e^- required i.e

$2 \times 96500 = 193000\,C$

$1.93 \times 10^5\,C$

(2) $Mn^{+7} + 5e^- \longrightarrow Mn^{+2}$

5 mole e^- required

$5 \times 96500 =$

$4.825 \times 10^5\,C$

Question How many gram of Cu will get deposited by passing 2A for 30 minutes in aquous $CuSO_4$ solution and what will be wt. of O_2 released at anode?

$Cu^{+2} + 2e^- \longrightarrow Cu$

$$E = \frac{63.5}{2}$$

$$W = \frac{Eit}{F} = \frac{63.5 \times 2 \times 30 \times 60}{2 \times 96500}$$

$\Rightarrow$ **1.18g**

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

$$E = \frac{32}{4} = 8\,gm.$$

$$W = \frac{Eit}{F} = \frac{8 \times 2 \times 30 \times 60}{96500}$$

$\Rightarrow$ **0.29g**

Question Silver is electro-deposited on a vessel of total surface area 800 cm^2 by passing a current of 0.2 A for 3 Hours. Calculate the thick mass of silver deposited (density of silver is deposited is 9.67 g/cm^3

$$W = \frac{Eit}{F} = \frac{108 \times 0.2 \times 3 \times 60 \times 60}{1 \times 96500} \Rightarrow \frac{7776 \times 3}{9650} =$$

2.41 g

$800 \times \text{Thickness} \times 9.67 = 2.41$

$\text{Thickness} = \dfrac{2.41}{800 \times 9.67} = \dfrac{1}{4 \times 800} = \dfrac{1}{3200} = 0.0312 \times 10^{-2}$

$\Rightarrow \boxed{3.12 \times 10^{-4}\ cm}$

Question In an aquous solution of silver nitrate a variable current is passed for 4 second. Calculate of silver deposited.

$i = 2t \quad 0 \le t \le 2$

$i = 8.2t \quad 2 \le t \le 4$

$q_1 = \int i\,dt \Rightarrow 2\int_0^2 t\,dt \Rightarrow 2\left[\dfrac{t^2}{2}\right]_0^2 = 4C$

$q_2 = i\int dt \Rightarrow 8.2\int t\,dt \Rightarrow 49.2C$

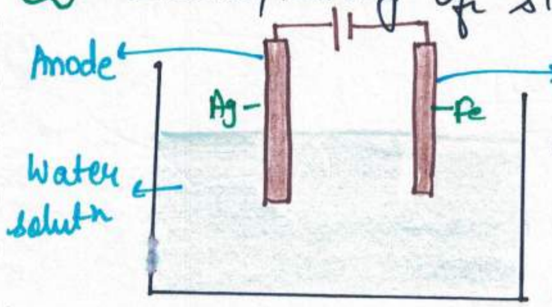
$W_1 = \dfrac{108 \times 4}{96500}$ $\quad W_2 = \dfrac{108 \times 49.2}{96500}$

$W = W_1 + W_2 \Rightarrow \dfrac{108}{96500}(4 + 49.2) \Rightarrow \dfrac{5745.6}{96500}$

$\Rightarrow \boxed{0.0059\ g}$

Electroplatting

Electroplatting of sliver and Gold on the rod :-



In this process, at anode and at cathode following reaction will occur:–

Anode $\quad Ag \longrightarrow Ag^+ + e^-$ ✓

$2H_2O \longrightarrow O_2 + 4H^+ + 4e$

Cathode $\quad Ag^+ + e^- \longrightarrow Ag$ ✓

$H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Ag will deposit from anode to iron on the Cathode. Fe will not deposite as Ag is more preferable than Fe.

CHEMICAL KINETICS

when one or more substance undergo a change which results in the formation of a new product, called chemical reaction.

CHEMICAL KINETICS, is the branch of chemistry which deals with the study of rates of chemical reaction their mechanism and the conditions in which rates can be altered.

ON THE BASIS OF SPEED

i) VERY FAST REACTION: Some reaction such as ionic reactions occur very fast e.g $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

ii) VERY SLOW REACTION: Some reactions are very slow i.e takes months to years in combletion

e.g. Rusting of iron in the presence of air and moisture

- Formation of coal and petrolium

iii) MODERATE REACTION: Those reactions which are neither very slow nor very fast but takes place at moderate speed.

e.g inversion of cane sugar

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

ON THE BASIS OF NUMBER OF STEPS ⇒

ELEMENTARY REACTIONS

The reactions taking place in one step are called elementary reaction

COMPLEX REACTIONS

when a sequence of elementary reactions gives us the product called complex reaction, each step in a complex reaction is called elementary Rxn.

Slowest step is called rate determining step.

RATE OF CHEMICAL REACTION :

It is the change in molar concenteration of species taking part in the chemical reaction per unit time.

For the reaction $A \longrightarrow B$

Rate of disappearance of A

$$= \frac{\text{Decrease in conc. of A}}{\text{Time taken}} = -\frac{\Delta[A]}{\Delta t}$$

Rate of disappearance of B

$$= \frac{\text{Increase in conc. of B}}{\text{Time taken}} = +\frac{\Delta[B]}{\Delta t}$$

NOTE The concentration of reactant decreases, so it represent by −ve sign, while the conc. of product increases so it represented by +ve sign.

TYPES OF RATE OF REACTION :

Average Rate

change in molar conc. of reactant and product at a given interval of time

Instantaneous Rate

change in molar conc. of reactant and product at a given instant of time.

$$R \longrightarrow P$$

Avg. Rate of Reaction $-\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$

Inst. Rate of Reaction $-\frac{d[R]}{dt} = +\frac{d[P]}{dt}$

RELATION BETWEEN RATE OF REACTION AND STOICHIOMETRY

•) $A + B \longrightarrow C + D$

Rate of Rxn $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$

•) $2A \longrightarrow C + D$

It is clear from stoichiometry of reaction that the rate of disappearance of A is twice the velocity of formation of C & D

So, rate of reaction can be given as below

$$\text{Rate of Rxn} \quad -\frac{1}{2}\frac{d[A]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$$

e.g. $5Br^-_{(aq.)} + BrO_3^-{}_{(aq.)} + 6H^+_{(aq.)} \longrightarrow 3Br_{2(g)} + 3H_2O_{(l)}$

$$\text{Rate of Reaction} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

UNIT OF RATE OF REACTION

$$\frac{\Delta C}{\Delta t} = \frac{\text{Mol } L^{-1}}{\text{sec or min or hr}} \Rightarrow \text{Mol } L^{-1} \sec^{-1} \text{ or Mol } L^{-1} \min^{-1} \text{ or Mol } L^{-1} hr^{-1}$$

Consider a general reaction:

$$aA + bB \longrightarrow cC$$

$$\text{Rate of reaction} \Rightarrow -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt}$$

rate of disappearance of $A = -\frac{d[A]}{dt}$

rate of disappearance of $B = -\frac{d[B]}{dt}$

Rate of appearance of $C = +\frac{d[C]}{dt}$

Q $A + 2B \longrightarrow 3C + 2D$, the rate of disappearance of B is 1×10^{-2} mol L^{-1} s^{-1} what will be

(i) Rate of Rxn (ii) Rate of change in conc. of A and C

Ans: Rate of disappearance B, $-\frac{d[B]}{dt} = 1\times10^{-2}$ mol L^{-1} s^{-1}

$$\text{Rate of Rxn} = -\frac{1}{1}\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt} = +\frac{1}{2}\frac{d[D]}{dt}$$

$$\therefore \text{Rate of Rxn} \quad -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{2}\times1.0\times10^{-2} = 0.5\times10^{-2} \text{ mol } L^{-1}s^{-1}$$

(ii) Rate of change in conc. of A

$$-\frac{d[A]}{dt} = R.O.R \Rightarrow 0.5\times10^{-2} \text{ mol } L^{-1}s^{-1}$$

Rate of change in conc. of C

$$+\frac{d[C]}{dt} = 3 \times R.O.R \Rightarrow 3 \times 0.5 \times 10^{-2}$$

$$1.5 \times 10^{-2} \, mol \, L^{-1} s^{-1}$$

FACTORS AFFECTING RATE OF REACTION

• CONCENTERATION OF REACTANT: It is observed that rate of reaction decreases with time. We know that initially the conc. of reactant is maximum so the rate of change in conc. is also maximum. As the conc. of reactant decreases when the rate of reaction also decreases. It means that the rate of reaction is directly proportional to the conc. of reactant.

• TEMPERATURE OF SYSTEM: Generally, the rate of all reactions approximately increases on increasing temp. In other words, the rate of reaction also decreases on decreasing temp. Generally, the rate of reaction mixture increases two to three times on increasing temp. upto 10°C

• NATURE OF REACTANT: In a chemical reaction old bonds are broken and new bonds are formed. So, the reactivity of substance depends on breaking and formation of specific bonds.

$$2NO + O_2 \longrightarrow 2NO_2 \text{ (fast)}$$

$$2CO + O_2 \longrightarrow 2CO_2 \text{ (Slow)}$$

• EFFECT OF CATALYST: Catalyst are those substance which increase the rate of reaction without undergoing any chemical change in them.

It is considered that presence of catalyst decrease the activation energy of reactant which increase the rate of rxn.

SURFACE AREA

Greater the surface area of reactant, higher is the rate of reaction. It is observed that if reactant is a solid substance then rate of reaction depends upon the size of its particles

e.g A piece of wood burns slowly but it burns rapidly when cut into small pieces.

EXPOSURE TO RADIATION :

The rate of some reactions increases rapidly in presence of radiation (UV and visible

Photons of UV and visible light having high energy dissociates chemical bonds of reactants rapidly which increase the rate of reaction.

$$H_2 + Cl_2 \xrightarrow{\text{In dark}} 2HCl \text{ (Slow)} \qquad H_2 + Cl_2 \xrightarrow[\text{light}]{\text{Sun}} 2HCl \text{ (with explosion)}$$

RATE LAW

Rate of Reaction is directly proportional to the product of molar concenteration of reactant and each raise to the power their coefficient on which rate of reaction actually depends.

$$aA + bB \longrightarrow \text{Product}$$

actual used: $a \downarrow \alpha$, $b \downarrow \beta$

$$\text{Rate of Rxn} = K[A]^{\alpha}[B]^{\beta}$$

K: Rate Constant or specific Reaction rate

↳ Rate law for any reaction can not be predicted theoretically but must be determined experimentally

RATE CONSTANT :

rate constant is equal to rate of reaction when concenteration of each reactant becomes unity.

ORDER :

It is the sum of powers acc. to rate law expression.

$$\text{Rate of Rxn} = K[A]^{\alpha}[B]^{\beta} \Rightarrow \text{order} = \alpha + \beta$$

Characteristics of Rate Constant

- Indicates the speed of reaction, Greater the value of rate constant, faster is the reaction.
- Every reaction has a particular value of rate constant at a particular temperature.
- The rate constant for the same reaction differs with temperature.
- The value of rate constant for a reaction does not depend upon the concenteration of reactant
- The unit of rate constant is dependent on the order of reaction.

MOLECULARITY OF REACTION

The total number of atoms, ions or molecules of the reactant which collide effectively to give product is termed as its molecularity.

$A \longrightarrow$ Product, Molecularity = 1 ↳ $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$2A \longrightarrow$ Product, Molecularity = 2 ↳ $2HI \longrightarrow H_2 + I_2$

$A + B \longrightarrow$ Product, Molecularity = 2 ↳ $2NO + O_2 \longrightarrow 2NO_2$

$A + B + C \longrightarrow$ Product, Molecularity = 3

Characteristic of Molecularity :

- Molecularity of a reaction is always an integer.
- It can not have a fractional or zero values (a zero molecularity implies that no effective collisions b/w reactant molecule takes place i.e reaction doesn't occur at all).
- Molecularity can be judged by a balanced chemical Rxn
- For a complex reaction, molecularity has no significance

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ molecularity = 1

$2HI \longrightarrow H_2 + I_2$ mole. = 2

ORDER OF REACTION

The order of a reaction is defined as the sum of powers to which the concenteration terms are raised in rate law equation.

$$A + 2B \longrightarrow C + D$$

Rate law $\qquad R = K[A]^m[B]^n$ (experimentally determined.)

order w.r.t $A = m$, order w.r.t $B = n$

Overall order of given reaction $= m+n$

Q. what is the order of reaction?

Ans: Rate law, $\quad R = K[A]^{1/2}[B]^2$

Order of reaction: $2\frac{1}{2}$ or 2.5

Characteristics of Order of a Reaction :

- It represents the number of species whose concenteration affects the rate of reaction directly.
- Reaction order can be obtained by adding all the exponents of the concenteration terms in rate expression.
- The stoichiometric coefficients corresponding to each species in the balanced reaction have no effect on the order of the reaction
- The reaction order of a chemical reaction is always defined with the help of reactant concenteration and not with product concenteration.
- For a complex reaction, the slowest step is rate determining step.

Zero Order Reaction:

Rate : $K[A]^0$ $\quad H_2 + Cl_2 \xrightarrow{h\nu} 2HCl \quad ; \quad 2N_2O \longrightarrow 2N_2 + O_2$

First Order Reaction:

Rate : $K[A]^1 \qquad 2H_2O_2 \longrightarrow 2H_2 + O_2$

Second Order Reaction

Rate = $K[A]^2$

e.g. $C + O_2 \longrightarrow CO + O$

$2NO_2 \longrightarrow 2NO + O$

UNIT OF RATE CONSTANT

$K = (mol\ L^{-1})^{1-n}\ sec^{-1}$ $K = (atm)^{1-n}\ sec^{-1}$

Zero order $n=0$ $K = (mol\ L^{-1})^{1-0}\ sec^{-1} \Rightarrow mol\ L^{-1}\ sec^{-1}$

First order $n=1$ $K = (mol\ L^{-1})^{1-1}\ sec^{-1} \Rightarrow sec^{-1}$

Second order $n=2$ $K = (mol\ L^{-1})^{1-2}\ sec^{-1} \Rightarrow mol^{-1}\ L^{1}\ sec^{-1}$

Half order $n=1/2$ $K = (mol\ L^{-1})^{1-\frac{1}{2}}\ sec^{-1} \Rightarrow mol^{1/2}\ L^{-1/2}\ sec^{-1}$

Q. Identify the reaction order

(i) $K = 2.3 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$ → Order = 2

(ii) $K = 3 \times 10^{-4}\ s^{-1}$ → Order = 1

Q. The conversion of molecules X to Y follows second order kinetics, if concentration of X is increased to three times how will it affect the rate of formation of Y?

Ans: The reaction is $X \longrightarrow Y$

Acc. to rate law

rate = $K[X]^2$

If [X] is increased to 3 times, then

$rate' = K[3X]^2$

$rate' = 9\,K[X]^2$

$\Rightarrow 9 \times rate$

Thus, rate of reaction becomes 9 times and hence rate of formation of increases 9-times.

Integrated Rate Equation

First Order

Those reaction whose rate depends upon one concenteration term of reactant.

$R \longrightarrow P$

Rate of Reaction $\propto [R]^1$

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

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

I.B.S (Integerating both Sides)

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

$$-\ln R = Kt + I \quad \text{— (1)}$$

(I = integeration constant)

to get the value of I

$t = 0, \; R = R_0$

$-\ln R_0 = I$

Put value of I in eq (1)

$$-\ln R = Kt + I$$

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

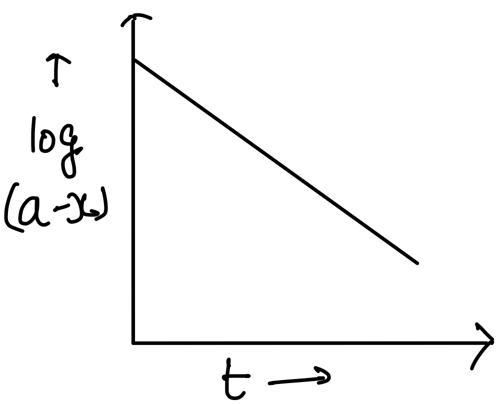
$$\ln R_0 - \ln R = Kt$$

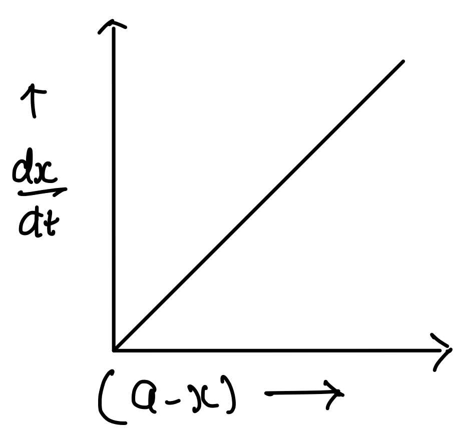
$$\ln \frac{R_0}{R} = Kt$$

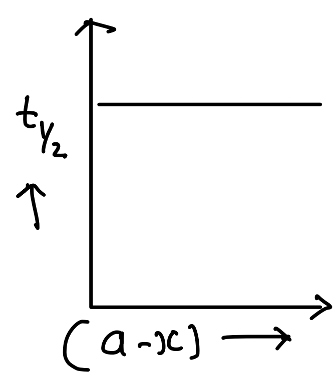
$$\frac{2.303}{K} \log \frac{R_0}{R} = t$$

UNIT = $mol\,L^{-1}s^{-1}$

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







Zero Order Reaction

Those reaction whose rate depends upon zero concenteration terms of reactant.

$R \longrightarrow P$

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

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

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

I.B.S (Integerating both sides)

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

$$-R = Kt + I \quad \text{—(1)}$$

← Integeration constant

to get the value of I

$t = 0, \quad R = R_0$

$$-R_0 = I$$

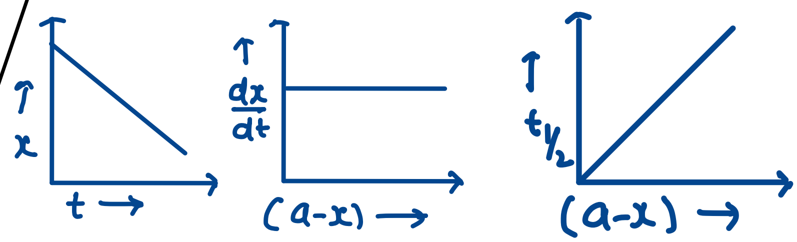
Put I in equation 1

$$-R = Kt + I$$

$$-R = Kt - R_0$$

$$R_0 - R = Kt$$

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



Half life of a Reaction:

The time in which the concenteration of a reactant is reduced to one half of its initial conc. It is represented by $t_{1/2}$.

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

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

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

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

} first order

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

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

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

Q write general expression for half life period of a reaction of nth order

Ans:

$$t_{1/2} = \frac{1}{[R_0]^{n-1}}$$

PSEUDO FIRST ORDER REACTION

Reaction which are not truely of the first order but under certain conditions become reactions of first order are called pseudo first order Reactions.

eg Acid catalysed inversion of cane sugar

$$C_{12}H_{22}O_{11} + \underset{\text{(excess)}}{H_2O} \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

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

Acid catalysed hydrolysis of ethyl acetate.

$$CH_3COOC_2H_5 + \underset{\text{(excess)}}{H_2O} \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\text{Rate} = K[CH_3COOC_2H_5]$$

Both of the above reactions are biomolecular but are found to be the first order because water is present in such a large excess that its concenteration remains almost constant during the reaction.

P.Y.Q

Q. A reaction is second order, w.r.t a reactant. How is the rate of reaction affected if the concenteration of reactant is **NCERT (2009, 2012, 2014)**

(i) doubled (ii) reduced to half

Ans: $\text{Rate} = K[A]^2$

$[A] = 2a$, $\text{rate} = K(2a)^2 = 4Ka^2$
$= 4$ times

$[A] = \frac{1}{2}a$, $\text{rate} = K\left[\frac{a}{2}\right]^2 = \frac{1}{4}Ka^2 = \frac{1}{4}$th

Q. A first order is found to have a rate constant $K = 5.5 \times 10^{-14}\ sec^{-1}$. Find half life of the reaction.

NCERT

Ans: Half life for a first order Reaction is

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{5.5 \times 10^{-14}} = 1.26 \times 10^{13} s$$

Q The half life for radioactive decay of ^{14}C is 5730 Y. An archaelogical artifact contained wood that had only 80% of the C^{14} found in living tree. Estimate age of the sample

NCERT

Ans: Radioactive decay follows first order Kinetics

$$\text{Decay } [K] = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}$$

$$t = \frac{2.303}{K} \log \frac{[A_0]}{[A]} = \frac{2.303 \times 5730}{0.693} \times 0.0969$$

$= 1845$ year.

Q A First order reaction takes 20 minutes for 20% decomposition. Calculate $t_{1/2}$. ($\log \frac{100}{80} = 0.0969$)

Ans. $K = \frac{2.303}{t} \log \frac{a}{a-x}$

$$= \frac{2.303}{20} \log \frac{100}{80} = \frac{2.303}{20} \times 0.0969$$

$$= 0.011158 = 11.158 \times 10^{-3}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{11.158 \times 10^{-3}} = 62.1 \text{ min.}$$

All the Best ☺

→ Effect of Temperature on rate of reaction:-

The rate of reaction increases with increase in temperature

Arrhenius proposed an equation that related temperature and rate constant for a reaction quantitavely

Acc. to Arrhenius Equation

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

where

K = rate constant of the Rx^n

A = Arrhenius factor / Frequency factor / pre exponential factor

E_a = Activation Energy

R = Universal Gas Constant

T = Temp. in Kelvin (absolute scale)

Taking ln both sides

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

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

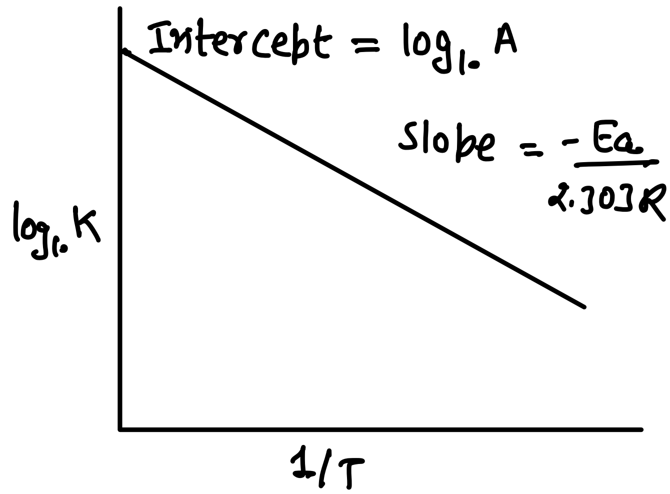
↳ At temp T_1,

$$\ln K_1 = \ln A - \frac{E_1}{RT_1} \quad \text{--- (1)}$$

↳ At temp T_2,

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

Operating (2) − (1)



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

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

$$2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_2 T_1}\right)$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R}\left(\frac{T_1 - T_2}{T_2 T_1}\right)$$

where

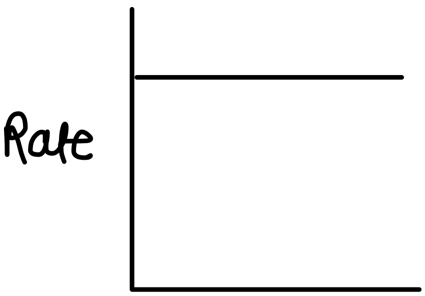
E_a → Activation Energy

R → Gas Constant

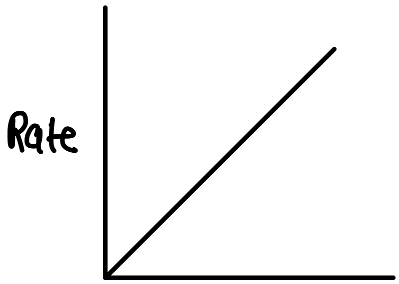
Methods to Determine Order of Reaction

i) Graphical Method

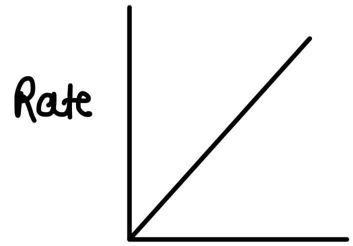
In this method, rate of reaction is plotted against the concenteration.



Zero Order
[A]



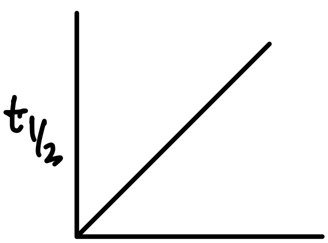
[A]
First Order



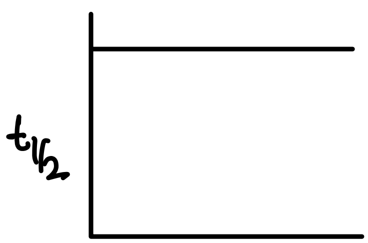
$[A]^2$
Second Order

ii.) Half life Method

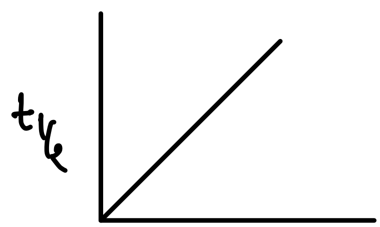
In general half life period of ($t_{1/2}$) of a reaction of nth order is related to initial concenteration of reactant



$[A]_0$
Zero order



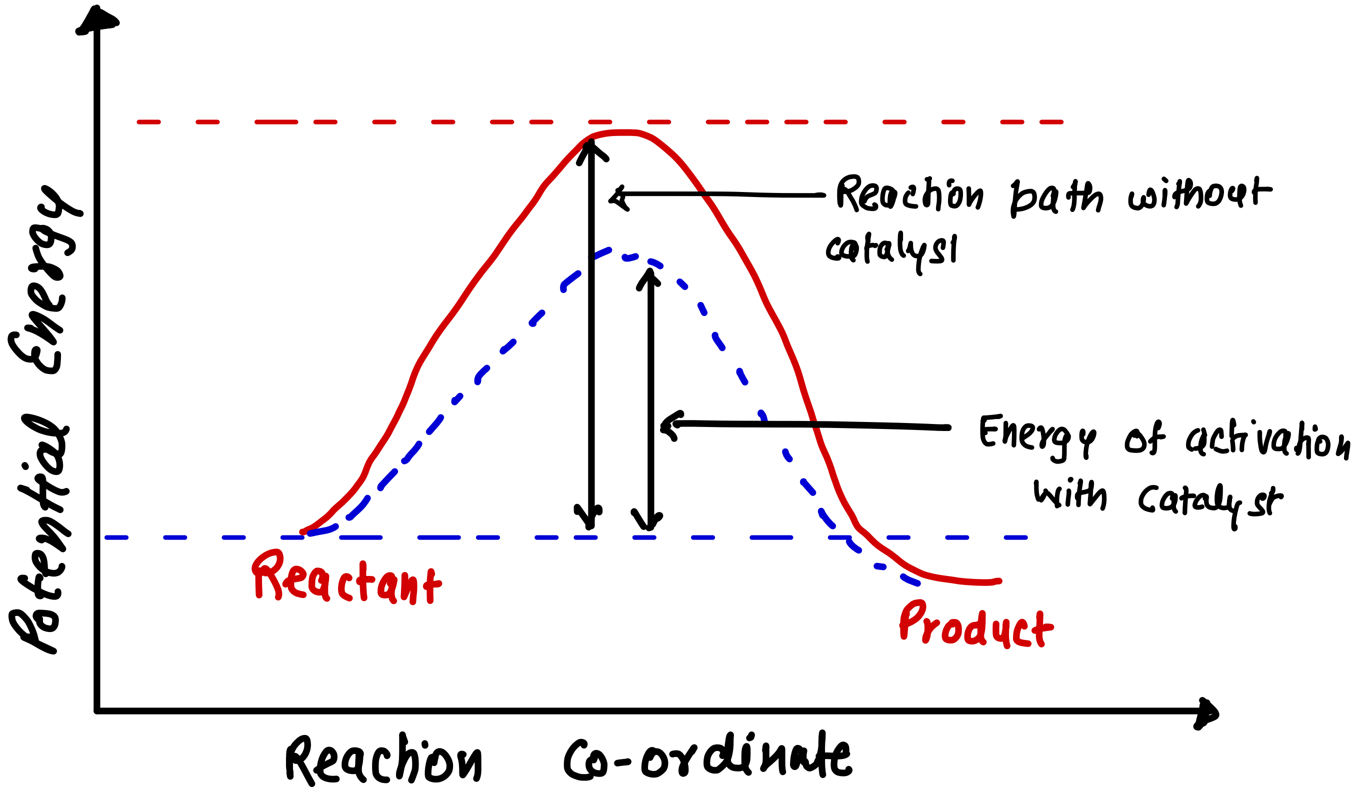
$[A]_0$
First order



$1/[A]_0$
Second Order

Rate of Catalyst in a Chemical Reaction –

A catalyst is a chemical substance which alters the rate of a reaction without itself undergoing any permanent chemical change



Catalyst provide an alternate path by reducing the activation energy between reactants and products and hence, lowering the potential energy.

➔ Collision Theory of chemical reactions

- Reaction occur 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 which is equal to activation energy + energy possessed by reacting species) and proper orientation.

Collision Frequency

no. of collisions per second per unit volume of reacting mixture. It is generally denoted by Z

Consider the biomolecular reaction

$$A + B \longrightarrow Product$$

Acc. to Collision Theory...

$$Rate = Z_{AB}\, e^{-Ea/RT}$$

where

Z_{AB} = Collision frequency of reactant A & B

E_a = Activation Energy

R = Universal Gas Constant

T = Temperature in absolute scale.

CONDITIONS FOR EFFECTVE COLLISIONS -

- Molecules must collide with sufficient energy called threshold energy
- Molecules must be oriented properly in order to break old bonds and form new bonds.
- another factor, P called the probability or steric factor is introduced to explain effective collisions

So,

$$rate = P\, Z_{AB}\, e^{-Ea/RT}$$

d- and f- block elements

d-Block elements

Those elements in which the last e⊖ enters in the d-subshell of penultimate shell

General Electronic Configuration → $(n-1)d^{1-10}\,ns^{0-2}$

Periodic Table of the Elements

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanide Series	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide Series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

They are subdivided into four series..

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

→ The d-block elements in which the atoms or ions have incomplete d-orbitals are called transition elements.

→ Zn, Cd and Hg have completely filled (n-1) d-orbitals so they do not show much resemblance with other transition elements.

There are four series of d-block elements.

- 3d Series (Sc to Zn)
- 4d Series (Y to Cd)
- 5d Series (La and Hf to Hg)
- 6d Series (Ac and Rf to Cn)

Electronic Configuration:

By - Bharat Panchal Sir

21. Sc – Scandium $[Ar]^{18}\ 3d^1 4s^2$
22. Ti – Titanium $[Ar]^{18}\ 3d^2 4s^2$
23. V – Vanadium $[Ar]^{18}\ 3d^3 4s^2$
24. Cr – Chromium $[Ar]^{18}\ 3d^5 4s^1$
25. Mn – Manganese $[Ar]^{18}\ 3d^5 4s^2$
26. Fe – Iron $[Ar]^{18}\ 3d^6 4s^2$
27. Co – Cobalt $[Ar]^{18}\ 3d^7 4s^2$
28. Ni – Nickel $[Ar]^{18}\ 3d^8 4s^2$
29. Cu – Copper $[Ar]^{18}\ 3d^{10} 4s^1$
30. Zn – Zinc $[Ar]^{18}\ 3d^{10} 4s^2$

$_{24}Cr^{2+} \rightarrow [Ar]^{18}\ 3d^4 4s^0$

$_{24}Cr^{3+} \rightarrow [Ar]^{18}\ 3d^3 4s^0$ (Stable due to half filled t_{2g})

$_{29}Cu^{1+} \rightarrow [Ar]^{18}\ 3d^{10} 4s^0$ (fully filled)

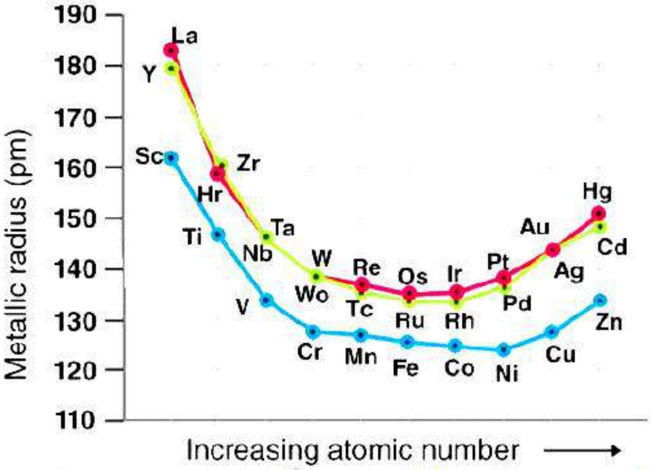
$_{29}Cu^{2+} \rightarrow [Ar]^{18}\ 3d^9 4s^0$

$_{23}Sc^{3+} \rightarrow [Ar]^{18}\ 3d^0 4s^0$

$_{26}Fe^{3+} \rightarrow [Ar]^{18}\ 3d^5 4s^0$ (half filled)

Atomic Radius

As we from left to right, atomic radii first decreases largely, then decreases slowly and increases in the end of the series.



This decrease in atomic radii in the beginning is due to the increase in effective nuclear charge with the increase in atomic number.

with the increase in number of e⊖ in (n-1)d subshell the screening effect of these d-electrons on the outermost ns-electrons also increases. This increased screening effect counterbalances the effect of increased nuclear charge, therefore the atomic radii remains almost same.

in the end of the series e⊖ - e⊖ repulsion takes place so the size of atom increases.

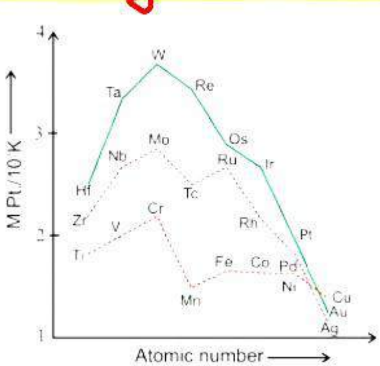
IONIC RADIUS

in general, ions of the same oxidation state in a given series show progressive decrease in radius with increase in atomic number due to the increase in effective nuclear charge

$$\text{Ionic Radius} \propto \frac{1}{\text{Oxi. State}}$$

[ionic Radii $Fe^{2+} > Fe^{3+}$]

Melting and Boiling Point



High m.pt and B.Pt

First increase and then decrease due to increase and decrease in number of unpaired electrons because the strength of bond depends on number of unpaired e⊖

Note → Tungsten (W) has the highest M.pt
→ Mercury (Hg) is the only metal in liquid form.

Metallic Character

• Show all the properties of general metals.

• Strength of metallic bond ∝ number of unpaired e⊖ which increase the chance and make the bond strong.

• Cr is a hard metal while Zn is a soft metal.

Enthalpy of Atomisation:

They have strong metallic bond due to which they have high enthalpy of atomization

By - Bharat Panchal Sir

Ionisation Energy:-

Lies b/w s- and p-block elements (more than s-block but less than p-block elements)

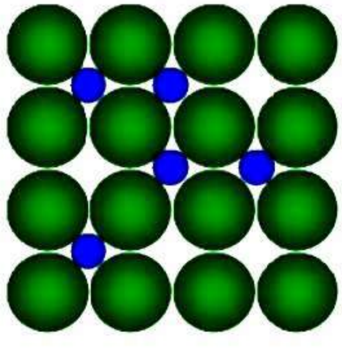
I.E increases from left to right in a period as the effective nuclear charge increases.

I.E ∝ Effective Nuclear charge

• I.E of Zn, Cd and Hg is very High due to fully filled orbitals

• I.E of 5d and 6d series elements is more than 3d and 4d elements due to lanthanide and Actinide contraction.

Formation of Interstitial Compounds:-



Transition metals have a tendency to form interstitial compounds with H, C, B or N atoms.

They are usually non-stoichiometric and are neither typically ionic nor covalent.

e.g TiC, Mn_4N, Fe_3N, $VH_{0.56}$ and $TiH_{1.7}$ etc

ce• The interstitial compounds are very hard, retain metallic conductivity, have high m.pt and are chemically inert.

Alloy Formation :-

Alloys are homogeneous solid solution. Many of d-block elements form alloys because they have similar atomic radii due to which they can easily replace the atom of other metal.

Alloys thus formed and often have high m.pt.

e.g Brass (Cu + Zn) & Bronze (Cu + Sn)

By - Bharat Panchal Sir

Magnetic Properties:-

Diamagnetic substances are rebelled by magnetic field while paramagnetic substances are attracted by magnetic field.

→ Those substance which are attracted very strongly by the applied field are called ferromagnetic

Many of the d-block elements and their compounds are paramagnetic in nature it is due to the presence of unpaired e⊖ in incomplete d-orbitals

→ The paramagnetic Nature ∝ no. of unpaired e⊖

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

n is number of unpaired e⊖

B.M → Bohr Magneton

Complex Formation:-

Many of d-block elements form complex compounds because

(i) They have small atomic radii

(ii) High Nuclear charge

(iii) Presence of vacant d-orbital so they can accept lone pair of e⊖ from ligands.

Catalytic Properties:-

By - Bharat Panchal Sir

Transition elements and their compounds show catalytic properties due to variable oxidation state and their ability to adopt multiple oxidation state.

e.g

$$2SO_2 + O_2 \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3 \quad \text{(Contact Process)}$$

$$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3 \quad \text{(Haber Process)}$$

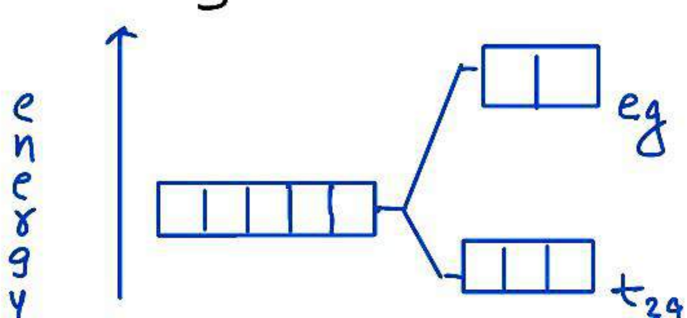
The presence of unpaired e⊖'s in incomplete d-orbitals, hence possess the capacity to absorb and re-emit wide range of energies which is used as an activation energy.

Formation Of Coloured Ions:-

• if unpaired e⊖ is present, complex is coloured due to d-d transition and also paramagnetic in nature

if unpaired e⊖ is absent, complex or compound is due to the absence of d-d transition and diamagnetic in nature

e.g $CuSO_4$ is blue in colour while $ZnSO_4$ is colourless



Oxidation State :-

Show large number of oxidation state due to the participation of both (n-1)d and ns electrons in bonding in different compounds.

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

- Mn shows maximum number of oxidation state due to the presence of maximum number of unpaired e^-
- Osmium (Os) show +8 oxidation state

→ Cu^{2+} is more stable than Cu^{1+} because it undergoes disproportionation Reaction in aqueous soln

$$2Cu^{1+} \longrightarrow Cu^{2+} + Cu$$

Note) The ability of oxygen to stabilise these high oxidation state exceeds that of fluorine because oxygen can form double bond while fluorine form single bond.

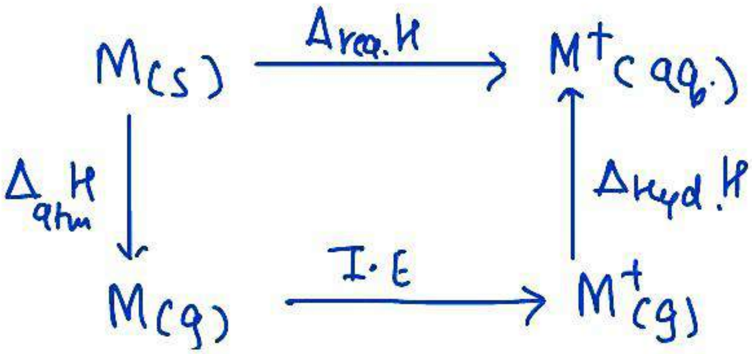
As a result highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7.

Electrode Potential :-

The stability of a compound depends upon electrode potential and it further depends upon.

(i) Enthalpy of atomisation / sublimation
(ii) Ionisation enthalpy
(iii) Hydration enthalpy

By - Bharat Panchal Sir



Δ atomisation H = +ve

Δ ionisation H = +ve

Δ Hydration H = −ve

Table 8.4: Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M^{II} to M.

Element (M)	$\Delta_a H^\ominus$ (M)	$\Delta_i H^\ominus_1$	$\Delta_i H^\ominus_2$	$\Delta_{hyd} H^\ominus(M^{2+})$	$E^\ominus$/V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

There is no regular trend for M^{2+}/M standard electrode potential due to the irregularities in ionisation enthalpies and enthalpy of atomisation

→ Copper is the only metal having positive value of E° so it does not liberate the hydrogen gas from acids

Chemical Reactivity :-

By - Bharat Panchal Sir

$$\text{chemical reactivity} \propto \frac{1}{E^\circ}$$

- $E^\circ (M^{2+}/M)$ is very less (more −ve) except Cu so these metals are highly reactive
- Oxidising power $\propto E^\circ$
- Reducing Power $\propto \frac{1}{E^\circ}$

Oxide Formation:-

Many of the d-block elements forms oxides of different types because of the presence of so many different oxidation state.

Note Acidic character $\propto$ Oxi. State
Ionic character $\propto$ Oxi. State.

f-Block Elements :-

Elements in which last $e^{\ominus}$ enters in f-orbital of pre-penultimate shell

General Electronic Configuration = $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

57 138,9 **La** lantani	58 140.1 **Ce** ceri	59 140,9 **Pr** praseodimi	60 144,2 **Nd** neodimi	61 [145] **Pm** prometi	62 150,4 **Sm** samari	63 152,0 **Eu** europi	64 157,3 **Gd** gadolini	65 158,9 **Tb** terbi	66 162,5 **Dy** disprosi	67 164,9 **Ho** holmi	68 167,3 **Er** erbi	69 168,9 **Tm** tuli	70 173,1 **Yb** iterbi	71 175,0 **Lu** luteci
89 [227] **Ac** actini	90 232,0 **Th** tori	91 231,0 **Pa** protactini	92 238,0 **U** urani	93 [237] **Np** neptuni	94 [244] **Pu** plutoni	95 [243] **Am** americi	96 [247] **Cm** curi	97 [247] **Bk** berkeli	98 [251] **Cf** californi	99 [252] **Es** einsteini	100 [257] **Fm** fermi	101 [258] **Md** mendelevi	102 [259] **No** nobeli	103 [262] **Lr** lawrenci

By - Bharat Panchal Sir

4f Series
or
Lanthanoid Series
or
Ist Inner Transition Series

4f-block elements (lanthanides)

Valence shell electronic Configuration $4f^{0,2\ to\ 14}5d^{0,1}6s^2$

57 **La** lanthanum 138.905 $4f^05d^16s^2$	58 **Ce** Cerium 140.116 $4f^25d^06s^2$	59 **Pr** Praseodymium 140.908 $4f^35d^06s^2$	60 **Nd** Neodymium 144.243 $4f^45d^06s^2$	61 **Pm** Promethium 144.913 $4f^55d^06s^2$	62 **Sm** Samarium 150.360 $4f^65d^06s^2$	63 **Eu** Europium 151.964 $4f^75d^06s^2$	64 **Gd** Gadolinium 157.250 $4f^75d^16s^2$
65 **Tb** Terbium 158.925 $4f^95d^06s^2$	66 **Dy** Dysprosium 162.500 $4f^{10}5d^06s^2$	67 **Ho** Holmium 164.930 $4f^{11}5d^06s^2$	68 **Er** Erbium 167.259 $4f^{12}5d^06s^2$	69 **Tm** Thulium 168.934 $4f^{13}5d^06s^2$	70 **Yb** Ytterbium 173.055 $4f^{14}5d^06s^2$	71 **Lu** Lutetium 174.967 $4f^{14}5d^16s^2$	

Oxidation State:-

The common oxidation state of lanthanoids is +3 with +2 and +4.

Electronic Configuration

General electronic configuration of lanthanoids are $6s^2\ 5d^{0-1}\ 4f^{1-14}$

→ Only Cerium, Gadolinium and lutetium have e⊖ in 5d-orbital as well.

Name	Symbol	Atomic#	Electron configuration
lanthanum	La	57	$(Xe)5d^1\ 6s^2$
Cerium	Ce	58	$(Xe)4f^1\ 5d^1\ 6s^2$
Praseodymium	Pr	59	$(Xe)4f^3\ 6s^2$
Neodymium	Nd	60	$(Xe)4f^4\ 6s^2$
Promethium	Pm	61	$(Xe)4f^5\ 6s^2$
Samarium	Sm	62	$(Xe)4f^6\ 6s^2$
Europium	Eu	63	$(Xe)4f^7\ 6s^2$
Gadolinium	Gd	64	$(Xe)4f^7\ 5d^1\ 6s^2$
Terbium	Tb	65	$(Xe)4f^9\ 6s^2$
Dysprosium	Dy	66	$(Xe)4f^{10}\ 6s^2$
Holmium	Ho	67	$(Xe)4f^{11}\ 6s^2$
Erbium	Er	68	$(Xe)4f^{12}\ 6s^2$
Thulium	Tm	69	$(Xe)4f^{13}\ 6s^2$
Ytterbium	Yb	70	$(Xe)4f^{14}\ 6s^2$
Lutetium	Lu	71	$(Xe)4f^{14}\ 5d^1\ 6s^2$

Atomic and Ionic Radii – The atomic and ionic radii decreases from lanthanum to lutetium. Which is known as LANTHANOID CONTRACTION.

CAUSE –

In case of lanthanide series elements, the last e⊖ enters into the 4f-orbital. Since, the shielding or screening effect of "f-orbita" is much less than 's' and 'p' orbital even less than that of d-orbital the effective nuclear charge increases by one at each step. Hence, the size of entire 4f subshell reduces.

CONSEQUENCES OF LANTHANOID CONTRACTION-

- **Increase in Covalent character-**

Covalent properties of lanthanide metal hydroxide compounds regularly increases according to fajan's Rule.

- **Similar Size and Charge**

Since all the lanthanide ions are of about the same size and also carry the same charge due to lanthanoid contraction, their properties are almost identical. This makes separation of lanthanides from one another is very difficult.

- **Basic Character of Hydroxides of Lanthanoids**

As we move from left to righ basic character of hydroxides of lanthanoides decreases.

- **Atomic and Ionic Radii of 4d & 5d Series**

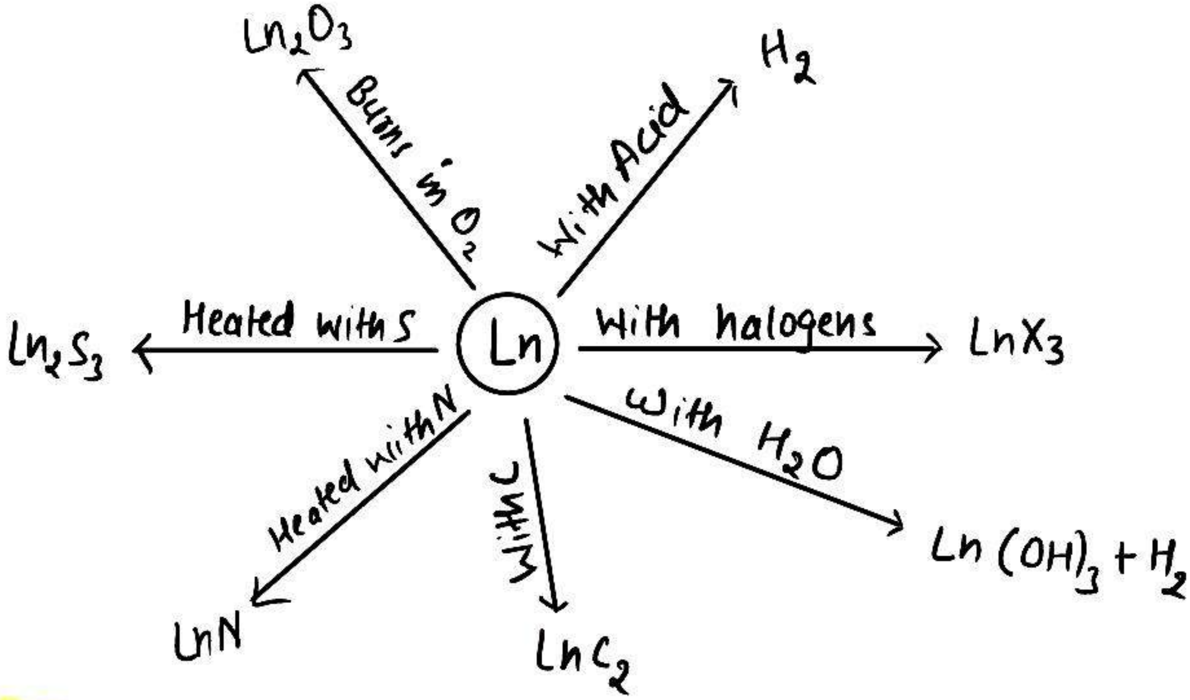
Due to lanthanide contraction, the atomic and ionic radii of the next and before on the lanthanide elements with same group

4d	Zr 145	Nb 134	Mo 129
5d	Hf 144	Ta 134	W 130

- **The decrease in chemical reactivity**

Due to lanthanoid contraction, the ionization energy of the next on the lanthanoid elements increases. This decreases their chemical reactivity.

Chemical Reactivity



Uses

i) Lanthanoids are used for the production of alloy steels for plates and pipes

ii) Mischmetal alloy of lanthanoid is used in Mg-based alloy to produce bullets, shell and lighter flint.

(iii) Mixed oxides of lanthanoids are used as catalyst in cracking of petroleum

(iv) Some lanthanum oxides are used as phosphorus in television screen

ACTINOIDS

These are the elements in which last e⊖ filled in 5f-orbitals. The actinoids are radioactive elements

Electronic Confi^{n}

The general electronic confi. $5f^{1-14}6d^{0-1}7s^2$

irregularities in the electronic configuration of actinoids is due to stabilities of f^0, f^7, f^{14} occupancies of 5f-orbital.

Similarities btw Lanthanoids and Actinoids

- Both exhibit +3 oxidation state predominantly.
- Both are electropositive and have high reactivity.
- Like lanthanoid contraction, there is actinoid contraction also.

Difference b/w lanthanoids and Actinoids

Lanthanoids	Actinoids
They show mainly +3 Oxi. State. +2 and +4 Oxidation State also exist	They show +3 Oxi. State. Higher oxidate like +4, +5, +6 and +7
They have poor shielding effect	They have even poor shielding effect
They are paramagnetic and their paramagnetic character can be explained easily	They are also paramagnetic but their magnetic character can't be explained easily
They have less tendency to form complexes	They have more tendency to form complexes
These are non-radioactive except promethium	These are radioactive substance.

Application of Actinoids

- Actinoids are used in nuclear reactors for the production of electricity.
- Actinoids are also used for the synthesis of transuranic elements.

COMPOUNDS OF TRANSITION ELEMENTS

- Potassium Dichromate ($K_2Cr_2O_7$)
- Potassium Permanganate ($KMnO_4$)

→ **Potassium Dichromate ($K_2Cr_2O_7$)**

it is prepared from chromite ore

Step-1 Conversion of ferrochromate into sodium chromate

$$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Yellow

Step-2 Conversion of sodium chromate into sodium dichromate

$$Na_2CrO_4 + 2HCl \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

Orange

Step-3 Conversion of sodium dichromate into potassium dichromate

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

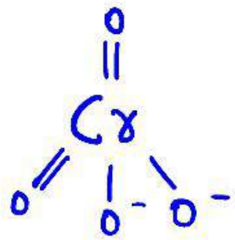
Orange Crystals

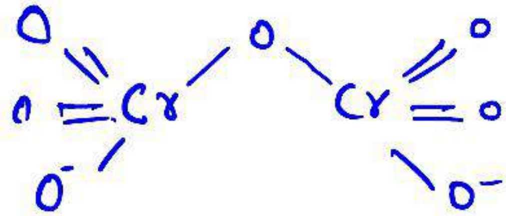
→ Chromates and dichromates are interconvertible

$$Cr_2O_7^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CrO_4^{2-}$$

Structure..

chromate ion (CrO_4^{2-}) dichromate ion ($Cr_2O_7^{2-}$)





Properties

1.) These are orange red crystals, moderately soluble in cold water but readily soluble in hot water

2.) Action Of heat

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

3.) Action Of Alkali –

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

$$2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

$$Cr_2O_7^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} 2CrO_4^{2-}$$

4.) Oxidising Property – $K_2Cr_2O_7$ behave as a powerful oxidising agent in Cr (VI) is changed into Cr(III)

Ionic Reaction

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

Molecular Reaction

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

- It oxidise

$I^- \rightarrow I_2$

$Fe^{2+} \rightarrow Fe^{3+}$ (Ferrous Salt to Ferric)

$H_2S \rightarrow S$ (Sulphide to Sulphur)

$SO_3^{2-} \rightarrow SO_4^{2-}$ (Sulphite to Sulphate)

$SO_2 \rightarrow H_2SO_4$ (Sulphur di oxide to Sulphuric Acid)

$HX \rightarrow X_2$ (Halogen Acid to Halogen)

ethyl alcohol → acetaldehyde → acetic acid

→ CHROMYL CHLORIDE TEST

This test is done for the identification of Cl^- ions during salt analysis, potassium dichromate is heated with conc. H_2SO_4 and a salt having Cl^- (eg NaCl, KCl) and reddish brown vapours of chromyl chloride are obtained.

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$$

→ Potassium Permanganate ($KMnO_4$)

$KMnO_4$ is prepared from pyrolusite (MnO_2) ore.

↳ Pyrolusite (MnO_2) react with alkali metal hydroxide (KOH) to give potassium manganate

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

(dark green)

↳ Potassium manganate disproportionate in acid or alkali to give potassium permanganate

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

Properties

$KMnO_4$ is dark purple black crystalline solid, soluble in warm water.

2.) Action of Heat -

On heating, it decomposes

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

3.) In Acidic Medium

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

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

→ it oxidise

$Fe^{2+} \longrightarrow Fe^{3+}$ (Ferrous salt into Ferric salt)

$H_2S \longrightarrow S$

Oxalic acid $\longrightarrow CO_2 + H_2O$

$SO_2 \longrightarrow H_2SO_4$

$I^- \longrightarrow I_2$

$H_2O_2 \longrightarrow O_2$

→ Oxidising Reactions in Neutral Medium...

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

$$MnO_4^- + 2H_2O + 3e^{\ominus} \longrightarrow MnO_2 + 4OH^-$$

→ It oxidise

$H_2S \longrightarrow S$

$MnSO_4 \longrightarrow MnO_2$

$Na_2S_2O_3 \longrightarrow Na_2SO_4$ (thiosulphate to sulphate

→ Oxidising Reactions in Alkaline Medium

$$2KMnO_4 + \cancel{2KOH} \longrightarrow \cancel{2K_2MnO_4} + H_2O + [O]$$

$$\cancel{K_2MnO_4} + H_2O \longrightarrow MnO_2 + \cancel{2KOH} + 3[O] \times 2$$

$$2KMnO_4 + H_2O \longrightarrow MnO_2 + 2KOH + [O]$$

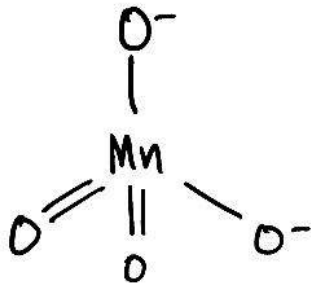
$$MnO_4^- + 2H_2O + 3e^{\ominus} \longrightarrow MnO_4^- + 4OH^-$$

NOTE

The overall reactions in alkaline medium is same as in neutral medium.

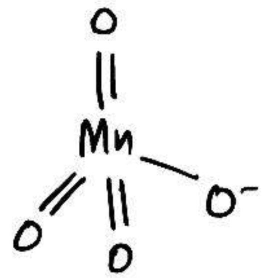
Structure of

MnO_4^{2-}



Tetrahedral manganate ion (green) (paramagnetic)

MnO_4^-



Tetrahedral permanganate ion purple (Diamagnetic)

CO-ORDINATION COMPOUNDS

Co-ordination Compounds Transition metals form a large no. complex compounds in which the metal atoms are bound to a number of anions or neutral molecule by sharing of e⊖. Such compound are known as co-ordination compounds.

Difference b/w Double Salt and Co-ordination Compound

Double Salt	Co-ordination Compounds.
→ They usually contain two simple salts in equimolar proportion	→ The simple salts from which they are formed may or may not be in equimolar prop.
→ They are ionic compound and do not contain any co-ordinate bond	→ They may or may not be ionic but the complex part always contain co-ordinate bond
• The properties of the double salts are the same as those of its constituent compounds.	The properties of the co-ordination compounds are different from its constituent.
• In the double salt metal ions show their normal valency	• In a co-ordination compound the metal ion satisfy its two type of valencies called primary and secondary valency.
• A double salt loses its identity in the solution	• A co-ordination compounds retain its identity in its solution.
e.g $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	e.g $K_4[Fe(CN)_6]$

→ **Types of Co-ordination Compounds**

Cationic Complex	Anionic Complex	Neutral Complex
complex ion carry +ve charge	complex ion carry -ve charge	complex doesn't carry any charge
$[Co(NH_3)_6]^{2+}$	e.g $[Fe(CN)_6]^{4-}$	e.g $[Ni(CO)_4]$

Ligands

The atoms, ions or molecules which can donate the lone pair of $e^{\ominus}$ to central metal atom by co-ordinate bond in co-ordination compounds are called ligands.

Denticity of ligands :-

The number of donor atoms present in the ligand is called its denticity. On the basis of denticity ligands are of different forms as:
monodentate, bidentate, tridentate, tetradentate, polydentate hexadentate etc.

Monodentate ligands

When a ligand is bound to a metal ion through a single donor atom

e.g Cl^-, Br^-, CN^-

$H_2\ddot{O}$:, $\ddot{N}H_3$, CO

Bidentate ligands

When a ligand can bind through two donor atoms.

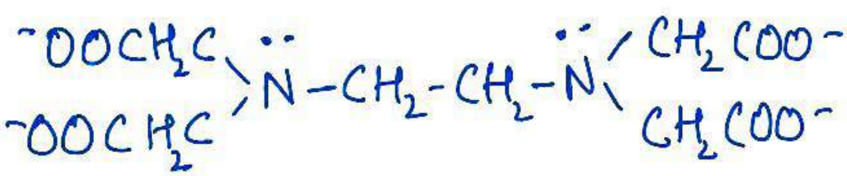
e.g oxalato, ethane-1,2-diamine, Glycinato (Gly)

$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \qquad \begin{matrix} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{matrix} \qquad H_2N-CH_2-COO^-$$

Polydentate ligands

When a ligand have more than two donating sites.

e.g EDTA (Ethylene Diamine Tetra Acetate Ion)



Donor Atoms → 6

Hexadentate ligands.

Ambidentate ligands

Those ligands which have two donor atoms but use one atom to attach with a central metal atom. So these are monodentate ligands

e.g. CN^- (Cyano) / NC^- (isocyano) ; SCN^- (thiocyano) / NCS^- (isothiocyano)

Negative ligands which have negative charge

Symbol of ligands	Name of ligands	charge on ligands
CN^-	Cyanido	-1
Cl^-	Chlorido	-1
Br^-	Bromido	-1
I^-	iodido	-1
NO_2^-	Nitrito-N	-1
ONO^-	Nitrito-O	-1
OH^-	Hydroxo	-1
NO_3^-	Nitrato	-1
SCN^-	thiocyano	-1
NCS^-	isothiocyano	-1
CH_3COO^-	Acetato	-1
H^-	Hydrido	-1
O^{2-}	oxo	-2
O_2^{2-}	peroxo	-2
SO_3^{2-}	Sulphito	-2
SO_4^{2-}	Sulphato	-2
CO_3^{2-}	Carbonato	-2

Bidentate

gly	glycenato	-1
Ox^{2-}	oxalato	-2

Neutral ligands

NH_3	ammine	0
$CH_3\text{-}NH_2$	Methylamine	0
H_2O	aqua	0
NO	Nitrosyl	0
CO	Carbonyl	0
CS	thio carbonyl	0
PH_3	Phosphine	0
	Triphenyl phosphine	0
H_2NCSNH_2	Thio urea	0
	Pyridine	0
CH_3	Methyl	0

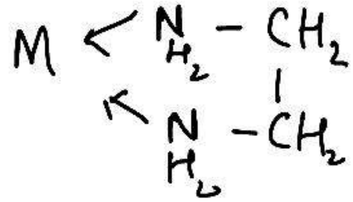
Bidentate

ethane-1,2-diamine	en	0

Chelating ligands:-

It is closed ring type compound formed by polydentate ligands (chelating ligand) on binding to central metal atom

e.g.



Importance

- it forms more stable complex, called chelating effect

Use

- in softening of Hard water
- Detection of metal ion
- separation of f-block elements.

Co-ordination Entity

The central metal atom and the ligands which are directly attached to it are enclosed in square bracket and called co-ordination sphere or co-ordination entity

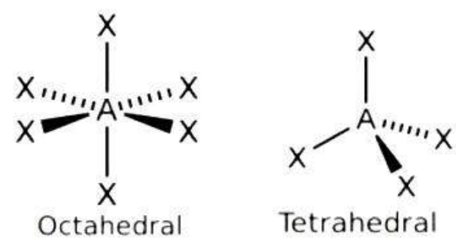
e.g $[Fe(CN)_6]^{4-}$ is called coordination sphere.

Counter Ion

The ionisable groups written outside the square bracket and are called counter ions. eg $K_4[Fe(CN)_6]$ where K_4 ions are called counter ions

Co-ordination Polyhedron

The spatial arrangement of the ligands around the central metal atom is called co-ordination polyhedron e.g



Co-ordination Number

The total number of co-ordinate bond formed by ligands with central metal atom

Co-ordination Number = $\sum$(Number of ligands X Denticity)

e.g $K_4[Fe(CN)_6]$ $[CoCl_2(en)_2]^{1+}$

$C.N = 6 \times 1 = 6$ $C.N = 2 \times 1 + 2 \times 2 = 6$

Oxidation Number

The charge present on the central metal atom in a co-ordination compound is called oxidation number. It is always positive.

e.g $K_4[Fe(CN)_6]$

$4(1) + x + 6(-1) = 0$

$x = 2$

ON THE BASIS OF LIGANDS

Homoleptic in which only one type of ligands are present
e.g $K_4[Fe(CN)_6]$

Heteroleptic in which different type of ligands are present
e.g $[CoCl_2(en)_2]Cl$

Nomenclature of Co-ordination Compounds

e.g
- $K_4[Fe(CN)_6]$ → potassium hexacyanido ferrate (II)
- $[CrCl_2(H_2O)_4]NO_3$ → tetraaqua dichlorido chromium (III) nitrate
- $[CoCl(NO_2)(NH_3)_4]NO_3$ → Tetraammine chlorido nitro-N-cobalt (III) nitrate
- $K_3[Fe(C_2O_4)_3]$ → potassium tri oxalato ferrate (III)
- $K_3[Co(CN)_5(NO)]$ → potassium penta cyanido nitrosyl cobaltate (II)
- $[CoCl_2(en)_2]SO_4$ → dichlorido bis (ethane-1,2-diamine) cobalt (IV) sulphate
- $[CoCl(ONO)(en)_2]^+$ → chlorido bis (ethane-1,2-diamine) nitrito-O-cobalt (III) ion
- $[Ni(CO)_4]$ → tetra carbonyl nickel (0)
- $Li[AlH_4]$ → lithium tetra hydrido aluminate (III)

Werner Theory

- Metals possess two types of valencies, called primary or ionisable valency (oxidation number and secondary or non-ionisable valency (Co-ordination Number)
- The primary valencies are non-directional.
- The complex compound do not show any property of the central metal atom and the ligands present in it.

Valence Bond Theory :

Acc. to this theory, metal-ligand bond arises due to the donation of electron pair from ligands to central metal atom

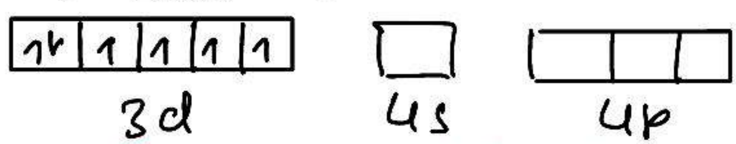
the metal atom or ion under the influence of ligands can use $(n-1)d$, ns, np, nd orbitals for hybridisation

Hybridisation	C.N	Geometry	Example
sp	2	linear	$[Ag(CN)_2]^-$
sp^2	3	Trigonal planar	$[HgI_3]^-$
sp^3	4	Tetrahedral	$[Ni(CO)_4]$
dsp^2	4	Square planar	$[Ni(CN)_4]^{2-}$
dsp^3	5	Square pyramidal	$Fe(CO)_5$
d^2sp^3	6	Octahedral (inner)	$[Cr(NH_3)_6]^{3+}$
sp^3d^2	6	Octahedral (outer)	$[FeF_6]^{3-}$

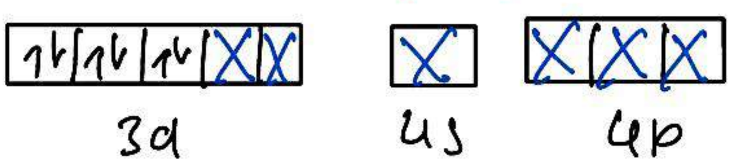
e.g $[Co(NH_3)_6]^{3+}$

$Co^{3+} \rightarrow [Ar]^{18}\, 3d^6$

$_{27}Co^{3+}$



$\because$ NH_3 is a strong ligand so pairing of $e^{\ominus}$ takes place



$\rightarrow$ it is diamagnetic

hybridisation $\rightarrow d^2sp^3$

Geometry $\rightarrow$ Octahedral

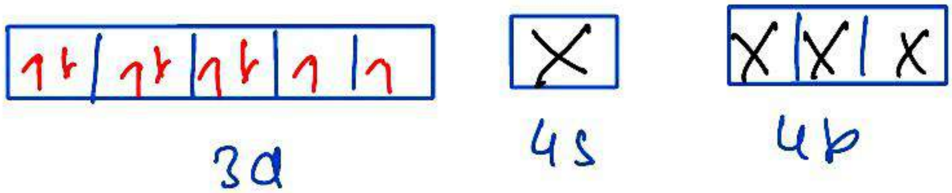
inner orbital Complex

$\mu = \sqrt{n(n+2)}$

$= 0$ B.M

- $[NiCl_4]^{2-}$

$_{28}Ni^{2+} \rightarrow [Ar]^{18}\ 3d^8\ 4s^0$



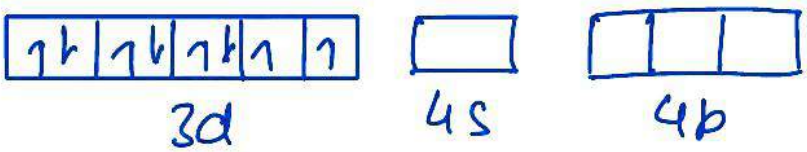
hybridisation → sp^3 Geometry → tetrahedral

It is paramagnetic in nature

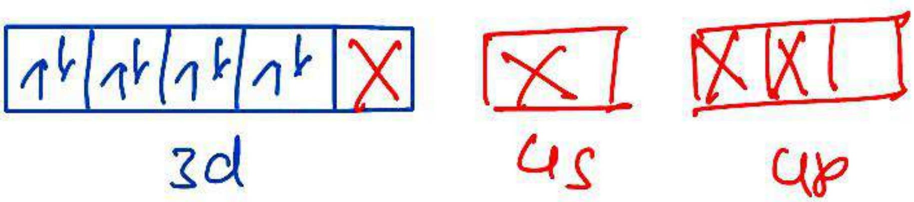
$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8}$ B.M

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

$_{28}Ni^{2+} \rightarrow [Ar]^{18}\ 3d^8 4s^0$



CN is a strong ligand so pairing of $e^{\ominus}$ takes place



hybridisation → dsp^2

Geometry → Square planar

It is diamagnetic in nature.

CRYSTAL FIELD THEORY:

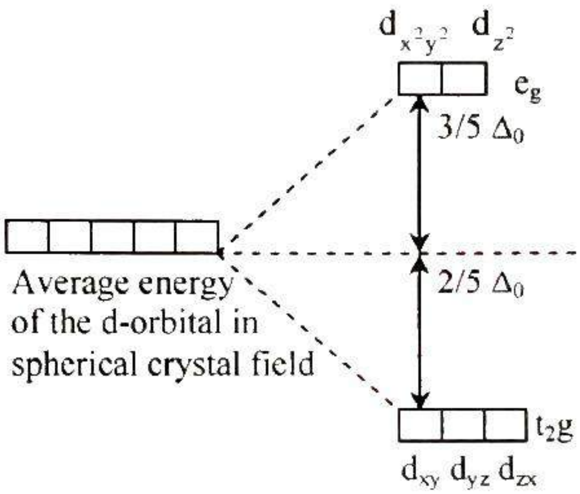
- Metal-ligand bond is ionic in nature. So, there is electrostatic force of attraction b/w metal and ligands
- The ligands are treated as negative centres and these negative centres are so arranged around central metal atom that there is minimum repulsion

b/w them.

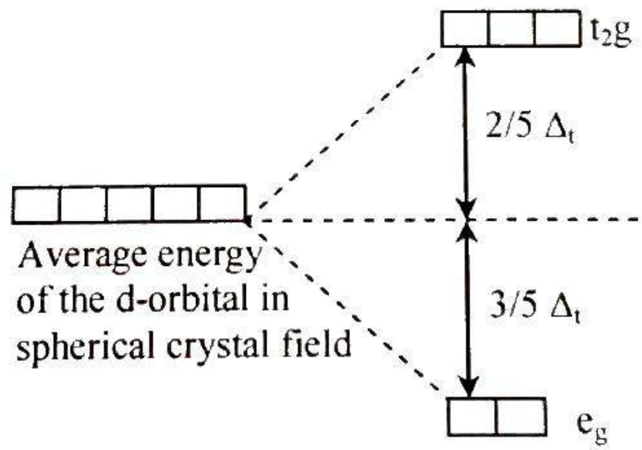
- In a free transition metal ion, all the five d-orbitals have equal energies (degenerate orbitals) but when it takes part in complex formation these d-orbitals split in two parts.

it is called d-d transition or crystal field splitting.

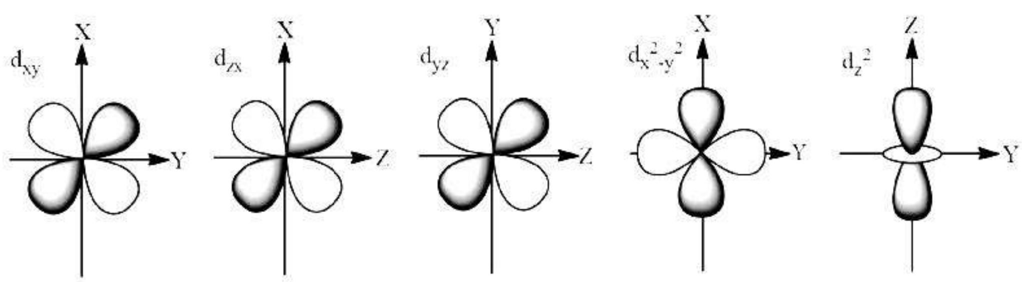
For Octahedral Complex



For Tetrahedral Complex



Shape of d-orbitals



$$\Delta_t = \frac{4}{9}\Delta_0$$

Spectrochemical Series:

arrangement of all ligands in order of increasing CFSE value is called spectrochemical series. The ligands with small value of CFSE are called weak ligands and the ligands with higher value of CFSE are called strong ligand

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < OX$

$< H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$

ISOMERISM

Two or more co-ordination compounds which have same molecular formula but have different ways of attachment of their ligands to the central metal atom and have different properties. These are called isomers. The phenomenon is known as isomerism.

ISOMERISM

- **Structural Isomers** — arises due to the difference in the str. of co-ordination compounds
  - Ionisation
  - Hydrate
  - Co-ordination
  - Linkage
- **Stereo Isomers** — arises due to the different spatial arrangement of ligands around the metal ion
  - Geometrical isomerism
  - Optical isomerism.

1.) IONISATION ISOMERISM

This isomerism arises due to exchange of ionisable anion with anionic ligands. e.g

e.g $[Co\,Br(H_2O)_5]^+Cl^-$ and $[CoCl(H_2O)_5]^+Br^-$

$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

2.) HYDRATE ISOMERISM OR SOLVATE ISOMERISM

In this isomerism, water is taken as solvent. It has different no. of water molecule in the co-ordination sphere and outside it e.g

$[Co(H_2O)_6]Cl_3$, $[Co(H_2O)_4Cl_2]Cl.2H_2O$,

$[Co(H_2O)_3Cl_3].3H_2O$

CO·ORDINATION ISOMERISM

This type of isomerism occurs when there is interchange of ligands b/w cationic and anionic complexes of different metal ion present in a complex.

e.g $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$

LINKAGE ISOMESISM

This type of isomerism is shown by the coordination compounds having ambidentate ligands

e.g $[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$

STEREO ISOMERISM

Geometrical Isomerism

This isomerism is common in complexes with C.N 4 & 6. Geometrical isomers are of two type

Cis

same ligands are present at adjacent position

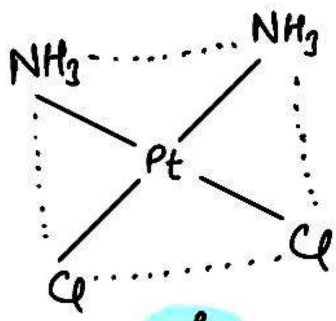
Trans

same ligands are present at opposite position

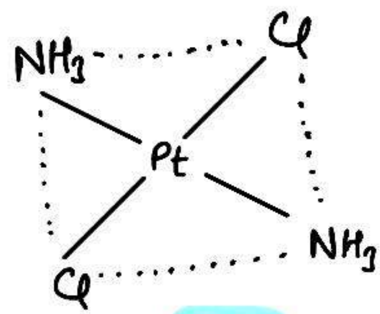
Optical Isomerism

These are the complexes which have chiral str. The pair of stereisomers are the mirror images of each other but may not be superimposed On the stereoisomers. These mirror images are called enantiomers. The enantiomers which rotate the plane polarised light in a clockwise direction is called dextrorotatory (d) or (+) and the enantiomer which rotate the plane polarised light in anti clockwise direction is laevorotatory (l) or (−)

- Tetrahedral complexes do not show Geometrical isomerism
- Square planar complexes of formula $[MX_2L_2]$ (X and L are unidentate ligands) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a cis-isomer or opposite to each other in a trans isomer



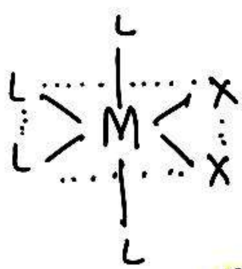
Cis



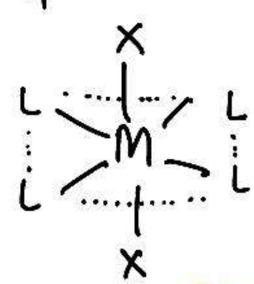
Trans

Octahedral complexes with C.N – 6

Type – MX_2L_4 e.g $[Co(NH_3)_4Cl_2]$

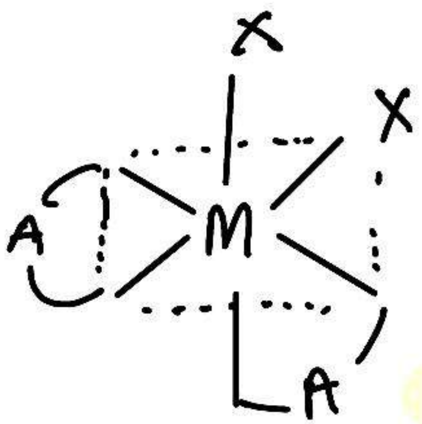


Cis

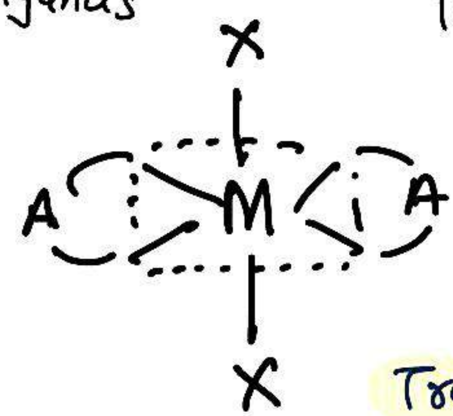


Trans

Type – MX_2A_2 (X- unidentate ligands A- Bidentate ligands)



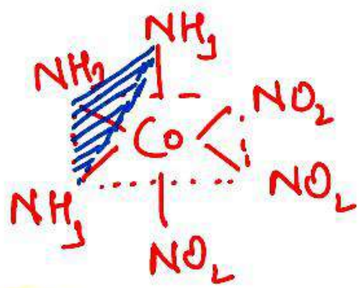
Cis



Trans

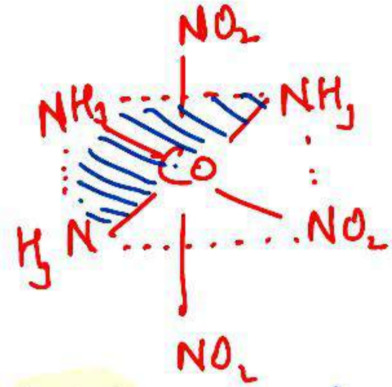
→ In Octahedral complexes of the formula $[MA_3X_3]$

eg $[Co(NH_3)_3(NO_2)_3]$



fac - facial

Same ligands occupy one face of an octahedron



mer - meridional.

same ligands are in one plane

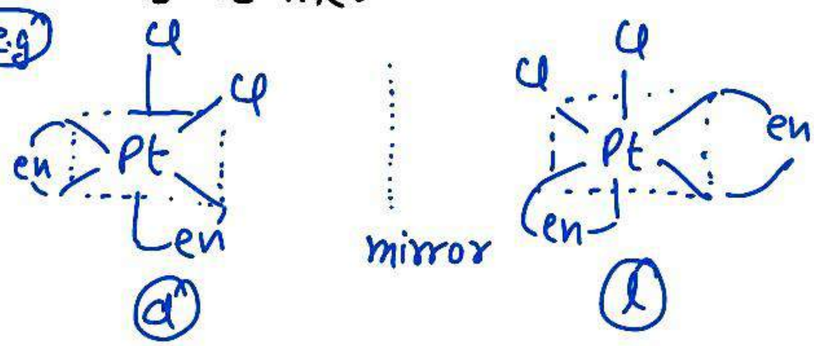
→ **OPTICAL ISOMERS**

→ optical isomerism is common in Octahedral complexes involving bidentate ligands

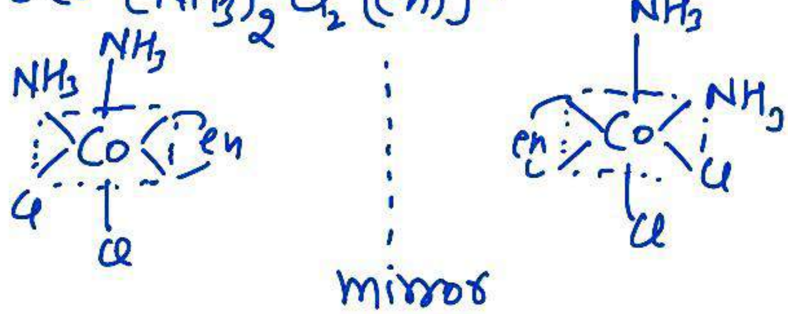
→ The equimolar mixture of 'd' and 'l' isomer is termed as the racemic mixture

→ Trans isomer can't show optical isomers

(e.g)

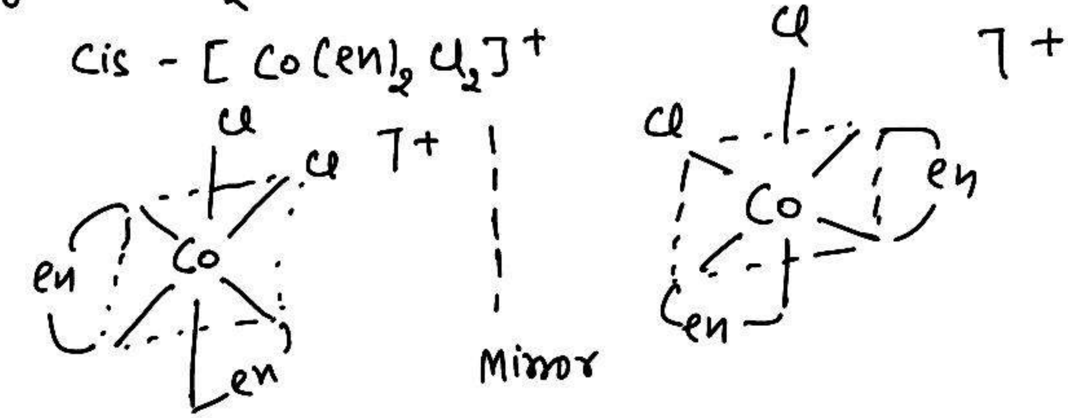


(eg) $[Co(NH_3)_2Cl_2(en)]^+$



eg $[M(AA)_2 X_2]^{n+}$

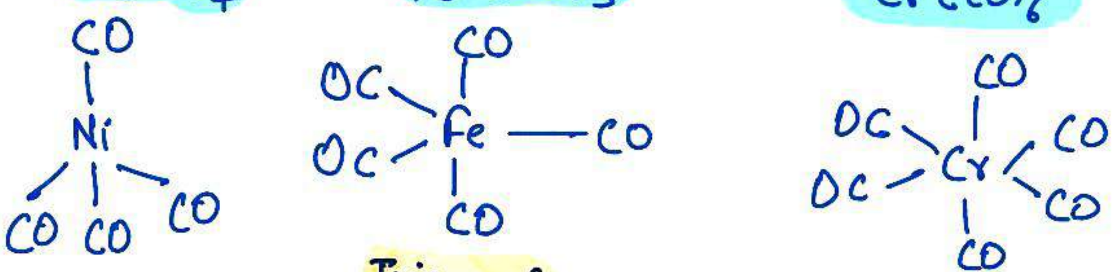
Cis - $[Co(en)_2Cl_2]^+$



METAL CARBONYLS

Complex compounds that contain carbonyl ligands only are termed as metal carbonyl

eg $Ni(CO)_4$ $Fe(CO)_5$ $Cr(CO)_6$



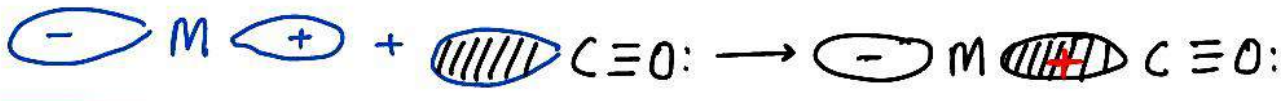
Tetrahedral   Trigonal Bipyramidal   Octahedral

BONDING IN METAL CARBONYLS

↳ In metal carbonyls, the metal-carbon bond has both s- and p-character, CO ligand attach itself to metal atom from the carbon atom to form metal-carbon bond It is a weak donor

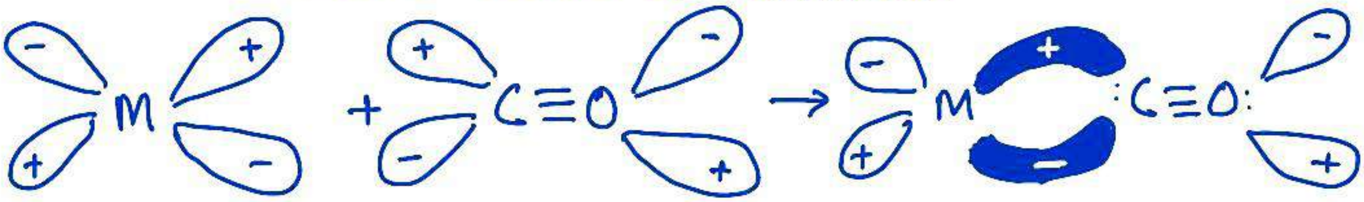
M-C σ bond is formed by the donation of lone pair of e⁻ on the carbonyl carbon to the vacant orbital of metal

↳ M-C π bond is formed by the donation of a pair of e⁻ from the filled d-orbital of the metal to vacant antibonding π* orbital of CO. This property of back bonding which stabilise the metal - ligand bond is termed as Synergic effect



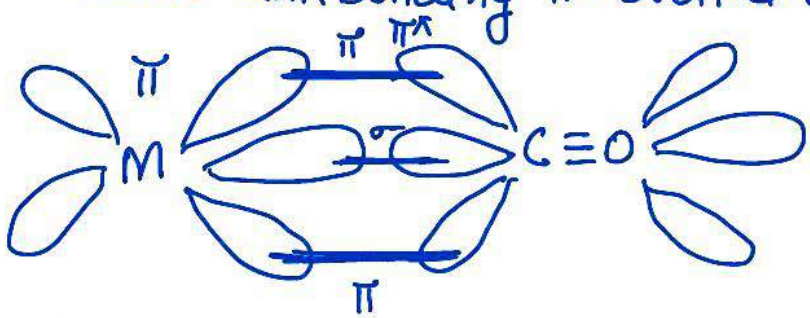
σ - overlap

Donation of lone pair of e⊖ from carbon atom into a vacant orbital of the metal.



π - overlap

Donation of e⊖ from a filled metal d-orbital into a vacant antibonding π-orbital of CO.



Factors Affecting Stability of a Complex

- Charge on central metal atom → as charge on central metal atom increases, stability of complex increases
- Nature of metal ion - stability order is 3d < 4d < 5d series
- Nature of ligands - strong field ligands form more stable complex
- Presence of chelate Ring: More the chelation, More is stability
- Effect of Multidentate ligands: If the ligands are multidentate, the stability of complex increases

→ Significance of Co-ordination Compounds

- In Biological System
- In Medicinal Chemistry
- In Analytical Chemistry
- In the extraction / Metallurgy of metals
- Estimation of Hardness of water
- In Catalysis
- In Photography

In Medicines

- Vitamin B_{12} is used to prevent anaemia
- A complex of Ca^{2+} with EDTA is used for the treatment of lead poisoning.
- A complex of platinum i.e cis-platin is used in the treatment of cancer in chemotherapy.

In Biological Importance

Many biological important natural compounds are co-ordination complexes e.g.

Chlorophyll : a complex of Mg^{2+}

Haemoglobin : a complex of Fe^{2+}

Vitamin B_{12} : a complex of Co^{3+}

Haloalkanes and Haloarenes

INTRODUCTION:-

The halogen derivatives of aliphatic and aromatic hydrocarbons are called alkyl halide (Haloalkanes) and aryl halide (Haloarenes)

Haloalkanes contain halogen atom attached to the sp^3 hybridised C-atom of an alkyl group. Whereas Haloarenes contain halogen atom attached to sp^2 hybridised C-atom of an aryl group.

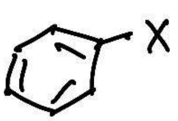
CLASSIFICATION OF HALOALKANES & HALOARENE

(*) On the basis of no. of halogen atoms

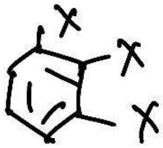
i) C_2H_5-X (Monohaloalkanes)

ii) CH_2-X / CH_2-X (Dihaloalkanes)

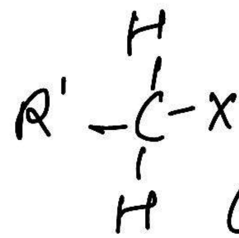
iii) CH_2-X / $CH-X$ / CH_2-X (Trihaloalkanes)

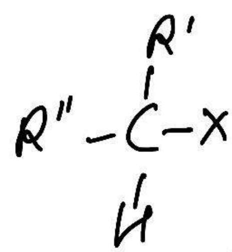

(monohaloarenes)

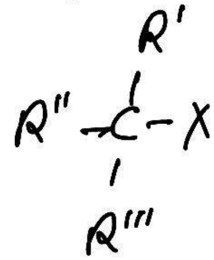

(Dihaloarenes)


(Trihaloarenes)

(*) On the basis of hybridisation state.


(1°-Primary)


(2°-Secondary)


(3° Tertiary Haloalkane)

X = F, Cl, Br, I

ALLYLIC HALIDES :-

the halogen is bonded to an sp^3 C-atom next to the C=C.

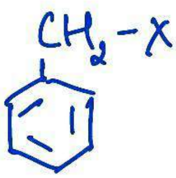
e.g. $R-CH=CH-CH_2-X$

Allylic carbon ↲

BENZYLIC HALIDE :-

the halogen atom is bonded to an sp^3 C-atom next to an aromatic ring

e.g



PROPAGYL HALIDE :-

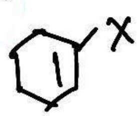
the halogen atom is bonded to an sp^3 C-atom, next to a C≡C bond.

e.g $R-C\equiv C-CH_2-X$

Vinyl Halide:

the halogen atom is bonded to an sp^2 C-atom

e.g $R-CH_2=CH-X$,



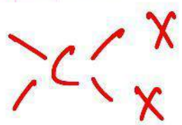
Aryl Halide :

the halogen atom is bonded to sp^2 C-atom of an aromatic ring.

NOMENCLATURE OF HALOALKANES

	Common Name	IUPAC Name
• CH_3-Cl	Methyl chloride	chloromethane
• $CH_3CH_2CH_2Br$	n-Propyl Bromide	Bromo propane
• $CH_3-CH(CH_3)-CH_2-Cl$	isobutyl chloride	1-chloro-2-methyl propane
• $CH_3-C(CH_3)_2-CH_2-Cl$	neopentyl chloride	1-chloro-2,2-dimethyl propane.

a) When both halogen atoms are attached to the same C-atom, these are called gem-dihalides also called alkylidene dihalide.

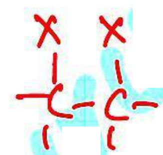


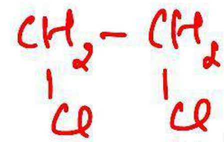
gem-dihalide

e.g $CH_3-CH<^{Cl}_{Cl}$

ethylidene dichloride

b) When two halogen atoms are present at adjacent C- then they are called vicinal dihalide also called alkylene dihalide



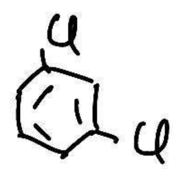


ethylene dichloride

NOMENCLATURE OF HALOARENES

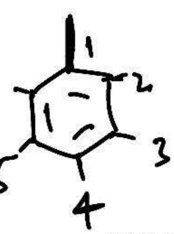
Chloro benzene

1,2-Dichlorobenzene (o-Dichloro benzene)

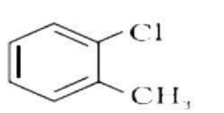
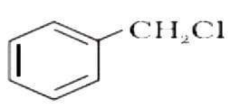


1,3-Dichloro benzene (m-Dichloro benzene)

1,4-Dichloro benzene (p-Dichloro benzene)



ओमपल
o, m, p

$CH_2 = CHCl$	Vinyl chloride	Chloroethene
$CH_2 = CHCH_2Br$	Allyl bromide	3-Bromopropene
	o-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

Nature of C-X Bond

the C-X bond is covalent but the electronegativity of halogen atom is more than C, due to which C-X bond is polar

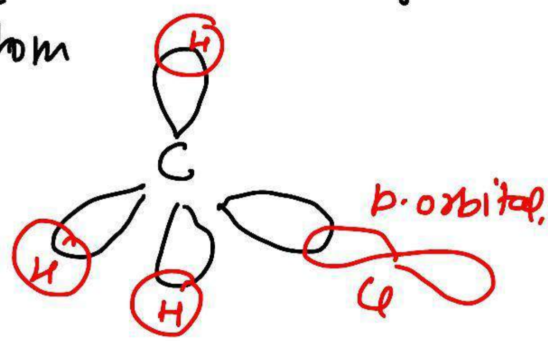
$$-\overset{|}{\underset{|}{C}}-X \longrightarrow -\overset{|}{\underset{|}{C}}^{\delta+}-X^{\delta-}$$ Polar Bond

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

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

• Molecular Structure of CH_3Cl

the C-X bond is formed by the overlaping of sp^3 hybrid orbital of C-atom and p-orbital of Cl-atom



METHODS OF PREPARATION OF HALOALKANES :-

1. From Alcohol

a) By the action of halogen acid

$$R-OH + HX \longrightarrow R-X + H_2O$$

1° & 2° alcohols form chloroalkanes, when hydrochloric acid gas is passed through alcohol in the presence of anhydrous $ZnCl_2$

This is known as "Groove's Process"

$ZnCl_2$ help in the cleavage of C-O bond.

→ 3' alcohols are very reactive, they react with conc. HCl at room temp. without $ZnCl_2$

$$CH_3-CH_2-OH + HCl \xrightarrow[ZnCl_2]{anhy} CH_3-CH_2-Cl + H_2O$$

$$CH_3-CH(CH_3)-OH + HCl \xrightarrow[ZnCl_2]{anhy} CH_3-CH(CH_3)-Cl + H_2O$$

$$CH_3-C(CH_3)_2-OH + HCl \xrightarrow[temp.]{Room} CH_3-C(CH_3)_2-Cl + H_2O$$

Note 2° & 3° bromides and iodides can not be prepared from the respective alcohols because 2° & 3° alcohols on heating with conc. H_2SO_4 undergo dehydration and form alkene

→ HF is least reactive. So fluoroalkane is not formed.

Order of reactivity of alcohol → 3° > 2° > 1°
Reactivity of halogens → HI > HBr > HCl

• By the action of Phosphorous Halides:

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$

$$R-OH + PCl_3 \longrightarrow R-Cl + H_3PO_3$$

Note PBr_3 & PI_3 are not stable, so they are prepared on the site of reaction (SITU)

• By the action of thionyl Chloride

$$R-OH + SOCl_2 \xrightarrow{Pyridine} R-Cl + SO_2\uparrow + HCl\uparrow$$

→ This method is preferred than other method because both the side products (SO_2 & HCl) are gaseous and can easily escape.

From Hydrocarbons

a) From Alkanes

Cl_2 & Br_2 reacts with alkanes in the presence of UV light to form haloalkanes. This reaction is "Free radical substitution reaction"

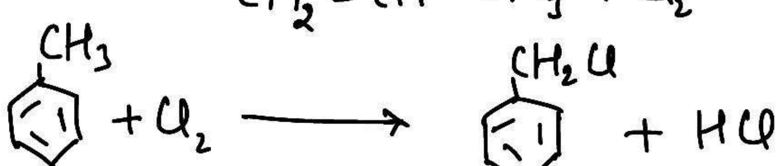
ex. $CH_3CH_2CH_3 \xrightarrow[\text{UV light}]{Cl_2} \underset{(45\%)}{CH_3CH_2CH_2Cl} + \underset{(55\%)}{CH_3\underset{Cl}{CH}CH_3}$

Note → The reactivity of different type of hydrogen in halocompound are

{ Benzylic = allylic > Alkyl > Vinyl = aryl }

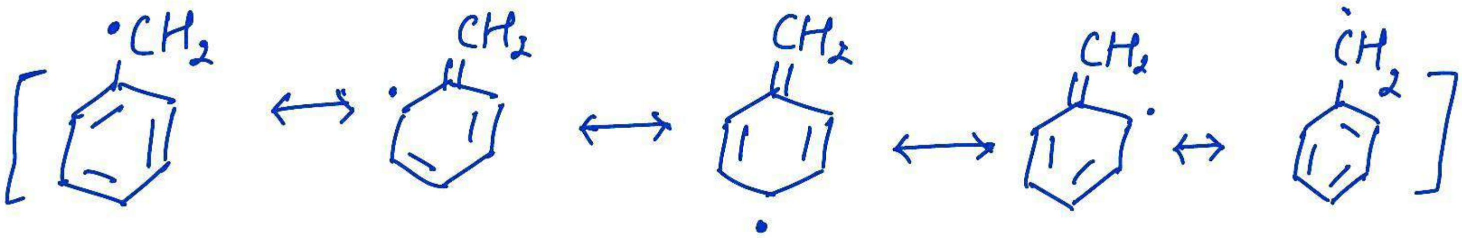
→ Allylic and benzylic halides can be easily prepared

· $CH_2=CH-CH_3 + Cl_2 \xrightarrow{\Delta} CH_2=CH-CH_2Cl + HCl$



→ Both are highly reactive and this can be explained in terms of stabilisation by resonance

$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$



From Alkenes

$$>C=C< + HX \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-$$

- It is possible in symmetrical alkenes (–CH=CH–)

Markovnikov's Rule:-

In unsymmetrical alkenes, the –ve part of the addendum goes to that carbon having lower no. of hydrogen

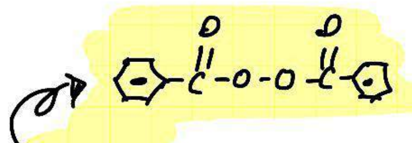
नटखट — Negative (–)
लाल — lower
हलवाई — Hydrogen

$$CH_3-CH=CH_2 + HX \longrightarrow CH_3-\underset{X}{\underset{|}{CH}}-CH_3$$

ANTI-MARKONIKOV'S RULE:-

↳ Applicable to HBr

↳ takes place in the presence of Organic peroxide



In unsymmetrical alkenes, the negative part of the additive goes to that carbon having higher no. of hydrogen

$$CH_3-CH=CH_2 + HBr \xrightarrow{Peroxide} CH_3-CH_2-\underset{Br}{\underset{|}{CH_2}}$$

Anti markovnikov's Rule is also known as peroxide effect or Kharasch effect.

नटखट — Negative (–)
हरा — Higher
हलवाई — Hydrogen.

Addition of Halogen:

When Br_2 & Cl_2 is added to alkenes the addition occur at the double bond forming vicinal dihalide

$$>C=C< + Br_2 \xrightarrow{CCl_4} >C(Br)-C(Br)<$$

(vicinal dihalides)

Note This test is used to check unsaturation because reddish brown colour of Br_2 disappeared when reacts with alkene

• By Halogen Exchange:-

$$R-X + NaI \xrightarrow[\text{Heat}]{\text{Acetone}} R-I + NaX \quad (X = Cl, Br)$$

Finkelstein Reaction

• Fluoroalkanes are difficult to prepare directly these are prepared by treating alkyl chloride and bromide with inorganic fluoride such as (Hg_2F_2, AgF, CoF_3, SbF_3) and this reaction is termed as **Swarts reaction**

$$CH_3-Br + AgF \longrightarrow CH_3-F + AgBr$$

• From Silver Salt of Acids:-

$$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + CO_2 + AgBr$$

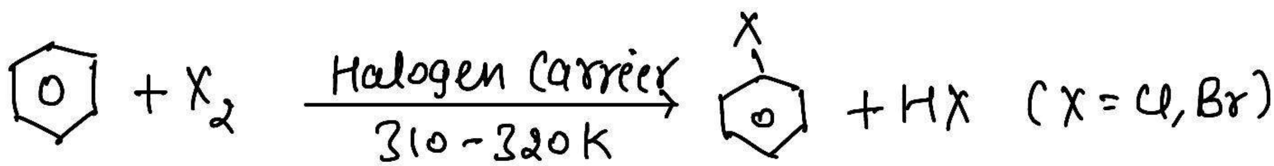
"Borodine Hunsdiecker Reaction"

$$2CH_3COOAg + I_2 \xrightarrow{CCl_4} CH_3COOCH_3 + CO_2 + 2AgI$$

"Birnbaum Simonini Reaction"

Methods of Preparation of Haloarenes

Electrophilic Substitution of Arenes OR Direct Halogenation of aromatic ring:



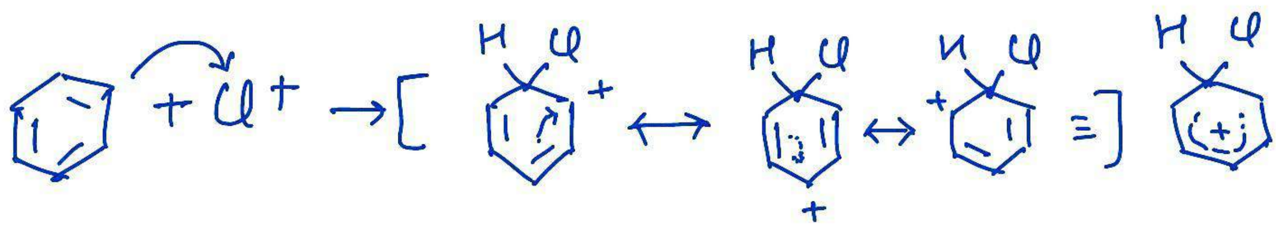
{Here Halogen carrier → $FeCl_3$ / $FeBr_3$ / $AlCl_3$
LEWIS ACID }

Mechanism:-

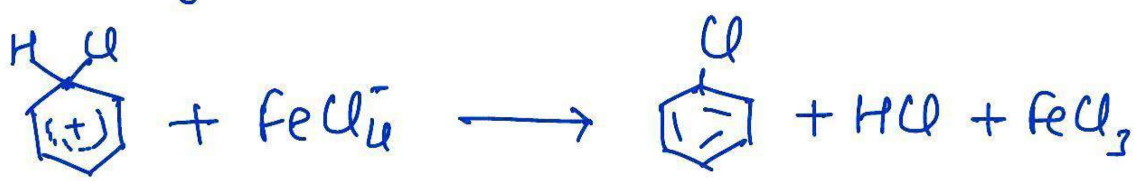
Step-1 Generation of electrophile

$$Cl_2 + FeCl_3 \longrightarrow FeCl_4^- + Cl^+$$

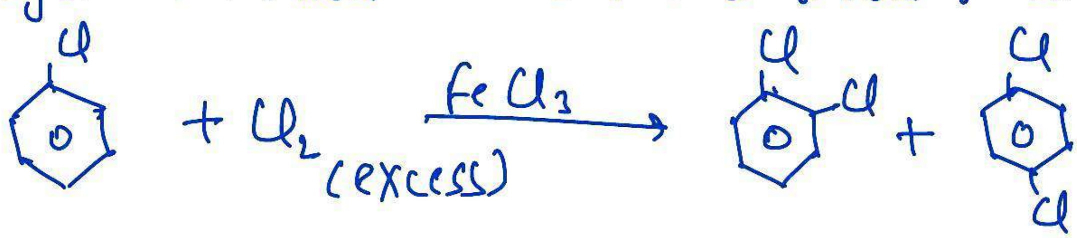
Step-2 Formation of carbocation intermediate



Step-3 loss of proton from the intermediate

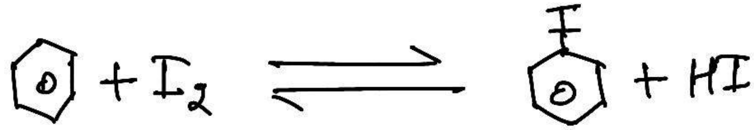


If excess of Halogen is used, the second halogen attached to ortho & para position



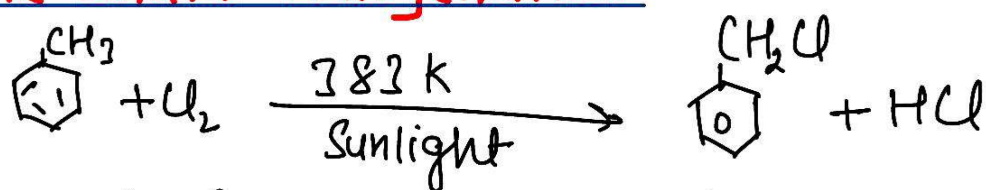
Note → The reaction with fluorine is violent or vigrous and can not be contbolled

→ The reaction with I_2 is not possible because when product is formed, HI reduce to back



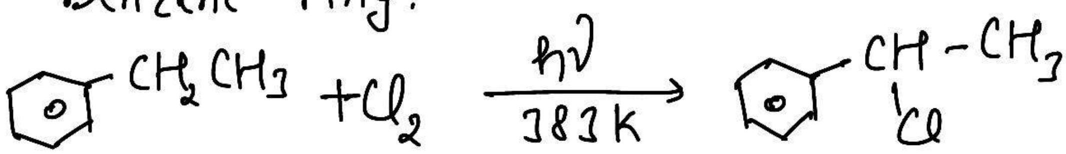
→ So the reaction is carried out in the presence of oxidising agent (HIO_3, HgO) to oxidise HI.

Side Chain Halogenation:



If Cl_2 is in excess than all "H" are replaced by "Cl"

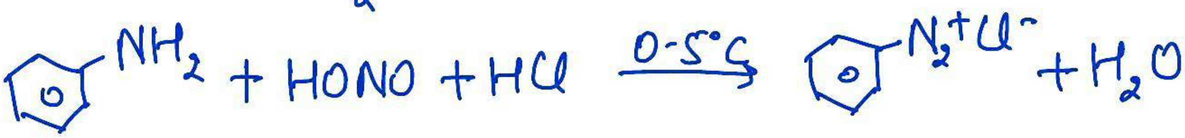
when the side chain is larger than a methyl group, halogenation occur at C-atom next to benzene ring.



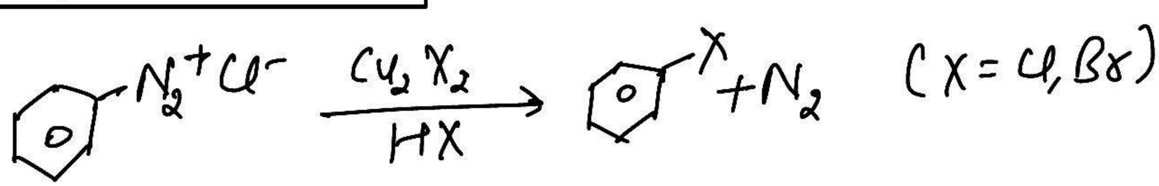
From Diazonium Salt:

- Diazotization Reaction

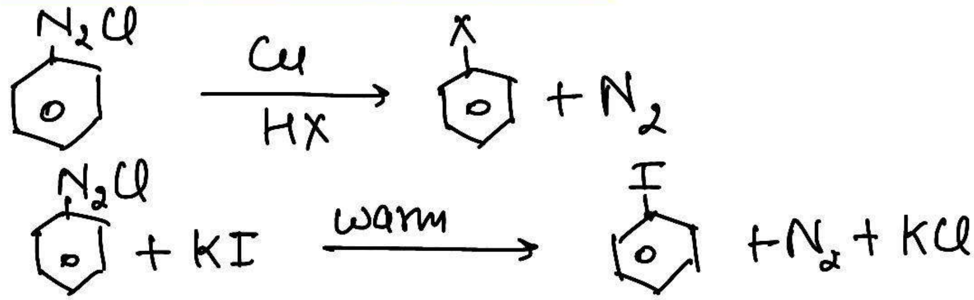
$$NaNO_2 + HCl \longrightarrow NaCl + HONO$$



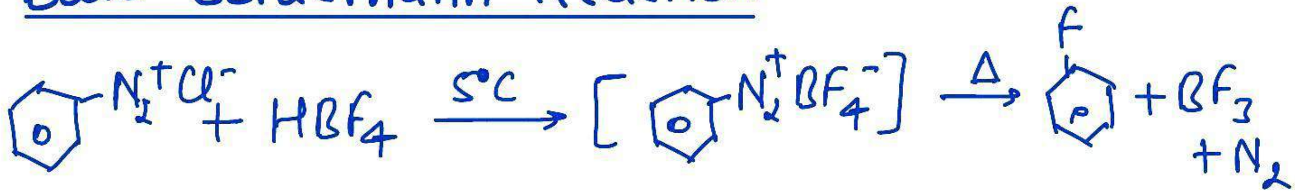
Sandmeyer Reaction



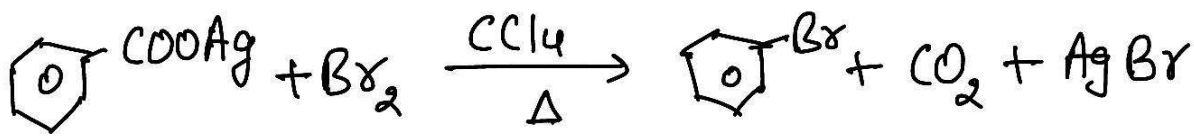
Gattermann Reaction



Balz- Schiemann Reaction



From Silver Salt of Aromatic Acid:



Note Haloarenes can't be prepared from phenol because it is difficult to replace –OH group. This is due to resonance in phenol.

Physical Properties of Haloalkanes :-

→ In general haloalkanes are colourless (when pure) sweet smelling liquids.

→ They are slightly soluble in water because of low tendency to form Hydrogen Bond.

→ Density : F < Cl < Br < I

more no. of H-atom, less is density

e.g $CH_2Cl_2 < CHCl_3$

→ Boiling Point

B.Pt ∝ Mol. Mass

B.Pt $\propto \frac{1}{\text{Branching}}$

Physical Properties of Haloarenes :

1. These are generally colourless liquid or crystalline solid.
2. The aryl halides are heavy than water. insoluble in water but soluble in organic solvents.
3. The m.pt & b.pt of aryl halides are nearly the same of alkyl halide containing the same no. of carbon atoms.

> B.Pt → ortho > Para > meta
> M.Pt → Para > ortho > meta

Chemical Properties Of Haloalkanes

*) **Nucleophilic Substitution Reaction :-**

$$>C-X \longrightarrow >C^{\delta+}-X^{\delta-} + Nu^{\ominus} \longrightarrow >C-Nu + X^{\ominus}$$

> Reactivity order :- R-I > R-Br > R-Cl > R-F

Types
- S_N1 (Unimolecular Nucleophilic Sub. Rxn)
- S_N2 (Bimolecular Nucleophilic Sub. Rxn)

S_N1

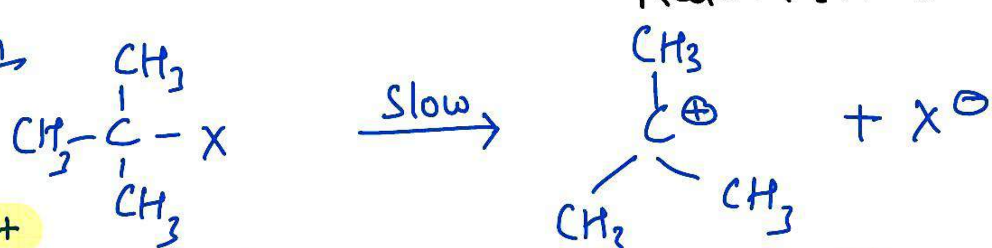
$$R-X + Nu^{\ominus} \longrightarrow R-Nu + X^{-}$$

Rate ∝ [R-X]

Mechanism

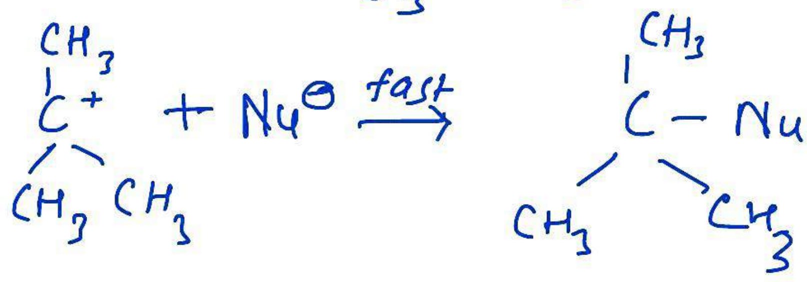
Step-1

Formation of C+



Step-2

Attack of Nucleophile



→ Retention as well as inversion of configuration takes place

Order of S_N1 reaction $(CH_3)_3C-X > (CH_3)_2CH-X > CH_3-CH_2-X > CH_3-X$

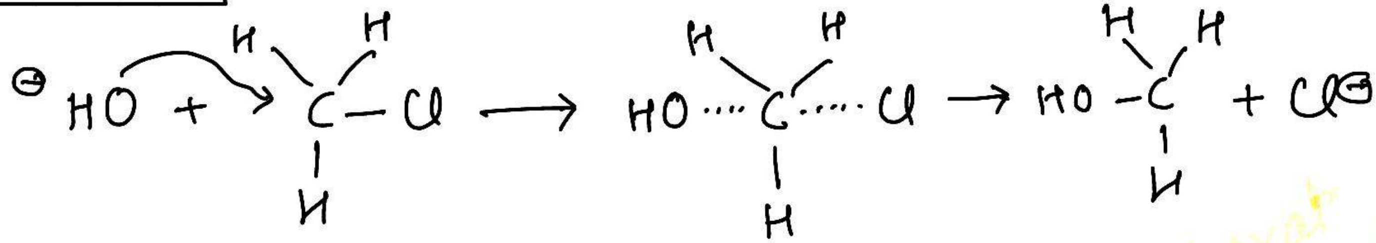
Allylic and benzylic halides show higher reactivity towards the S_N1 reaction.
The carbocation thus formed get stabilised through resonance.

S_N2 (Bimolecular Nucleophilic Substitution Rxn)

$$R-X + Nu^{\ominus} \longrightarrow R-Nu + X^{\ominus}$$

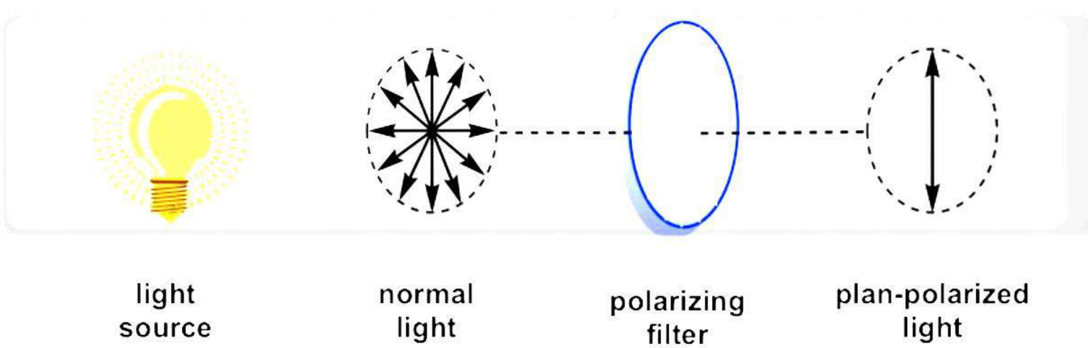
$$\text{Rate} \propto [R-X][Nu^{\ominus}]$$

Mechanism



Order of S_N2 reaction :- $CH_3X > 1° > 2° > 3°$

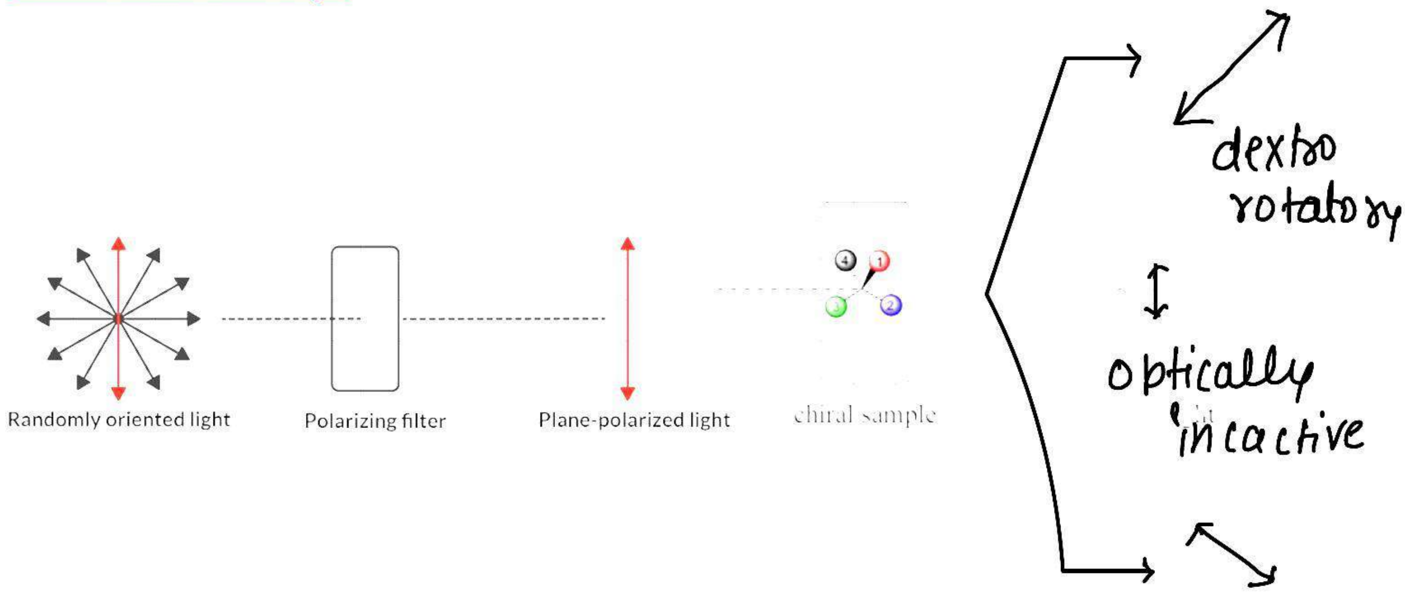
→ inversion of configuration takes place



A beam of ordinary light consist of electromagnetic waves vibrating in all planes when pass through Nicol prism, vibrates in one plane called PPL (Plane polarised light)

Dextro-Rotatory - which rotate PPL towards right

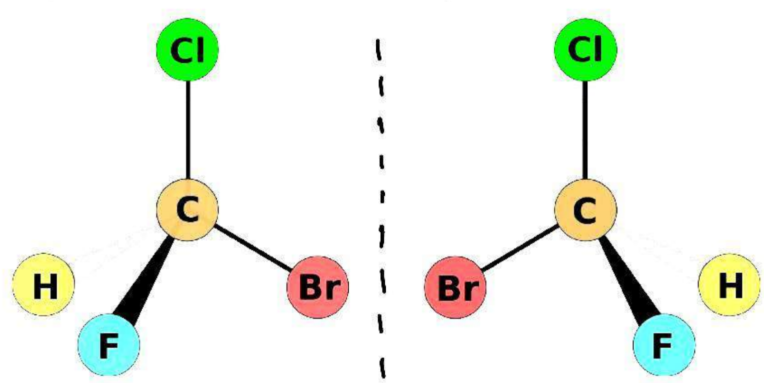
Levo-Rotatory - which rotate PPL towards left.



Racemic Mixture equimolar mixture of d and l, so that net rotation of PPL is zero.

Enantiomers

- The optical isomers are called enantiomers.
- These are distinguished by +/-, D/L or more correctly R/S.
- A 50/50 mixture of the two enantiomers is called a racemic mixture or a racemate.



Nucleophilic Substitution Reaction

Reagent	Nucleophile (Nu^-)	Substitution product R-Nu	Class of main product
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	$R'O^-$	ROR′	Ether
NaI	I^-	R—I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″NH	RNR′R″	Tert. amine
KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO_2	O=N—O	R—O—N=O	Alkyl nitrite
$AgNO_2$	Ag—Ö—N=O	$R—NO_2$	Nitroalkane
R′COOAg	R′COO	R′COOR	Ester
$LiAlH_4$	H	RH	Hydrocarbon
$R'^- M^+$	R'^-	RR′	Alkane

Substitution by Amino Group:

$$R-X + NH_3 \longrightarrow R-NH_2 + HX$$

when haloalkanes is in excess amount then all three of NH_3 is replaced by group (R)

$$\underset{(excess)}{R-X} + NH_3 \longrightarrow R_3N + HX$$

"Hoffman Ammonolysis reaction"

- $R-X + KNO_2 \xrightarrow{\Delta} R-O-N=O + KX$

$$R-X + AgNO_2 \xrightarrow{\Delta} R-N{=}O\,(\rightarrow O) + AgX$$

- **Substitution by -OH group.**

$$R\text{-}X + KOH \text{ or } AgOH \xrightarrow{\Delta} R\text{-}OH + KX \text{ or } AgX$$

- **Substitution by alkoxy group**

$$R\text{-}X + \overset{\oplus}{Na}\text{-}OR \xrightarrow{\Delta} R\text{-}O\text{-}R' + NaX$$

This reaction is known as Williamson Synthesis

- **Substitution by Cyano Group**

$$R\text{-}X + KCN \longrightarrow R\text{-}CN + KX$$

$$C_2H_5\text{-}I + KCN \longrightarrow C_2H_5CN$$

$$C_2H_5CN \xrightarrow{\text{Conc. HCl}} CH_3CONH_2$$

$$C_2H_5CN \xrightarrow{\text{Dil. HCl or NaOH}} CH_3COOH$$

$$C_2H_5CN \xrightarrow[\text{LiAlH}_4,\ \text{Ni/H}_2]{\text{Na, } C_2H_5\text{-OH}} CH_3CH_2NH_2$$

Mendius Reaction: The formation of 1° amines by reduction with nascent hydrogen obtained by the action of sodium on alcohol.

Substitution by Isocyanide group:

$$R\text{-}X + AgCN \longrightarrow R\text{-}NC + AgX$$

(Note) Ag activate N-group & K activate C-group

- **Substitution by azide group:**

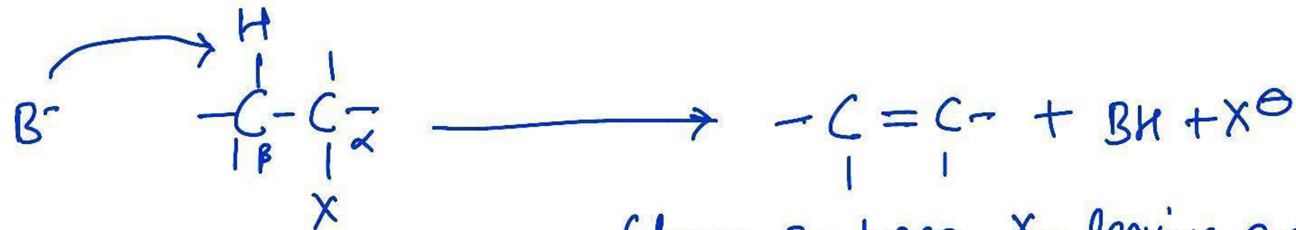
$$R\text{-}X + NaN_3 \longrightarrow R\text{-}N_3 + NaX$$

- **Substitution by Carboxyl group:**

$$R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\boxed{Ag + X}\text{-}R \xrightarrow{C_2H_5OH} R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR + AgX$$

• Elimination Reaction (Dehydrogenation)

when a haloalkane with β-H atom is heated with alc. KOH there is an elimination of H-atom from β-C and a halogen from α-C, result an alkene is formed



(here B- base, X- leaving group)

If there is a possibility of formation of more than one alkene due to availability of more than one β-H usually one alkene is formed as major product.

$CH_3-CH_2-CH_2-CH(Br)-CH_3 \rightarrow$

- $CH_3-CH_2-CH=CH-CH_3$ (81%)
- $CH_3-CH_2-CH_2-CH=CH_2$ (19%)

• Acc. to "Saytzeff's Rule", the alkene with greater no. of alkyl group is preferred [$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > RCH=CH_2$]

Note → A primary alkyl halide prefer a S_N2 reaction.

→ A sec. halide prefer S_N2 & S_N1 depending upon the strength of base/$Nu^\ominus$ and a tert. halide prefer S_N1

Reactivity → $3° > 2° > 1° > CH_3-X$ cas carbocation

→ Alcoholic KOH causes elimination, while aqueous solution of base leads to substitution

Reaction with active metals-

Reaction with Magnesium

$$R-X + Mg \xrightarrow[\text{ether}]{\text{Dry}} R-Mg\cdot X \quad (X \rightarrow Cl, Br, I)$$

Grignard Reagent

→ These grignard reagents are very reactive compounds. They react with any source of proton to form hydrocarbons. So it is very necessary to avoid traces of moisture from grignard reagent.

$$R-MgX + \underset{(H^+ \cdot OH^-)}{H_2O} \longrightarrow \underset{\text{Hydrocarbon}}{R-H} + Mg{<}^{X}_{OH}$$

Reaction with Na (Wurtz Rxn)

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

used to prepare symmetrical alkanes.

Reaction with Zn (Frankland Reaction)

$$2\,C_2H_5-Br + 2\,Zn \longrightarrow C_2H_5-Zn-C_2H_5 + ZnBr_2$$

diethyl zinc (frankland Reagent)

Reduction Reaction:

$$R-X + 2[H] \longrightarrow R-H + HX$$

$$C_2H_5Cl + 2[H] \longrightarrow C_2H_6 + HCl$$

Following reagents are used for reduction

Zn/HCl, Na/C_2H_5OH, $LiAlH_4$, Red P/HI

Rearrangement Reaction

$$CH_3CH_2CH_2Cl \xrightarrow[573\,K]{AlCl_3} CH_3-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_3$$

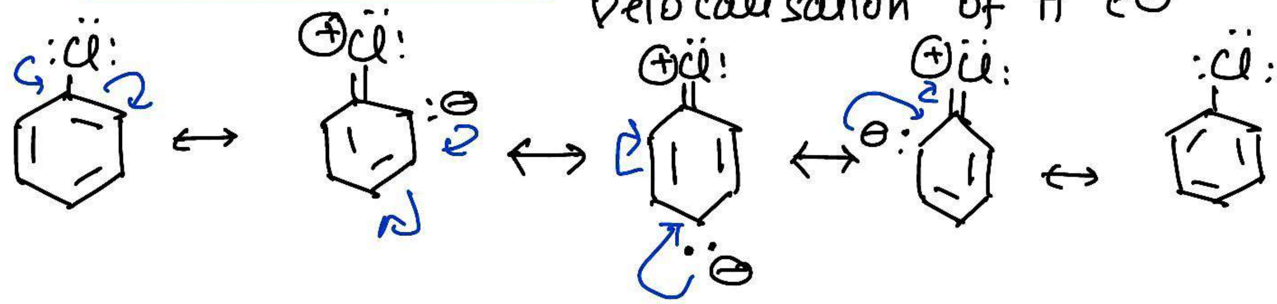
$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Cl \xrightarrow[573\,K]{AlCl_3} CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2-CH_3$$

Chemical Properties of Haloarenes:

Haloarenes are less reactive than Haloalkanes due to

1. **Resonance Effect →**

Delocalisation of π e⊖



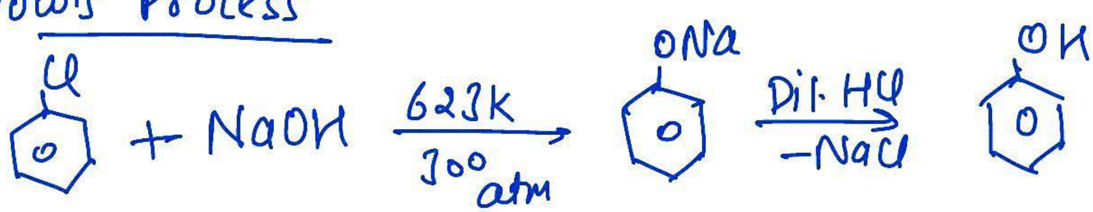
2. **Difference in hybridisation of C-X Bond**

more s-character more electronegative, so hold e⊖ pair more tightly, so less reactive

3. **Polarity of C-X Bond** In C-X bond of aryl halide polarity is less, so reactivity is less

(a) **Nucleophilic Substitution Reaction**

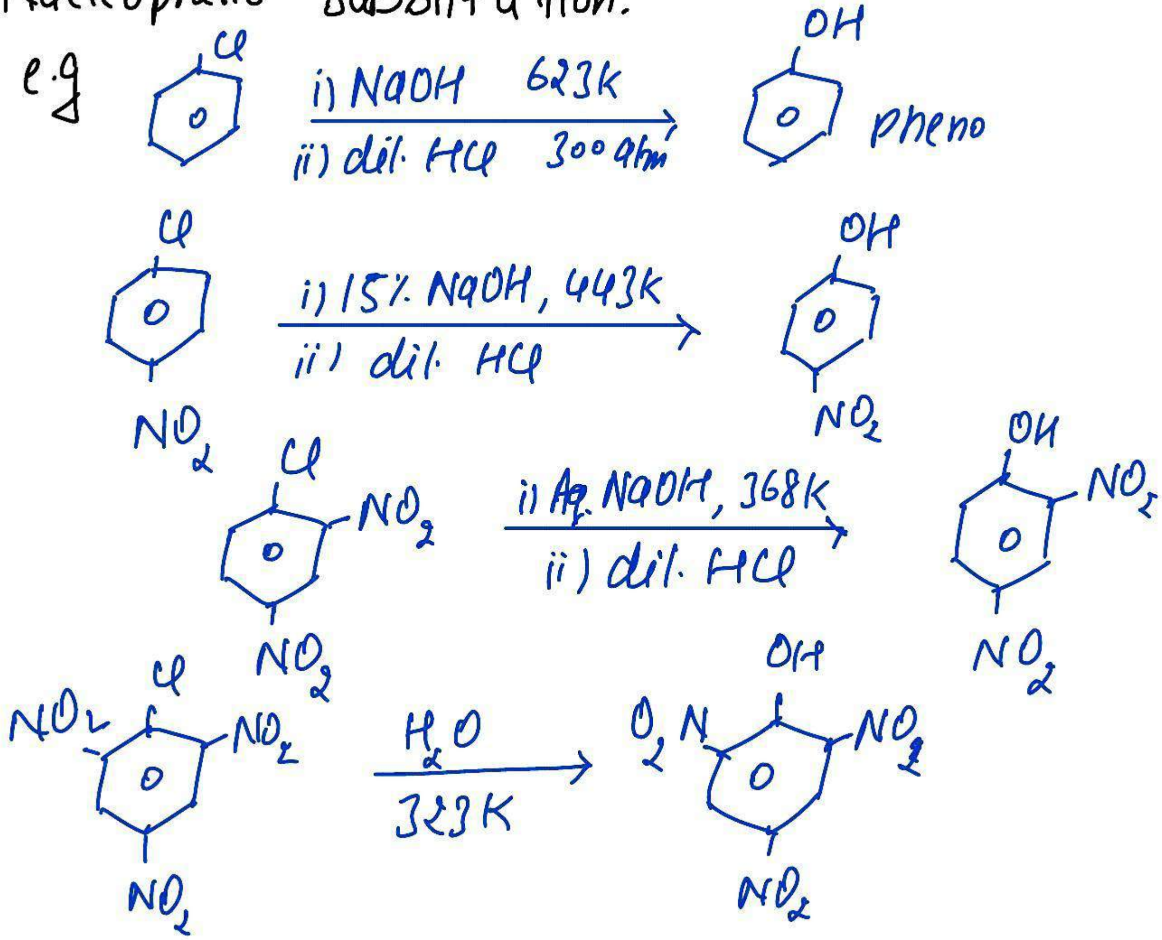
- Dow's Process



Effect of Substituent in Haloarenes on Reactivity:

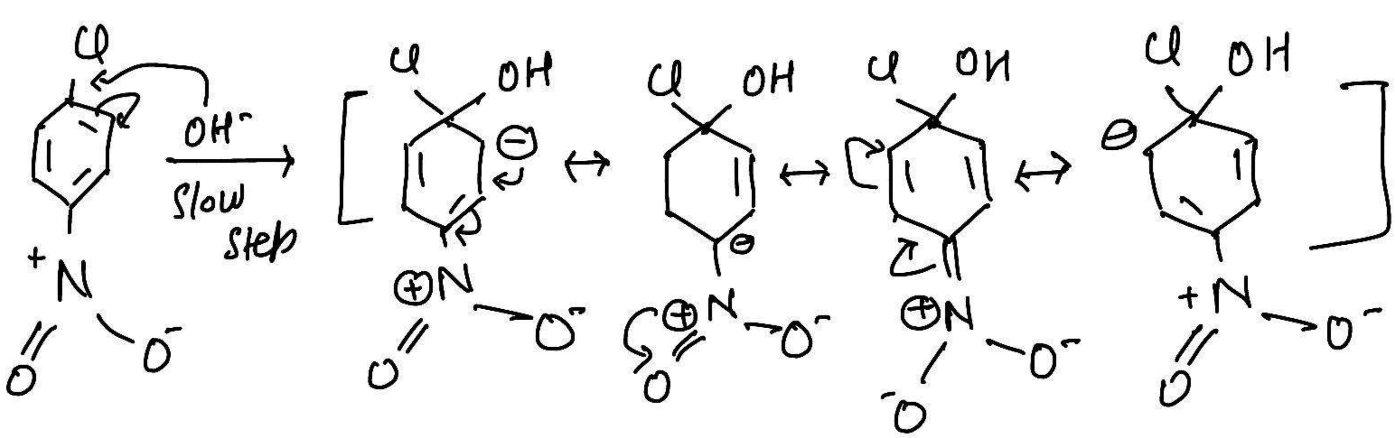
→ The presence of e⊖ withdrawing groups such as $-NO_2$, $-CN$, $-COOH$ etc. at ortho and para position to the halogen atom greatly activates the halogen towards Nucleophilic substitution.

e.g



NOTE → Nitro group ($-NO_2$) meta to the chlorine has no effect on reactivity.

Explanation :- NO_2 at para positions.



In case of ortho and para structures, one of the resonating structures bears a negative charge on the C-atom bearing the $-NO_2$ group.

These carboanions are stabilized by the $-NO_2$ group as well as π e⊖ of benzene ring.

However in case of m-structure, none of the resonating str. bear the -ve charge on carbon atom bearing the $-NO_2$ group.

∴ The $-NO_2$ groups does not stabilise the carboanion and thus has no effect towards Reactivity.

Q Out of chlorobenzene and cyclohexyl chloride, which one is more reactive toward nucleophilic substitution reaction and why?

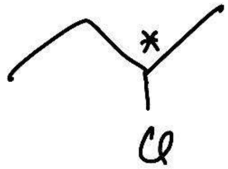
Ans. Cyclohexyl chloride is more reactive towards nucleophilic substitution reaction because C-Cl bond strength is less in cyclohexyl chloride than chlorobenzene.

In Cyclohexyl chloride, Cl-atom is bonded to sp^3 hybrid C-atom while in chlorobenzene Cl is bonded to sp^2 hybrid C-atom

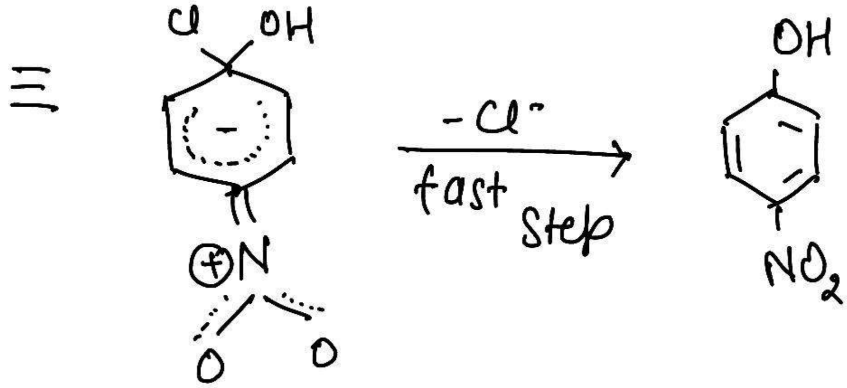
C-Cl bond is more strong in chlorobenzene and less reactive towards nucleophilic sub.

Q Identify the chiral molecule in the following pairs.

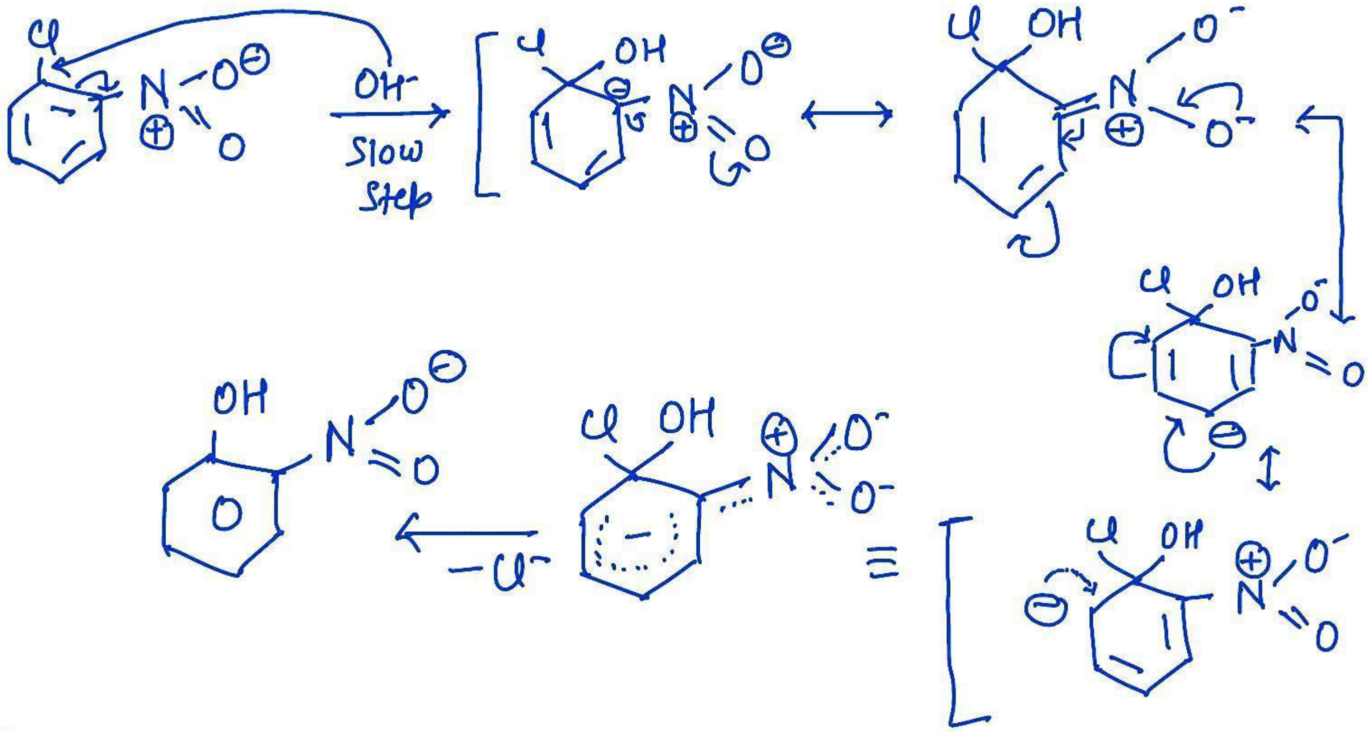
Ans.



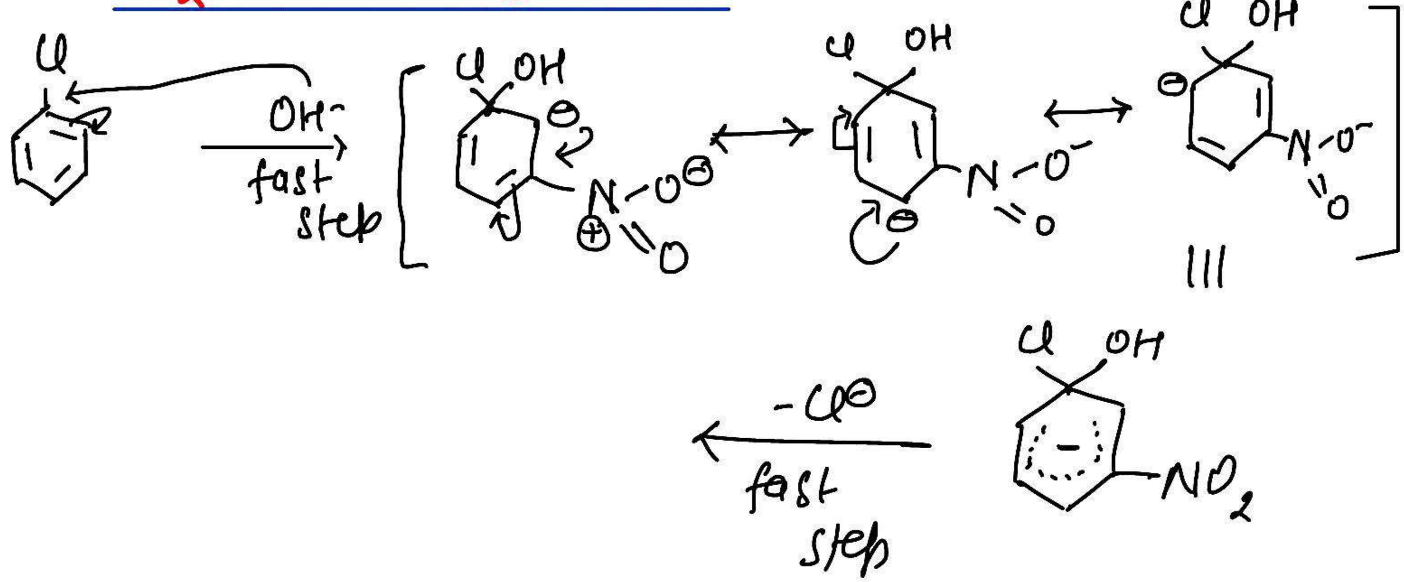
is chiral molecule as it contains an asymmetric C-atom which is denoted by *.



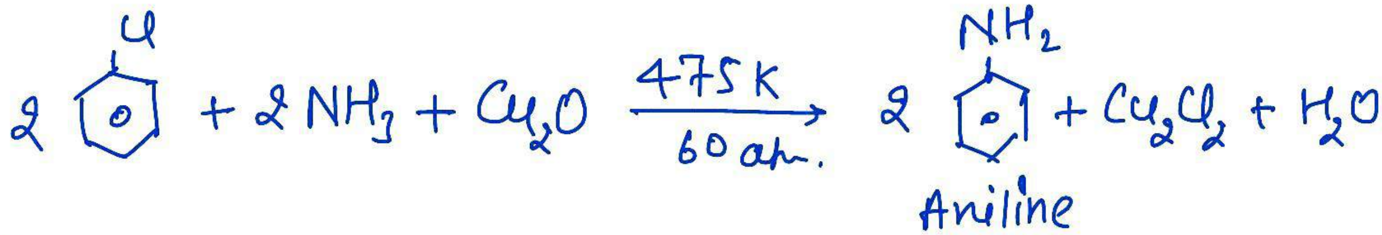
Cl → NO_2 at Ortho position :



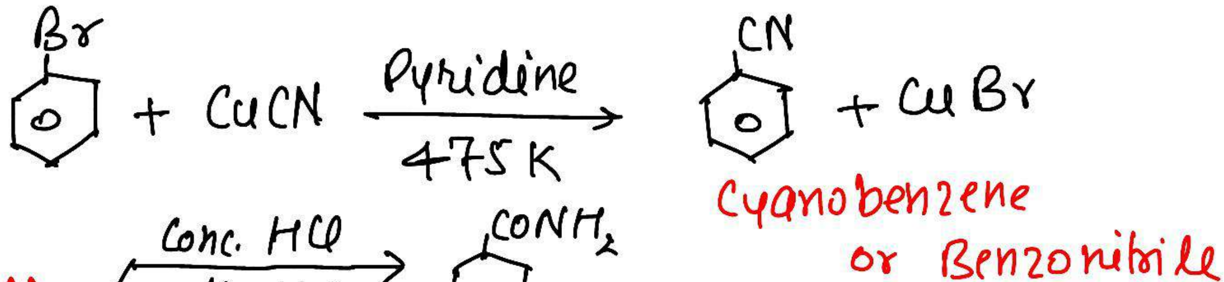
Cl → NO_2 at meta position

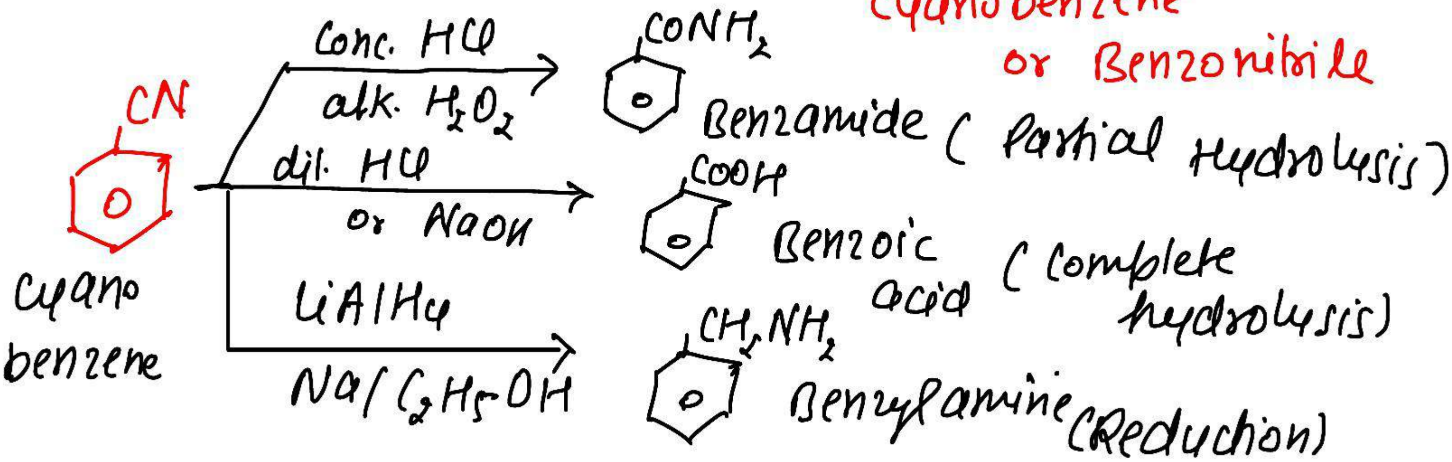


Substitution of Amino Group :

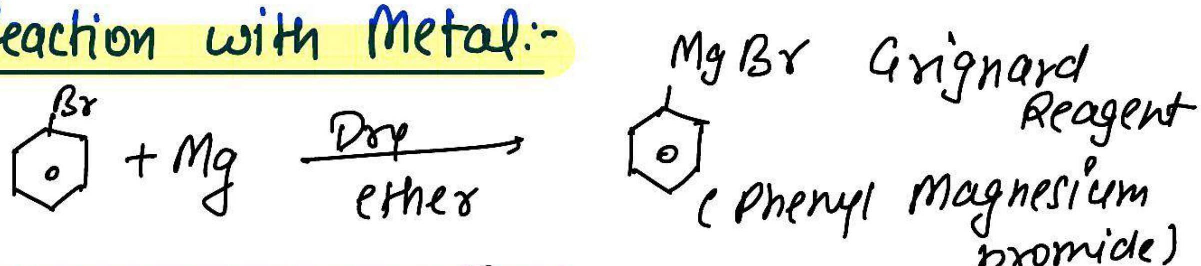


Substitution by Cyano Group





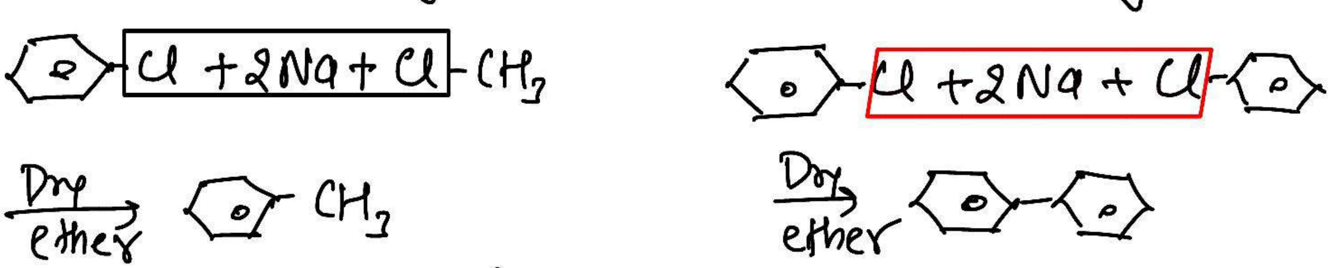
Reaction with Metal:-



Reaction with Sodium

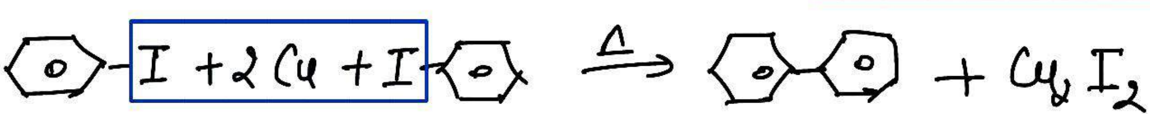
Wurtz-Fittig Rxn

Fittig Reaction

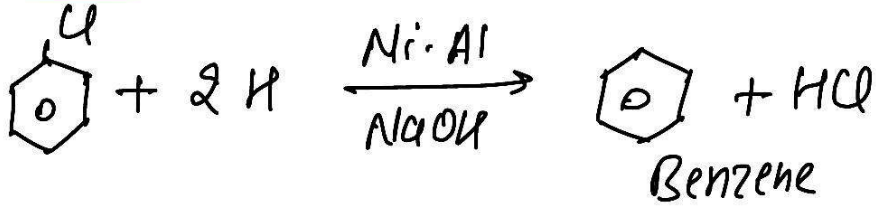


Reaction with Copper

Ullmann Reaction



Reduction

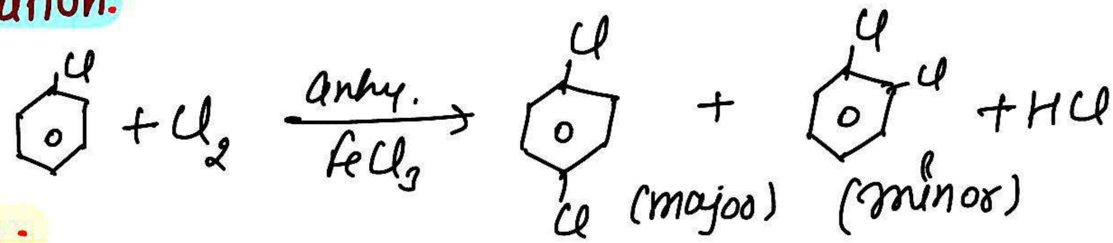


Electrophilic Substitution Reaction

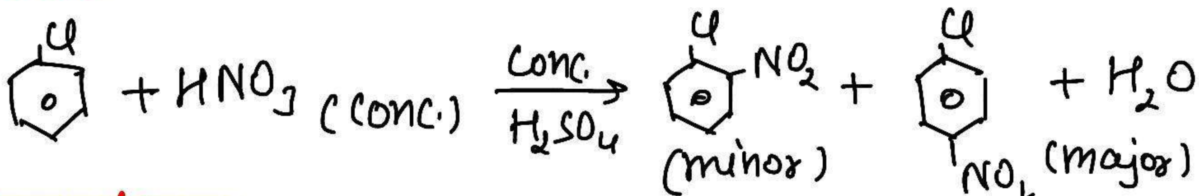
Note (i) Haloarenes undergo electrophilic substitution reaction slowly as compared to benzene

(ii) Halogen group is ortho and para directing

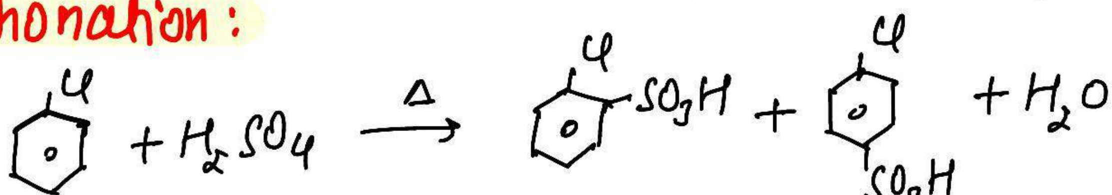
Halogenation:



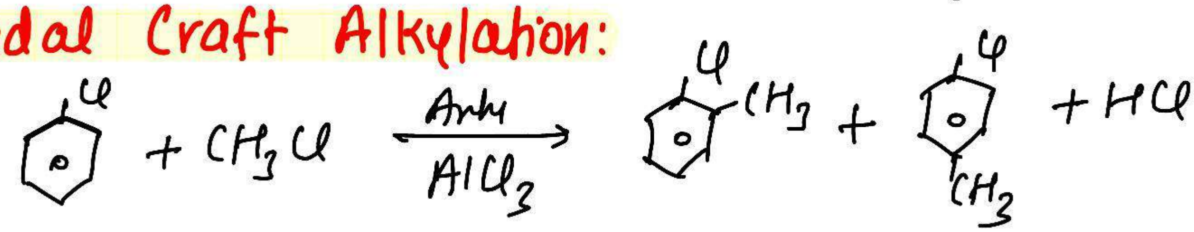
Nitration:



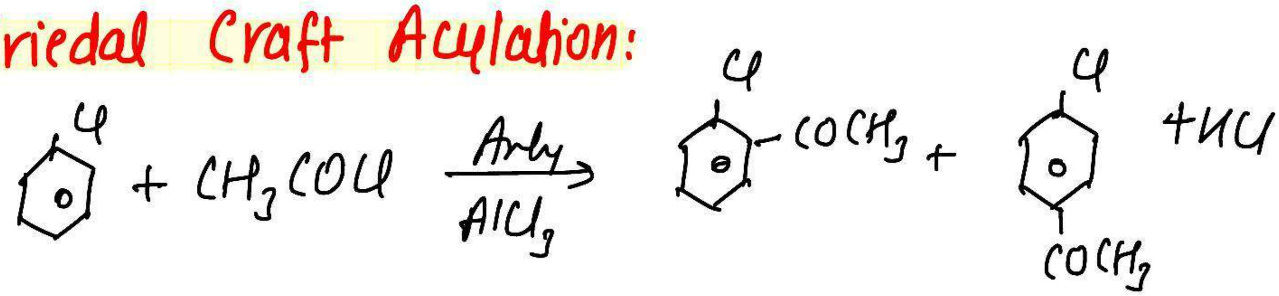
Sulphonation:



Friedal Craft Alkylation:



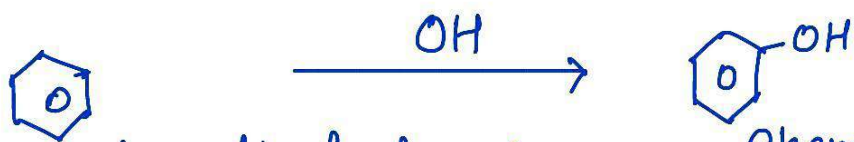
Friedal Craft Acylation:



Alcohols and Phenols :-

When a hydrogen of aliphatic or aromatic hydrocarbons is replaced by (−OH) group then the compounds which are obtained are called alcohols and phenols.

$$\underset{\text{Aliphatic Hydrocarbons}}{R-H} \xrightarrow{OH} \underset{\text{Alcohol}}{R-OH}$$



Aromatic hydrocarbons → Phenol

⇒ Also called Hydroxy derivatives of Hydrocarbons.

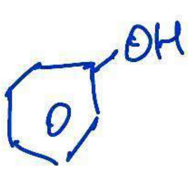
Classification of Alcohol and Phenols

- On the basis of no. of −OH groups -

Monohydric

CH_3-OH

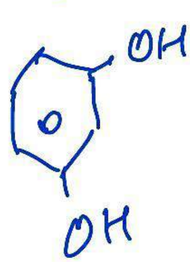
or



Dihydric

CH_2-OH
|
CH_2-OH

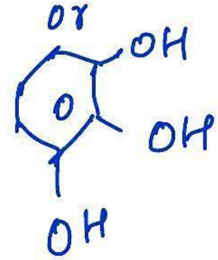
or



Tri or polyhydric

CH_2-OH
|
$CH-OH$
|
CH_2-OH

or



Primary (1°) | Secondary (2°) | Tertiary (3°)

CH_3-CH_2-OH

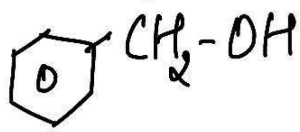
$CH_3-CH(OH)-CH_3$

$CH_3-C(CH_3)(OH)-CH_3$

- **Allylic Alcohols** In this type of alcohols, –OH group is attached to the sp^3 hybridised carbon which itself attached to a double bonded carbon atom

$CH_2=CH-CH_2-OH$ → Prop-2-en-1-ol

- **Benzylic Alcohols**: In this type of alcohol the –OH group is attached to the sp^3 hybridized carbon which itself attached to a benzene ring.



→ Benzylic alcohol.

- **Vinylic alcohol**: In this type of alcohols –OH group is attached to a double bonded carbon atom.

$CH_2=CH-OH$ → Vinylic Alcohol.

NOMENCLATURE :

$CH_3-C(CH_3)(C_2H_5)-CH(OH)-CH_3$ → 3,3-Dimethylpentan-2-ol

Compound	Common name	IUPAC name
CH_3-OH	Methyl alcohol	Methanol
$CH_3-CH_2-CH_2-OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_3$	Isopropyl alcohol	Propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	*n*-Butyl alcohol	Butan-1-ol
$CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_2-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
$CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_2-CH_3$	Isobutyl alcohol	2-Methylpropan-1-ol
$CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
$\underset{\underset{OH}{\mid}}{CH_2}-\underset{\underset{OH}{\mid}}{CH}-\underset{\underset{OH}{\mid}}{CH_2}$	Glycerol	Propane -1, 2, 3-triol

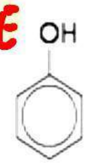
$$CH_3-\underset{\underset{CH_3}{\mid}}{C}=\underset{\underset{Br}{\mid}}{C}-CH_2-OH$$

3-Bromo-4-methyl pent-3-en-1-ol

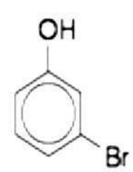
• Draw the str. of Hex-1-en-3-ol

$$CH_3-CH_2-CH_2-\underset{\underset{OH}{\mid}}{CH}-CH=CH_2.$$

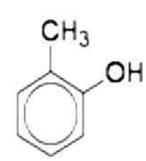
NOMENCLATURE OF PHENOL



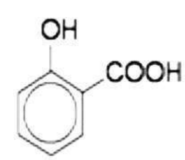
phenol



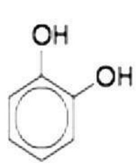
m-bromophenol



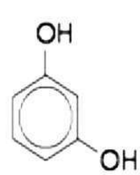
o-cresol



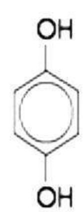
salicylic acid



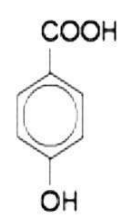
catechol



resorcinol

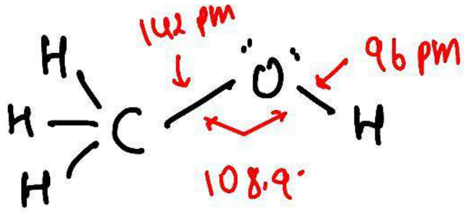


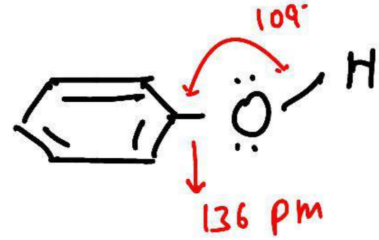
hydroquinone



p-hydroxybenzoic acid

• Structure of Alcohol and Phenol group:





Note

The C-O bond length in phenol is 136 pm which is less than alcohol due to

(i) In phenol, lone pair of oxygen is conjugation with π bond of aromating ring and acquire partial double bond character.

(ii) In phenol oxygen atom is attached to sp^2 hybridised carbon.

Preparation of Alcohols:

• **From Alkenes:** (By Hydration of Alkene)

$$CH_3-CH=CH_2 + H-O-H \xrightarrow{H^+} CH_3-\underset{}{\overset{OH}{|}}{CH}-CH_3$$

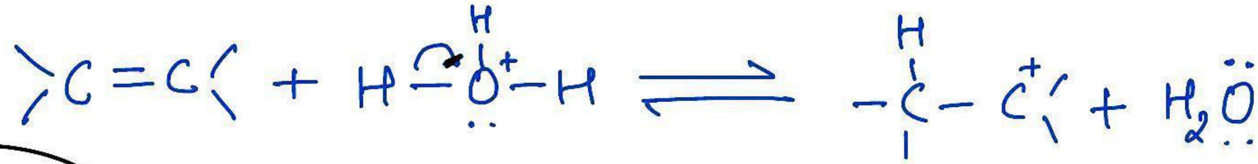
Propan-2-ol

when alkene react with water in the presence of acid catalysed, then alcohol is formed. On unsymmetrical alkene, when water molecule is added, then product is formed according to Markovnikov's Rule.

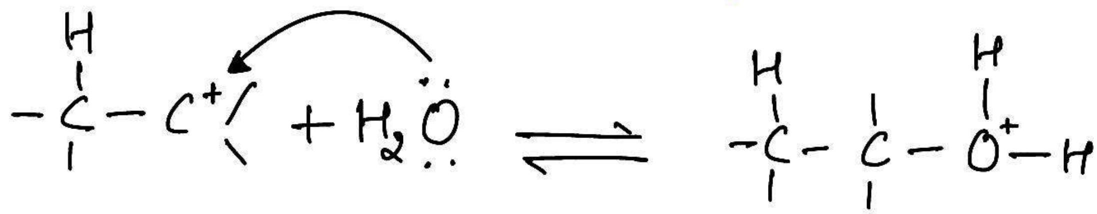
✲ Mechanism:

Step-1

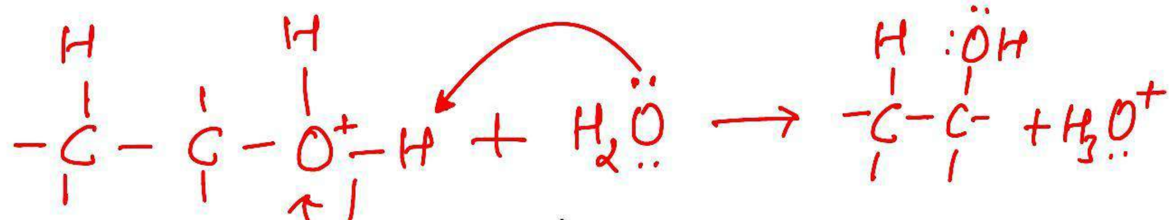
$$H_2O + H^+ \longrightarrow H_3O^+$$



Step 2:



Step 3:



• By Hydroboration- Oxidation:

$$3(CH_3-CH=CH_2) + \frac{1}{2}B_2H_6 \longrightarrow (CH_3-CH_2-CH_2)_3B$$

$$(CH_3-CH_2-CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3(CH_3-CH_2-CH_2-OH) + B(OH)_3$$

When alkene react with diborane (B_2H_6), then trialkyl borane is formed which gives alcohol by the oxidation of H_2O_2 in the presence of sodium hydroxide.

From Carbonyl Compound:

• By the reduction of aldehyde and ketones

Aldehydes and Ketones are reduced to the corresponding alcohols by hydrogen in the presence of reagent like Pt, Pd, Ni, $LiAlH_4$, $NaBH_4$ etc.

{In the presence of Pt/Pd we take H_2 & rest of these take 2H}

$$R-CHO + H_2 \xrightarrow{Pd} R-CH_2-OH \quad 1^\circ \text{ alcohol}$$

Aldehyde

$$R-\underset{\underset{O}{\parallel}}{C}-R + H_2 \xrightarrow{Pd} R-\underset{\underset{OH}{|}}{CH}-R \quad 2^\circ \text{ alcohol.}$$

• From the reduction of carboxylic acid & ester ⇒

$$\underset{\text{Carboxylic Acid}}{R-\underset{\underset{O}{\parallel}}{C}-OH} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Alcohol}}{R-CH_2-OH} + H_2O$$

$$\underset{\text{ester}}{R-\underset{\underset{O}{\parallel}}{C}\vdots O\cdot R'} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Alcohol}}{R-CH_2-OH} + R-OH$$

• From Grignard Reagent :

when grignard reagent react with aldehyde and ketone, then alcohol is formed.

$$>C=O + \overset{\delta-}{R}-\overset{\delta+}{Mg}-X \longrightarrow \underset{\text{Adduct}}{\left[>\underset{\underset{R}{|}}{C}-O^{-}\overset{+}{Mg}-X \right]} \xrightarrow{H_2O} >\underset{\underset{R}{|}}{C}-OH + Mg(OH)X$$

$$\underset{\text{formaldehyde}}{\begin{matrix}H\\H\end{matrix}>C=O} + R-Mg-X \longrightarrow H-\underset{\underset{R}{|}}{CH}-\underset{\underset{MgX}{|}}{O} \xrightarrow{H_2O} \underset{1^\circ\text{ alcohol}}{H-\underset{\underset{R}{|}}{CH}-OH} + Mg\begin{matrix}X\\OH\end{matrix}$$

$$\begin{matrix}R\\H\end{matrix}>C=O + R-MgX \longrightarrow R-\underset{\underset{R}{|}}{CH}-\underset{\underset{MgX}{|}}{O} \xrightarrow{H\cdot OH} \underset{2^\circ\text{ alcohol}}{R-\underset{\underset{R}{|}}{CH}-OH} + Mg\begin{matrix}X\\OH\end{matrix}$$

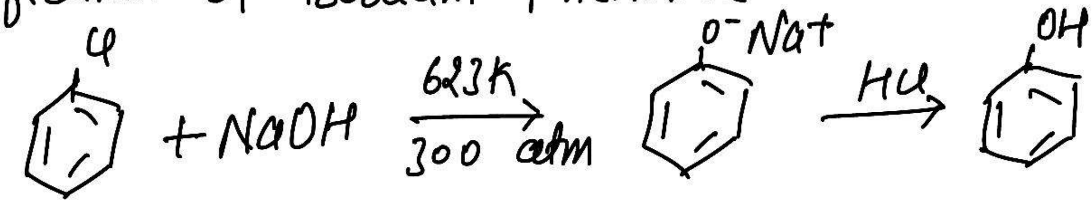
Ketones give 3° alcohol

$$\begin{matrix}R\\R\end{matrix}>C=O + R-MgX \longrightarrow \begin{matrix}R\\R\\R\end{matrix}-C-OMgX \xrightarrow{H\cdot OH} \underset{3^\circ\text{ alcohol}}{\begin{matrix}R\\R\\R\end{matrix}-C-OH} + Mg\begin{matrix}X\\OH\end{matrix}$$

Preparation of Phenol

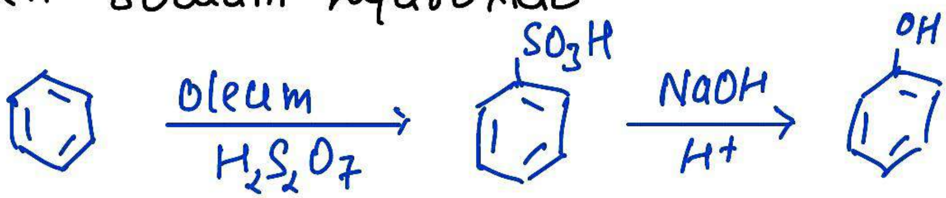
• From Haloarenes

Chlorobenzene is fused with NaOH at 623 K and 300 atm pressure. Phenol is obtained by acidification of sodium phenoxide



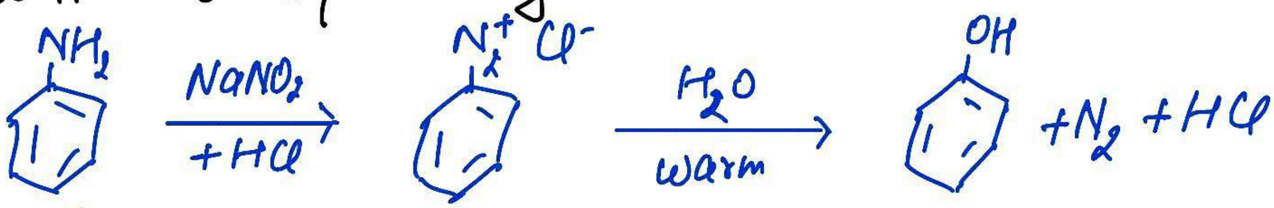
• From Benzene Sulphonic acid:

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide



• From Diazonium Salts:

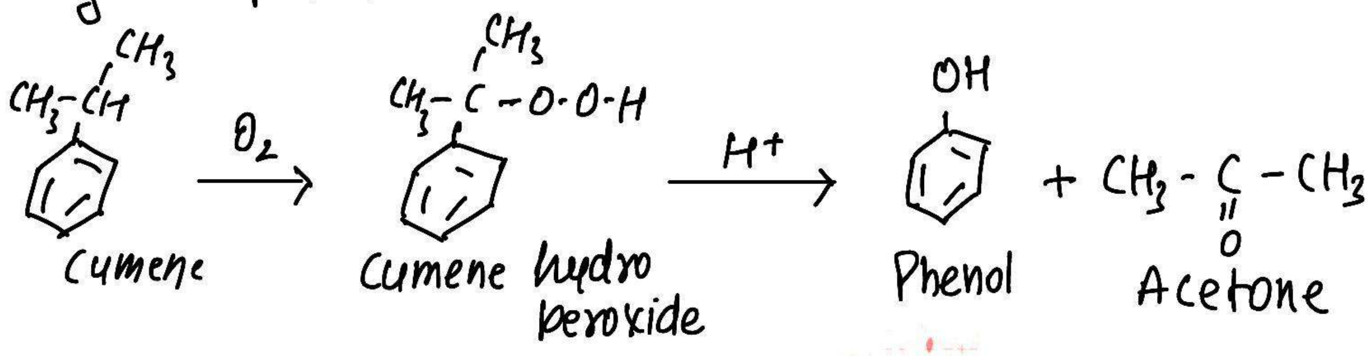
A diazonium salt is formed by treating an aromatic 1° amine with nitrous acid ($NaNO_2 + HCl$) at 273K - 278K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.



Aniline — Benzene diazonium Chloride — Phenol.

• From Cumene

In this method cumene is oxidised in the presence of air then cumene hydroperoxide is obtained. Now it react with dilute acid, gives phenol and acetone.



• Physical Properties

Boiling Point:

The b.pt of alcohols and phenols increase with increase in no. of carbon atoms (increase in van der waals forces)

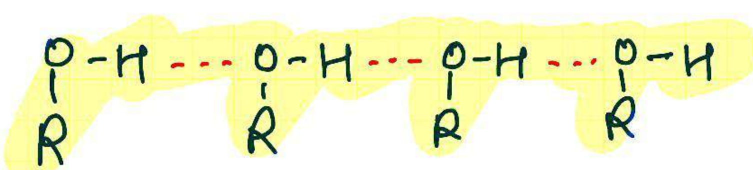
e.g Boiling Point of butanol is more than ethanol.

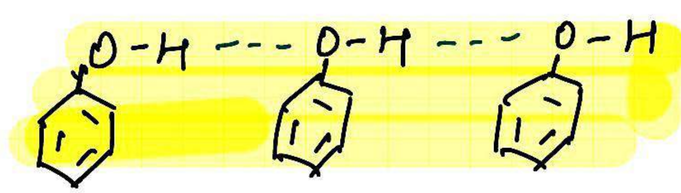
→ In isomeric alcohol, the B.Pt decreases with increase in branching. i.e B.Pt follows the order

$$1° \text{ alcohol} > 2° \text{ alcohol} > 3° \text{ alcohol}$$

[Because of decrease in van der waal forces with decrease in surface area]

→ The –OH group in Alcohols and phenols is involved in intermolecular Hydrogen Bonding.

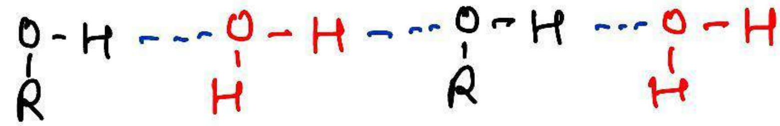




Solubility:

→ Solubility of alcohols and phenols in water is due to their ability to form Hydrogen Bonds with water molecules.

→ The solubility decreases with increase in size of alkyl / aryl (hydrophobic) groups.



Chemical Properties of Alcohols:

1. Rxn in which cleavage of -O÷H bond takes place
2. Rxn in which cleavage of -C÷OH bond takes place

Rxn in which cleavage of -O-H bond takes place

1° alcohol > 2° alcohol > 3° alcohol

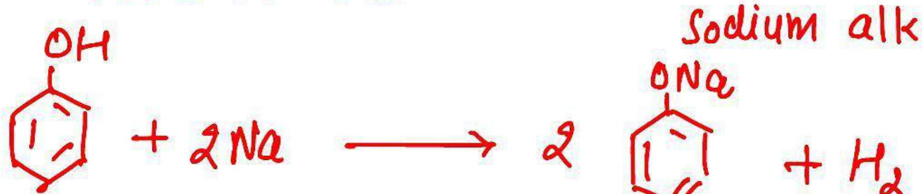
i) Acidic Nature of Alcohol and Phenol

a) Rxn with Metal

Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides / phenoxides and hydrogen.

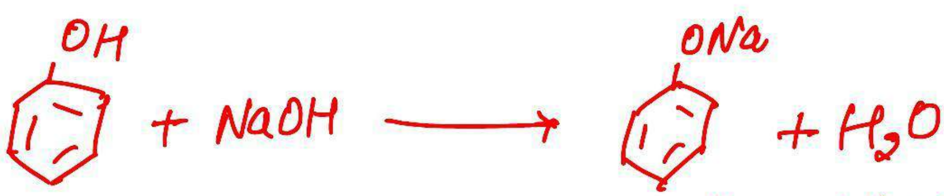
$$2\,R\text{-}O\text{-}H + 2Na \longrightarrow 2\,R\text{-}O\text{-}Na + H_2$$

Sodium alkoxide



Phenol

Sodium phenoxide



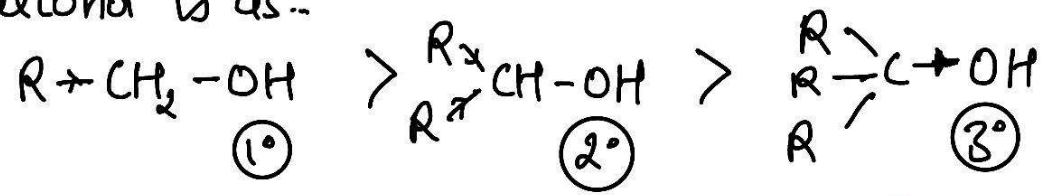
sodium phenoxide

b.) Acidity of Alcohol –

The acidic nature of alcohol is due to the polar nature of –OH bond.

- In alcohol an e⊖ releasing group ($-CH_3$, $-C_2H_5$) increase the e⊖ density on oxygen atom and decrease the polarity of –OH bond. Due to this the acidic strength of alcohol also decreases

Therefore the order of acidity of different alcohol is as..



Q. Why alcohols are weak acid than compare to water?

Ans: In alcohol, alkoxide ion is formed after removing H^+ ion and in water hydroxide ion is formed after removing H^+ ion.

But alkoxide ion is less stable than compare to OH^- ion due to the presence of more e⊖ density on oxygen atom. Therefore, alcohol act as weak acid than compare to water.

$$R-O \vdots H \longrightarrow R-O^- + H^+$$

Alkoxide ion (less stable)

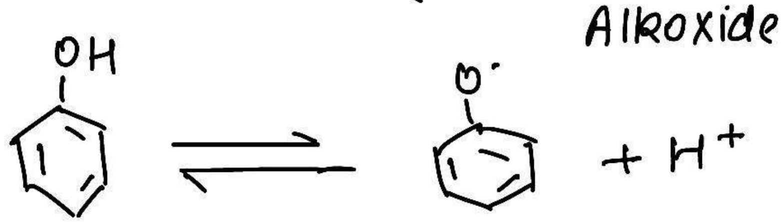
c) Acidity of Phenol :

Phenol is more acidic in nature than compare to alcohol.

Reason: The ionisation of alcohol and phenol takes place as -

$$R-OH \rightleftharpoons R-O^{\ominus} + H^+$$

Alkoxide ion



Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which -OH is attached, $e^{\ominus}$ density decreases on oxygen. This increase the polarity of OH bond and result in an increase in ionisation of phenols that that of alcohols.

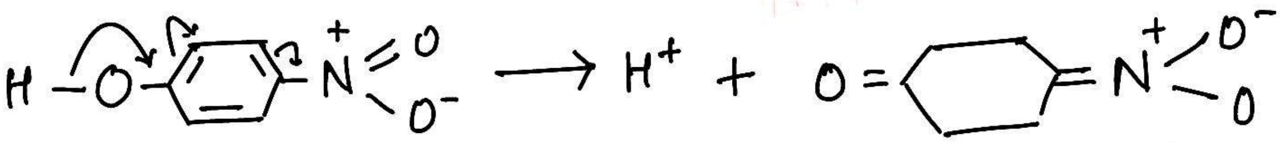
In alcohol, alkoxide ion is formed and in phenol, phenoxide ion after removing H^+ ion. Phenoxide ion is more stable due to resonance than compare to alkoxide ion.

Therefore phenol is more acidic than alcohol.

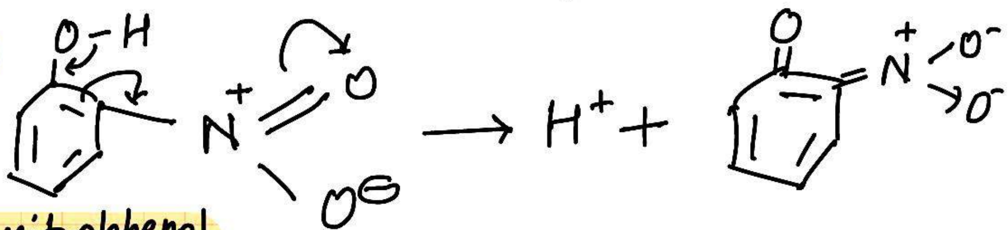
Q Explain the following observation -

o- and p- nitrophenols are more acidic than phenol.

Ans. NO_2 being an electron withdrawing group when present at ortho and para-positions withdraws $e^{\ominus}$ density from benzene ring thereby decreasing the $e^{\ominus}$ density of OH bond and thus make the release of proton easier.

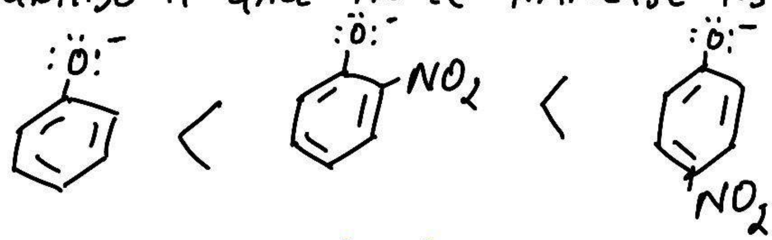


p-nitrophenol



o-nitrophenol

Also, the $-NO_2$ group intensifies the -ve charge of phenoxide ion and thus, stabilise it and hence increase its acidic strength as..



Hence ortho and para nitrophenol are more acidic than phenol.

Esterification of Alcohol –

Rxn with Carboxylic acid –

$$R-\underset{\underset{O}{\|}}{C}-OH + H-O-R \xrightleftharpoons{H^+} R-\underset{\underset{O}{\|}}{C}-O-R + H_2O$$

Acid   Alcohol

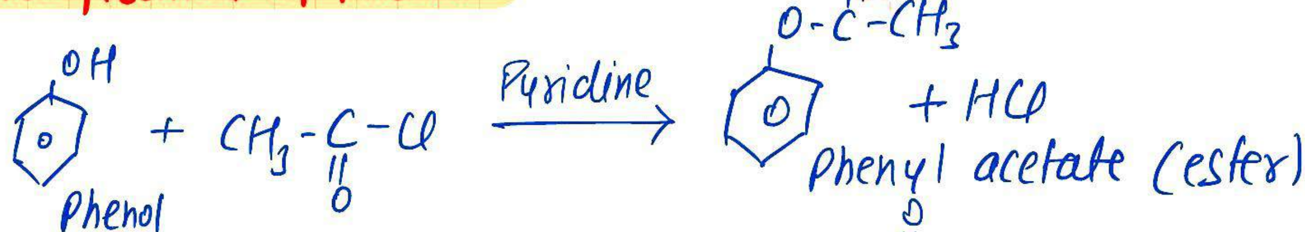
• Rxn with Acid Chloride –

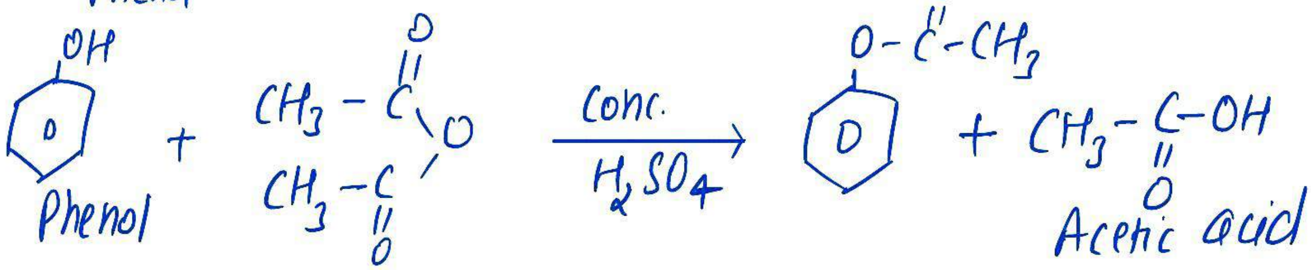
$$R-\underset{\underset{O}{\|}}{C}-Cl + H-O-R \xrightarrow{\text{Pyridine}} R-\underset{\underset{O}{\|}}{C}-OR + HCl$$

• Rxn with Acid Anhydride –

$$R-OH + (R-CO)_2O \xrightleftharpoons{H^+} R-\underset{\underset{O}{\|}}{C}-OR + R-\underset{\underset{O}{\|}}{C}-OH$$

• Esterification of Phenol –





Reaction in which cleavage of C-OH bond takes place:

In this type of reaction, alcohol behave as a electrophile

• Rxn with Hydrogen Halide

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$

mixture of $HCl + ZnCl_2$ ⟶ Lucas Reagent

e.g. $CH_3-CH_2-OH + HCl \xrightarrow{ZnCl_2} CH_3-CH_2-Cl$

Lucas Test:

1° alcohol

$CH_3-CH_2-OH \xrightarrow{HCl + ZnCl_2} CH_3-CH_2-Cl + H_2O$

Turbidity appears after heating

2° alcohol

$CH_3-CH(CH_3)-OH \xrightarrow{HCl + ZnCl_2} CH_3-CH(CH_3)-Cl + H_2O$

Turbidity appears after 5 min.

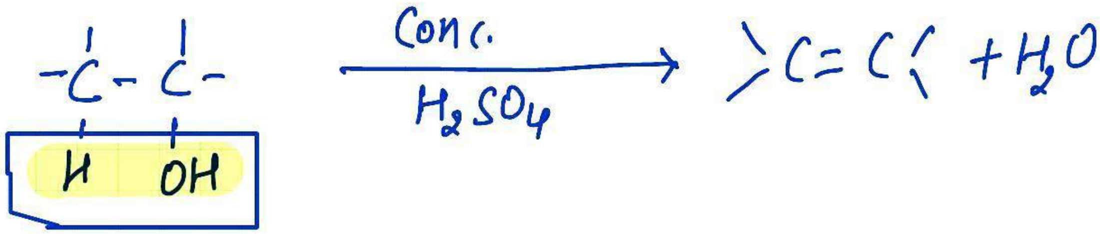
3° alcohol

$CH_3-C(CH_3)_2-OH \xrightarrow{HCl + ZnCl_2} CH_3-C(CH_3)_2-Cl + H_2O$

Turbidity appears immediately

Dehydration

Removing of water molecule from alcohol is called dehydration of alcohol. It is an elimination reaction in which conc. H_2SO_4, Phosphorous Pentaoxide (P_2O_5), Alumina (Al_2O_3) is used for dehydration and alkene is formed as product.



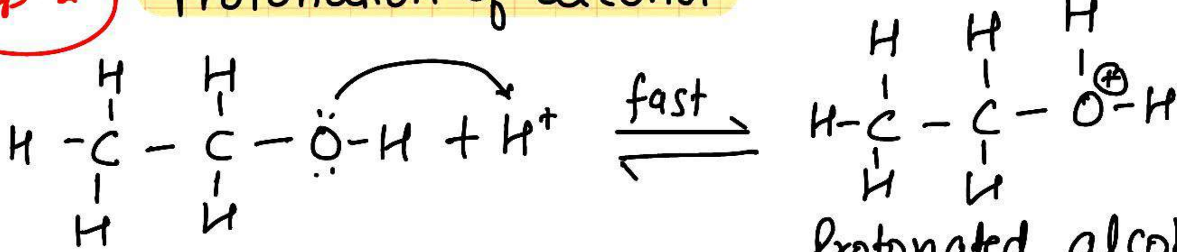
The order of reactivity of different alcohols

3° alcohol > 2° alcohol > 1° alcohol.

Mechanism of Dehydration of Ethanol:

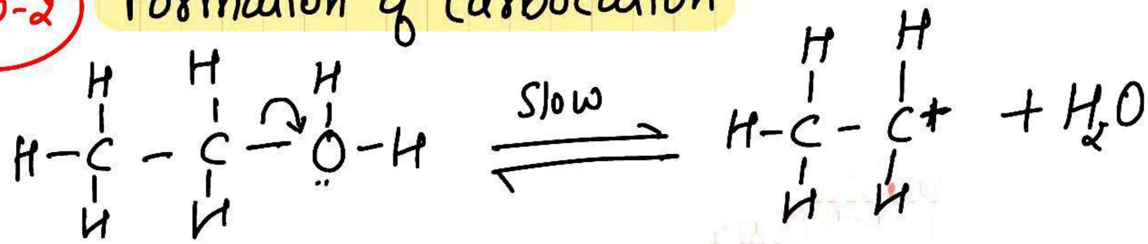
Dehydration of ethanol in the presence of conc H_2SO_4 involve the following steps:

Step-1 Protonation of alcohol

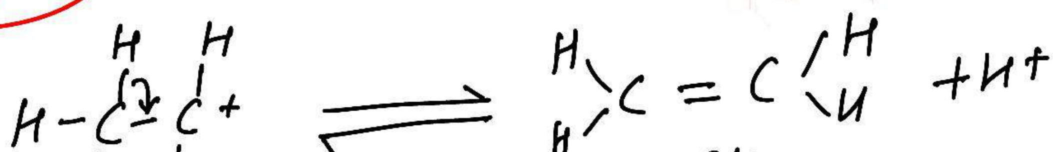


Protonated alcohol
(ethyl oxonium ion)

Step-2 Formation of Carbocation



Step-3 elimination of Proton



Ethene.

Oxidation-

oxidation of alcohol involve the formation of carbon-oxygen bond with cleavage of an 'O-H' bond and 'C-H' bond.

$$H-\underset{|}{\overset{|}{C}}-O-H \longrightarrow \; >C=O + H_2$$

➤ This process is also known as **dehydrogenation**

Primary Alcohol ⇒ It is oxidised into aldehyde which is further oxidised into an acid.

$$\underset{}{CH_3-CH_2-OH} \xrightarrow[-H_2O]{[O]} \underset{\text{Aldehyde}}{CH_3-CHO} \xrightarrow{[O]} \underset{\text{Acid.}}{CH_3-COOH}$$

Secondary Alcohol

It is oxidised into Ketone which is further oxidised into acid

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\! CH-OH + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7/H^+} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\! C=O \xrightarrow{3[O]} CH_3-COOH + HCOOH$$

Tertiary Alcohol

It is not oxidised in ordinary condition but in the presence of strong oxidising agent, a mixture of carboxylic acid is formed.

• Dehydrogenation:

$$CH_3-CH_2-OH \xrightarrow[\Delta]{Cu} CH_3-CHO + H_2$$

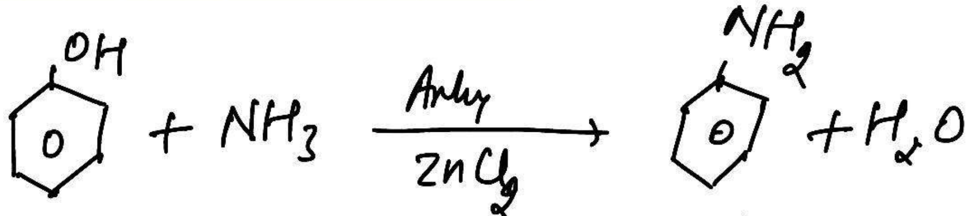
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\! CH-OH \xrightarrow[\Delta]{Cu} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\! C=O + H_2$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[\Delta]{Cu} CH_3-\overset{\overset{CH_2}{||}}{\underset{\underset{CH_3}{|}}{C}}$$

In case of 3° alcohol, dehydration takes place.

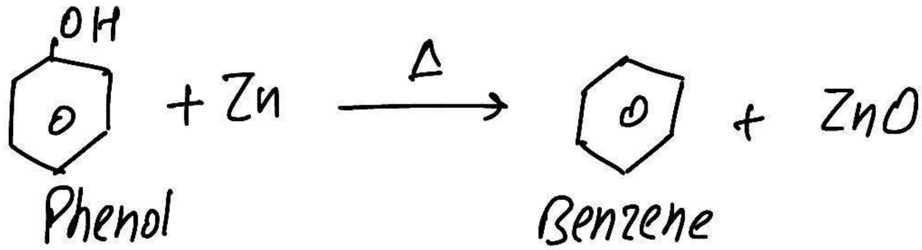
Rxn due to -OH group of phenol

• Rxn with Ammonia

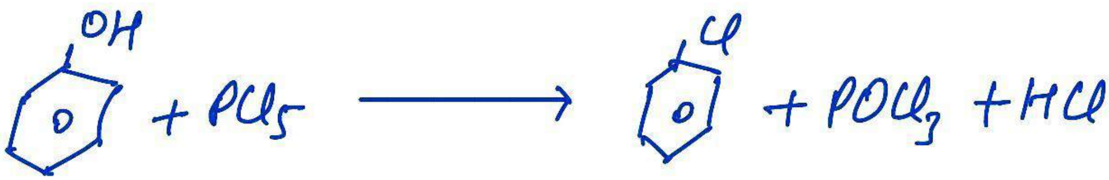


Aniline

- Rxn with Zinc Powder -

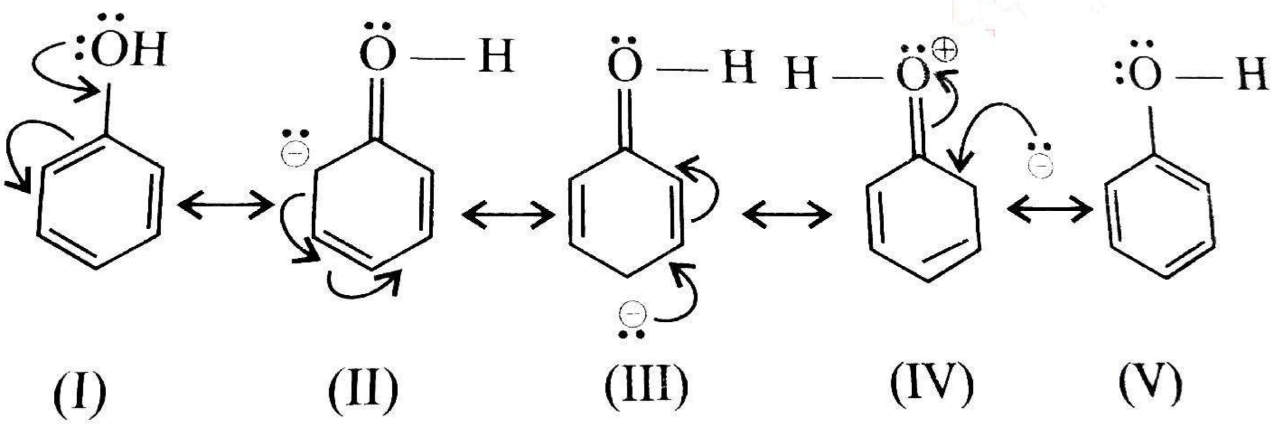


- Rxn with Phosphorous Pentachloride (PCl_5)



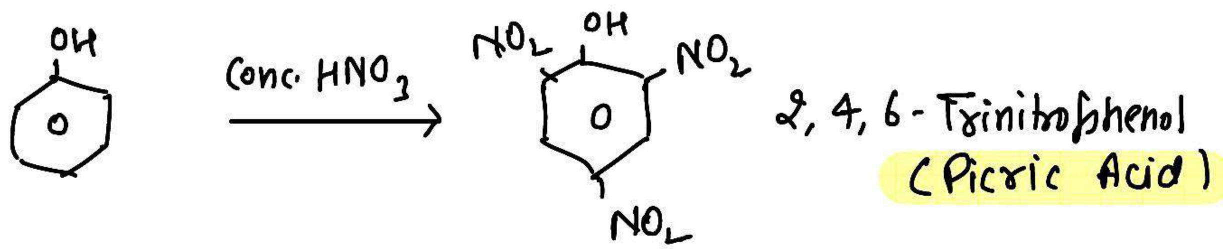
Rxn due to benzene ring of phenol

Resonance in phenol

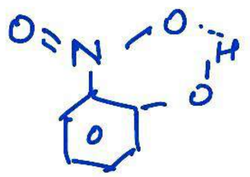


As a result of resonance, electrophilic substitution Rxn takes place at ortho and para position.

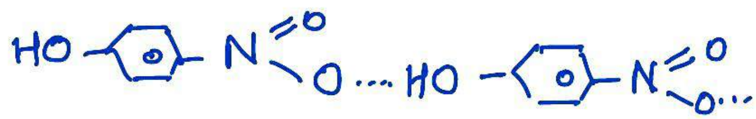
Nitration



Note The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular H-Bonding, while p-nitrophenol is less volatile due to inter molecular H-Bonding which causes the association of molecules



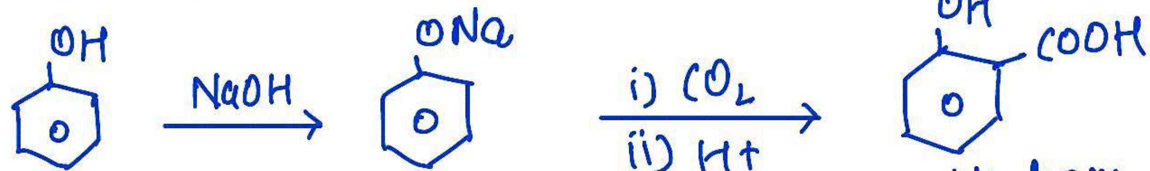
o-Nitrophenol
(intramolecular H-Bonding)



p-Nitrophenol
(intermolecular H-Bonding)

Kolbe's Reaction

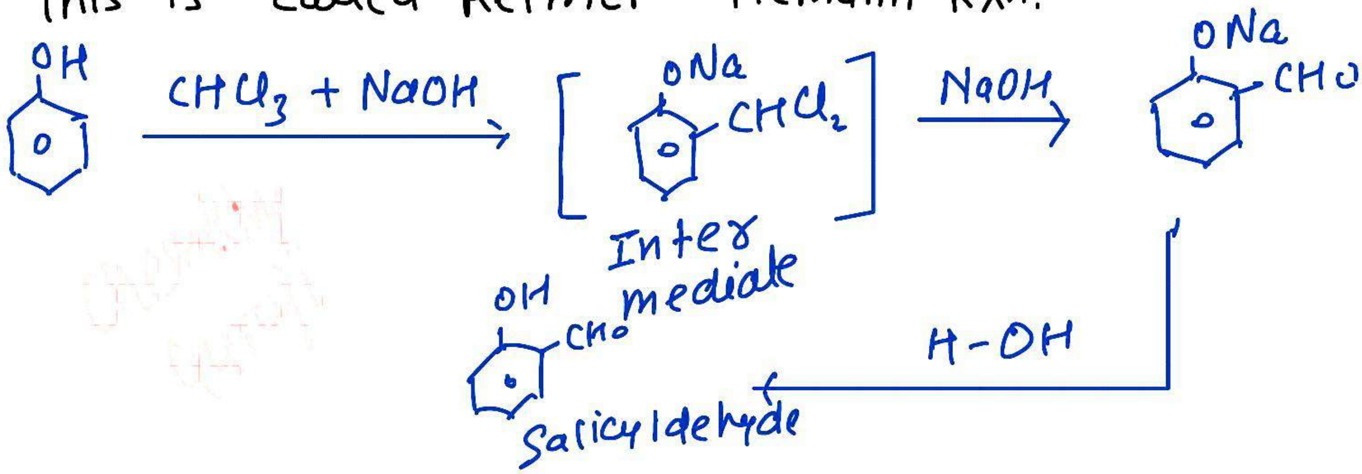
Phenoxide ion is more reactive than phenol towards electrophilic sub. reaction. Therefore when phenoxide ion react with CO_2, then salicylic acid is formed as a product. This reaction is called Kolbe's Reaction



Phenol → Sod. Phenoxide → 2-Hydroxy Benzoic acid (Salicylic Acid)

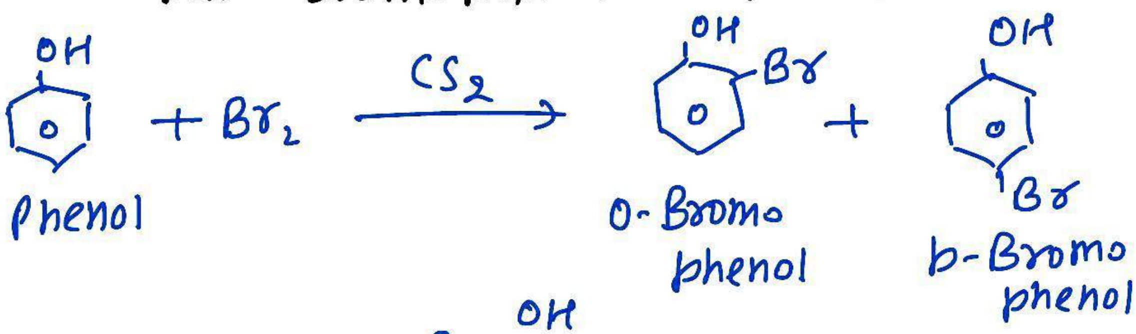
Reimer - Tiemann Rxn

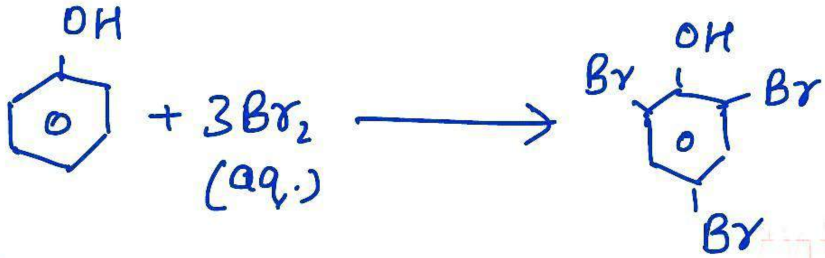
when phenol react with chloroform in the presence of sodium hydroxide then salicylaldehyde is formed as a product. This is called Reimer - Tiemann Rxn.



Halogenation

when phenol react with bromine in the presence of CS_2, $CHCl_3$ or CCl_4 at low temp, then ortho and para bromophenol is formed.

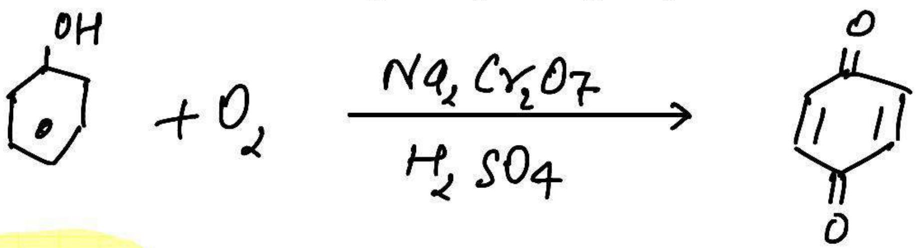




2,4,6 - Tribromo phenol.

Oxidation:

oxidation of phenol in the presence of air with chromic acid ($Na_2Cr_2O_7 + H_2SO_4$) form benzoquinone



Benzo quinone

Ethers (R-O-R)

- The general formula of ether is $C_nH_{2n+2}O$
- In ether two alkyl group are attached with the both side of oxygen atom R-O-R
- Ether is also known as Anhydride of Alcohol.

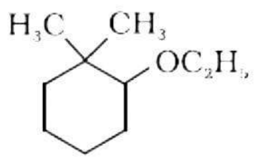
$$R-OH + HO-R \longrightarrow R-O-R + H_2O$$

Ether (Anhydride of Alcohol)

Types of Ethers

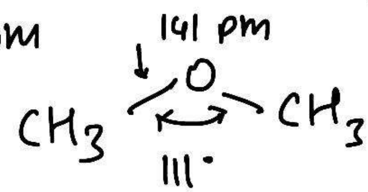
Simple ethers	Mixed Ethers
CH_3-O-CH_3, 	$C_2H_5-O-CH_3$, 

Common & IUPAC Name of Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O-CH(CH_3)-CH_3$	Methyl isopropyl ether	2-Methoxypropane
$C_6H_5-O-CH_2-CH_2-CH(CH_3)-CH_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

Structure of Ethers:

The bond angle b/w (C–O–C) is 111° due to rebulsion between alkyl groups, which are attached to oxygen atom



Preparation of Ethers

- By dehydration of alcohol

$$CH_3CH_2OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2$$

$$CH_3CH_2OH \xrightarrow[413K]{H_2SO_4} C_2H_5-O-C_2H_5$$

Mechanism

The formation of ether is S_N2 involving the attack of alcohol molecule on a protonated alcohol.

$$\text{(i)}\quad CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{+}{O}H_2$$

$$\text{(ii)}\quad CH_3CH_2-\ddot{O}H + CH_3-CH_2-\overset{+}{O}H_2 \longrightarrow CH_3-CH_2-\overset{+}{O}H-CH_2-CH_3 + H_2O$$

$$\text{(iii)}\quad CH_3-CH_2-\overset{+}{O}H-CH_2-CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$$

• Williamson Synthesis

when sodium or potassium alkoxide are heated with alkyl halide, then ether is formed. takes place by S_N2 mechanism

$$R-X + R'-O-Na \longrightarrow R-\ddot{O}-R' + NaX.$$

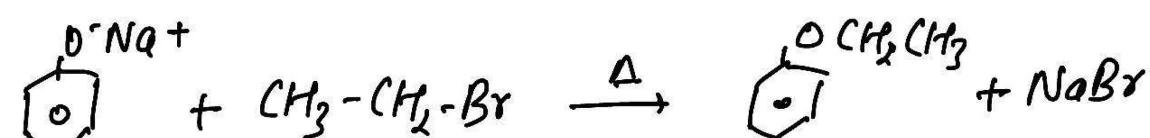
$$CH_3-C(CH_3)_2-\ddot{O}^-Na^+ + CH_3-Br \longrightarrow CH_3-\ddot{O}-C(CH_3)_2-CH_3 + NaBr$$

In case of 2° and 3° alkyl halides, elimination completes over substitution. If a 3° alkyl halide is used an alkene is the only reaction product and no ether is formed

$$CH_3-C(CH_3)_2-Br + Na^+-\ddot{O}-CH_3 \longrightarrow CH_3-C(CH_3)=CH_2 + NaBr + CH_3OH$$

2-Methyl propane

Phenols are also converted to ethers by this method.



Sod. Phenoxide — Ethoxy benzene

Physical Properties of Ethers

- Dimethyl ether and diethyl ether are gaseous and other ethers are liquid in nature.
- Ethers are lighter than water i.e density is less than water.
- Ethers are highly volatile in nature.
- **Solubility** ethers are partially soluble in water and are highly soluble in chloroform and Benzene.
- **Boiling Point** The b.pt of ether is very less than compare to isomeric alcohol because in ether intermolecular H- Bonding is not present.

  The b.pt of ether is similar to the molecular wt. of alkane.

Chemical Properties

i) **Hydrolysis**

$$C_2O_5-O-C_2H_5 + H_2O \xrightarrow[H_2SO_4\ \Delta]{Conc.} 2\,C_2H_5OH$$

ii) **Rxn with Halogen Acids:**

$$HI > HBr > HCl > HF$$

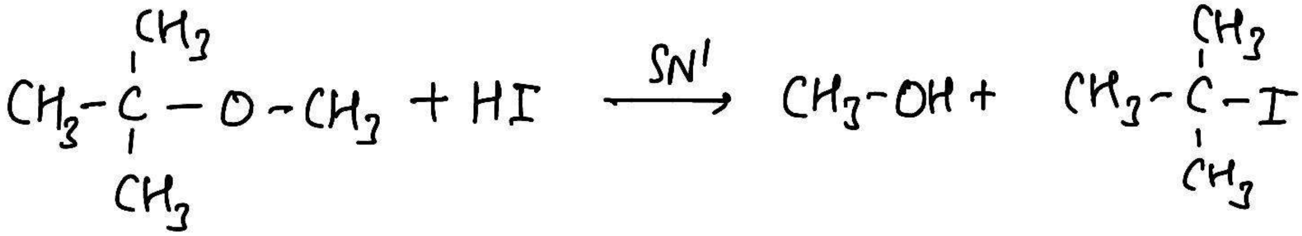
 # Reaction with HI: when ether react with HI in hot and cold medium, then different product is formed

$$C_2H_5-\overset{H-I}{\underset{I-H}{O}}-C_2H_5 \xrightarrow{Hot} 2\,C_2H_5-I + H_2O$$

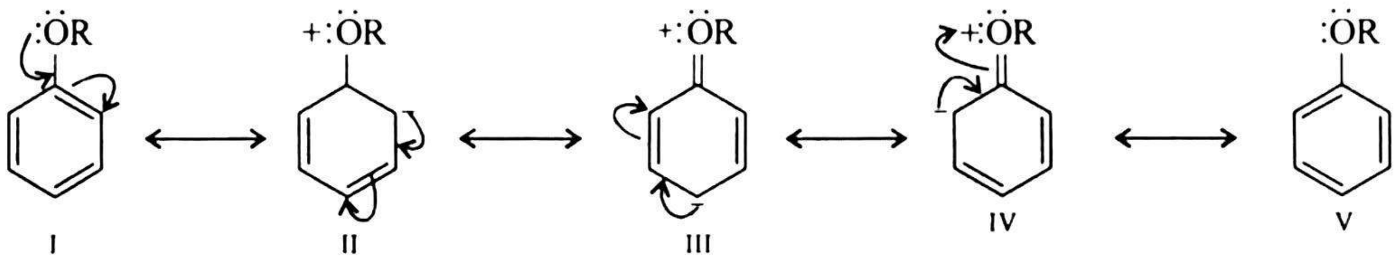
$$C_2H_5-O \div C_2H_5 \ (H \div I) \xrightarrow{Cold} \underset{\text{ethyl alcohol}}{C_2H_5-OH} + \underset{\text{ethyl iodide}}{C_2H_5-I}$$

Note

When one of the alkyl group is a tertiary group, the halide ion is formed is a tertiary halide.

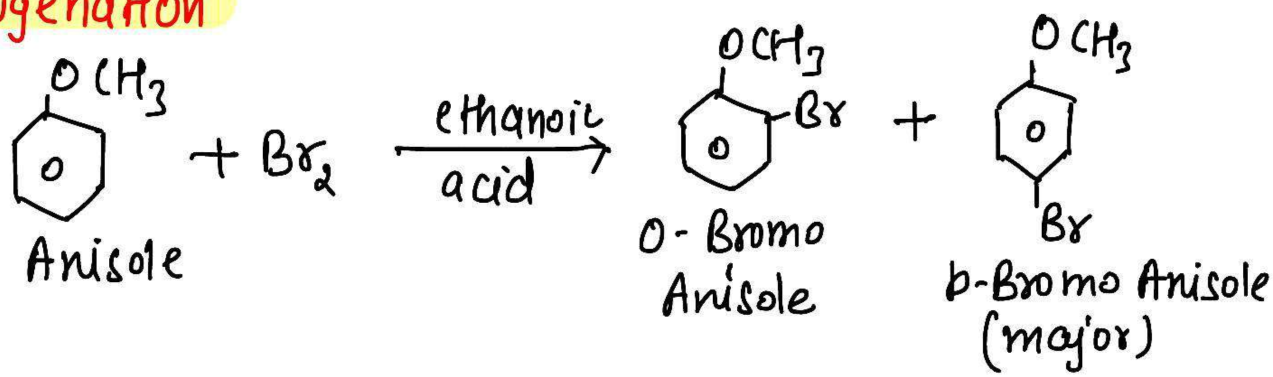


• Electrophilic Substitution Reaction

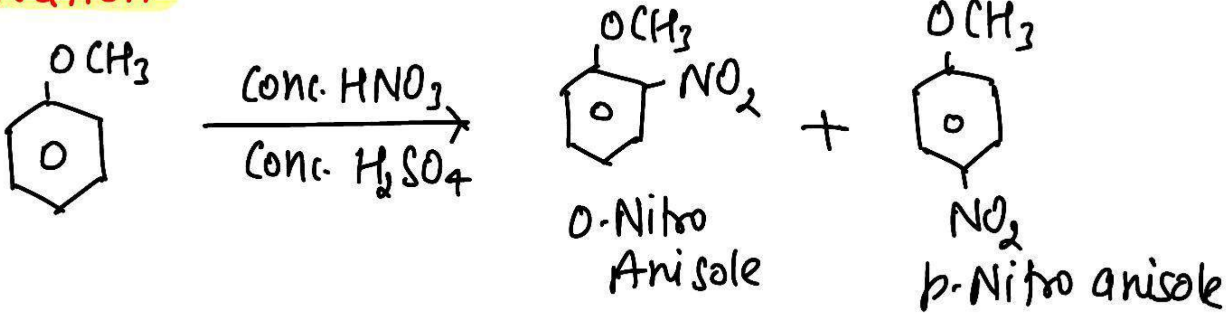


-OR group is ortho and para directing. Therefore electrophilic substitution takes place on ortho and para position of benzene ring.

Halogenation

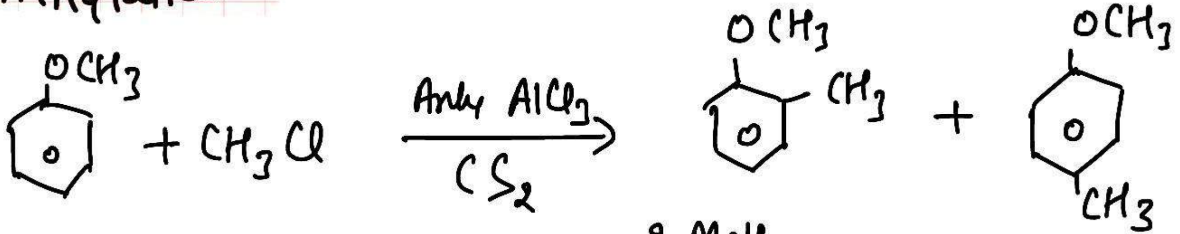


Nitration



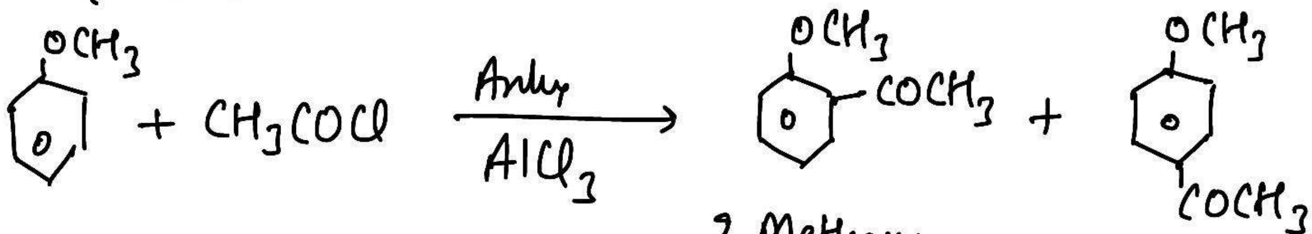
Friedal Craft Reaction

- Alkylation



2-Methoxy toluene (minor) 4-Methoxy toluene (major)

- Acylation



2-Methoxy acetophenone 4-Methoxy acetophenone

Denaturation of Alcohol

The commercial alcohol is made unfit for drinking by mixing it with some copper sulphate and methyl alcohol.

Power Alcohol-

Absolute alcohol mixed with petrol (roughly in the ratio 20: 80) is used in internal combustion engines. this is known as power alcohol. Mixing is done in presence of 1% benzene or 1% ether.

ALCOHOLMETRY -

The determination of the percentage of alcohol in a liquid, especially is alcohol is known as alcoholmetry.

SOME COMMERCIALLY IMPORTANT ALCOHOLS

1. Methanol, CH_3OH ↘ also known as wood spirit

Preparation

By catalytic hydrogenation of carbon mono oxide at high pressure and temp. in the presence of $ZnO-Cr_2O_3$ catalyst

$$CO + 2H_2 \xrightarrow[\substack{200-300\ atm \\ 573-673K}]{ZnO-Cr_2O_3} CH_3OH$$

Properties

- it is a colourless liquid and highly poisonous
- It is completely soluble in water.

Uses

- It is used as a solvent for paints.
- It is used for the manufacture of formaldehyde
- It is used as an antifreeze for automobile radiators.
- It is used for denaturing ethyl alcohol.

2. Ethanol (C_2H_5OH)

Ethanol is mainly obtained commercially by fermentation of sugar.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{zymase} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

Properties

Ethanol is a colourless liquid

The boiling point of ethanol is higher than methanol.

USES -

- as a solvent in paint industry
- it is used as an antiseptic in the form of rectified spirit.
- in the preparation of a no. of compounds such as ether, acetic acid, chloroform, iodoform etc.

FLOW CHART


Aldehydes Ketones & Carboxylic Acids
IUPAC Nomenclature
Ketone
Aldehyde
Preparation of Ketones and aldehyde
Physical Properties
B.P.
Solubility
Chemical Reactions
NAR
Reduction
Oxidation
Tollens Test
Fehling Test
Haloform Reaction
Aldol Reaction
Cannizzaro Reaction
ESR
Carboxylic Acid
IUPAC Nomenclature
Methods of preparation
Physical Properties
Acidic Nature
Chemical Reactions
Reactions involving
breaking of C–OH bond
–C(=O)–OH group
Reactions on hydrocarbon part

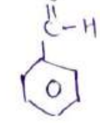
Aldehydes, Ketones and Carboxylic Acids

- Aldehydes: $H-\overset{O}{\overset{\|}{C}}-H$ | $R-\overset{O}{\overset{\|}{C}}-H$
- Ketones: $R-\overset{O}{\overset{\|}{C}}-R'$
- Carboxylic Acids: $R-\overset{O}{\overset{\|}{C}}-OH$

→ Nomenclature of carbonyl group —:

Important common names —:

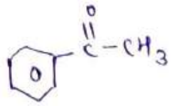
$CH_3-\overset{O}{\overset{\|}{C}}-H$ Acetaldehyde


Benzaldehyde

$\underset{\gamma}{CH_3}-\underset{\beta}{\overset{Br}{\overset{|}{CH}}}-\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H$

β-Bromobutyraldehyde

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ Acetone


Acetophenone


Benzophenone

IUPAC Name

→ For aliphatic aldehydes | ketones : Alkane − e + al / one → Alkanal → Alkanone

→ In case of aldehydes —: The longest carbon chain is numbered starting from the carbon of aldehyde group.

→ In case of Ketones —: Numbering begins from the end nearer to carbonyl group

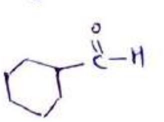
Example —: $\underset{2}{CH_3}-\underset{1}{\overset{O}{\overset{\|}{C}}}-H$: Ethanal ; $\underset{3}{CH_3}-\underset{2}{\overset{O}{\overset{\|}{C}}}-\underset{1}{CH_3}$: Propanone

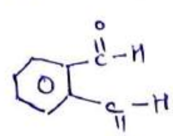
$\overset{7}{C}H_3-\overset{6}{C}H_2-\overset{5}{C}H_2-\overset{4}{C}H(Br)-\overset{3}{C}H(CH_3)-\overset{2}{C}H_2-\overset{1}{\overset{O}{\overset{\|}{C}}}-H$: 4-Bromo-3-methyl heptanal

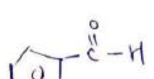
$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{\overset{O}{\overset{\|}{C}}}-H$: Pent-2-enal [2012 CBSE] (1M)

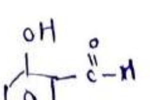
$\underset{1}{CH_3}-\underset{2}{\overset{CH_3}{\overset{|}{CH}}}-\underset{3}{\overset{O}{\overset{\|}{C}}}-\underset{4}{CH}(CH_3)-\underset{5}{CH_3}$ → 2,4-Dimethylpentan-3-one.

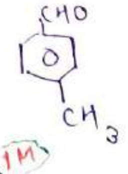
→ When aldehyde group is attached to cyclic ring, then special suffix is used —: [Carbaldehyde]


: Cyclohexanecarbaldehyde ;


→ Benzene-1,2-dicarbaldehyde


: Benzene Carbaldehyde [Benzaldehyde]


→ 2-Hydroxy benzene carbaldehyde [2014]

→  4 - Methylbenzenecarbaldehyde / (p - Methylbenzenecarbaldehyde) or 4 - Methylbenzaldehyde

[Delhi 2013 2014] (1M)

→ 3-Methylbutanal $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CHO$

Delhi 2013 / 2011 (1M)

→ $\overset{5}{CH_3}-\overset{4}{\underset{Cl}{\underset{|}{CH}}}-\underset{3}{CH_2}-\underset{2}{\overset{O}{\overset{||}{C}}}-\underset{1}{CH_3}$

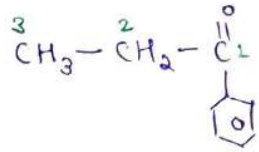
4 - Chloropentan - 2 - one

[2008 / 2011] (1M)

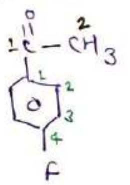
→ $\underset{1}{CH_3}-\underset{2}{\overset{O}{\overset{||}{C}}}-\underset{3}{CH}=\underset{4}{C}\langle^{CH_3}_{\underset{5}{CH_3}}$: 4 - Methylpent - 3 - en - 2 - one

[Delhi 2011 C] (1M)

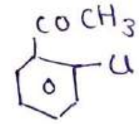
→ Benzene as substituent -: Phenyl

 : 1 - Phenylpropan -1- one

[Delhi 2011 / 2010]

 -: 4 - Fluorophenylethanone

[Delhi 2010] (1M)

 -: 2 - Chlorophenylethanone

(1M) [CBSE 2010]

→ Senior functional group makes 2° suffix and junior makes 2° prefix (substituent)

$\underset{5}{H_3C}-\underset{4}{CH_2}-\underset{3}{\overset{O}{\overset{||}{C}}}-\underset{2}{CH_2}-\underset{1}{\overset{O}{\overset{||}{C}}}-H$: 3 - Oxopentanal [Seniority : $-\overset{O}{\overset{||}{C}}-H > -\overset{O}{\overset{||}{C}}-$]

$\underset{4}{H_3C}-\underset{3}{\underset{OH}{\underset{|}{HC}}}-\underset{2}{H_2C}-\underset{1}{\overset{O}{\overset{||}{C}}}-H$: 3 - Hydroxybutanal [Seniority : $-\overset{O}{\overset{||}{C}}-H > -OH$]

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$: 4 - Hydroxypentan - 2 - one [Seniority : ketone > Alcohol]

(1M) [CBSE 2014]

Preparation of aldehydes and ketones

(1.) Oxidation of alcohols -:

$R-CH_2-OH \xrightarrow{CrO_3} R-\overset{O}{\overset{||}{C}}-H$

$R-\underset{R}{\underset{|}{CH}}-OH \xrightarrow{CrO_3} R-\overset{O}{\overset{||}{C}}-R$

(2.) Dehydrogenation of alcohols -:

$R-CH_2-OH \xrightarrow{Cu / 300^{\circ}C} R-\overset{O}{\overset{||}{C}}-H$

$R-\underset{R}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH \xrightarrow[300^{\circ}C]{Cu} R-\overset{O}{\overset{||}{C}}-R$

3.) Ozonolysis of alkene :-

$$R-CH=CH-R \xrightarrow[\text{(2) } Zn/H_2O]{\text{(1) } O_3} 2\ R-\overset{O}{\overset{\|}{C}}-H$$

$$R-\underset{R}{\underset{|}{C}}=C\begin{smallmatrix}R\\R\end{smallmatrix} \xrightarrow[\text{2) } Zn/H_2O]{\text{1) } O_3} 2\ R-\overset{O}{\overset{\|}{C}}-R$$

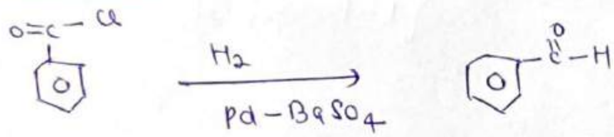
4.) Hydration of alkyne :-

$$CH\equiv CH \xrightarrow[H_2SO_4(aq.)]{HgSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2SO_4]{HgSO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

Preparation of Aldehydes

→ (i) Rosenmund reduction of acid chloride :-



(ii) Stephen's Reduction :-

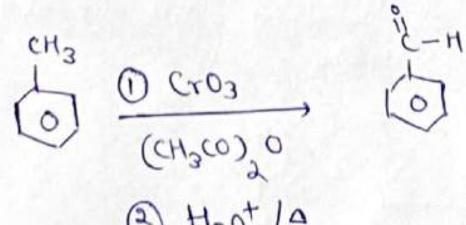
$$R-C\equiv N \xrightarrow{SnCl_2 + HCl} R-CH=NH \xrightarrow{H_3O^+} R-\overset{O}{\overset{\|}{C}}-H$$

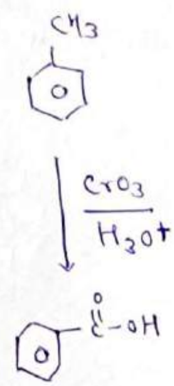
→ (iii) By DIBAL-H -:

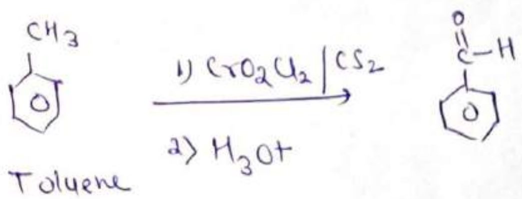
a.) $$R-C\equiv N \xrightarrow[\text{2) } H_2O]{\text{1) } AlH(iBu)_2} R-\overset{O}{\overset{\|}{C}}-H$$

b.) $$C_2H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\text{ii) } H_2O]{\text{i) } AlH(iBu)_2} C_2H_5-\overset{O}{\overset{\|}{C}}-H$$

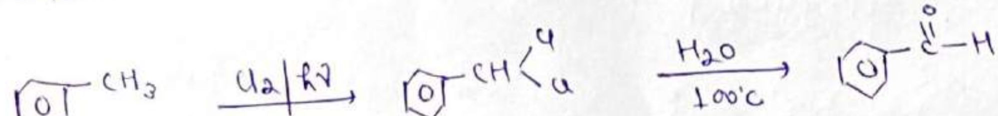
iv) From Hydrocarbon -:



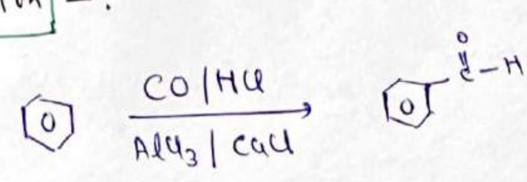


→ 

: Etard Reaction (Delhi 2017) → (1M)

→ 

Gattermann - Koch Reaction -:



Preparation of Ketones

→ (i) From acyl chlorides –:

$$R'-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\Downarrow\; R^{\ominus}]{R_2Cd} R'-\overset{O}{\overset{\|}{C}}-R$$

$$\rightarrow 2RMgBr + CdCl_2 \longrightarrow R_2Cd + 2Mg\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

$$\rightarrow CH_3MgBr + CdCl_2 \longrightarrow (CH_3)_2Cd \xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-Cl} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

(ii) From Nitrile –:

$$CH_3-CH_2-C\equiv N + C_6H_5MgBr \xrightarrow{ether} CH_3-CH_2-\underset{C_6H_5}{C}=N^{\ominus}\overset{\oplus}{Mg}Br$$

$C_6H_5MgBr \Downarrow C_6H_5^{\ominus}\ \overset{\oplus}{Mg}Br$

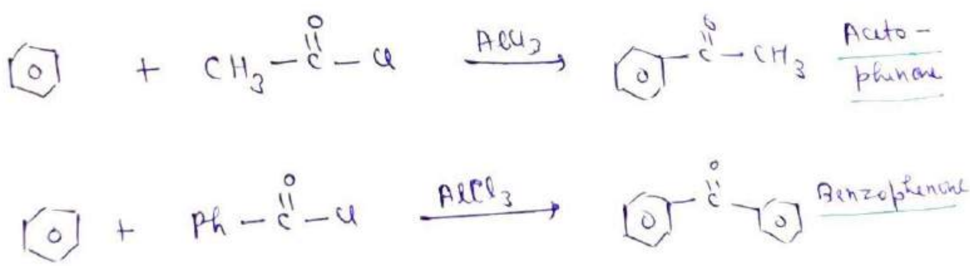
$\downarrow H_3O^+$

[1-Phenylpropanone] $C_2H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$

(iii) From Benzene :–

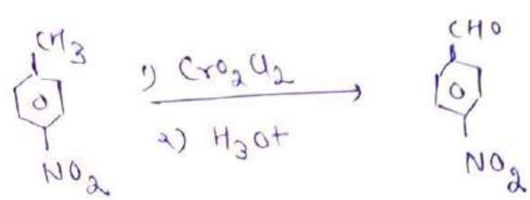
⇓

Friedel-Crafts Acylation reaction



(1M) [Delhi 2012]

$$\# \quad CH_3-C\equiv C-H \xrightarrow[H_2SO_4]{Hg^{2+}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$



→ [Delhi 2012]

Physical properties

→ **Boiling Point** –: The boiling points of aldehydes and ketones are higher than hydrocarbons and ether of comparable molecular mass. It is due to dipole dipole interaction.

B.P. : $CH_3-CH_2-CH_2-\overset{O^{-\delta}}{\overset{\|}{C}}{}^{+\delta}-H > CH_3-CH_2-CH_2-CH_2-CH_3$

$> CH_3-CH_2-O-CH_2-CH_3$

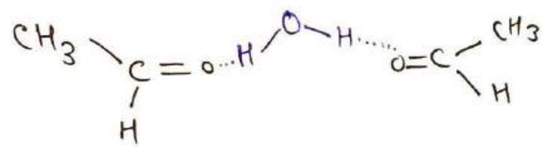
→ Boiling points of aldehydes and ketones are lower than those of alcohol of similar molecular masses due to absence of hydrogen bonding.

B.P. : $CH_3-CH_2-CH_2-CH_2-OH$ > $CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-H$

(Hydrogen Bonding) (Dipole - Dipole interaction)

Solubility → solubility of aldehydes and ketones decreases ⇒ size of alkyl group ↑es.

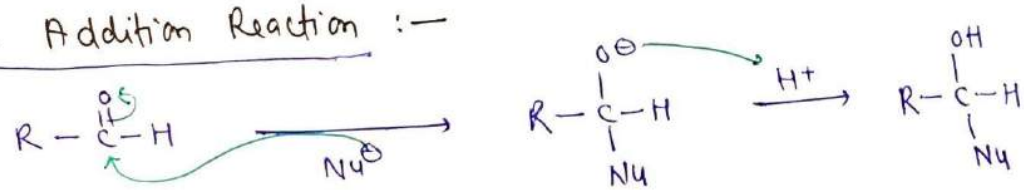
→ Methanal | Ethanal | propanone are miscible with water because they form hydrogen bond with water.



Chemical Reactions

Nucleophilic Addition Reaction :—

Reaction :—



Aldehyde : Planar — Tetrahedral intermediate — Addition Product

Reactivity :→ Aldehydes > ketones

$R\rightarrow\overset{O}{\overset{||}{C}}-H$ > $R\rightarrow\overset{O}{\overset{||}{C}}\leftarrow R$

↳ Electrophilicity decreases means that partial ⊕ve charge decreases.

→ As size of alkyl group ↑es, approach of Nucleophile to carbonyl carbon ↓es.

→ Reactivity order : $H-\overset{O}{\overset{||}{C}}-H$ > $CH_3-\overset{O}{\overset{||}{C}}-H$ > Acetone

: Acetaldehyde > Acetone > Methyl t-butyl ketone

: $CH_3-\overset{O}{\overset{||}{C}}-H$ > $CH_3-\overset{O}{\overset{||}{C}}-CH_3$ > $CH_3-\overset{O}{\overset{||}{C}}-C(CH_3)_3$

(1M) [CBSE 2012]

→ $C_6H_5-\overset{O}{\overset{||}{C}}-CH_3$ < $CH_3-\overset{O}{\overset{||}{C}}-CH_3$ < $CH_3-\overset{O}{\overset{||}{C}}-H$

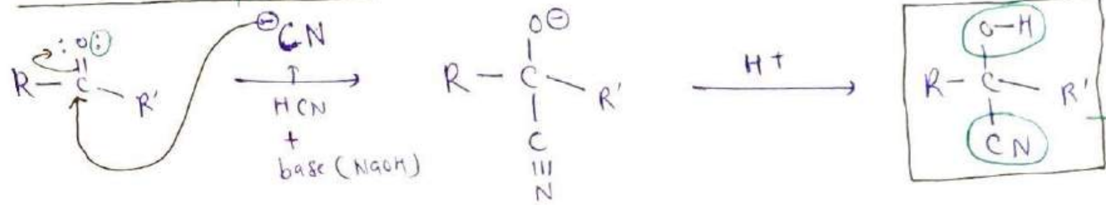
[1M] ← [Delhi 2015]

→ Reactivity for NAR :-

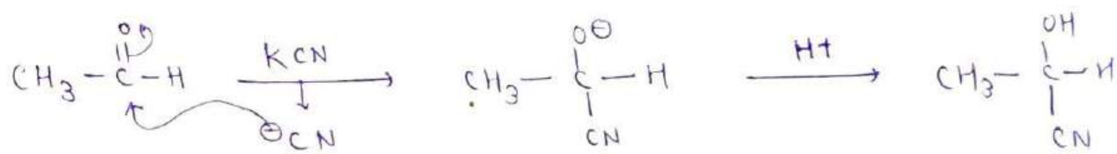
Because polarity of carbonyl group is reduced in benzaldehyde due to resonance.

Partial ⊕ve charge less → Electrophilicity less

⇒ Addition of HCN -:



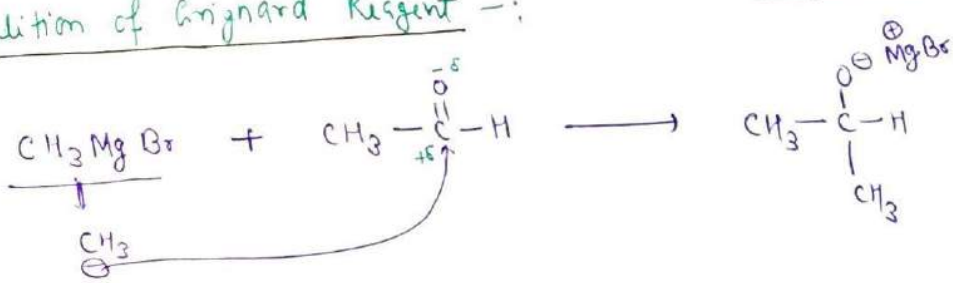
Cyanohydrin



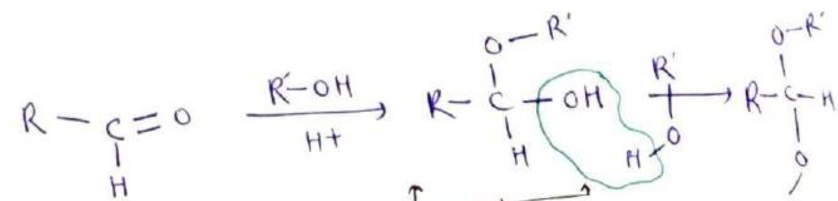
⇒ Addition of sodium hydrogen sulphite :- [$NaHSO_3$]

Crystalline ← [Addition Product]

⇒ Addition of Grignard Reagent -:

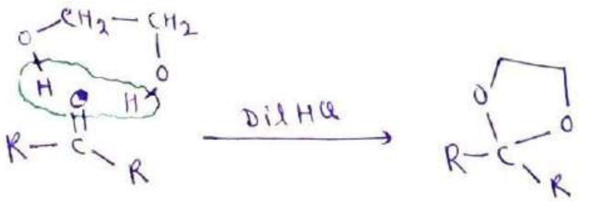


⇒ Addition of alcohols -:

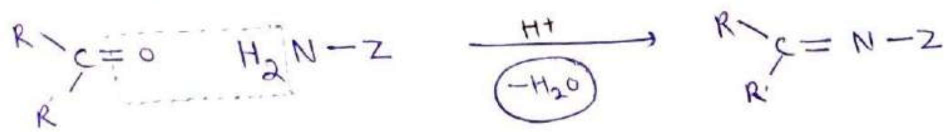


Hemiacetal

Acetal



⇒ Addition of Ammonia and its derivatives :-



$\rightarrow$ $R'R'C=O + H_2N-H \longrightarrow RR'C=NH$ — Imine

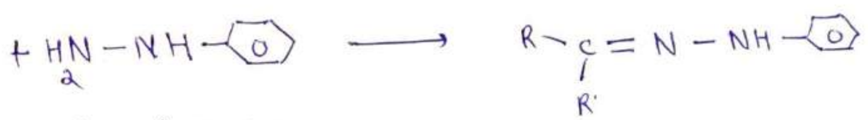
$+ H_2N-R \longrightarrow RR'C=N-R$ — Substituted imine

$+ H_2N-OH \longrightarrow RR'C=N-OH$ — Oxime

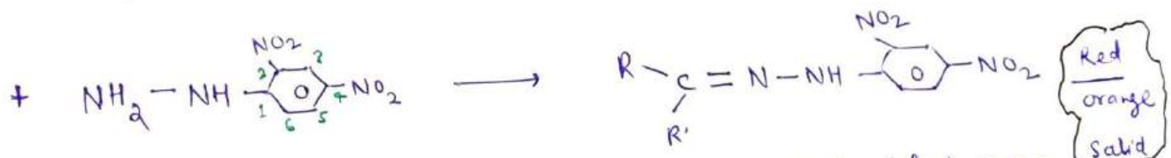
Hydroxylamine

$+ H_2N-NH_2 \longrightarrow RR'C=N-NH_2$ — Hydrazone

Hydrazine



Phenylhydrazine



2,4 - Dinitrophenyl hydrazine

2,4 - Dinitrophenyl hydrazone

$+ NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow RR'C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$

Semicarbazide

Semicarbazone

Reduction :-

(i) Reduction to alcohols -:

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[2)\ H_2O]{1)\ NaBH_4} R-CH_2-OH$$

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[2)\ H_2O]{1)\ NaBH_4\ |\ LiAlH_4} R-\underset{R}{\underset{|}{C}}H-OH$$

(ii) Reduction to hydrocarbons -:

a.) Clemmensen Reduction :-

$$RR'C=O \xrightarrow[HCl]{Zn-Hg} R-CH_2-R'$$

[Delhi 2017] → [1M]

b.) Wolff - Kishner Reduction :-

$$RR'C=O \xrightarrow{H_2N-NH_2} RR'C=N-NH_2 \xrightarrow[\Delta]{KOH} RR'CH_2 + N_2$$

[Delhi 2016 | 2017 | 2010] → [1M]

Oxidation :- Aldehyde $[R-\overset{O}{\overset{\|}{C}}-H]$ $\xrightarrow[\downarrow]{\text{oxidising agent}}$ $R-\overset{O}{\overset{\|}{C}}-OH$

→ HNO_3 | $KMnO_4$ | $K_2Cr_2O_7$

→ Tollen's Reagent

→ Fehling Reagent

$R-\overset{O}{\overset{\|}{C}}-R$

$\not\downarrow$ T.R. | F.R

$R-\overset{O}{\overset{\|}{C}}-OH$

→ **Tollen's Test -:** Tollen's Reagent → $NH_4OH + AgNO_3 \longrightarrow [Ag(NH_3)_2]^+$

$$\underset{\text{Alkyl / Aryl}}{(R)}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[Ag(NH_3)_2]^+} R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H_2O + NH_3$$

↓ Reduction: (Ag) → Silver Mirror

oxidation

: [Delhi 2010] → (1M)

→ Above reaction is not possible with ketone. By using above reagent aldehyde and ketone can be identified.

Fehling's Test -: Two parts
- → Solution A : $CuSO_4$ (aq.)
- → Solution B : Sodium Potassium Tartarate (Rochelle Salt)

oxidation

$$\underset{\text{Alkyl group}}{(R)}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{Solution A + Sol}^n \text{ B}} R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Cu_2O\downarrow$$

⇓ (Cu^{+2}) — Reduction → (Here Cu^{+})

(Red - brown)

→ $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[Cu^{+}]{Cu^{+2}} CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

$C_6H_5-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\quad\times\quad}$

→ **Haloform Reaction :-** (oxidation of methyl ketone) Reagent -: $\frac{NaOH + X_2}{NaOX}$ (X = Cl | Br | I)

→ $CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5 \xrightarrow{NaOI} \overset{\oplus}{Na}\,\overset{\ominus}{O}-\overset{O}{\overset{\|}{C}}-C_2H_5 + CHI_3\downarrow$ (Yellow ppt)

→ $\xrightarrow{NaOCl} C_2H_5-\overset{O}{\overset{\|}{C}}-O^{\ominus}\,\overset{\oplus}{Na} + CHCl_3$

$\xrightarrow{NaOBr} C_2H_5-\overset{O}{\overset{\|}{C}}-O^{\ominus}\,Na^{+} + CHBr_3$

→ $CH_3-CH(OH)-C_2H_5 \xrightarrow{NaOX} (CH_3-C(=O))-C_2H_5 \longrightarrow \overset{\ominus}{O}-C(=O)-C_2H_5\ \overset{\oplus}{Na} + CHX_3$

→ $C_6H_5-C(=O)-CH_3 \xrightarrow[I_2]{NaOH} C_6H_5-C(=O)-O^{\ominus}Na^{\oplus} + CHI_3\downarrow$

Aldol Reaction / Aldol Condensation

→ Reaction :— $2\,CH_3-C(=O)-H \underset{}{\overset{Dil\,NaOH}{\rightleftharpoons}} \overset{4}{C}H_3-\overset{3}{C}H(OH)-\overset{2}{C}H_2-\overset{1}{C}(=O)-H \xrightarrow{\Delta} CH_3-CH^{\beta}=CH^{\alpha}-CH=O$

(α- Carbon; γ, β, α labels)

β- Hydroxyaldehyde

α, β -unsaturated aldehyde.

→ $CH_3-CH=O + H_2CH-C(=O)-H \xrightarrow[2)\ \Delta]{1)\ Dil\,NaOH} CH_3-CH=CH-C(=O)-H$

→ Aldehyde $\xrightarrow{Dil\,NaOH}$ β-Hydroxyaldehyde : Aldol Reaction

Aldehyde $\xrightarrow[②\ \Delta]{①\ Dil\,NaOH}$ α-β-unsaturated aldehyde : Aldol condensation

→ $2\,CH_3-C(=O)-CH_3 \underset{}{\overset{Ba(OH)_2}{\rightleftharpoons}} \overset{5}{C}H_3-\overset{4}{C}(OH)(CH_3)-\overset{3}{C}H_2-\overset{2}{C}(=O)-\overset{1}{C}H_3 \xrightarrow{\Delta} (CH_3)_2\overset{4}{C}=\overset{3}{C}H-\overset{2}{C}(=O)-\overset{1}{C}H_3$

4-Hydroxy-4-methylpentan-2-one

4-methylpent-3-en-2-one

[Delhi 2012] → [1M]

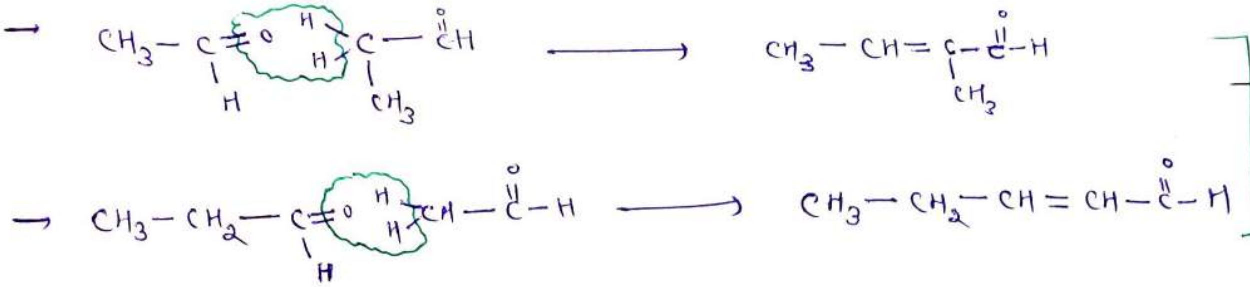
⇒ **Cross Aldol Condensation** :— Aldol reaction between two different aldehyde or ketones.

→ $CH_3-C(=O)-H + CH_3-CH_2-C(=O)-H \xrightarrow[2)\ \Delta]{1)\ NaOH}$ How many products are possible?

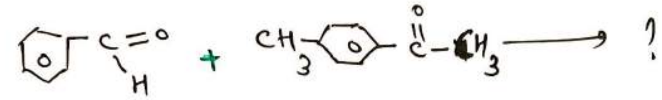
a.) $CH_3-CH=O + H_2CH-C(=O)-H \longrightarrow CH_3-CH=CH-C(=O)-H$

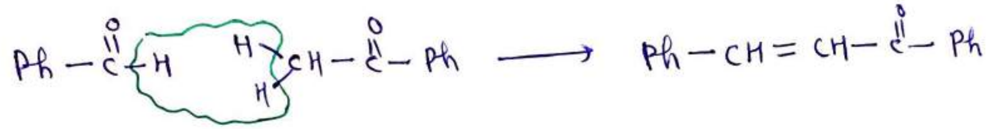
b.) $CH_3-CH_2-CH=O + H_2C(CH_3)-C(=O)-H \longrightarrow CH_3-CH_2-CH=C(CH_3)-C(=O)-H$

] → Self-Aldol



→ Cross aldol Product.





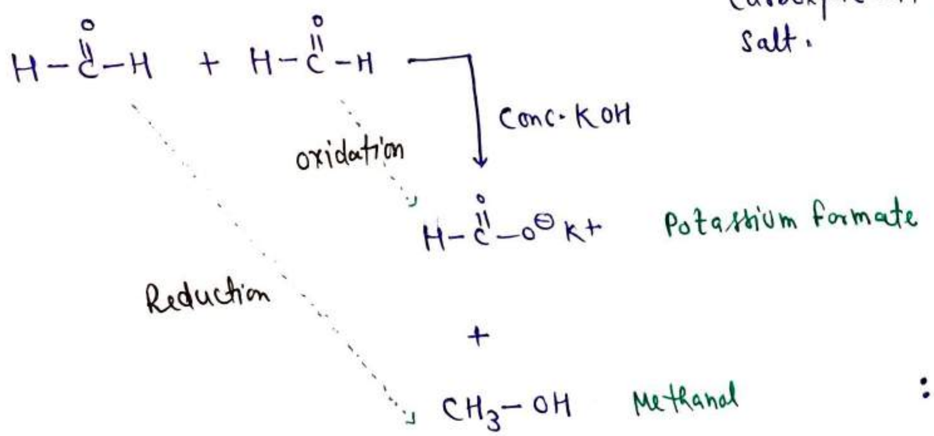
[Delhi 2010] (1M)

Cannizzaro Reaction

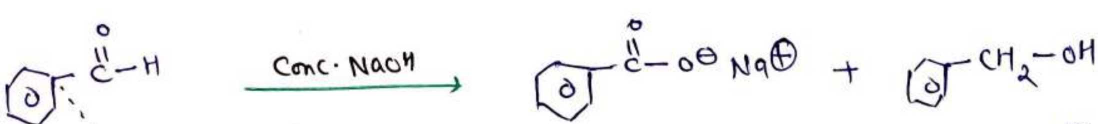
[Delhi 2017 | 2011] → (1M)

→ Con. NaOH | KOH → No, α – Hydrogen → Disproportionation Reaction

Carboxylic and salt ← Oxidation ← Aldehyde → Reduction → Alcohol



: [Delhi 2013] → [1 M]

→ 

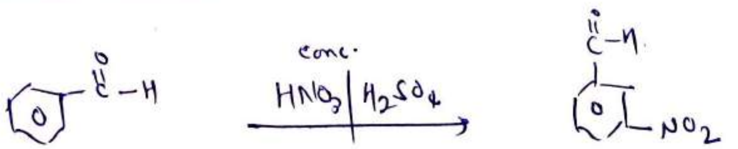
[Delhi 2016C]

No α Hydrogen

Sodium benzoate.

Benzyl alcohol

Electrophilic Substitution Reaction :- ($-\overset{O}{\overset{\|}{C}}-H$: meta – Directing in nature)



[CBSE 2016C | Delhi 2015C 2013] → [1 M]

m – Nitrobenzaldehyde.

Question :— $C_9H_{10}O$ → 2, 4 - DNP Derivative : Presence of Carbonyl group

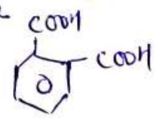
[CBSE 2012]

→ Reduces Tollen's Reagent : Presence of aldehyde

→ gives Cannizaro Reaction : No, α Hydrogen

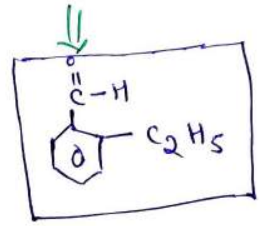
Oxidation ↓

(1, 2)- Benzene dicarboxylic



means that substitution at 1,2 position in reactant.

Then predict the structure.



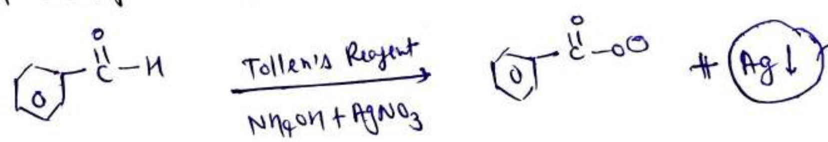
→ Describe a chemical test to distinguish between →

a.) Ethanal and propanal :— $CH_3-\overset{O}{\overset{||}{C}}-H \xrightarrow{NaOH + I_2} CHI_3\downarrow$ Yellow ppt.

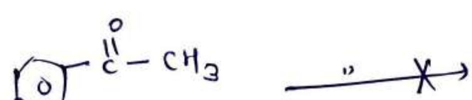
[Delhi 2010] [2M]

$CH_3-CH_2-\overset{O}{\overset{||}{C}}-H \xrightarrow[+ I_2]{NaOH}$ No reaction

b.) Benzaldehyde and acetophenone —:



Silver mirror



Yellow ppt

c.) Propan-2-one and pentan-3-one :— $CH_3-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[+ I_2]{NaOH} CHI_3\downarrow$

$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3 \xrightarrow{\ \ "\ \ }$ No Reaction.

Complete the reactions —:

a.) $CH_3-\underset{H}{\underset{|}{C}}=O + H_2N-NH-\overset{O}{\overset{||}{C}}-NH_2 \xrightarrow[(-H_2O)]{H^+} CH_3-CH=N-NH-\overset{O}{\overset{||}{C}}-NH_2$

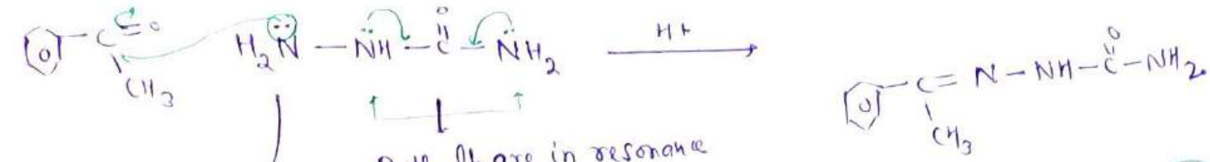
[Semicarbazone of CH_3-CHO]

CBSE [2015] (2M)

b.) $CH_3-\underset{CH_3}{\underset{|}{C}}=O + H_2N-OH \xrightarrow{H^+} CH_3-\underset{CH_3}{\underset{|}{C}}=N-OH$ Propanone oxime

Propanone Hydroxyl amine

→ c.)



Both lp are in resonance with $-\overset{O}{\overset{\|}{C}}-$.

This lp is free to attack on carbonyl carbon

[Delhi 2012] → (1M)

d.) $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{C_2H_5MgCl\ (\Rightarrow C_2H_5^{\ominus})} CH_3-\underset{C_2H_5}{\overset{OMgCl}{C}}-H \xrightarrow{H_2O} \boxed{CH_3-\underset{C_2H_5}{\overset{OH}{C}}-H} \xrightarrow[H_2SO_4]{Conc.} CH_3-CH=CH-CH_3$

(3M)

$CH_3-CH=CH-CH_3 \xrightarrow{HBr,\ Peroxide} \boxed{CH_3-\underset{Br}{CH}-\underset{H}{CH}-CH_3}$

[Delhi 2011 C]

[CBSE 2019] → [1M]

Wolf Kishner Reduction

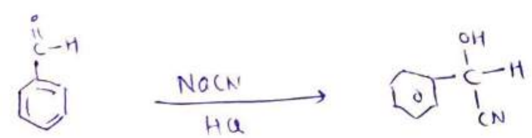
e.) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[b)\ KOH,\ Glycol/\Delta]{a)\ NH_2-NH_2} CH_3-CH_2-CH_3$

[CBSE 2019] → [1M]

f.) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{Conc.\ NaOH} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus}$

→ No α Hydrogen = Cannizzaro Reaction

g.]



Cyanohydrin : [Delhi 2019] → [1M]

h.] Organic Compound (A) [C_3H_8O] $\xrightarrow[573\ K]{Cu}$ (B) $\xrightarrow[Solution]{Fehling}$ ✗

(B) $\xrightarrow{I_2/NaOH}$ Compound C (Yellow ppt)

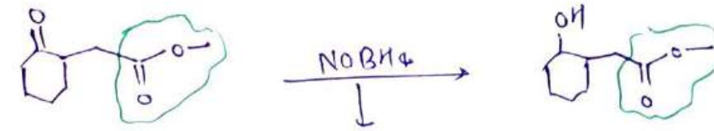
→ B to C conversion is iodoform test, means that B has $-\overset{O}{\overset{\|}{C}}-CH_3$ group and C ⇒ ($CHI_3\downarrow$).

→ A is alcohol as it has only one oxygen, which is oxidised by Cu.

(A) ($CH_3-\overset{OH}{CH}-CH_3$) $\xrightarrow{Cu}$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (B) $\xrightarrow[Sol^n]{Fehling}$ No Response

(B) $\xrightarrow{I_2/NaOH}$ $CHI_3\downarrow$. (C)

I.]



It reduces only aldehyde easily. So, No effect on ester.

Carboxylic Acid → $R-\overset{O}{\overset{||}{C}}-OH$

Nomenclature –: Alkane – e + oic acid = Alkanoic acid

→ In numbering the carbon chain, the carboxylic carbon is numbered one.

$H-\overset{O}{\overset{||}{C}}_1-OH$: Methanoic acid [formic acid] ; $\underset{2}{CH_3}-\overset{O}{\overset{||}{C}}_1-OH$: Ethanoic Acid [Acetic Acid]

$\underset{1}{COOH}-\overset{2}{COOH}$: Ethanedioic acid [Oxalic Acid]

→ OMSGAP

O → Oxalic Acid (n=0): COOH–COOH

M → Malonic Acid (n=1): COOH–CH_2–COOH

S → Succinic Acid (n=2): COOH–$(CH_2)_2$–COOH

G → Glutaric Acid (n=3)

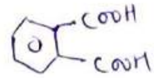
A → Adipic Acid (n=4)

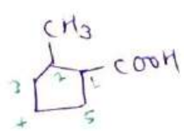
P → Piemelic Acid (n=5)

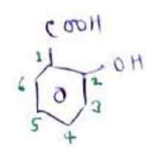
General: COOH–$(CH_2)_n$–COOH

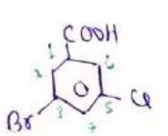
→ If $-\overset{O}{\overset{||}{C}}-OH$ group is present on ring then suffix : Carboxylic acid


: Benzene carboxylic acid ;


: (Phthalic acid) Benzene-1,2-dicarboxylic acid


: 2-Methylcyclohexane-1-carboxylic acid ;


: 2-Hydroxybenzoic acid or 2-Hydroxybenzene carboxylic acid. [Delhi 2014] 1M


: 3-Bromo-5-chlorobenzoic acid

[CBSE 2011C] 1M

→ $\underset{4}{CH_3}-\underset{\underset{OH}{|3}}{CH}-\underset{2}{CH_2}-\overset{O}{\overset{||}{C}}_1-OH$: 3-Hydroxybutanoic acid [CBSE 2014] 1M

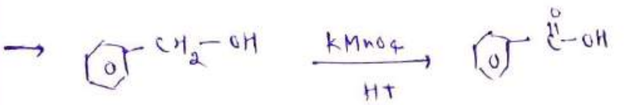
→ $\overset{6}{C}H_3-\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{C}H=\overset{2}{C}H-\underset{\underset{O}{||}}{\overset{1}{C}}-OH$: Hex-2-en-4-yn-1-oic acid [Delhi 2011C] 1M

Methods of preparation :-

(i) From 1° Alcohols / Aldehyde :- $R-\overset{O}{\overset{\parallel}{C}}-H$ / $R-CH_2-OH \xrightarrow{KMnO_4} R-\overset{O}{\overset{\parallel}{C}}-OH$

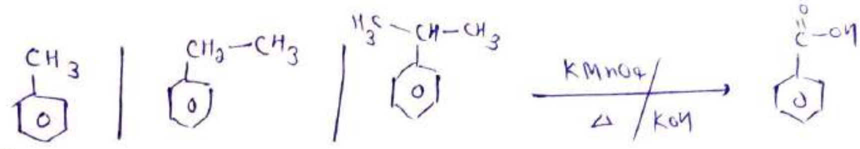
(Neutral / Basic / Acidic)

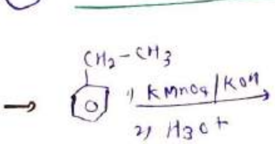
→ $CH_3-\overset{O}{\overset{\parallel}{C}}-H \xrightarrow[OH^-]{KMnO_4} CH_3-\overset{O}{\overset{\parallel}{C}}-OH$



H_2CrO_4 ⟵ CrO_3 | H^+ or $K_2Cr_2O_7$

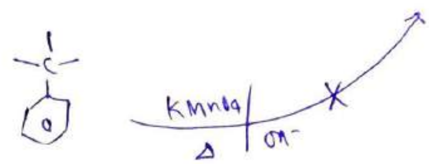
(ii) From Alkylbenzene :-





: [Delhi 2019]

: [Delhi 2015]



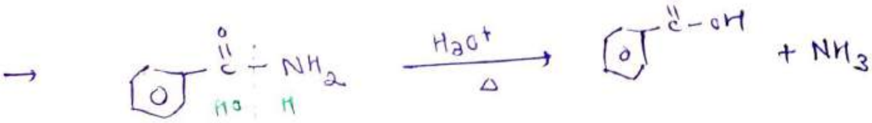
(iii) From nitriles and amides :-

$R-C\equiv N \xrightarrow[\Delta]{H^+} R-\underset{\underset{O-H}{|}}{C}=NH \rightleftharpoons R-\overset{}{\underset{\underset{O}{\parallel}}{C}}-NH_2 \xrightarrow[\Delta]{H^+} R-\overset{O}{\overset{\parallel}{C}}-OH$

($R-C\equiv N \xrightarrow[\Delta]{OH^-}$) HO : H

→ $CH_3-\overset{O}{\overset{\parallel}{C}}-NH_2 \xrightarrow[\Delta]{H_3O^+} CH_3-\overset{O}{\overset{\parallel}{C}}-OH + NH_3$

Ethanamide



Benzamide

→ Ethanal to 2-Hydroxypropanoic acid

$CH_3-\underset{\underset{H}{|}}{C}=O \xrightarrow{HCN} CH_3-\underset{H}{C}(OH)-C\equiv N \xrightarrow{H_2O / HCl} CH_3-\underset{\underset{OH}{|}}{CH}-COOH$

[CBSE 2013]

(iv) From Grignard Reagents :- $\overset{-\delta\ +\delta}{RMgX} + \underset{-\delta}{O}=\underset{+\delta}{C}=\underset{-\delta}{O} \longrightarrow R-\overset{O}{\overset{\parallel}{C}}-O^{\ominus}\ \overset{\oplus}{Mg}X$

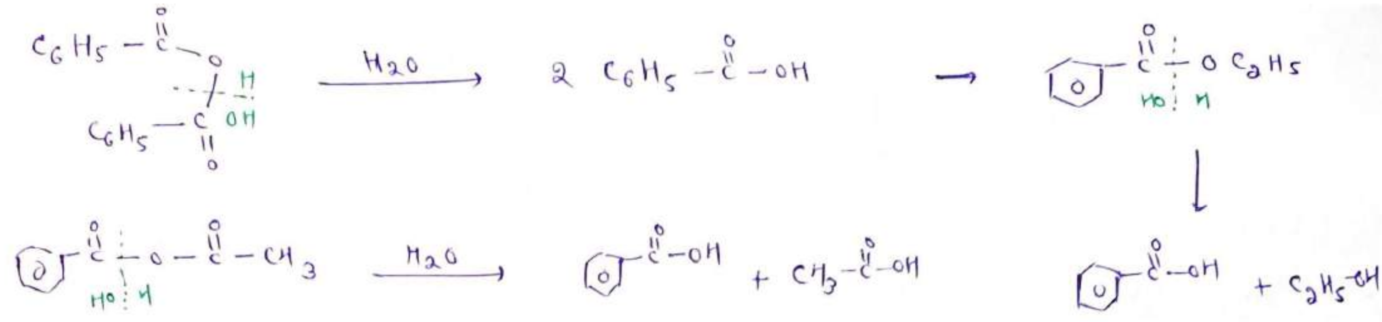
($R^{\ominus}$)

→ $CH_3MgBr + O=C=O \longrightarrow CH_3-\overset{O}{\overset{\parallel}{C}}-OMgBr \xrightarrow{H_3O^+} CH_3-\overset{O}{\overset{\parallel}{C}}-OH$

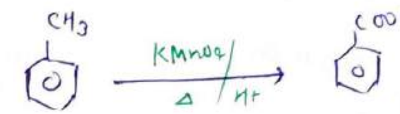
(v) Acyl Halide : $R-\overset{O}{\overset{\parallel}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\parallel}{C}}-OH + HCl$

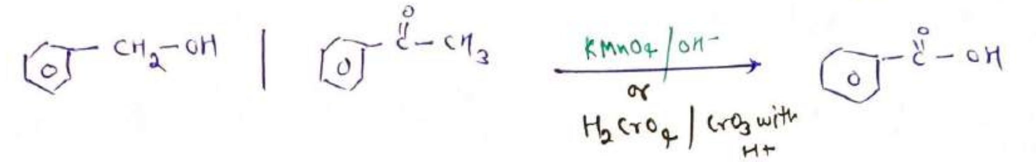
Anhydride : $R-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-R \longrightarrow 2\,R-\overset{O}{\overset{\parallel}{C}}-OH$

Ester : $R-\overset{O}{\overset{\parallel}{C}}-OR \longrightarrow R-\overset{O}{\overset{\parallel}{C}}-OH + R-OH$

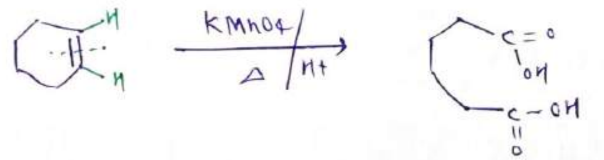


(vi) KMnO4 | KOH or KMnO4 | H2SO4 | Δ :-





: [Delhi 2011C] → 1M

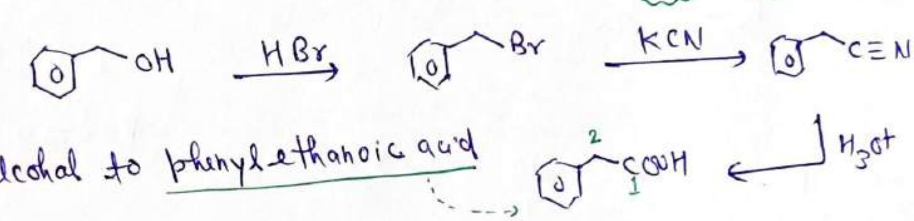


: [Delhi 2011C] → [1M]

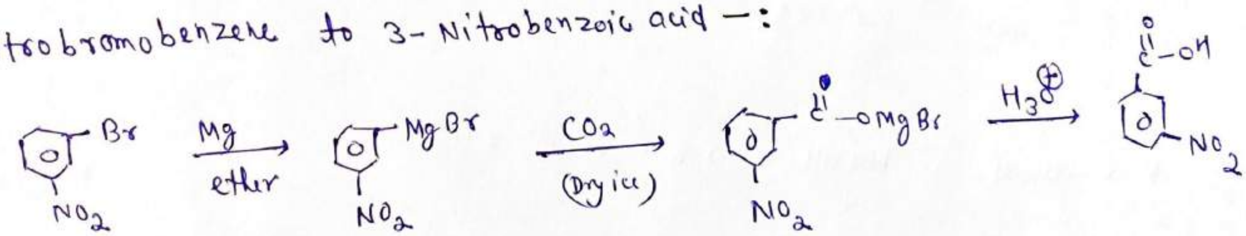
→ Conversions :-

1M ← [CBSE 2010]

(a) Benzyl alcohol to phenylethanoic acid



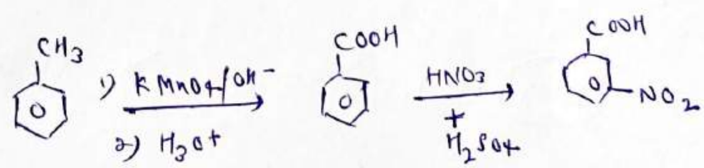
(b) → 3-Nitrobromobenzene to 3-Nitrobenzoic acid -:



(c) → Acetylene to acetic acid -: $H-C\equiv C-H \xrightarrow[Hg^{2+}]{Dil\ H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-OH$

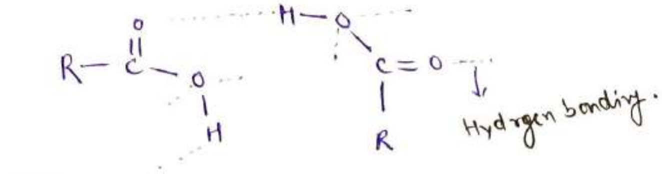
CBSE [2013C] → [2M]

(d) → Toluene to m-nitrobenzoic acid -:

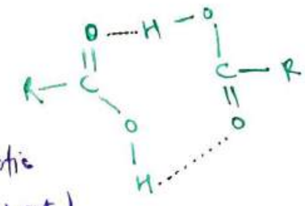


Physical Properties

→ Carboxylic acids are higher boiling liquids than aldehydes; ketones and even alcohols of comparable mass. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

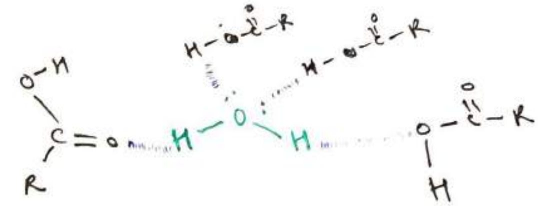


→ Association of carboxylic acid as dimer (in vapour / aprotic solvent)



Solubility

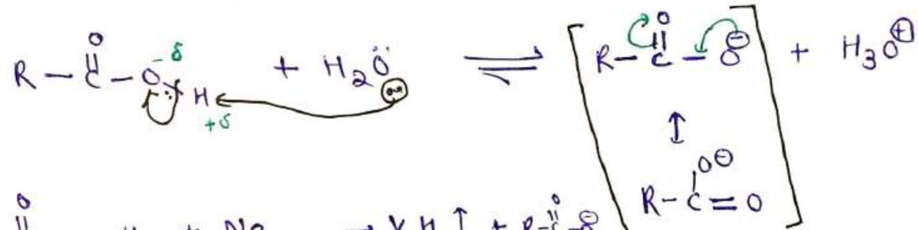
→ Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to formation of hydrogen bonding with water.



→ As No. of Carbon ↑ ⇒ Solubility ↓

→ solubility order : $CH_3-CH_2-CH_2-COOH > CH_3(CH_2)_6COOH$

Acidic Nature of Carboxylic Acid

→  : Acidic Nature

→ $R-\overset{O}{\overset{\|}{C}}-O-H + Na \longrightarrow \frac{1}{2}H_2\uparrow + R-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ Na^{\oplus}$

$R-\overset{O}{\overset{\|}{C}}-O-H \downarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ H^{\oplus}$; $Na \downarrow Na^+ + e^-$

→ $R-\overset{O}{\overset{\|}{C}}-O-H + NaHCO_3$

$R-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ H^{\oplus}$; $Na^+\ HCO_3^-$

$\downarrow$

$R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} + H_2CO_3$

$H_2CO_3 \rightarrow H_2O + CO_2$

→ $R-\overset{O}{\overset{\|}{C}}-O-H + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ Na^{\oplus} + H_2O$

$R-\overset{O}{\overset{\|}{C}}-O-H \downarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ H^{\oplus}$; $NaOH \downarrow Na^+\ OH^-$

→ Effect of substituents on acidity of carboxylic acids :-

$(EWG) \leftarrow CH_2-\overset{O}{\overset{\|}{C}}-O-H > (EDG) \rightarrow CH_2-\overset{O}{\overset{\|}{C}}-O-H$: Ka

$F \leftarrow CH_2-\overset{O}{\overset{\|}{C}}-OH > CH_3 \rightarrow CH_2-\overset{O}{\overset{\|}{C}}-OH$: Ka

$-H^+ \downarrow\uparrow$ $\quad\quad \downarrow\uparrow -H^+$

$F \leftarrow CH_2 \leftarrow \overset{O}{\overset{\|}{C}}-O^{\ominus} > CH_3 \rightarrow CH_2 \rightarrow \overset{O}{\overset{\|}{C}}-O^{\ominus}$: stability of conjugate base of acid.

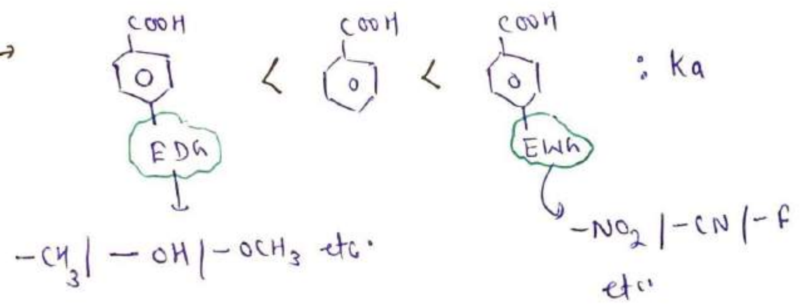
⇒ **Acidity (Ka) ∝ Stability of conjugate base**

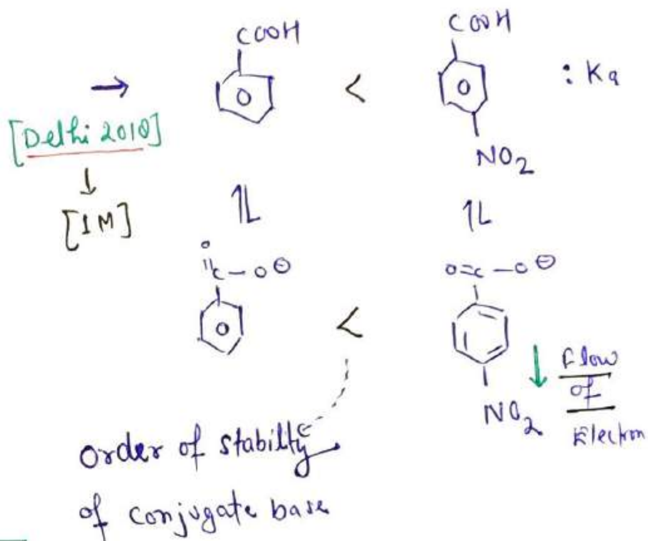
→ $CF_3-\overset{O}{\overset{\|}{C}}-O-H$ > $CCl_3-\overset{O}{\overset{\|}{C}}-O-H$: Ka (F is more electronegative than Cl.)

→ $F-CH_2-\overset{O}{\overset{\|}{C}}-OH$ > $Cl-CH_2-\overset{O}{\overset{\|}{C}}-OH$ > $Br-CH_2-\overset{O}{\overset{\|}{C}}-OH$ > $I-CH_2-\overset{O}{\overset{\|}{C}}-OH$: Ka

→ | F > B > A : Ka | means that, HCOOH > $C_6H_5-\overset{O}{\overset{\|}{C}}-OH$ > CH_3-COOH : Ka

F → Formic Acid; B → Benzoic Acid; A → Acetic Acid

→ 



Reactions involving breaking of C–OH bond

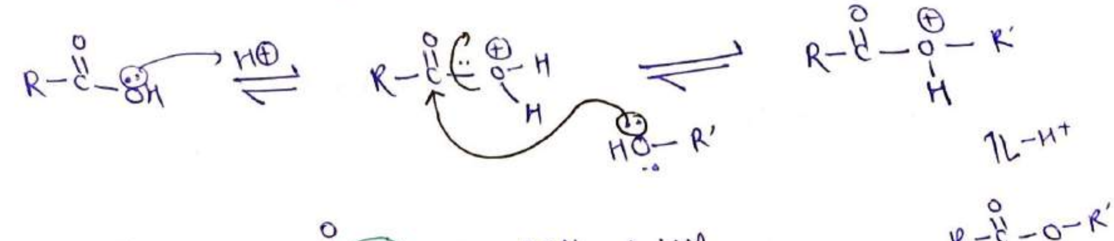
① **Formation of anhydride :–** (By using dehydrating agent : Conc. H_2SO_4 / P_2O_5, Δ)

$$CH_3-\overset{O}{\overset{\|}{C}}-O-H + HO-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(-H_2O)]{P_2O_5\,/\,\Delta} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

② **Esterification :–**

$$R-\overset{O}{\overset{\|}{C}}-OH + H-O-R' \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O$$

Mechanism :–



③ $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{PCl_5} R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$

$3\,R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{PCl_3} 3\,R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + HCl\uparrow$

→ side products are gases and escape the reaction mixture making pure $R-\overset{O}{\overset{\|}{C}}-Cl$.

→ [4] Reaction with ammonia —:

$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{-\delta}{O}-\underset{+\delta}{H} + \ddot{N}H_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ \overset{\oplus}{N}H_4$$

Ammonium Acetate

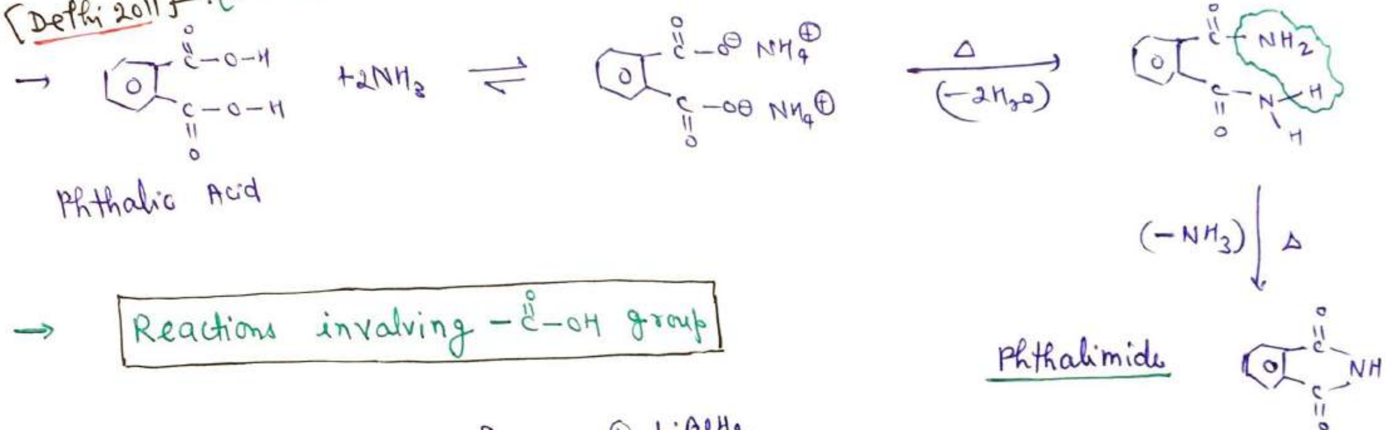
$$\xrightarrow[(-H_2O)]{Heat} CH_3-\overset{O}{\overset{\|}{C}}-NH_2$$

Acetamide

→ $$C_6H_5-\overset{O}{\overset{\|}{C}}-O-H + NH_3 \rightleftharpoons C_6H_5-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ \overset{\oplus}{N}H_4 \xrightarrow{(-H_2O)} C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2$$

Ammonium Benzoate — Benzamide

[Delhi 2011] —: [2.5 M]



Phthalic Acid

Phthalimide

→ **Reactions involving $-\overset{O}{\overset{\|}{C}}-OH$ group**

1.] Reduction :—

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{② } H_3O^{\oplus}]{\text{① } LiAlH_4 \text{ or } B_2H_6} R-CH_2OH$$

B_2H_6 is best for acid.

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaBH_4}$ ✗

2.] Decarboxylation :— [Removal of CO_2] → [Delhi 2012] → [1M] [Delhi 2017] → [2M]

→ Soda - Lime Decarboxylation :

NaOH + CaO : Reagent

$$R-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[CaO]{NaOH +} R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} \longrightarrow R-H + Na_2CO_3$$

→ $$CH_3-\boxed{\overset{O}{\overset{\|}{C}}-O}-H \xrightarrow[CaO/\Delta]{NaOH +} CH_3-H\ (CH_4) + Na_2CO_3$$

(methane)

→ Acid to alkane Conversion

→ Kolbe Electrolysis —:

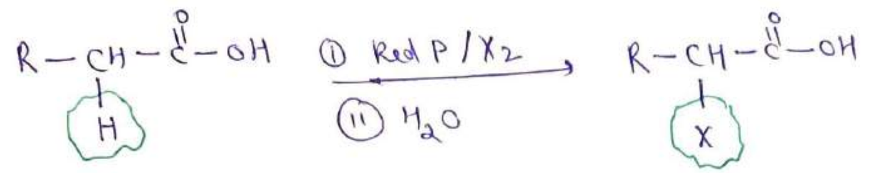
$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaOH} CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} \xrightarrow{Electrolysis} CH_3-CH_3$$

$$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-ONa \xrightarrow{Electrolysis} C_6H_5-CH_2-CH_2-C_6H_5$$

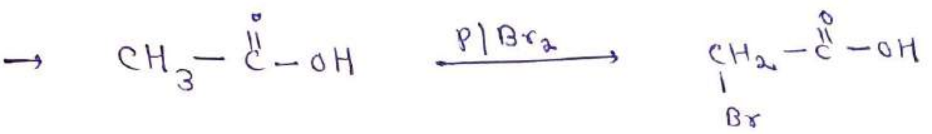
Reaction on hydrocarbon part

[Delhi 2017] - [2M] (CBSE 2010)

(i) Halogenation :— Hell - Volhard - Zelinsky Reaction (HVZ Reaction)

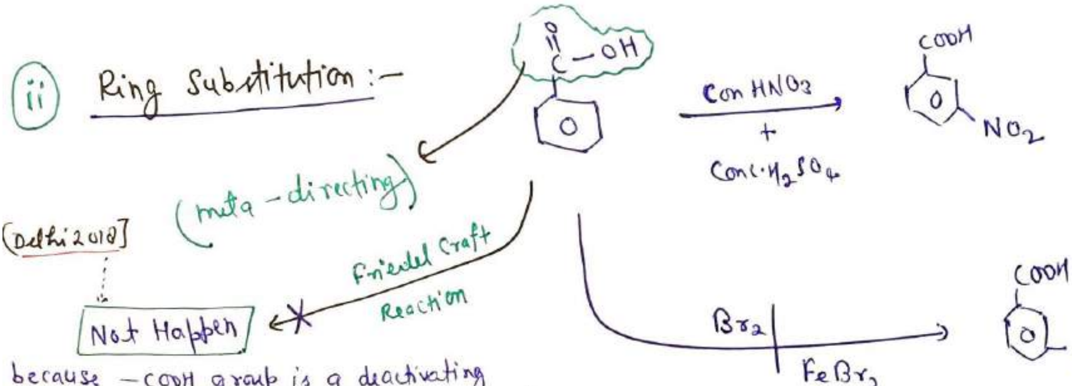


α- Halocarboxylic acid



[Delhi 2014] → [1M]
[Delhi 2013C] → [1M]
[CBSE 2016] → [1M]

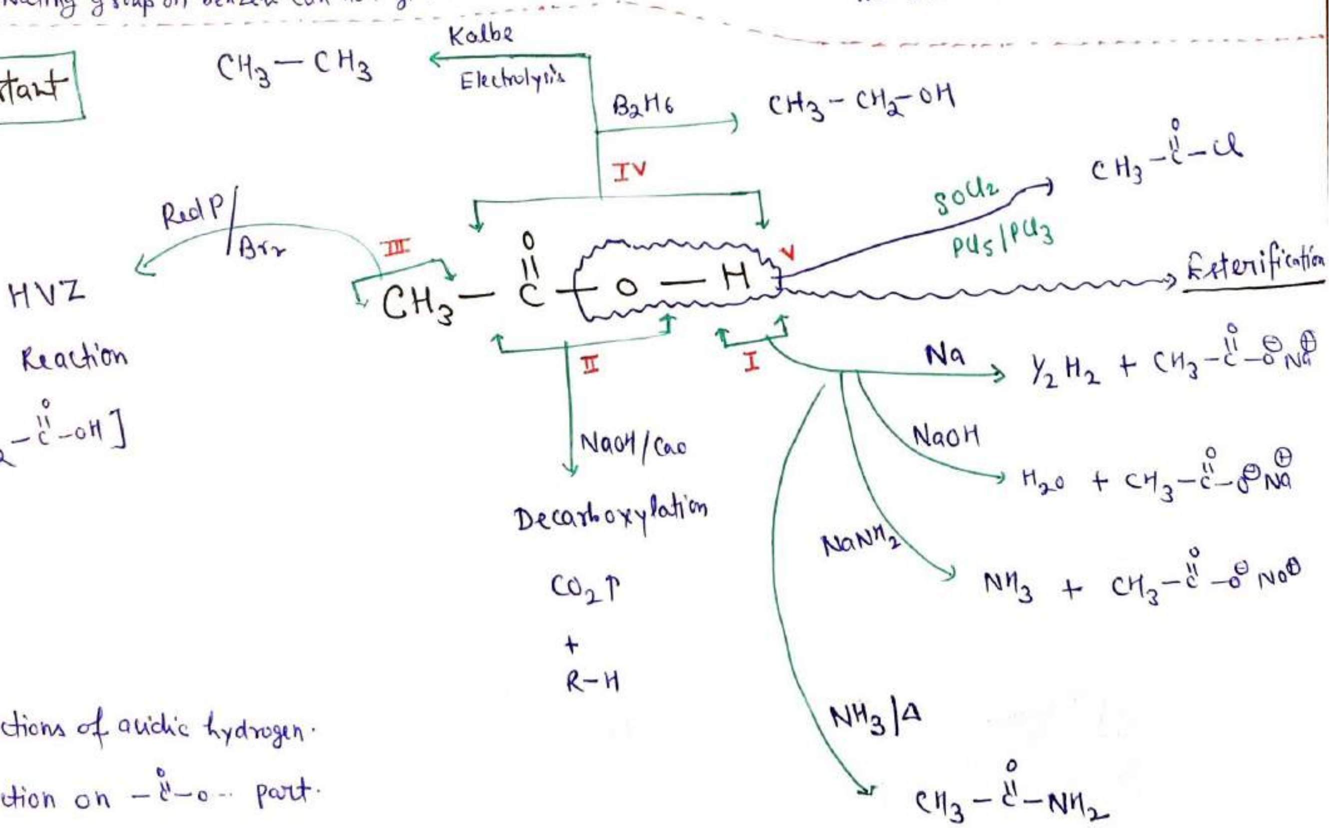
(ii) Ring Substitution :-



because —COOH group is a deactivating group. Deactivating group on benzene can not give FCR.

[Delhi 2012C] [1M]

Important

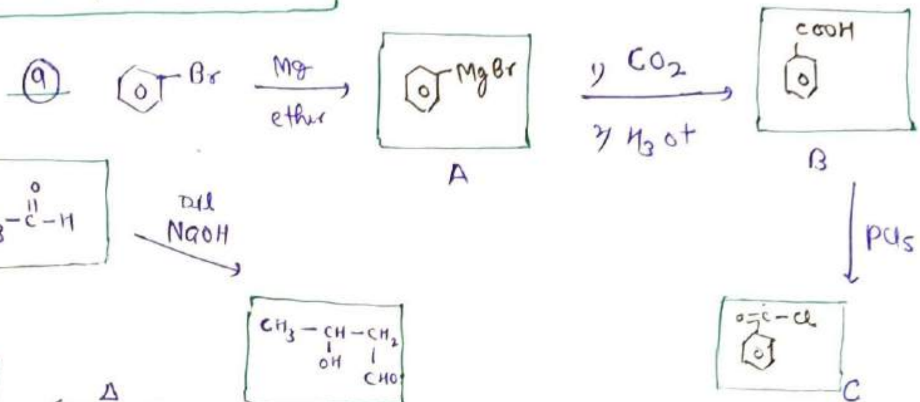


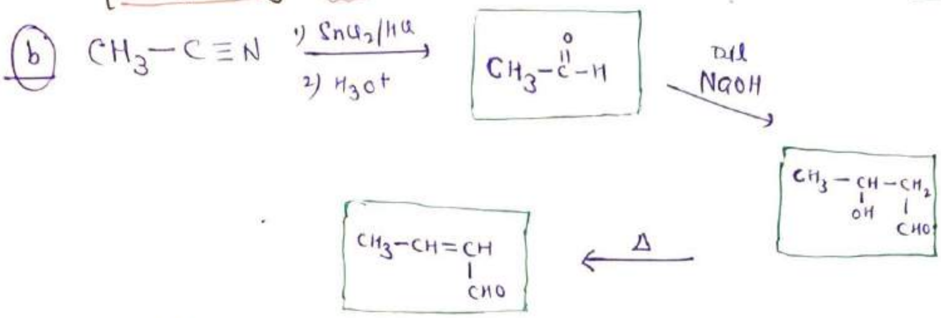
I → Reactions of acidic hydrogen.
II → Reaction on —C(=O)—O— part.
III → Reaction on hydrocarbon part.
IV → Reaction on —C(=O)—OH.
V → Reactions on —OH part.

Important Previous Year Questions

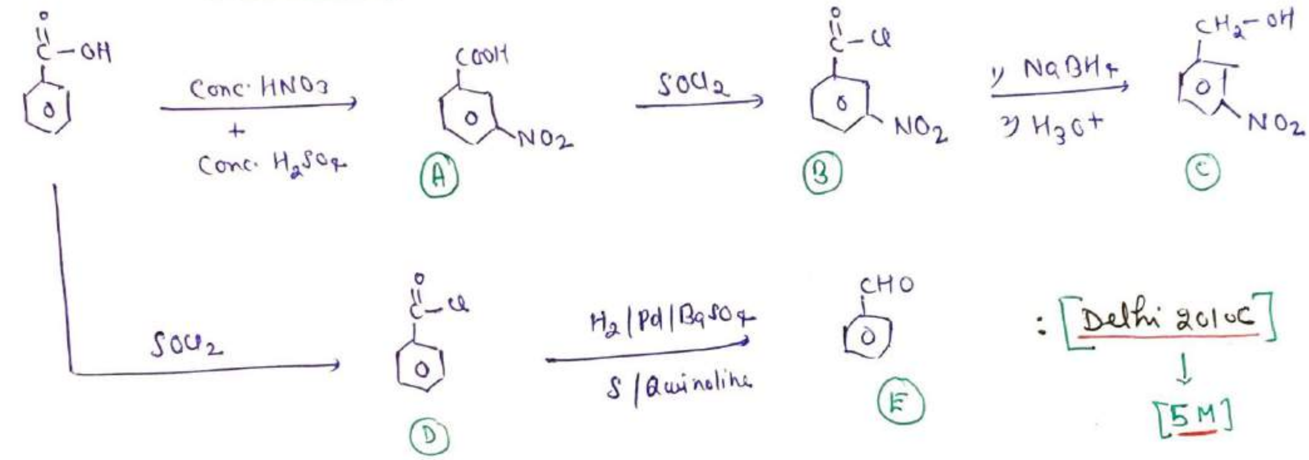
(1) Structure of A / B / C :-

[Delhi 2017] → (3M)





(2) →



: [Delhi 2010C] → [5M]

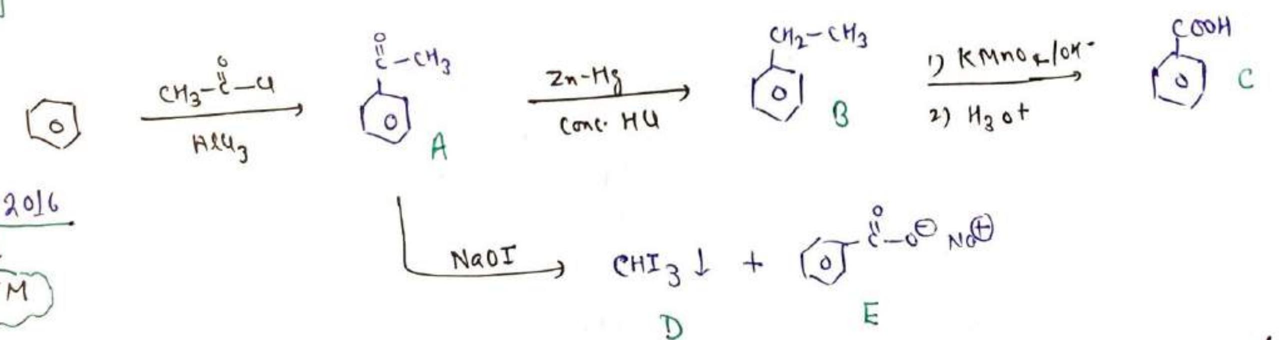
(3) → Acidity Order :

$$F \leftarrow CH_2-\overset{O}{\overset{\|}{C}}-OH > Cl \leftarrow CH_2-\overset{O}{\overset{\|}{C}}-OH > CH_3 \rightarrow \overset{O}{\overset{\|}{C}}-OH$$

–F / –Cl both are –I group; –CH_3 +I group.

[CBSE 2015, Delhi 2013C] → [1M]

(4) →



Delhi 2016 → (5M)

(5.) → Two moles of organic compound A $\xrightarrow{\text{strong base}}$ B + C $\xrightarrow{\text{Acidification}}$ D (Carboxylic acid) $[CH_2O_2]$

B $\xrightarrow{\text{Dehydrogenation with Cu}}$ A

[Delhi 2013] → [5M]

Answer :- D ⇒ Carboxylic acid → $H-\overset{O}{\overset{\|}{C}}-OH$

C → $H-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

B → Alcohol → CH_3-OH $\xrightarrow{Cu}$ A $(H-\overset{O}{\overset{\|}{C}}-H)$

Then A must be $H-\overset{O}{\overset{\|}{C}}-H$ as strong base represent cannizzaro.

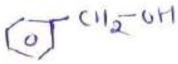
6.] Organic compound A $\xrightarrow{NaOH}$ B + C

[CBSE 2013 | 2012C] → (3M)

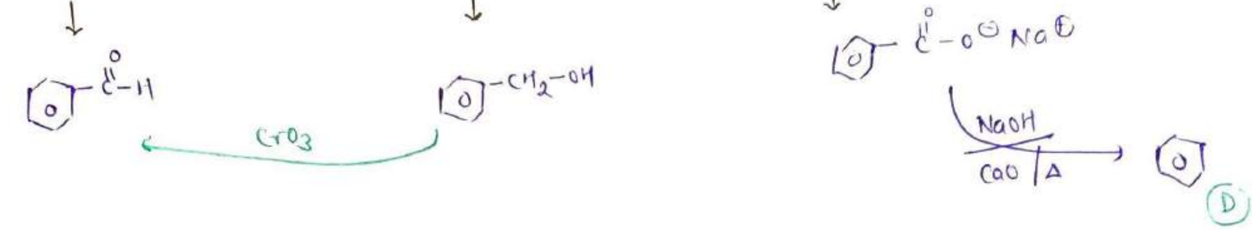
B $[C_7H_8O]$ $\xrightarrow{CrO_3}$ A

C: Sodium salt of acid $\xrightarrow{\text{Soda-lime}/\Delta}$ D (Aromatic Hydrocarbon)

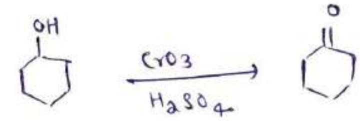
→ Answer

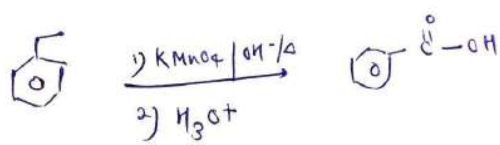
B (C_7H_8O) has only one oxygen : Alcohol : 

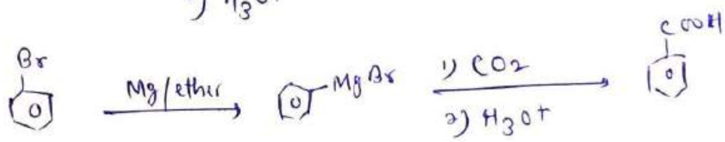
(A) Aldehyde $\xrightarrow{NaOH}$ Alcohol (B) + Salt of acid (C)



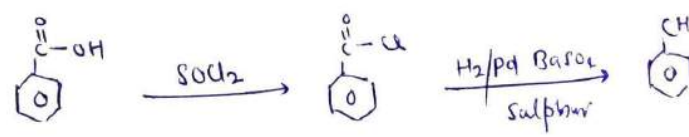
7.] How the following conversions can be brought about?

a.] Cyclohexanol to cyclohexan-1-one 

b.] Ethyl benzene to benzoic acid  : [Delhi 2017]

c.] Bromobenzene to benzoic acid 

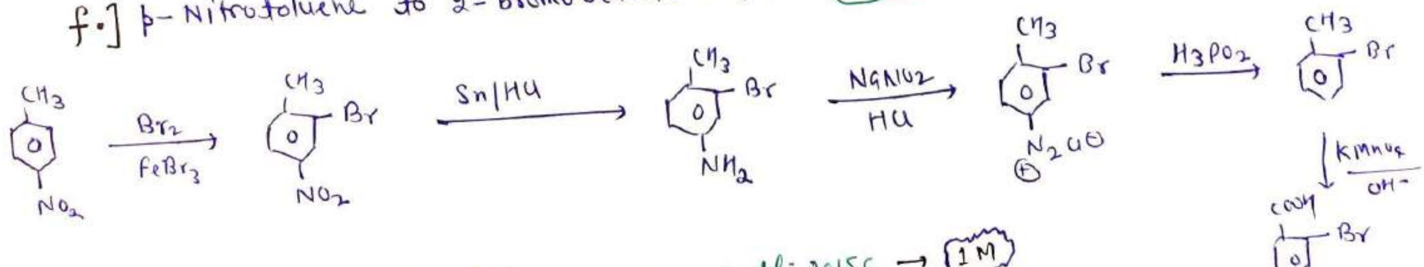
[3M] → [CBSE 2010 | Delhi 2009]

d.] Benzoic acid to benzaldehyde [2015] → (1M) 

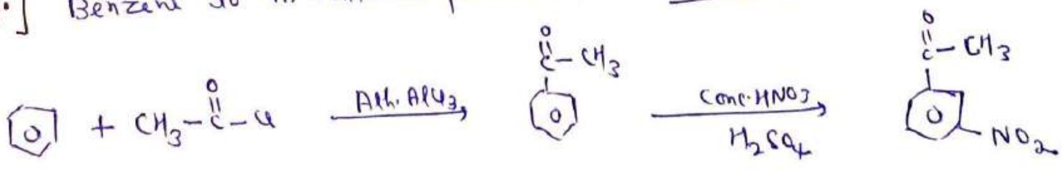
e.] Propanone to propene $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaBH_4} CH_3-\underset{OH}{CH}-\underset{H}{CH_2} \xrightarrow[H_2SO_4]{Conc.} CH_3-CH=CH_2$

[Delhi 2017] → (2M)

f.] p-Nitrotoluene to 2-bromobenzoic acid :- (2019)



g.] Benzene to m-nitroacetophenone :- Delhi 2015C → (1M)



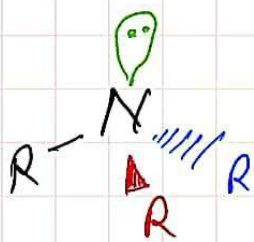
Benzene. m-Nitroacetophenone.

Amines

These are alkyl or aryl derivatives of Ammonia

H–N(H)–H	R–N(H)–H	R–N(R)–H	R–N(R)–R
Ammonia	1° amine	2° amine	3° amine

Structure of Amines



Structure – trigonal pyramidal

3 Bond Pair + 1 Lone Pair

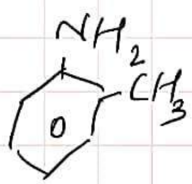
Hybrid. → sp^3

Nomenclature ⇒

$CH_3-CH_2-CH_2-NH_2$ Propan-1-amine

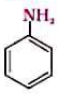
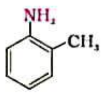
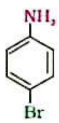
$CH_3-NH-CH_2-CH_3$ N-Methyl ethanamine

Aniline



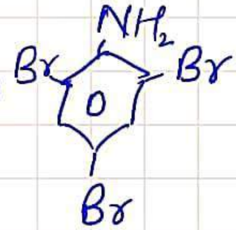
2-Amino toluene

NCERT Ques.

Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-Propylamine	Propan-1-amine
$CH_3-CH(NH_2)-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-N(H)-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3-N(CH_3)-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
$C_2H_5-N(C_2H_5)-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	*N,N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Methylaniline
	*p*-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	*N,N*-Dimethylaniline	N,N-Dimethylbenzenamine

P.Y.Q

(D-2016)

(•) 

2,4,6-Tribromo aniline

(•) $CH_3-N(CH_3)-CH_2-CH_3$ (A.I-2013)

N,N-Dimethyl ethanamine

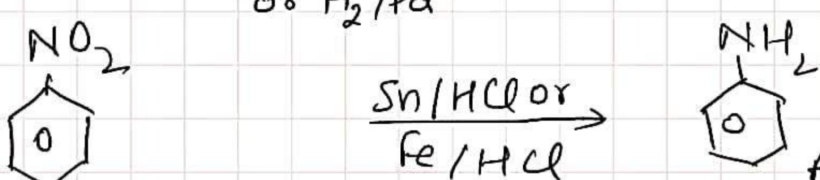
(•) $CH_2=CH-CH(CH_3)-NH_2$ (D-2012)

But-3-en-2-amine.

• Preparation of Amines ⇒

- Reduction of Nitro Compounds -

$$R-NO_2 \xrightarrow[\text{or } H_2/Pd]{Sn/HCl \text{ or } Fe/HCl} R-NH_2$$



Nitrobenzene → Aniline

- Reduction of Amides →

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{or } C_2H_5-OH/Na]{LiAlH_4/\text{ether}} R-CH_2-NH_2$$

$$C_2H_5-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} C_2H_5-CH_2-NH_2$$

• Hoffmann Bromamide Degradation

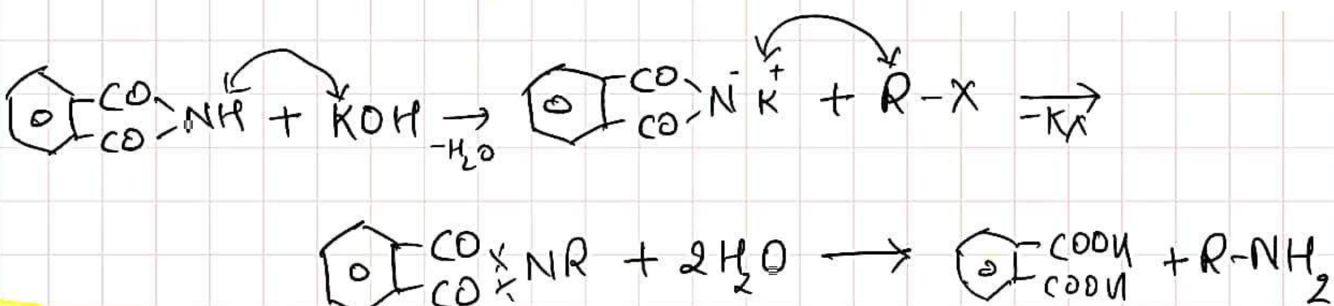
Trick - Baby को Base पसंद है।

$$R-CO-NH_2 + Br_2 + 4KOH \xrightarrow[-2KBr \; -K_2CO_3 - 2H_2O]{\Delta} R-NH_2$$

$$\underset{\text{Propanamide}}{C_2H_5-CO-NH_2} + Br_2 + 4KOH \xrightarrow[-2KBr,\, \cdot 2H_2O \; -K_2CO_3]{\Delta} \underset{\text{Ethanamide}}{C_2H_5-NH_2}$$

• Gabriel phthalimide synthesis :-

Trick - गाब्बर Basement में R-X को H₂O पीला।



P.T.R

Aromatic 1° amines can't be prepared by this method because aryl halides do not undergo nucleophilic sub. with the anion formed by phthalimide.

• Reduction of Nitriles :-

$$R-C\equiv N + 4[H] \xrightarrow{LiAlH_4} R-CH_2-NH_2$$

$$C_2H_5-C\equiv N + 4[H] \xrightarrow{LiAlH_4} C_2H_5-CH_2-NH_2$$

- **Hoffmann Ammonolysis of Alkyl Halide**

$$H-\underset{H}{\underset{|}{N}}-H + R-X \xrightarrow[-HX]{} \underset{\boxed{1^\circ amine}}{R-\underset{H}{\underset{|}{N}}-H} + R-X \xrightarrow[-HX]{} \underset{\boxed{2^\circ amine}}{R-\underset{H}{\underset{|}{N}}-R} + R-X \xrightarrow[-HX]{} \underset{\boxed{3^\circ amine}}{R-\underset{R}{\underset{|}{N}}-R}$$

$$H-\underset{H}{\underset{|}{N}}-H + C_2H_5-Cl \xrightarrow[-HCl]{} \underset{\boxed{1^\circ amine}}{C_2H_5-\underset{H}{\underset{|}{N}}-H} + C_2H_5-Cl \xrightarrow[-HCl]{}$$

$$\underset{\boxed{2^\circ amine}}{C_2H_5-\underset{H}{\underset{|}{N}}-C_2H_5} + C_2H_5-Cl \xrightarrow[-HCl]{} \underset{\boxed{3^\circ amine}}{C_2H_5-\underset{C_2H_5}{\underset{|}{N}}-C_2H_5}$$

→ Physical Properties of Amines :-

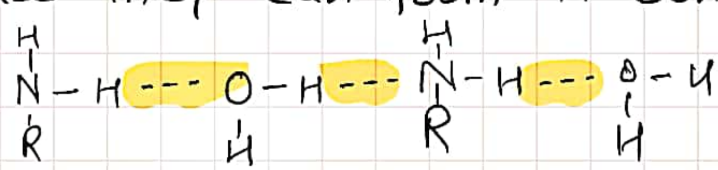
- **Physical State :-**

Lower amines are gases and liquids but higher amines are solids. The lower aliphatic amines are gases with fishy odour.

Arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

- **Solubility :-**

Lower aliphatic amines are soluble in water because they can form H-Bond with water



Primary and secondary amines are soluble in water due to H-bonding while 3° amines are insoluble in water.

- The solubility decrease with increase in size of hydrophobic alkyl part.

P.T.R The solubility of amines is less than that of alcohol of comparable molecular mass because alcohols are more polar than amines and form stronger H-Bond.

· Boiling Point ⇒

The order of b.pt isomeric amines
1° amines > 2° amines > 3° amines

- 3° amines do not have intermolecular H-Boding because no H- is attached to N-atom.
- 1° amines have maximum amount of H-Bonding because two H-atoms are attached to N-atom.

Basic Character of Amines

→ Amines are basic in nature due to the presence of lone pair of e⊖ on nitrogen atom.

→ Aliphatic amines are stronger bases than ammonia due to +I effect of Alkyl group.

→ Aromatic amines are weaker bases than ammonia due to -I effect or Aryl group.

→ **Besides inductive effect, effects like steric effect, solvation effect, resonance effect also affect the basic strength of amines.**

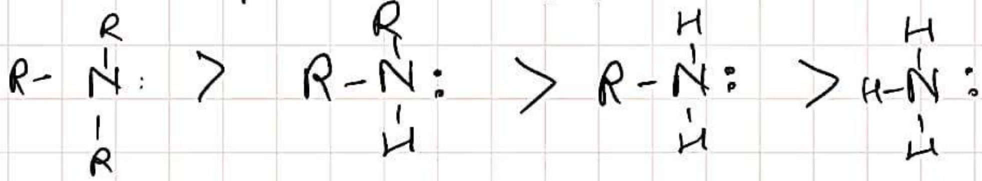
Amines are basic in nature and reats with acids to form salts.

$$R-\ddot{N}H_2 + HX \longrightarrow R-\overset{\oplus}{N}H_3 X^{\ominus}$$

Ammonium Salt.

→ Order of basic character of amines in gaseous phase (Acc. to +I effect)

3° amines > 2° amines > 1° amines > NH_3



However in aqueous phase :-

There is subtle interplay of Inductive effect, steric effect and Solvation effect

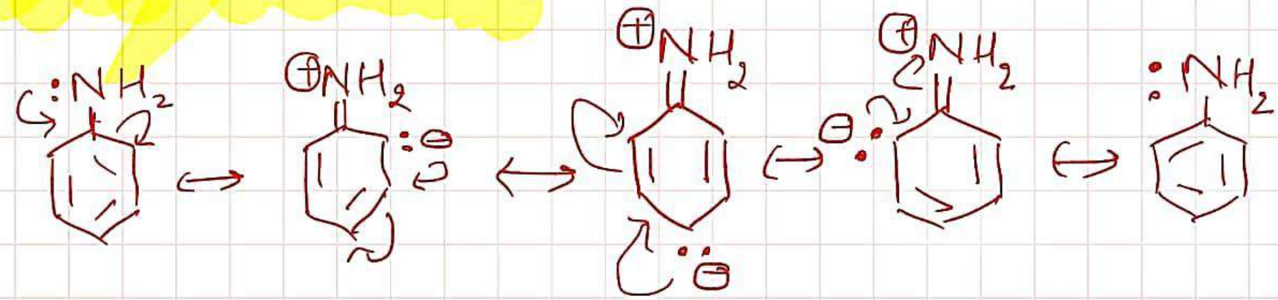
$$(CH_3CH_2)_2-NH > (CH_3CH_2)_3N > CH_3CH_2NH_2 > NH_3$$

2°   3°   1°

$$(CH_3)_2NH > CH_3-NH_2 > (CH_3)_3N > NH_3$$

2°   1°   3°

Resonance in Aniline



• Carbylamine Reaction

$$R\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R\text{-}N\equiv C + 3KCl + 3H_2O$$

$$C_2H_5\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_2H_5\text{-}NC + 3KCl + 3H_2O$$

$$C_6H_5\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_6H_5\text{-}NC + 3KCl + 3H_2O$$

• Reaction with Grignard Reagent ⇒

$$R\text{-}NH_2 + CH_3\text{-}MgI \longrightarrow CH_4 + R\text{-}NH\text{-}MgI$$

$$R_2NH + CH_3\text{-}MgI \longrightarrow CH_4 + R_2\text{-}N.MgI$$

$$C_6H_5\text{-}NH_2 + C_2H_5\text{-}MgI \longrightarrow C_2H_6 + C_6H_5\text{-}NH.MgI$$

P.T.R Tertiary amines do not react with Grignard reagents as they do not contain active H-atoms.

ALKYLATION

⇒ $C_2H_5\text{-}NH_2 + C_2H_5\text{-}Br \xrightarrow[-HBr]{} (C_2H_5)_2\text{-}NH$

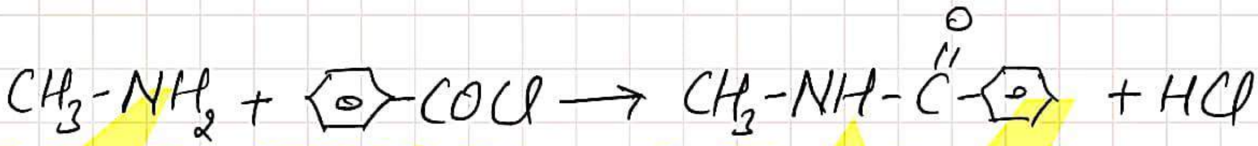
$+ C_2H_5\text{-}Br \xrightarrow[-HBr]{} (C_2H_5)_3N + C_2H_5\text{-}Br$

$\xrightarrow[-HBr]{} (C_2H_5)_4N^+Br^-$ Tetraethyl ammonium bromide

⇒ $C_6H_5\text{-}NH_2 + CH_3I \xrightarrow{\Delta} C_6H_5\text{-}NH\text{-}CH_3 + CH_3I \xrightarrow{\Delta}$

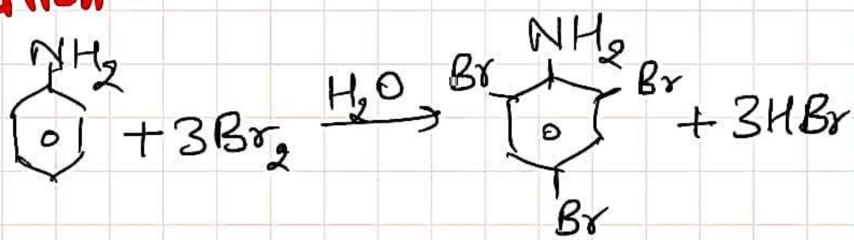
$\xrightarrow{\Delta} C_6H_5\text{-}N(CH_3)_2 + CH_3I \xrightarrow{\Delta} C_6H_5\text{-}N^+(CH_3)_3I^-$

· **Acylation**

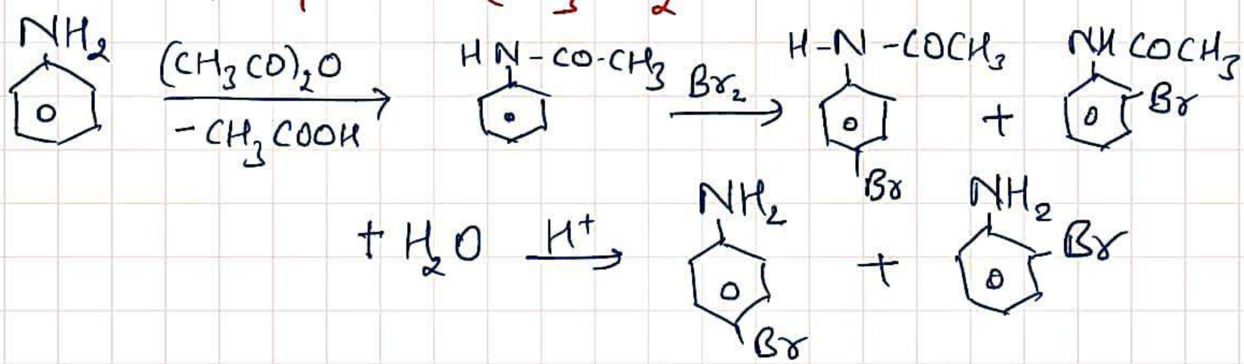


- Electrophilic Substitution Reaction ⇒

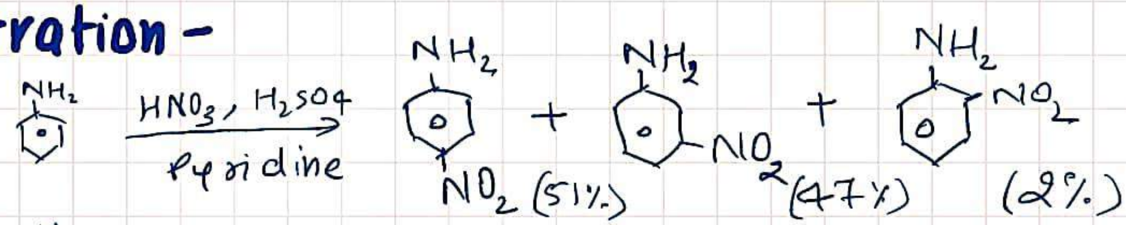
(i) Bromination -

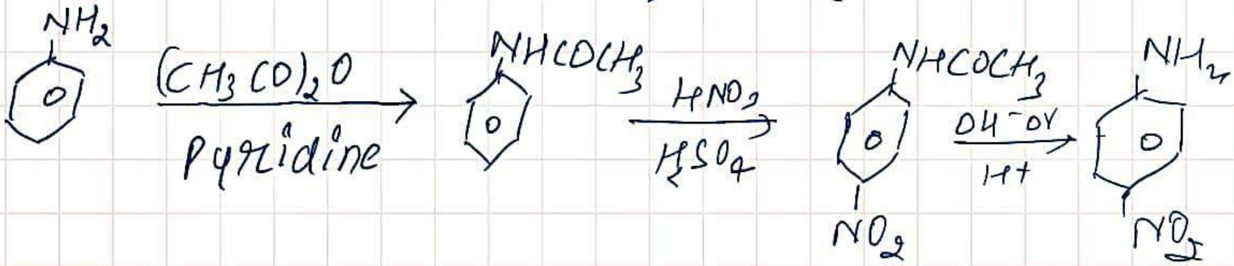


P.T.R For monobromination, treat aniline with acetic anhydride $(CH_3CO)_2O$

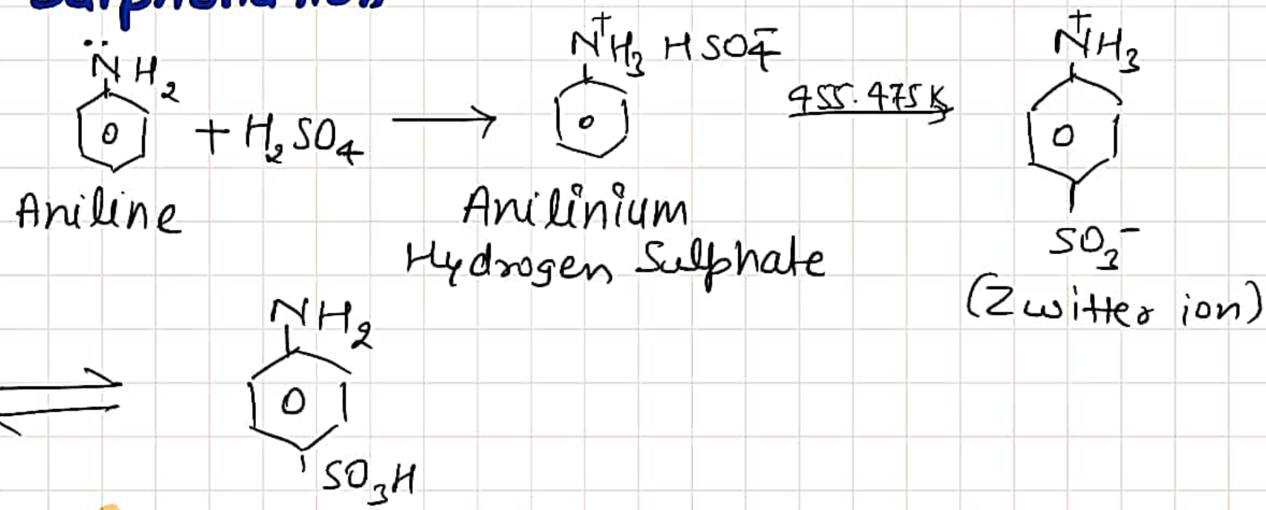


(ii) Nitration -





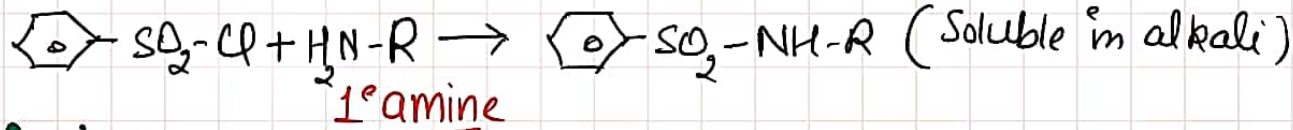
Sulphonation



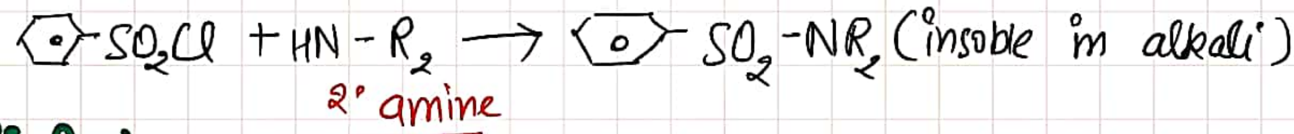
Hinsberg Test (benzene sulphonyl Chloride)

(Hinsberg Reagent)

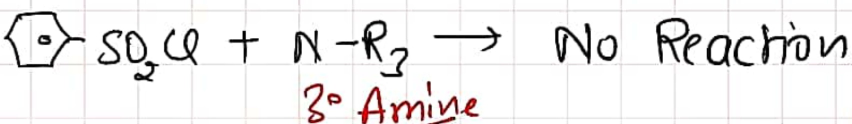
1° Amines



2° Amines

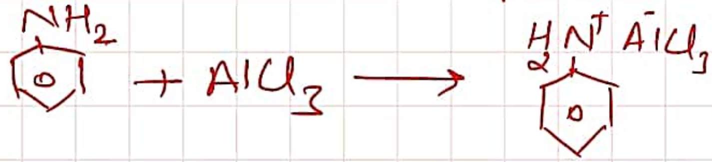


3° Amines



P.T.R **Friedal craft Rxn are not possible for** 

because it form salt with anhy. $AlCl_3$ that is used as catalyst in the reaction.

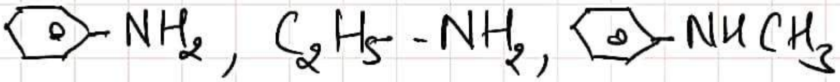


(due to +ve charge it act as strong deactivating group)

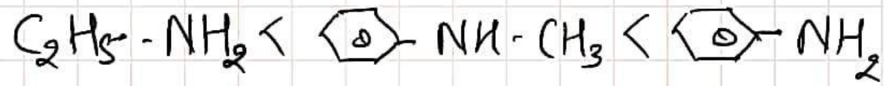
Basic Character $\propto K_b$

Basic Character $\propto \frac{1}{pK_b}$

- Arrange the following in the increasing order of pK_b values: (C.B.S.E - 2018)



Solution :-

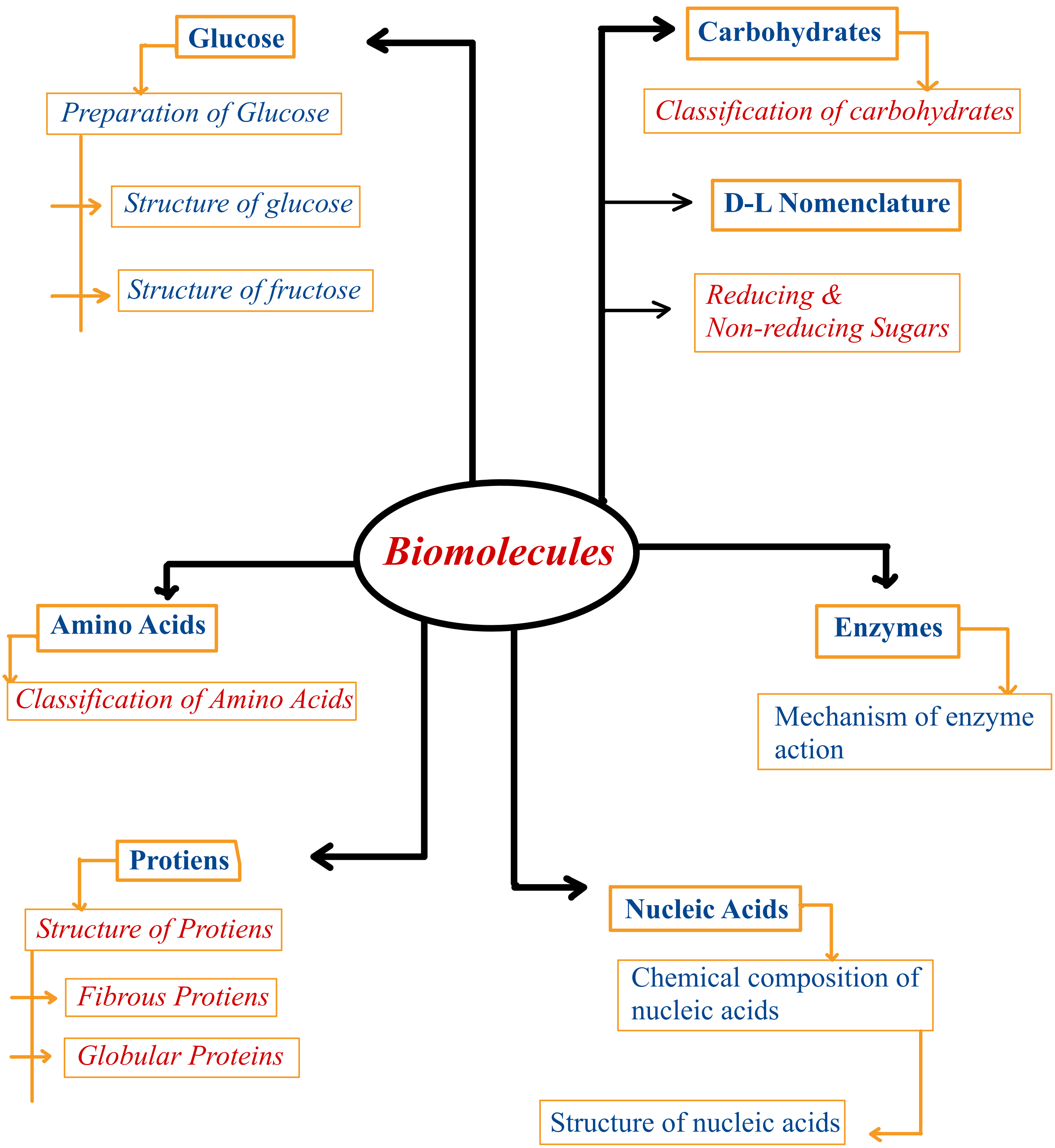


(•) Give reasons: $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution (C.B.S.E - 2018)

Ans: $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution due to less steric hindrance.

Biomolecules

Flow Chart Of Biomolecules



Biomolecules

→ The branch of chemistry that deals with the molecules involved in living system, is called Biochemistry.

→ Carbohydrates, proteins, vitamins and nucleic acids are some of the major components of our body. These are collectively called Biomolecules.

Carbohydrates :- Carbohydrates are optically active polyhydroxy aldehydes or ketones or substances that will yield these types of compounds on hydrolysis.

Carbohydrates ↓ Hydrates of Carbon

$C_x(H_2O)_y$: General Formula.

Example -: $C_6(H_2O)_6 \Rightarrow C_6O_6H_{12}$ ($C_6H_{12}O_6$: Glucose / Fructose)

Classification of Carbohydrates :-

→ This classification is based on hydrolysis.

a.] **Monosaccharides :-** A carbohydrate that can not be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketones is called a monosaccharide. [CBSE 2010] → (1M)

For example -: Glucose / Fructose / Ribose

b.] **Oligosaccharides :-** Carbohydrates that produce 2 to 10 monosaccharide units on hydrolysis, are called oligosaccharide.

→ **Disaccharide** : It produce 2 unit of monosaccharide.

[CBSE 2019] (1M) Example → Sucrose, Lactose [Sucrose $\xrightarrow{\text{Hydrolysis}}$ Glucose + Fructose]

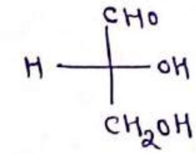
c.] **Polysaccharides -:** Carbohydrates that produce a large no. of monosaccharide units on hydrolysis are called polysaccharide.

Example -: Starch / Cellulose / Glycogen.

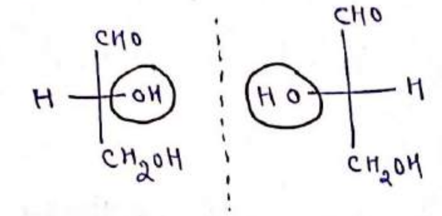
→ Polysaccharides are not sweet in taste. Hence they are also called non-sugars.

D-L Nomenclature :-

Standered for this Nomenclature :



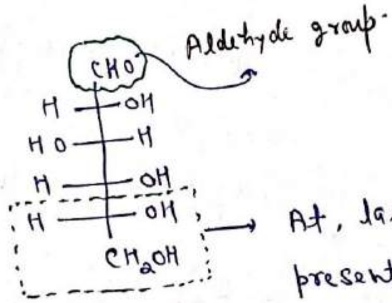
Glyceraldehyde

→ 

D-Glyceraldehyde Mirror L-Glyceraldehyde

→ (+) and (−) represents dextrorotatory nature and leavorotatory nature of a compound, means that optical active nature can be defined by ⊕ or ⊖. But remember that D and L have no relation with optical activity of a Compound, they represents only Configuration of a compound.

→ Structure of Glucose −:



→ At, last chiral carbon −OH group is present at right side ⇒ D−Glucose.

Reducing and Non-reducing Sugars :- [Delhi 2010C] (1M)

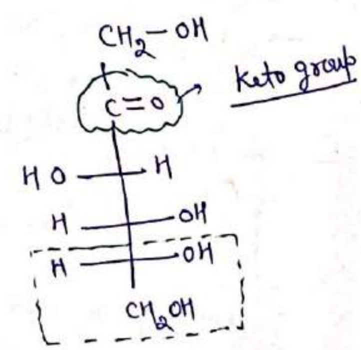
→ Reducing Sugars −: All those carbohydrates which reduce Tollen's reagent and fehling reagent are called reducing sugars. [CBSE 2010] (1M)

→ All monosaccharides are reducing sugars. (Example → Glucose and fructose)

→ Non-reducing Sugars −: Carbohydrates which can not reduce Tollen's reagent and Fehling solution are called non-reducing sugars.

For example → Sucrose

Classification of monosaccharides :-



D-Fructose

Aldose −: Monosaccharide containing aldehyde group.

Ketose −: Monosaccharide containing Keto group.

→ Glucose is an example of Aldose, while fructose is an example of Ketose.

Different Types of Monosaccharides

Carbon atoms	Aldehyde	Ketone
3	Aldotriose	Ketotriose
4	Aldotetrose	Ketotetrose
5	Aldopentose	Ketopentose
6	Aldohexose	Ketohexose

Glucose

→ It occurs freely in nature as well as combined form. It is present in sweet fruits, honey and ripe grapes.

Preparation of glucose

(1M) [CBSE 2010/2013 and Delhi 2014]

(i) From Sucrose [Cane Sugar]

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{Acidic Hydrolysis}]{H_3O^+} \underset{\text{Glucose + Fructose}}{C_6H_{12}O_6 + C_6H_{12}O_6}$$

(ii) From starch :- $[C_6H_{10}O_5]_n$

$$[C_6H_{10}O_5]_n \xrightarrow{H_3O^+} \underset{\text{Glucose}}{n\ C_6H_{12}O_6}$$

Linear structure of glucose -:

$CHO-(CHOH)_4-CH_2OH$

Molecular formula : $C_6H_{12}O_6$

Supporting Evidence for this structure -:

a.] Six Carbon in straight chain -:

[CBSE 2012] → (1M)

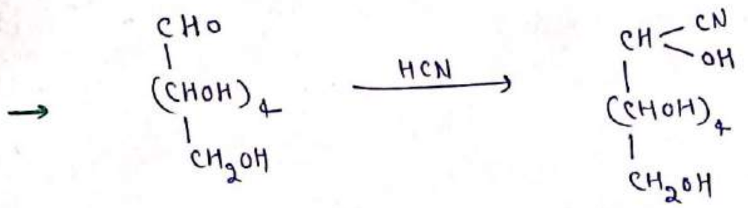
$$CHO-(CHOH)_4-CH_2OH \xrightarrow[\text{Heating with HI}]{\text{Prolonged}} CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \text{ (n-Hexane)}$$

b.] Presence of carbonyl group -:

$$H-C(=O)-(CHOH)_4-CH_2OH + H_2N-OH \xrightarrow[\text{Hydroxyl amine}]{NH_2-OH} H-C(=N-OH)-(CHOH)_4-CH_2OH$$

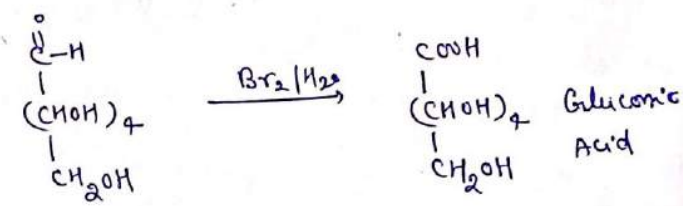
CBSE 2015

(1M)

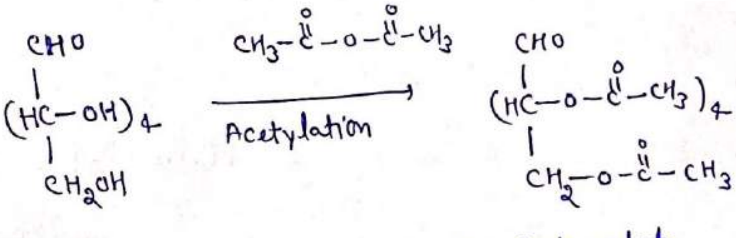


[CBSE 2019]
(1M)

c.] Presence of aldehyde group —:
[CBSE 2019 / 2018]
(1M)



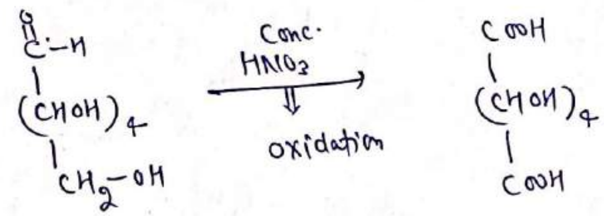
d.] Presence of 5 OH groups —:
[CBSE 2019]
(1M)



Glucose Pentaacetate

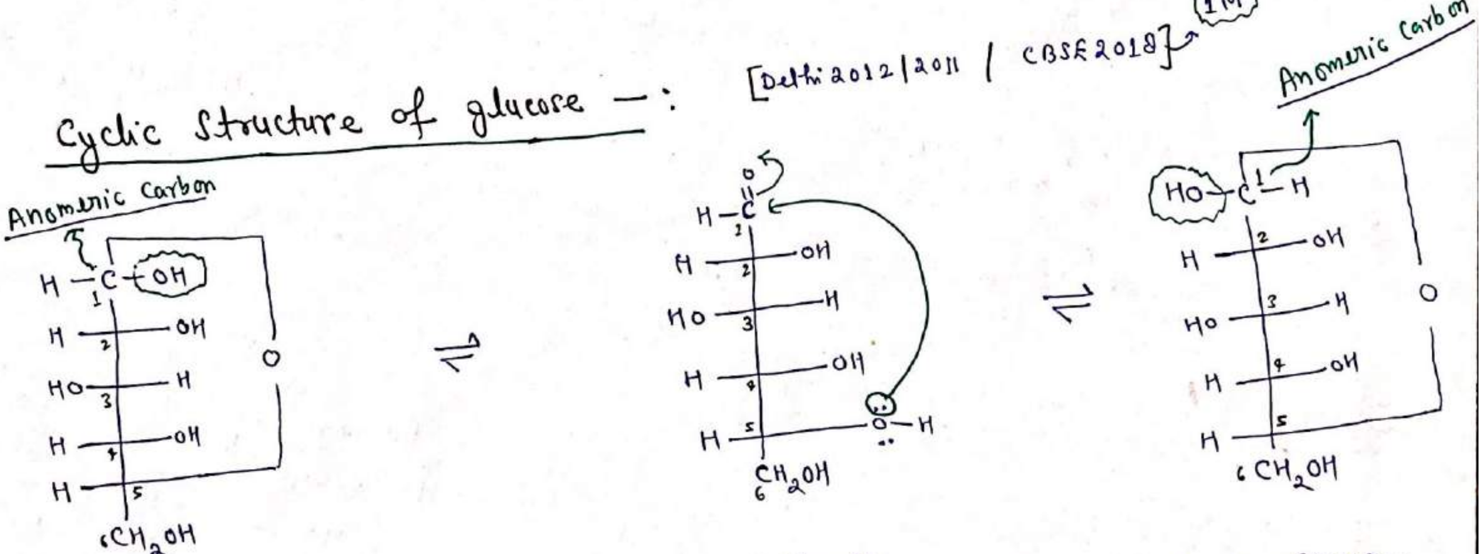
e.] Presence of 1° alcoholic group (—OH) :—
[CBSE 2018] (1M)

Conc. HNO_3 oxidises only aldehyde and 1° alcohol.



Cyclic Structure of glucose —:

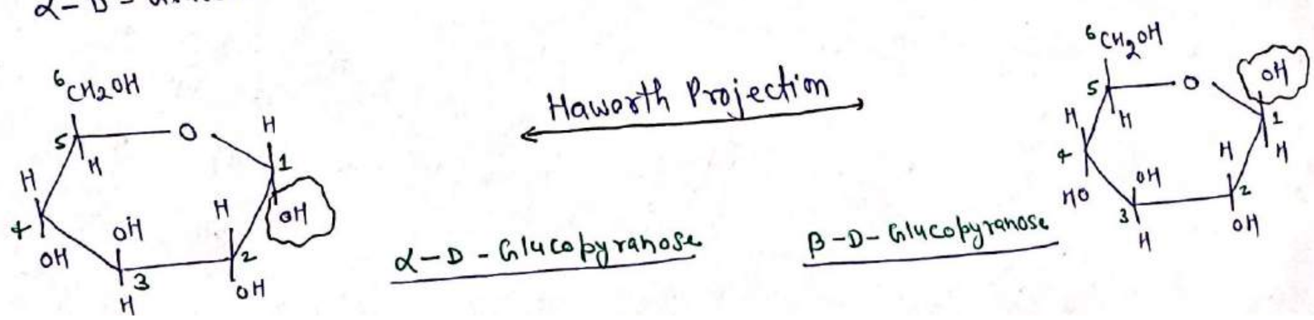
[Delhi 2012 | 2011 | CBSE 2018] (1M)



α-D-Glucose

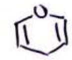
D-Glucose

β-D-Glucose.



α-D-Glucopyranose

β-D-Glucopyranose

→ In Haworth Projection, the six membered cyclic structure of glucose is called Pyranose structure. (In analogy with Pyran ).

→ **Anomers -:** Anomers are isomers that differ in the configuration at the acetal or hemiacetal carbon atom of a sugar in its cyclic form.

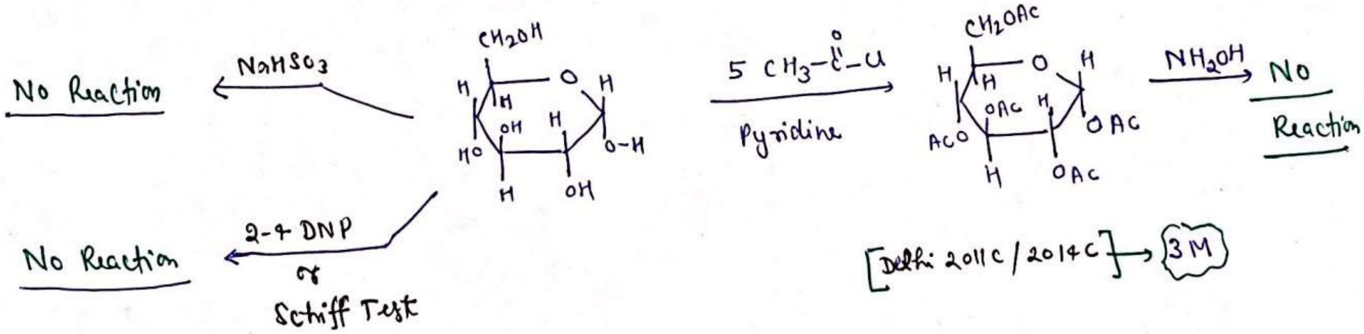
CBSE 2014 ↓ (1M)

For example -: α - D - Glucose and β - D - Glucose are Anomers.

Cyclic structure of glucose : Supporting Evidence :- [CBSE 2010C / 2011 / 2011C] ↳ (2M)

(i) Despite having aldehyde group, glucose does not give 2,4 - DNP test, Schiff test and it does not form adduct with $NaHSO_3$.

(ii) Pentaacetate of glucose does not react with NH_2-OH indicating the absence of free -CHO group.

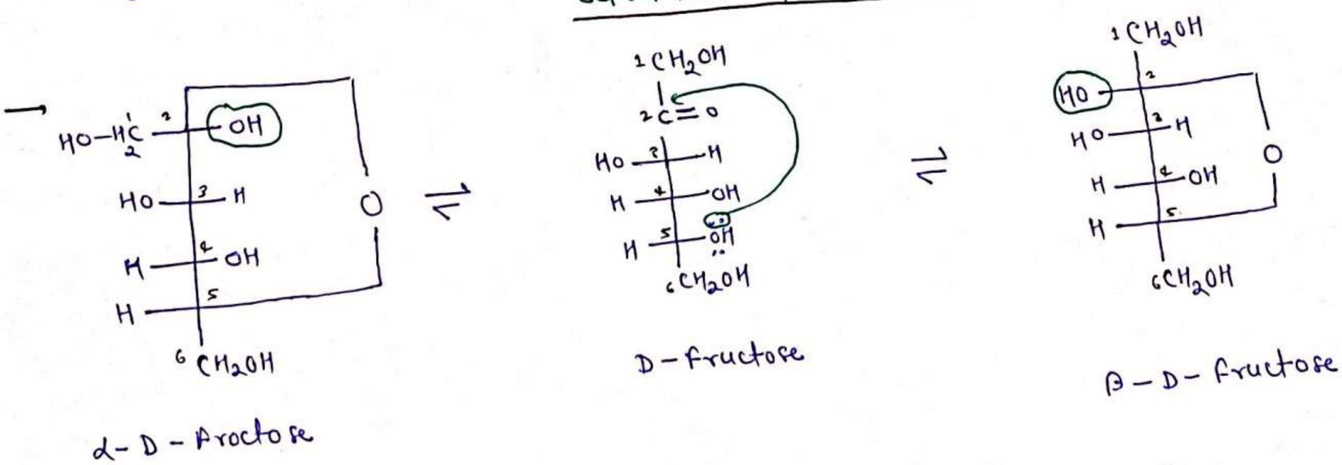


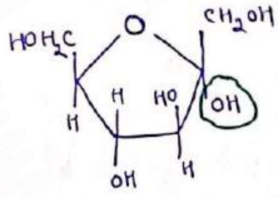
[Delhi 2011C / 2014C] → (3M)

(iii) Glucose is found to exist in two different crystalline forms which are named as α and β. They both have different melting point and different temperature for crystallisation.

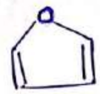
Structure of Fructose -:

→

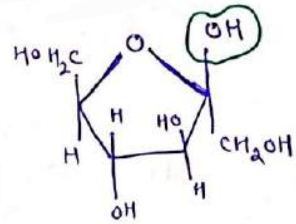




α- D - fructofuranose



furan



β - D - fructofuranose

Amino Acids

Amino group ($-NH_2$) ← → Carboxyl group ($-\overset{O}{\overset{\|}{C}}-OH$)

→ **α - Amino Acid -:** $R-\overset{\alpha}{C}H_2-COOH$ with NH_2 on the α-carbon R → Side chain

20 Amino Acids ↓

- Glycine
- Alanine
- Valine
- Leucine
- Isoleucine
- Arginine
- Lysine
- Glutamic Acid
- Aspartic Acid
- Glutamine
- Asparagine
- Threonine
- Serine
- Cysteine
- Methionine
- Phenylalanine
- Tyrosine
- Tryptophan
- Histidine
- Proline

Classification of amino acids -: (1M)

(i) Depending on nature of synthesis -: [CBSE 2010 / Delhi 2010] [CBSE 2014C] → (3M)

a.) **Non - Essential Amino acids** → The amino acids which can be synthesised in body are known as non-essential amino acids.

→ 10 amino acids are non - essential.

For example → alanine, Glycine, Asparagine

b.) **Essential Amino acids** -: Those amino acids which can not be synthesised in our body and must be obtained through diet.

For example → P V T - T I M H A L L

P → Phenyl alanine
V → Tryptophan
T → Threonine
A → Arginine

(ii) On the basis of functional group -:

a.) **Neutral Amino Acids** :- One $-NH_2$ and one $-\overset{O}{\overset{\|}{C}}-OH$ group.

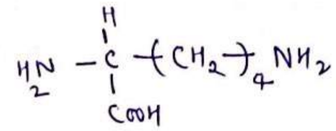
For Example → Glycine $H-CH(NH_2)-\overset{O}{\overset{\|}{C}}-OH$

b.) **Acidic Amino Acids** -: One $-NH_2$ and 2 $-\overset{O}{\overset{\|}{C}}-OH$ group.

For example → Aspartic acid $H_2C(COOH)-HC(NH_2)-COOH$

c.) <u>Basic Amino Acid</u> -: More no. of amino group than carboxyl group.

<u>For example</u> → Lysine



<u>NOTE</u> -: Amino acids are crystalline solids. These are water soluble and behave like salts rather than simple amines or carboxylic acids.

<u>Zwitter Ion</u> -: Due to presence of both acidic (Carboxyl group -COOH) and basic ($-NH_2$ group) in the same molecule, in aqueous solution $-\overset{O}{\overset{\|}{C}}-OH$ group can lose a proton and $-NH_2$ group can accept a proton giving rise to a dipolar ion. This dipolar ion is known as zwitter ion. [CBSE 2011C], (1M)

Amino Acid

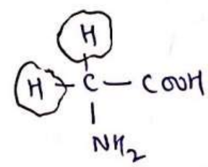
<u>Zwitter Ion</u>

→ This is neutral but contain both ⊕ and ⊖ charge.

→ This can react with both acid and base. So, has amphoteric character. [CBSE 2015 / 2019] (1M)

→ All α-amino acids are optically active except Glycine. Because there is no chiral Carbon in glycine.

Glycine →

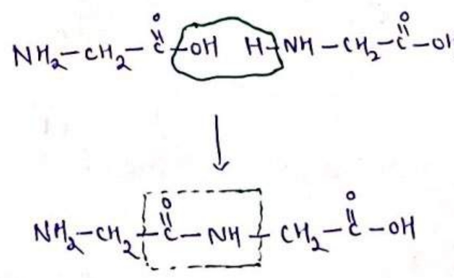


Proteins

→ Proteins are most abundant biomolecules of the living system.

→ Proteins are the polymers of α-amino groups and they are connected to each other by <u>peptide bond</u> or <u>peptide linkage</u>. (1M) [CBSE 2014C / CBSE 2013 / CBSE 2015 / 2016 / Delhi 2017]

chemically, peptide linkage is an amide linkage formed between $-\overset{O}{\overset{\|}{C}}-OH$ group of one α-amino acid and $-NH_2$ group of other α-amino acid formed by the loss of water molecule.



Peptide linkage

→ Dipeptide —: Combination of 2 amino acid by peptide bond is know as dipeptide.

→ Similarly, a tripeptide contains 3 amino acids linked by 2 peptide linkages.

→ Polypeptide —: Combination of 10 or more than 10 amino acids by peptide bonds, is known as poly peptide. (1M) [Delhi 2010]

→ Protein is a polypeptide.

Proteins $\xrightarrow{\text{Hydrolysis}}$ Peptides $\xrightarrow{\text{Hydrolysis}}$ α- Amino Acids.

[CBSE 2010 / 2016 / Delhi 2019] → (1M)

Classification of Proteins :— Two types on the basis of their molecular shape.

a.) Fibrous Proteins :— When polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre like structure is formed.

→ Such proteins are insoluble in water.

→ Example —: Keratin [hair / wool / silk] and myosin [present in muscles].

b.) Globular Proteins —: The chains of polypeptides coil around to give a spherical shape. These are usually soluble in water.

→ Example :— Insulin and albumins.

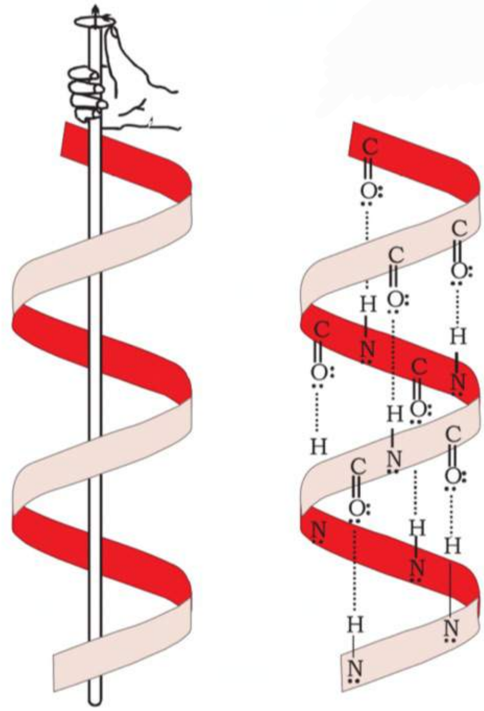
→ Structure and shape of proteins can be studied at four different levels

→ Primary, secondary, tertiary and quaternary, each level being more complex than previous one.

a.) Primary Structure of proteins :— In a protein molecule, one or more poly peptide chains may be present. Each polypeptide chain in a protein is linked together in a specific sequence of amino acids. This sequence of amino acids is termed as primary structure of proteins. [CBSE 2015] (1M)

b.) 2° Structure of proteins :— It refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures → α - Helix & β - Sheet.

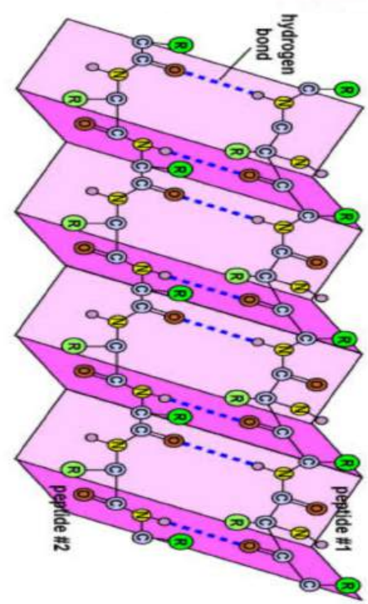
→ These structures aries due to regular folding of backbone of polypeptide chain due to hydrogen bonding between $-\overset{O}{\underset{}{C}}-$ and $-NH-$ groups of peptide bond.



α - Helix –: It is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix). This hydrogen bond is in between $-NH-$ group of each amino acid to the $-\overset{O}{\underset{}{C}}-$ group of an adjacent turn of helix. [Delhi 2013 / CBSE 2018] → (1M)

β - pleated sheet –: In β - structure, all peptide chains are stretched out to maximum extent and then laid side by side (which are held together by intermolecular hydrogen bonding).

→ The structure resembles the pleated folds of drapery and therefore is known as β - pleated sheet.



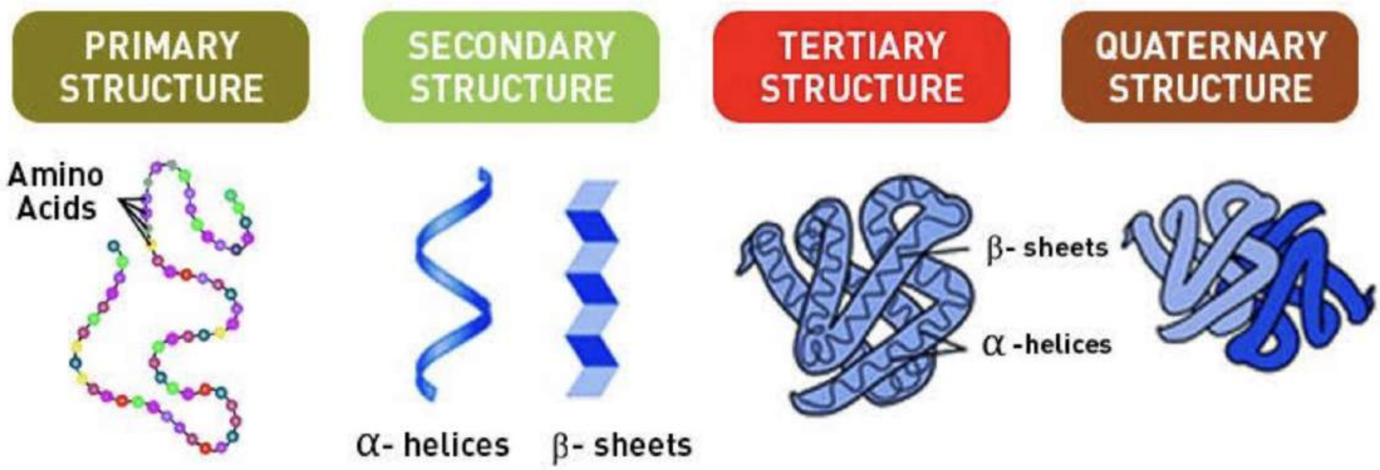
c.> **Tetiary structure of proteins** –: It represents further folding of secondary structure. It gives rise to two major molecular shapes → fibre and globular.

→ Stability of this structure depends on H-bonding, disulphide linkages, Vander Waals force of attraction and electrostatic forces of attraction.

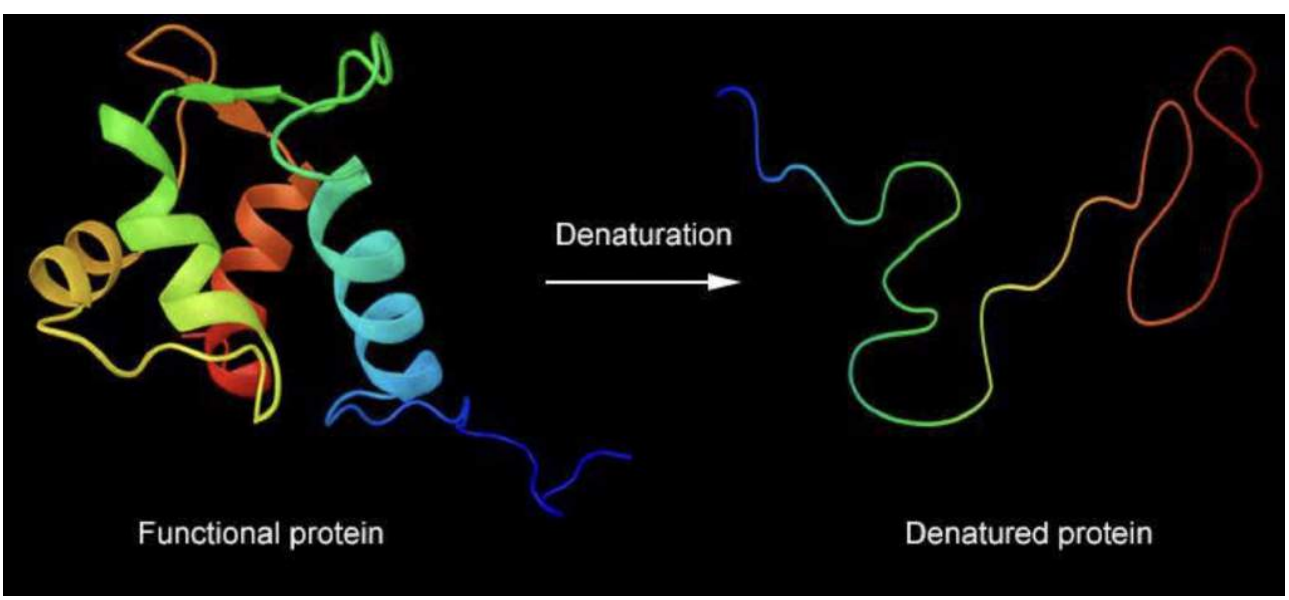
d.> **Quaternary structure of proteins** :— The spatial arrangement of sub units of proteins [which are composed of two or more polypeptide chains] with respect to each other is known as quaternary structure.

Denaturation of Proteins –:

Native Protein → Protein found in a biological system with a unique three dimensional structure (3D) and biological activity is called native protein.



Desaturation of Protiens



→ When a native form of protein is subjected to a physical change (like change in temperature) or chemical change (like change in pH) hydrogen bonds are disturbed. Due to this unfolding of proteins or uncoiling of helix happens and protein loses its biological activity. This is called <u>Denaturation of protein.</u>

→ During denaturation 2°/3° structures are destroyed but 1° structure remains intact. [Delhi 2013/2014 CBSE 2010/2015] (1M)

<u>Example</u> → <u>The coagulation of egg white on boiling</u> → upon boiling the egg, denaturation followed by coagulation occurs. The water present in egg gets adsorbed / absorbed in coagulated proteins through Hydrogen bonding.

→ Curdling of milk [Delhi 2010C] → (1M)

Nucleic Acids

→ Nucleus of a living cell is responsible for the transmission of inherent characters

→ The particles in nucleus of cell (responsible for heredity), are called chromosomes.

→ Chromosomes are made up of proteins and nucleic acids.

→ [Deoxyribonucleic acid] DNA ⟵ <u>Nucleic Acids</u> ⟶ RNA [Ribonucleic Acid]

<u>Chemical Composition of nucleic acids</u> —: [Delhi 2012/2011 | CBSE 2011 2014] (1M)

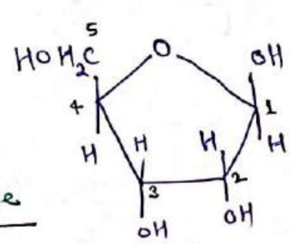
→ Nucleic Acid $\xrightarrow{\text{Hydrolysis}}$ Pentose sugar + Phosphoric acid + base

↑ Nitrogen containing heterocyclic Compounds.

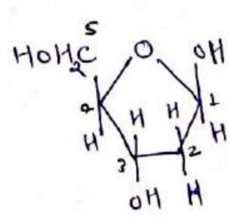
→ <u>DNA</u> ⇒ β-D-2-deoxyribose + Phosphoric acid + [A G C T]

→ <u>RNA</u> ⇒ β-D-ribose + Phosphoric acid + [A G C U]

<u>Pentose sugar</u> →

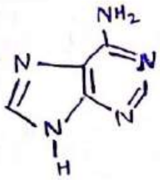


<u>β-D-ribose</u>

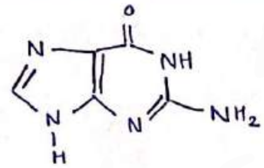


<u>β-D-2-deoxy ribose</u>

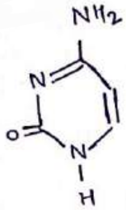
→ Adenine (A)



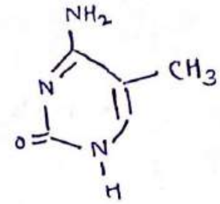
→ Guanine (G)



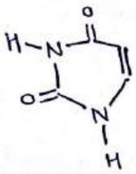
→ Cytosine (C)



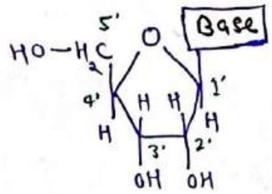
→ Thymine (T)



→ Uracil (U)



[Delhi 2010C / 2014]

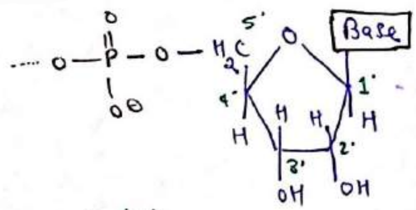


← Nucleoside

→ Nucleoside = Sugar + base

→ Nucleotide = phosphate + Nucleoside

= phosphate + sugar + base



Nucleotide

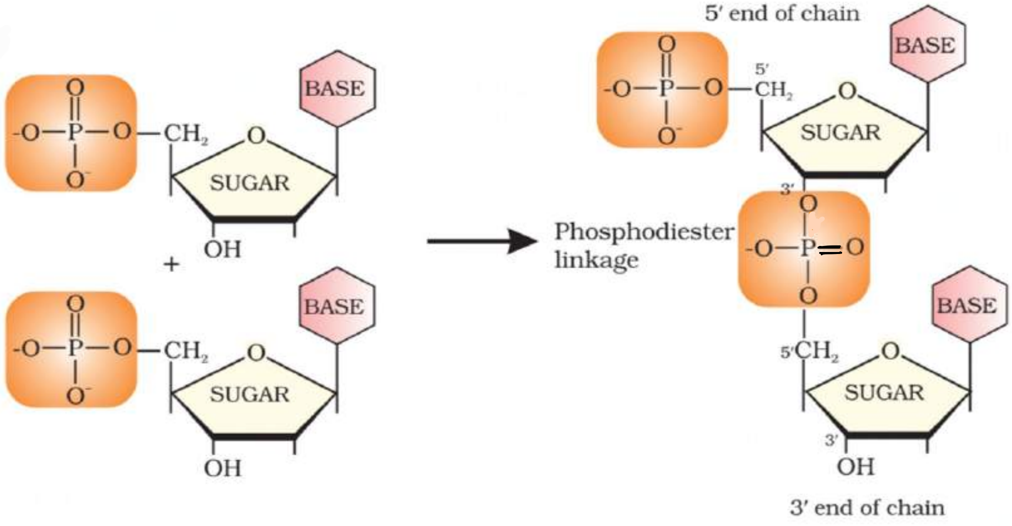
→ Nucleic Acid = Many nucleotides = Polynucleotides

= Long chain polymer of nucleotides.

Nucleic Acid ⇒ ---- — Sugar (Base) — phosphate — sugar (Base) — Phosphate — sugar (Base) -------

→ In a nucleotide, base is connected to 1' carbon of sugar and phosphate is connected to 5' carbon of sugar.

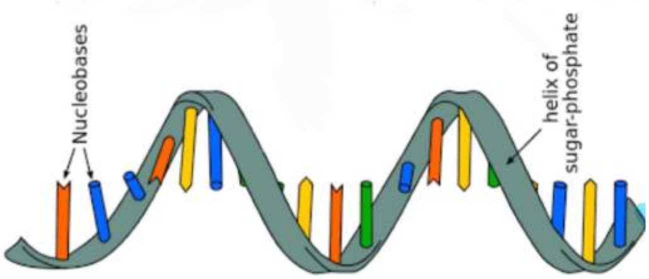
→ Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar.

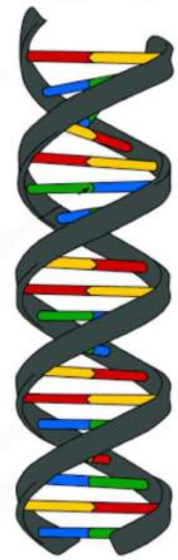


→ Double Strand helix structure for DNA —: The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with Thymine, whereas Cytosine forms hydrogen bonds with Guanine. [G≡C | A=T] [Delhi 2010]

G≡C → 3 Hydrogen bonds

A=T → 2 Hydrogen bonds.





RNA —: Structure —: Single stranded helix.

→ RNA molecules are of 3 types. [Delhi 2013] → (1M)

(i) messenger RNA [m-RNA]

(ii) Ribosomal RNA [r-RNA]

(iii) Transfer RNA [t-RNA]

Biological functions of Nucleic Acids :— DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. Another important function of nucleic acids is the protein synthesis in the cell.