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CHEMICAL KINETICS

➤ **Rate of reaction (ROR)** = $\frac{\text{Rate of disappearance of reactant (appearance of products)}}{\text{Stoichiometric coefficient of reactant (products)}}$

➤ **For a reaction :**

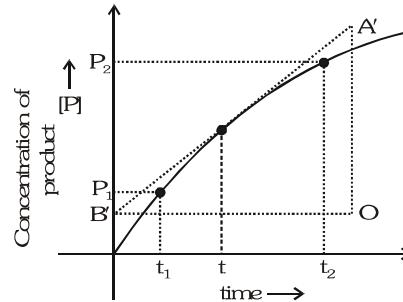
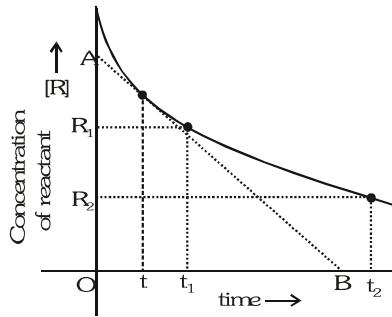


➤ **Instantaneous rate** : $-\frac{1}{a}\left(\frac{d[A]}{dt}\right) = -\frac{1}{b}\left(\frac{d[B]}{dt}\right) = \frac{1}{c}\left(\frac{d[C]}{dt}\right) = \frac{1}{d}\left(\frac{d[D]}{dt}\right)$

Relationship between rate of reaction and rate of disappearance of reactant (rate of appearance of product).

◆ **Average rate** : $-\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[B]}{\Delta t}\right) = \frac{1}{c}\left(\frac{\Delta[C]}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta[D]}{d\Delta t}\right)$

⇒ Graphical method for determining rate :



$$\text{Avg. Rate} = -\left(\frac{[R]_2 - [R]_1}{t_2 - t_1}\right) = \frac{([P]_2 - [P]_1)}{t_2 - t_1}$$

$$\text{Instantaneous rate} = -\left(\frac{OA}{OB}\right) = +\frac{OA'}{OB'} = \pm \text{slope of tangent}$$

➤ **Important kinetic expression for reaction of type $A \longrightarrow B$:**

Order	Zero	1st	2nd	<i>n</i> th
Differential rate law	Rate = k	Rate = k[A]	Rate = k[A] ²	Rate = k[A] ⁿ
Integrated rate law	$[A_0] - [A] = kt$	$kt = \ln \frac{[A_0]}{[A]}$	$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$	$kt = \frac{1}{(n-1)} \left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$
Half life ($t_{1/2}$)	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$	$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{[A]_0^{n-1}} \right]$
($t_{3/4}$)	$t_{3/4} = 1.5 t_{1/2}$	$t_{3/4} = 2 t_{1/2}$	$t_{3/4} = 3 t_{1/2}$	$t_{3/4} = (2^{n-1} + 1) t_{1/2}$

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 ➤ *Graphs of various order*

Order	Rate vs [A]	[A] vs t	log [A] vs t	$\frac{1}{[A]} \text{ vs } t$
<i>Zero order</i>				
<i>First order</i>				
<i>Second order</i>				

Where
 $[A]_0 \Rightarrow$ initial concentration

 $[A] \Rightarrow$ concentration at time t
 $t_{1/2} \Rightarrow$ time taken for initial concentration of reactant to finish by 50%

 $t_{3/4} \Rightarrow$ time taken for initial concentration of reactant to finish by 75%

 ➤ *Monitoring Kinetics Experimentally :*

The kinetics of reaction can be followed (i.e. order, rate constant etc. can be established) by measuring a property which changes with time.

- e.g. (i) Total pressure in a gaseous reaction.
 (ii) Volume of a reagent (Acidic, Basic, oxidising or reducing agent)
 (iii) Volume of a gaseous mixture (V)
 (iv) Optical rotation (R)

For a Reaction -

$$\begin{array}{ccc}
 A_n & \longrightarrow & nB \\
 t = 0 & c & 0 & c_0 \Rightarrow \text{conc. at } t = 0 \\
 t = t & c - x & nx & c_t \Rightarrow \text{conc. at } t = t \\
 t = \infty & 0 & nc & c_\infty \Rightarrow \text{conc. at } t = \infty
 \end{array}$$

For any measurable property X proportional to the concentration of reaction mixture at various times, following relations can be expressed.

In terms of -

(i) X_0 and x	(ii) X_0 and X_t	(iii) X_∞ and X_t	(iv) X_0 , X_t , and X_∞
$k = \frac{1}{t} \ln \frac{X_0}{X_0 - x}$	$k = \frac{1}{t} \ln \frac{(n-1)X_0}{nX_0 - X_t}$	$k = \frac{1}{t} \ln \frac{(n-1)X_\infty}{n(X_\infty - X_t)}$	$k = \frac{1}{t} \ln \left(\frac{X_\infty - X_0}{X_\infty - X_t} \right)$

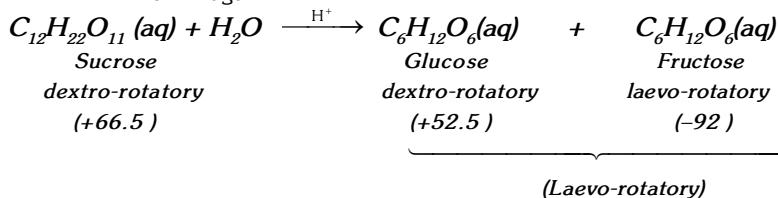
where

 $x \Rightarrow$ amount of reactant reacted in time ' t '.

 $X_0 \Rightarrow$ measured property at $t = 0$
 $X_t \Rightarrow$ measured property at $t = t$
 $X_\infty \Rightarrow$ measured property at $t = \infty$

➤ **Examples : (For Monitoring Kinetics Experimentally)**

(i) Inversion of cane sugar :



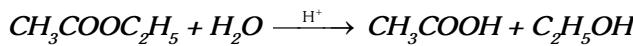
$$k = \frac{2.303}{t} \log \left(\frac{r_\infty - r_t}{r_\infty - r_0} \right)$$

r_0 = rotation at time, $t = 0$

r_t = rotation at time, $t = t$

r_∞ = rotation at time, $t = \infty$

(ii) **Acidic hydrolysis of ethyl acetate :**



$$k = \frac{2.303}{t} \log \left(\frac{V_\infty - V_t}{V_\infty - V_0} \right)$$

V_0 = Volume of NaOH solution used at time, $t = 0$

V_t = Volume of NaOH solution used at time, $t = t$

V_∞ = Volume of NaOH solution used at time, $t = \infty$

Note : Here NaOH acts as a reagent. Acetic acid is one of the product the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution.

➤ **Important characteristics of first order reaction :**

- ◆ $t_{1/2}$ is independent of initial concentration.
- ◆ In equal time interval, reactions finishes by equal fraction.

Reactant conc.	$t = 0$	$t = t$	$t = 2t$
	a_0	a_0x	a_0x^2
	x = fraction by which reaction complete in time ' t '.		
	$t = 3t \dots$		
	$a_0x^3 \dots \dots \dots$		

◆ Graph of $\ln[A]$ vs t is straight line with slope = $\frac{k}{2.303}$

◆ Graph of $[A]$ vs t is exponentially decreasing.

➤ **Zero order :**

- $t_{1/2}$ of zero order is directly proportional to initial concentration.
 - In equal time interval, reaction finishes by equal amount.
- | | | | |
|---------|-----------|------------|------------------|
| $t = 0$ | $t = t$ | $t = 2t$ | $t = 3t \dots$ |
| C_0 | $C_0 - x$ | $C_0 - 2x$ | $C_0 - 3x \dots$ |
- Graph of $[A]$ vs t is straight line.

A zero order reaction finishes in
$$t = \frac{[A]_0}{k}$$

➤ **Temperature dependence :**

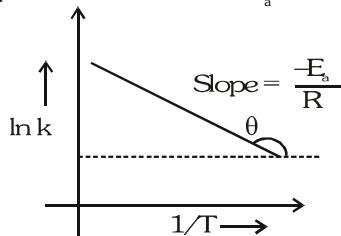
- Arrhenius equation : $k = A \cdot e^{-E_a/RT}$
- E_a = minimum energy over and above the avg. energy of reactant which must be possessed by reacting molecule for collision to be successful.
- A = frequency factor - proportional to number of collisions per unit volume per second.

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- $e^{-E_a/RT}$ = Fraction of collision in which energy is greater than E_a .
- A and E_a are constant i.e. do not vary with temperature

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

Graph : Graphical determination of E_a .

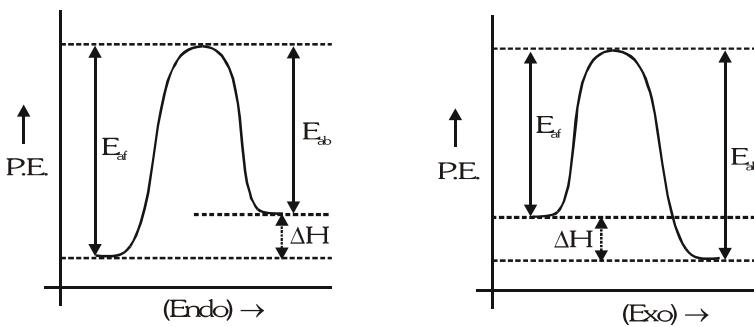


$$\text{Temperature coefficient} = \frac{k_{T+10}}{k_T}$$

By default T = 298 K

$$\text{Variation of rate constant with temparture} \Rightarrow \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

➤ **Endothermic and exothermic reactions :**



$$\boxed{\Delta H = E_{af} - E_{ab}}$$

➤ **Parallel reaction :** $A \xrightarrow{k_1} B$ $A \xrightarrow{k_2} C$

(i) Rate = $(k_1 + k_2) [A]$ - (differential rate law)

(ii) $\frac{k_1}{k_2} = \frac{[B]}{[C]}$

(iii) $t_{1/2} = \frac{0.693}{k_1 + k_2}$

(iv) % of B = $\frac{k_1}{k_1 + k_2} \times 100$; % of C = $\frac{k_2}{k_1 + k_2} \times 100$

(v) $[A] = [A]_0 e^{-(k_1+k_2)t}$

➤ **Pseudo-order reaction :**

Rate law → rate = $k [A]^m [B]^n$

Pseudo rate law :

rate = $k_1 [A]^m$

[B] assumed constant in two cases :

- (i) B in large excess (ii) B → CATALYST

NUCLEAR CHEMISTRY

- All nuclear reactions are first order :

Two types of nuclear reaction : (a) Artificial radioactivity (b) Radioactivity (spont.)
First order

$$\lambda t = 2.303 \log \frac{N_0}{N_t}$$

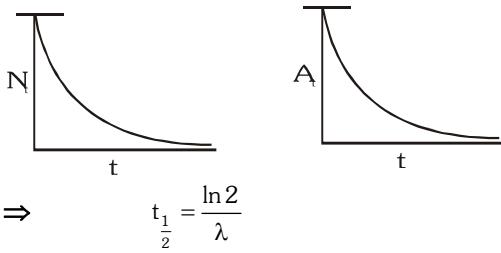
$\lambda \rightarrow$ Decay constant

$N_0 \rightarrow$ Initial nuclei

$N_t \rightarrow$ Nuclei at 't'

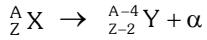
$$\text{Activity} = A_t = \frac{-dN_t}{dt} = \lambda N_t ; \text{ Nuclei/sec.}$$

A_t = Rate of decay



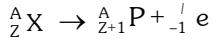
$$\Rightarrow t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$$

- α decay = ${}^4_2\text{He}$ Particles at high velocity



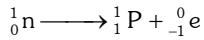
To \downarrow size of large nuclei

- β decay = ${}^0_{-1}\text{e}$ at high velocity



To $\downarrow \frac{n}{p}$ ratio.

Nuclear change in β decay



- γ -decay :

Photons from excited nuclei after α - or β - decay

No effect on n/p ratio

High energy e/m radiation.

$$\text{Mean life} , t_{\text{avg}} = \frac{1}{\lambda}$$

- Parallel decay :

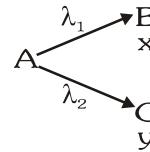
$$t = 0 \quad N_0$$

$$t = t \quad N_0 - x - y$$

$$\lambda_{\text{eff.}} = \lambda_1 + \lambda_2$$

$$\frac{1}{t_{\text{eff.}}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}$$

$\lambda \rightarrow$ No dependence on temp.



THERMODYNAMICS

➤ **THERMODYNAMICS :**

- ◆ Study of heat and work interaction between system and surrounding.
- ◆ A macroscopic science.
- ◆ Thermodynamic laws are experimentally verified.

➤ **Important terms and concepts in thermodynamics.**

- ◆ System - Portion of universe under investigation.
- ◆ Surrounding - Anything apart from system.
- ◆ Boundary - Real or hypothetical line or surface between system and surrounding.
- ◆ Wall - A real boundary.

Rigid wall - Immovable wall ($w = 0$)

Non-rigid wall - Movable wall ($w \neq 0$)

Adiabatic wall - Insulated wall ($q = 0$)

Diathermic wall - Non-insulated wall ($q \neq 0$)

- ◆ State variable - Variable which defines state of system.
- ◆ State of system - A condition defined by fixed value of state variables.
- ◆ State of thermodynamic equilibrium - A condition in which state variables do not vary with time.

➤ **Extensive state variable :** State variable whose value depends upon size of system.

Examples - mass, volume, charge, mole etc.

➤ **Intensive state variable :** State variable whose value does not depend upon size of system.

Examples - concentration, density, temperature etc.

➤ **Path variable :**

- ◆ **Heat :** Mode of energy transfer between system and surrounding due to temperature difference.
- ◆ **Work :** Mode of energy transfer between system and surrounding due to difference in generalized force.(Net force).

THE FIRST LAW

- (i) Energy of universe is conserved
- (ii) Internal energy (U) of a system is state function.
- (iii) $\Delta U = q + w$

ΔU = Increase in internal energy of system.

q = Heat absorbed by the system

w = work done on the system

- (iv) In a cyclic process
$$\sum_{Cyclic} \Delta U = 0$$

If a cyclic process involves n steps with heat absorbed and work done on the system, q_i and w_i respectively, then -

$$\sum_{Cyclic} \Delta U = \sum_{i=1}^{i=n} (q_i + w_i) = \sum_{i=1}^{i=n} q_i + \sum_{i=1}^{i=n} w_i = 0$$

$$\Rightarrow Q_{net} = -W_{net} \quad (\text{in a cyclic process})$$

(v) If two states 1 and 2 are connected by n paths involving q_i and w_i , heat and work respectively, then

$$\Delta U = q_1 + w_1 = q_2 + w_2 = \dots \dots \dots q_n + w_n$$

(vi) q and w are path dependent quantities (indefinite quantities) but their sum is a definite quantity (ΔU).

◆ **Enthalpy** : A state function defined by first law

$$H = U + PV$$

(i) Enthalpy is (pressure volume energy + internal energy of system)

(ii) Enthalpy is also called heat content of system.

◆ **Heat absorbed at constant volume and constant pressure.**

$q_V = \Delta U$ Heat absorbed by a system in isochoric process is equal to change in internal energy of system.

$q_p = \Delta H$ Heat absorbed at constant pressure by a system is equal to change in enthalpy.

◆ **Enthalpy change :**

For General process -

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1 \dots \dots \text{(i)}$$

For Isobaric change -

$$\Delta H = \Delta U + P \Delta V \dots \dots \text{(ii)}$$

For Isochoric change -

$$\Delta H = \Delta U + V(\Delta P) \dots \dots \text{(iii)}$$

For a differential change

$$dH = dU + PdV + VdP \dots \dots \text{(iv)}$$

➤ **Ideal gas processes : (See table page no. 11)**

◆ **Enthalpy of phase transition**

ΔH_{vap} = heat absorbed at constant temperature and pressure to convert one mole liquid into its vapours.
= molar enthalpy of vapourisation.

ΔH_{fusion} = heat absorbed at constant temperature and pressure to convert one mole solid into liquid.
= molar enthalpy of fusion.

$\Delta H_{\text{sublimation}}$ = heat absorbed at constant temperature and pressure to convert one mole solid into its vapours.
= molar enthalpy of sublimation.

$\Delta H = \Delta U + P(V_f - V_i)$ since phase transitions are isobaric and isothermal processes.

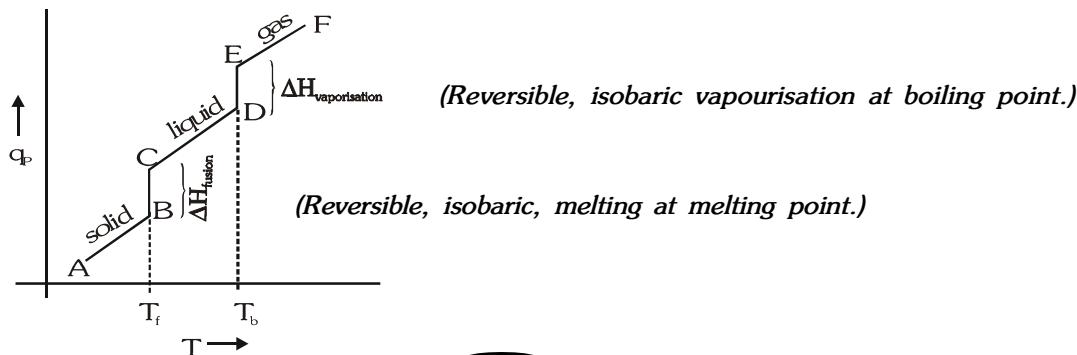
◆ **Relationship between ΔH and ΔU for phase transitions.**

For vapourisation $\Delta H_{\text{vap}} = \Delta U_{\text{vap}} + RT$

For sublimation $\Delta H_{\text{sublimation}} = \Delta U_{\text{sublimation}} + RT$

For fusion $\Delta H_{\text{fusion}} \approx \Delta U_{\text{fusion}}$

◆ **Heating curve at constant pressure :**



- ◆ **Enthalpy of reaction ($\Delta_r H$) :** The enthalpy of reaction is heat exchanged at constant pressure and temperature to convert the stoichiometric amount of reactant into product with specified physical state according to balanced chemical reaction at constant temperature and pressure.

for $aA + bB \longrightarrow cC + dD$

$$\Delta_r H = q_p = \text{enthalpy of reaction}$$

$$\Delta_r H = (cH_C + dH_D - aH_A - bH_B) \quad \text{where } H_A, H_B, H_C, H_D \text{ are molar enthalpies of A,B,C and D.}$$

- ◆ **Relationship between $\Delta_r H$ and $\Delta_r U$**

$$\Delta_r H = \Delta_r U + \Delta n_g RT \quad (\text{for ideal gas})$$

$$\Delta_r H = \Delta_r U + P(V_f - V_i) \quad (\text{for non ideal conditions})$$

- ◆ **The stoichiometric coefficient of solids and liquids in not considered in calculation of Δn_g (because $V_s \sim V_L \ll V_g$)**

- ◆ **Standard state for**

(i) Ideal gas : 1 bar pressure ; any temperature.

(ii) Solid / Liquid : 1 bar pressure ; any temperature.

(iii) Solute : Molar concentration of 1 mole/L at $P = 1$ bar.

Standard enthalpy, internal energy change for reaction.

$\Delta_r H$ and $\Delta_r U$ are change in thermodynamics function of a system under standard conditions.

SECOND LAW

- **Spontaneous process :**

- A process which takes place on its own without any external help.
- Spontaneous process ≡ Irreversible process ≡ Natural process.

- **Second law :** During a spontaneous process.

- $\Delta S_{\text{universe}} > 0$
- ⇒ $\Delta S_{\text{system}} + \Delta S_{\text{surr.}} > 0$
- S is a state function. S is measure of disorder of a system.

- (A) Change in entropy of system is given by :

$$dS_{\text{system}} = \frac{dq_{\text{rev.}}}{T}$$

- (i) Entropy change for ideal gas process :

$$\bullet \quad \Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

- (ii) Entropy change for system in phase transition :

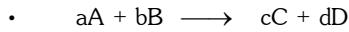
$$\bullet \quad \Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T_b}$$

$$\bullet \quad \Delta S_{\text{fusion.}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$\bullet \quad \Delta S_{\text{sublimation}} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{Sub.}}}$$

(iii) Entropy change of system for a chemical reaction :

For a reaction -



$$\Delta_r S = cS_c + dS_D - aS_A - bS_B$$

S_A , S_B , S_C and S_D are molar absolute entropies which is obtained by third law.

(B) Entropy change in surrounding :

(i) Ideal gas process : $\Delta S_{\text{surr.}} = \frac{-q_{\text{actual}}}{T}$

(ii) Phase transition : $\Delta S_{\text{surr.}} = \frac{-\Delta H}{T}$

(iii) Chemical reaction : $\Delta S_{\text{surr.}} = -\frac{\Delta_r H}{T}$

For reversible processes : $\Delta S_{\text{system}} + \Delta S_{\text{surr.}} = 0$
 $\Delta S_{\text{system}} = -\Delta S_{\text{surr.}}$

For irreversible processes : $\Delta S_{\text{system}} + \Delta S_{\text{surr.}} > 0$
 $\Delta S_{\text{total}} \geq 0$

◆ *Prediction of sign of $\Delta_r S$ from inspection :*

(i) If $\Delta n_g > 0$; $\Delta_r S > 0$.

(ii) If Solid \longrightarrow liquid }
 liquid \longrightarrow gas } $\Delta_r S > 0$

(iii) If cyclisation taken place $\Delta_r S < 0$.

➤ *Gibb's function : $G = H - TS$*

$$\Delta G = \Delta H - T\Delta S \quad \rightarrow \text{For isobaric change}$$

$$\Delta G = -T(\Delta S_{\text{Total}})$$

$$\Rightarrow (\Delta G)_{T,P} \leq 0 \quad \rightarrow \text{Process spontaneous}$$

(A) Change in ΔG for phase transition :

(i) For reversible phase transitions : $\Delta G = 0$.

(ii) For irreversible phase transition : $\Delta G_{P,T} = \Delta H_{P,T} - T\Delta S_{P,T}$

(B) Change in ΔG for chemical reaction :



$$\Delta_r G = cG_C + dG_D - aG_A - bG_B \quad \dots\dots(i)$$

$$\Delta_r G = \Delta_r H - T\Delta_r S \quad \dots\dots(ii)$$

$$\Delta_r G = \Delta_r G + RT \ln Q \quad \dots\dots(iii)$$

Where, $Q \equiv$ Reaction quotient

➤ **$\Delta G / \Delta_r G$ and state of chemical equilibrium :**

At equilibrium :

- $\Delta G = 0 \Rightarrow G_{\text{product}} = G_{\text{reactant}}$
- $\Delta G = -RT \ln K_{\text{eq.}}$
- At equilibrium the system gibb's function is at minimum value.

➤ **$\Delta_r G$ and $\Delta_r^{\circ}G$:**

$\Delta_r G$ = change in Gibb's function when all the reactants and products have arbitrary activities.

$\Delta_r^{\circ}G$ = change in Gibb's function when all the reactants and products are at unit activities.

⇒ All gases at 1 bar pressure.

⇒ All solute at molar concentration 1 M.

➤ **Factors on which $\Delta_r G$ depends -**

- (i) Stoichiometric coefficients of a balanced chemical reaction.
- (ii) the temperature.
- (iii) the $\Delta_r G$ is independent of actual pressure or concentration of reactants or products.

➤ **Gibb's function and non-PV work :**

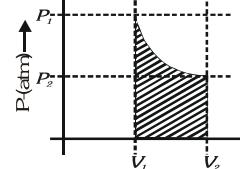
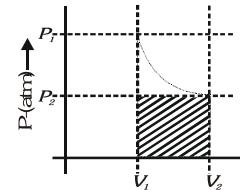
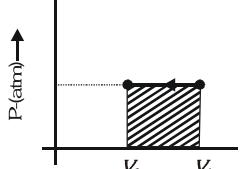
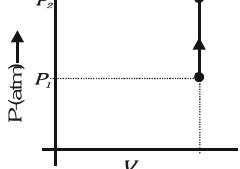
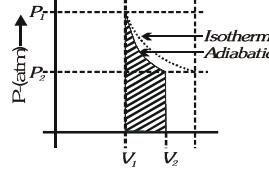
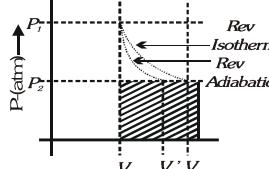
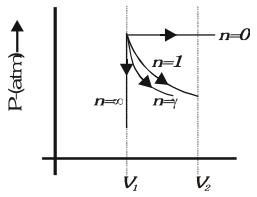
$$-(\Delta G)_{T, P} = W_{\max}$$

decrease in Gibb's function at constant temperature and pressure is equal to maximum non-PV work obtainable from system reversibly.

$$-\Delta_r G = -\Delta_r H + T\Delta_r S$$

Decrease in Gibb's function = heat given out to surrounding + $T\Delta_r S$.

IDEAL GAS PROCESSES :

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
<i>Reversible isothermal process</i>	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \left(\frac{V_2}{V_1} \right)$ $q = nRT \ln \left(\frac{P_1}{P_2} \right)$	0	0	
<i>Irreversible isothermal process</i>	$w = -P_{ext}(V_2 - V_1)$ $= -P_{ext} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$q = P_{ext}(V_2 - V_1)$	0	0	
<i>Isobaric process</i>	$w = -P_{ext}(V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_p\Delta T$	$\Delta U = nC_v\Delta T$	$\Delta H = nC_p\Delta T$	
<i>Isochoric process</i>	$w = 0$	$q = \Delta U = nC_v\Delta T$	$\Delta U = nC_v\Delta T$	$\Delta H = nC_p\Delta T$	
<i>Reversible adiabatic process</i>	$w = nC_v(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	$\Delta U = nC_v\Delta T$	$\Delta H = nC_p\Delta T$	
<i>Irreversible adiabatic process</i>	$w = nC_v(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$				
<i>Polytropic process</i>	$w = \frac{P_2 V_2 - P_1 V_1}{n-1}$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$q = \int_{T_1}^{T_2} C_v dT$ $+ \int_{T_1}^{T_2} \frac{R}{1-n} dT$	$\Delta U = nC_v\Delta T$	$\Delta H = nC_p\Delta T$	

 V_2 = Final volume P_2 = Final pressure V_1 = Initial volume P_1 = Final pressure

THERMOCHEMISTRY

- $\Delta_r H = q_p$ = Heat of reaction at constant pressure
 $\Delta_r E = \Delta_r U = q_v$ = Heat of reaction at constant volume.
- For mix. of reacting ideal gases at constant Temperature :
 $\Delta_r H = \Delta_r U + (\Delta n_g) RT$.
- **Exothermic Reaction :**

$$\begin{array}{ll} H_p > H_r & U_p > U_r \\ \Delta_r H > 0 & \\ \Delta_r U > 0 & \end{array}$$

- **Endothermic Reaction :**

$$\begin{array}{ll} H_p < H_r & U_p < U_r \\ \Delta_r H < 0 & \\ \Delta_r U < 0 & \end{array}$$

- **Reversible Phase Transition**

Isothermal and Isobaric

Example :

- Melting or Freezing at MP
- Vaporisation or condensation at B.P.
- Sublimation at sublimation point.
- Interconversion of allotropic forms at Transition temperature.

- $S_g \gg S_\ell > S_s ; \quad V_g \gg V_\ell > V_s ;$
 $V_g \gg V_\ell < V_s$ (Water) ; $H_g \gg H_\ell > H_s ;$
 $U_g \gg U_\ell > U_s ; \quad \Delta H_{\text{sub}} \gg \Delta H_{\text{vap}} > \Delta H_{\text{fus.}}$

At same Pressure and Temperature

$$\Delta H_{\text{sub}} = \Delta H_{\text{vap}} + \Delta H_{\text{fus.}}$$

- For reversible phase transition.

$$W = - P_{\text{ext}} [\Delta V]$$

$$\Delta S_{\text{trans.}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}}$$

$$q = \Delta H_{\text{trans}}$$

$$\Delta U_{\text{trans}} = \Delta H_{\text{trans}} + w$$

- $\Delta_r H = \sum V_p H_{\text{(product)}} - \sum V_R H_{\text{(Reactant)}}$
 $\Rightarrow V_p, V_R$ – Stoichiometric coefficient of reactants & products
 $\Delta_r G = \sum V_p G_{\text{(product)}} - \sum V_R G_{\text{(reactants)}}$

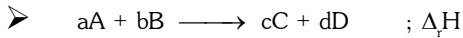
- **Determining $\Delta_r H$ for reaction :- 3 methods**

- $\Delta_r H = \sum V_p \Delta H_f(P) - \sum V_R \Delta H_f(R)$
- $\Delta_r H = \sum V_R \Delta H_{\text{comb.}}(R) - \sum V_p \Delta H_{\text{comb.}}(P)$
- $\Delta_r H = \sum \Delta H_{\text{atomisation}}(R) - \sum \Delta H_{\text{atomisation}}(P)$

- ΔH_f (Element in solid state) = 0.

$$\Delta H_f(\text{CO}_2, g) = \Delta H_{\text{comb.}}(\text{C, grap.})$$

$$\Delta H_f (H_2O, l) = \Delta H_{\text{comb.}} (H_2, g)$$



$\Delta_r H$ = change in enthalpy when

a mol of A react ; b mol of B react ; c mol of C formed ; d mol of D formed

➤ $\Delta_r G = \sum V_p \Delta G_f (P) - \sum V_R \Delta G_f (R)$ OR $\Delta_r G = \Delta_r H - T \Delta_r S$

➤ Gibbs enthalpy is function of P, T.

$$P \uparrow \Rightarrow G \uparrow$$

$$T \uparrow \Rightarrow G \downarrow$$

➤ $\Delta H_f (H^+, aq) = 0$

$$\Delta G_f (H^+, aq) = 0$$

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

$$S_m (H^+, aq) = 0$$

By convention

➤ $q = \int ms dt$

$$= \int nC_m dt$$

$$= \int C dt$$

$$\begin{matrix} mS & = & nC_m & = & C \\ \downarrow & & \downarrow & & \downarrow \end{matrix}$$

specific molar Total

heat heat heat

capacity capacity capacity

➤ For strong Acid and strong base

$$\Delta H_{\text{neutr.}} = - 57.1 \text{ kJ/mol.}$$

when 1 eq. H^+ (acid) reacts with 1 eq. OH^- (base)

➤ If acid or base is weak

$$\Delta H_{\text{neut.}} = - 57.1 + \Delta H_{\text{ionisation}} \Rightarrow + ve$$

➤ Heat evolved in SA + SB titration = (no. of eqv. of limiting reagent) 57.1 kJ

➤ Resonance enthalpy = R.E. < 0 = (Energy of R.H.) - (Energy of stablest R.S.)

➤ $\Delta H_{\text{Actual}} - \Delta H_{\text{theoretical}} = [\sum V_p RE (P) - \sum V_R RE (R)]$

□ $\Delta H_{\text{hydration}} [CuSO_4, s]$

$$\Delta H_{\text{solution}} [CuSO_4, s] - \Delta H_{\text{solution}} [CuSO_4 \cdot 5H_2O, s]$$

➤ **Enthalpy of atomisation :**

$$\Delta H_{\text{atomisation}} (O_2, g) = BE (O = O)$$

$$\Delta H_{\text{atomisation}} (C_6H_6, l) = \Delta H_{\text{vap.}} + 3\epsilon (C = C) + 3\epsilon (C - C) + 6\epsilon (C - H) \quad \epsilon = \text{Bond enthalpy}$$

$$\Delta H_{\text{atomisation}} (Fe, s) = \Delta H_{\text{sub}}$$

$$\Delta H_{\text{atomisation}} (I_2, s) = \Delta H_{\text{sub}} + \epsilon (I - I)$$

CHEMICAL EQUILIBRIUM



- | | |
|--|--|
| (1). K_c not very large or very small
(2). Both R and P present at equilibrium
(3). R and P stability comparable | (1). $K_c \ggg 1$
(2). $[P] \ggg [R]$ at equilibrium
(3). Stability $P \ggg R$ |
|--|--|

At equilibrium for reaction mix. properties like P, V, T, n, magnetism, colour, density become constant.

➤ **For gaseous reactions.**

$$K_p = K_c (RT)^{\Delta n_g}$$

$$\begin{array}{lll} K_p > K_c & \text{if} & \Delta n_g > 0 \\ K_p < K_c & \text{if} & \Delta n_g < 0 \\ K_p = K_c & \text{if} & \Delta n_g = 0 \end{array}$$

$$\text{Units of } K_p = (\text{atm})^{\Delta n_g}$$

$$\text{Units of } K_c = (M)^{\Delta n_g}$$

$$K_p = \frac{A_f}{A_b} e^{-\Delta_r H^\circ / RT}$$

both K_p & K_c depend only on temperature for given reaction.

➤ For pure solids & pure liquids (solvent) :

Active mass = 1 [Kinetically]

Activity = 1 [thermodynamically]

$$\text{Molarity} = \frac{\text{Density}}{\text{Molar mass}} = \text{Constant}$$

➤ **Reaction Quotient (Q_c / Q_p)**

(i) Used to find direction of reaction mixture – Fwd./Bwd.

(ii) $Q_c < K_c$ or $Q_p < K_p \Rightarrow$ FWD.

$Q_c > K_c$ or $Q_p > K_p \Rightarrow$ BWD.

$Q_c = K_c$ or $Q_p = K_p \Rightarrow$ Equilibrium

$$(iii) Q_p = Q_c (RT)^{\Delta n_g}$$

➤ If

(1) $[K_p \ggg 1 \text{ or } K_c \ggg 1]$

or

(2) $[K_p \lll 1 \text{ or } K_c \lll 1]$

no need to solve equation but use approximation.

In 1st case $[R]_{eq} \approx 0$

In 2nd case $[P]_{eq} \approx 0$

➤ **Degree of dissociation, α**

$$\frac{\Delta n}{n_0} = \frac{\Delta P}{P_0} = \frac{\Delta m}{m_0} = \frac{\Delta V}{V_0}$$

n, P, m, V → mols, partial pressure, mass, partial volume of reactant respectively.

% dissociation = % reactant converted to product = 100 α

$\alpha \leq 1$ [Equality for irreversible reaction]

□ $X_{gas} = \frac{P_{gas}}{P_T} = \frac{V_{gas}}{V_T} = \frac{n_{gas}}{n_T}$

For a reacting mixture of 'n' gases :

$$2VD_{mix} = M_{avg.} = \sum_{i=1}^n x_i m_i$$

- $M_{avg.}$ & VD_{mix} is a function of mixture composition.
- For mixture of reacting gas $M_{avg.}$ changes & becomes constant at equilibrium.

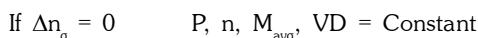
- $M_{avg.}$ (or VD_{mix}) $\propto \frac{1}{\text{moles of gases in mixture}}$

➤ $\frac{(VD)_i}{(VD)_f} = \frac{M_i}{M_f} = \frac{n_f}{n_i} = \frac{P_f}{P_i}$

Used to find ' α ' from M_{avg} or VD data for reactions with $\Delta n_g \neq 0$

- On going FWD.

If $\Delta n_g > 0$



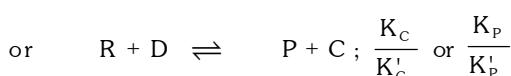
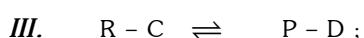
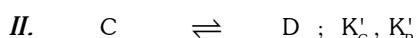
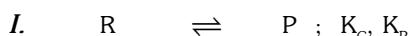
➤ For a reaction with $\Delta n_g \neq 0$

α depends on - K_p or K_c , Temperature, Initial concentration, Initial moles, Initial pressure, volume of vessel

➤ For a reaction with $\Delta n_g = 0$;

α depends only on - K_p or K_c , Temperature

➤ K_p or K_c depend on the way of writing a reaction :



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➤ Relative Humidity (R.H.)

$$= \left(\frac{\text{Partial pressure of water vapour}}{\text{Aqueous tension}} \right) \times 100$$

If RH < 100% \Rightarrow Partial pressure < Aqueous tension \Rightarrow Unsaturated air sample

If RH \geq 100% \Rightarrow Saturated air sample

➤ Le Chatelier Principle

Case I : [R] increased \Rightarrow Forward shift

[P] increased \Rightarrow Backward shift

□ If R or P is pure solid / Pure liquid \Rightarrow No effect.

Case II : Total P increased (or V decreased)

If $\Delta n_g > 0$ \Rightarrow backward

If $\Delta n_g < 0$ \Rightarrow forward

If $\Delta n_g = 0$ \Rightarrow no effect

Case III : V Increased

\Rightarrow Same effect as P decreased

If $\Delta n_g > 0$ \Rightarrow forward

If $\Delta n_g < 0$ \Rightarrow backward

If $\Delta n_g = 0$ \Rightarrow no effect

Case IV : T Increased

If $\Delta_r H > 0$ \Rightarrow forward

If $\Delta_r H < 0$ \Rightarrow backward

T decreased

If $\Delta_r H > 0$ \Rightarrow backward

If $\Delta_r H < 0$ \Rightarrow forward

Case V : Using Catalyst

No effect on K_C , K_p or equilibrium concentration

Only time required to attain equilibrium is lesser.

Case VI : Adding inert gas at constant V.

\Rightarrow No effect

Case VII : Adding inert gas at constant Pressure

\Rightarrow Same effect as Pressure decrease or volume increase

➤ Thermodynamics state of Equilibrium :

$$\begin{aligned} G_{\text{mix}} &\rightarrow \text{Minimum} \\ \Delta_r G &\rightarrow 0 \\ \sum V_p G_p &= \sum V_R G_R \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{at } P, T \text{ constant}$$

If $\Delta_r G < 0 \Rightarrow \sum V_p G_p < \sum V_R G_R$

- ⇒ Reaction shifts forward to attain equilibrium.
If $\Delta_r G > 0 \Rightarrow \sum V_p G_p > \sum V_R G_R$
- ⇒ Reaction shifts backward to attain equilibrium.
If $\Delta_r G = 0 \Rightarrow$ Equilibrium state
- ◻ $\Delta_r G = \Delta_f G + RT \ln(Q)$
 $\Delta_r G$ = Standard Gibbs energy of reaction (when all Reactants & Products are in standard states)

➤ **Standard State**

Gas → Ideal gas

Activity=Partial pressure=1 bar ≈ 1 atm.

Solute → Ideal solution

Activity = concentration = 1M

Solid/Liquid → Pure activity = 1

- ◻ Q contains activity of species i.e., partial pressure in bar (or atm) for gas molarity for solute is unity for solid or liquid.

- ◻ At equilibrium $\Delta_r G = 0$ & $Q = K_{eq}$

$$\Rightarrow \Delta_r G = -RT \ln K_{eq}$$

$$K_{eq} = e^{-\Delta_r G^\circ / RT}$$

- ◻ For gaseous homogeneous reaction,

$$\Delta_r G = -RT \ln K_p$$

For homogeneous reaction in solution phase

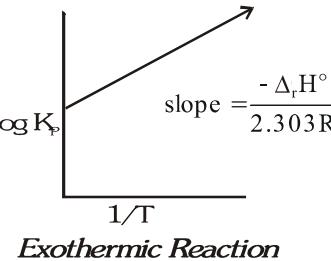
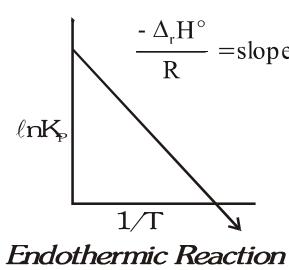
$$\Delta_r G = -RT \ln K_c$$

- ◻ BP, M.P. & Sublimation point all increase in increasing pressure

Exception – M.P. of H_2O decrease on increasing pressure

➤ **Von't Hoff Equation :**

$$\frac{d[\ln K_p]}{dT} = \frac{\Delta_r H^\circ}{RT^2}; \quad \ln K_p = -\frac{\Delta_r H^\circ}{RT} + \ln \frac{A_f}{A_b}; \quad \log \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta_r H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$



IONIC EQUILIBRIUM
➤ ACCORDING TO STRENGTH IONIC CONDUCTORS ARE OF 2 TYPES :

1. **Strong electrolyte** : Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

Ex. Na^+Cl^- , K^+Cl^- , etc.

- (a) Strong acid $\rightarrow \text{H}_2\text{SO}_4$, HCl , HNO_3 , HClO_4 , H_2SO_5 , HBr , HI
- (b) Strong base $\rightarrow \text{KOH}$, NaOH , Ba(OH)_2 , CsOH , RbOH
- (c) All Salts $\rightarrow \text{NaCl}$, KCl , CuSO_4

2. **Weak electrolytes** : Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex.

- (a) Weak acid $\rightarrow \text{HCN}$, CH_3COOH , HCOOH , H_2CO_3 , H_3PO_3 , H_3PO_2 , B(OH)_3
- (b) Weak base $\rightarrow \text{NH}_4\text{OH}$, Cu(OH)_2 , Zn(OH)_2 , Fe(OH)_3 , Al(OH)_3

➤ ACIDS BASES AND SALTS :

Arrhenius concept :

Arrhenius Acid : Substance which gives H^+ ion on dissolving in water (H^+ donor)

Ex. HNO_3 , HClO_4 , HCl , HI , HBr , H_2SO_4 , H_3PO_4 etc.

◆ H_3BO_3 is not Arrhenius acid.

➤ **Arrhenius base** : Any substance which releases OH^- (hydroxyl) ion in water (OH^- ion donor).

◆ First group elements (except Li.) form strong bases

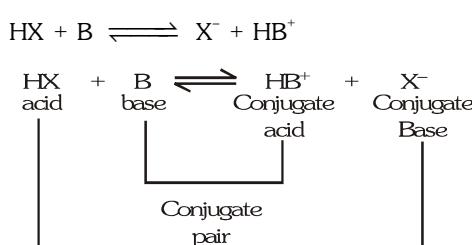
➤ **Bronsted - Lowery concept : (Conjugate acid - base concept) (Protonic concept)**

Acid : substances which donate H^+ are Bronsted Lowery acids (H^+ donor)

Base : substances which accept H^+ are Bronsted Lowery bases (H^+ acceptor)

➤ **Conjugate acid - base pairs :**

In a typical acid base reaction



Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	H_2O	H_3O^+
HSO_4^-	SO_4^{2-}	RNH_2	RNH_3^+
H_2O	OH^-		

Ex :

➤ **LEWIS CONCEPT (electronic concept) :**

An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Acid → e^- pair acceptor

Ex.	Electron deficient molecules	: BF_3 , AlCl_3
	Cations	: H^+ , Fe^{2+} , Na^+
	Molecules with vacant orbitals	: SF_4 , PF_3

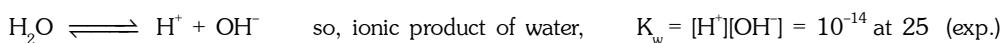
A base is any molecule/ion which has a lone pair of electrons which can be donated.

Base → (One electron pair donor)

Ex.	Molecules with lone pairs	: NH_3 , PH_3 , H_2O , CH_3OH
	Anions	: OH^- , H^- , NH_2^-

➤ **IONIC PRODUCT OF WATER :**

According to arrhenius concept



Dissociation of water is endothermic, so on increasing temperature K_w increases.

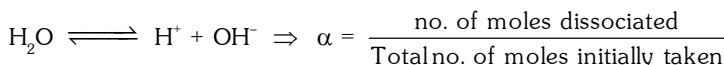
K_w increases with increase in temperature.

Now $\text{pH} = -\log[\text{H}^+] = 7$ and $\text{pOH} = -\log[\text{OH}^-] = 7$ for water at 25°C (experimental)

$$\left. \begin{array}{l} \text{pH} = 7 = \text{pOH} \Rightarrow \text{neutral} \\ \text{pH} < 7 \text{ or } \text{pOH} > 7 \Rightarrow \text{acidic} \\ \text{pH} > 7 \text{ or } \text{pOH} < 7 \Rightarrow \text{Basic} \end{array} \right\} \text{at } 25^\circ\text{C}$$

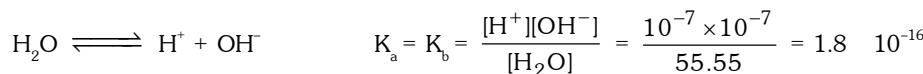
◆ Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

➤ **Degree of dissociation of water :**



$$= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7} \% \quad [\text{at } 25^\circ\text{C}]$$

➤ **Absolute dissociation constant of water :**



$$\text{So, } \text{pK}_a = \text{pK}_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

□ **ACIDITY AND pH SCALE :**

Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.

So greater the tendency to give H^+ , more will be the acidic strength of the substance.

Basic strength means the tendency of a base to give OH^- ions in water.

So greater the tendency to give OH^- ions, more will be basic strength of the substance.

The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale.

pH is defined as negative logarithm of activity of H^+ ions.

$$\therefore \text{pH} = -\log a_{\text{H}^+} \quad (\text{where } a_{\text{H}^+} \text{ is the activity of } \text{H}^+ \text{ ions})$$

Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a dilute solution.

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The pH scale was marked from 0 to 14 with central point at 7 at 25 °C taking water as solvent.

If the temperature and the solvent are changed, the pH range of the scale will also change. For example

0 - 14 at 25 °C ($K_w = 10^{-14}$) Neutral point, pH = 7

0 - 13 at 80 °C ($K_w = 10^{-13}$) Neutral point, pH = 6.5

pH can also be negative or > 14

➤ pH Calculation of different Types of solutions :

(a) Strong acid solution :

- (i) If concentration is greater than 10^{-6} M.

In this case H^+ ions coming from water can be neglected,

so $[H^+] = \text{normality of strong acid solution}$

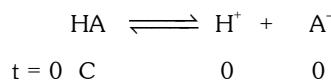
- (ii) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected.

So $[H^+] = \text{normality of strong acid} + H^+ \text{ ions coming from water in presence of this strong acid}$

(b) pH of a weak acid (monoprotic) Solution :

- ◆ Weak acid does not dissociate 100 % therefore we have to calculate the percentage dissociation using K_a dissociation constant of the acid.
- ◆ We have to use Ostwald's Dilution law (as have been derived earlier)



$$t_{eq} \quad C(1 - \alpha) \quad C\alpha \quad C\alpha \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha^2}{1 - \alpha}$$

If $\alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$ (is valid if $\alpha < 0.1$ or 10%)

$$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \text{ So } pH = \frac{1}{2}(pK_a - \log C)$$

on increasing the dilution $\Rightarrow C \downarrow = \alpha \uparrow$ and $[H^+] \downarrow \Rightarrow pH \uparrow$

(c) pH of a mixture of weak acid (monoprotic) and a strong acid solution :

- ◆ Weak acid and Strong acid both will contribute H^+ ion.
- ◆ For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- ◆ To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.
- ◆ If the total $[H^+]$ from the acid is more than 10^{-6} M, then contribution from the water can be neglected, if not then we have to take $[H^+]$ from the water also.

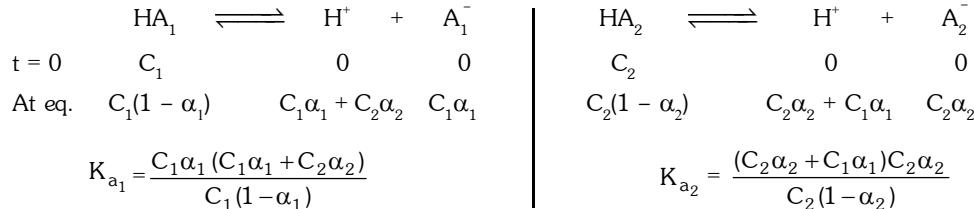
➤ Relative strength of weak acids and bases :

For two acids of equimolar concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

(d) pH of a mixture of two weak acid (both monoprotic) solution :

- ◆ Both acids will dissociate partially.
- ◆ Let the acids are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then



(Since α_1 , α_2 both are small in comparison to unity)

$$K_{a_1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 \quad ; \quad K_{a_2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \quad \Rightarrow \quad \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} + \frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} \Rightarrow [\text{H}^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

(e) pH of a solution of a polyprotic weak acid :

- Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid (H_2A) in water whose concentration is c M.

In an aqueous solution, following equilibria exist.

If

α_1 = degree of ionization of H_2A in presence of HA^-

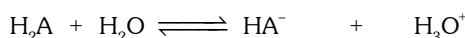
K_{a_1} = first ionisation constant of H_2A

α_2 = degree of ionisation of HA^- in presence of H_2A

K_{a_2} = second ionisation constant of H_2A

I step

II step



$$\text{at eq. } c(1 - \alpha_1) \quad c\alpha_1(1 - \alpha_2) \quad (c\alpha_1 + c\alpha_1\alpha_2) \quad \text{at eq. } c\alpha_1(1 - \alpha_2) \quad c\alpha_1\alpha_2 \quad (c\alpha_1 + c\alpha_1\alpha_2)$$

$$(K_{eq})_1 [H_2O] = \frac{[H_3O^+][HA^-]}{[H_2A]} = K_{a_1}$$

$$(K_{eq})_2 [H_2O] = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = K_{a_2}$$

$$\therefore K_{a_1} = \frac{(ca_1 + ca_1 a_2)[c a_1 (1 - a_2)]}{c(1 - a_1)}$$

$$K_{a_2} = \frac{(ca_1 + ca_1a_2)[ca_1a_2])}{ca_1(1-a_2)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1} \quad \dots \dots \text{ (i)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)]\alpha_2}{1-\alpha_2} \quad \dots\dots \text{(ii)}$$

Knowing the values of K_{a_1} , K_{a_2} , and c , the values of α_1 and α_2 can be calculated using equations (i) and

(ii) After getting the values of α_1 and α_2 , $[\text{H}_3\text{O}^+]$ can be calculated as

$$[\text{H}_3\text{O}^+]_T = c\alpha_1 + c\alpha_1\alpha_2$$

Finally, for calculation of pH

- ◆ If the total $[H_3O^+] < 10^{-6} M$, the contribution of H_3O^+ from water should be added.
 - ◆ If the total $[H_3O^+] > 10^{-6} M$, then $[H_3O^+]$ contribution from water can be ignored.

Using this $[H_3O^+]$, pH of the solution can be calculated.

Approximation :

For diprotic acids, $K_{a_2} \ll K_{a_1}$ and α_2 would be even smaller than α_1

$$\therefore 1 - \alpha_2 \approx 1 \text{ and } 1 + \alpha_2 \approx 1$$

$$\text{Thus, equation (i) can be reduced to } K_{a_1} = \frac{C\alpha_1 \times \alpha_1}{1 - \alpha_1}$$

This is expression similar to the expression for a weak monoprotic acid.

- ◆ Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} \ll K_{a_1}$

➤ **SALTS :**

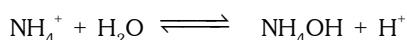
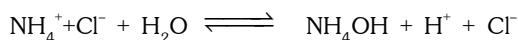
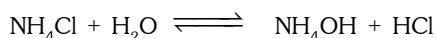
Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.

Classification of salts :**(1) Simple salts****(2) Normal salt :** (i) Acid salts (ii) Basic salts**(3) Double salts****(4) Complex salts****(5) Mixed salts**

➤ **TYPES OF SALT HYDROLYSIS :**

(1) Hydrolysis of strong acid - weak base [SA - WB] type salt -

Ex. $CaSO_4$, NH_4Cl , $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$



➤ **Summary :**

$$(1) K_h = \frac{K_w}{K_b}$$

$$(2) h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}$$

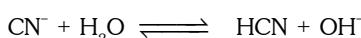
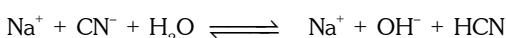
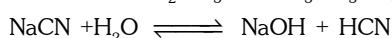
$$(3) [H^+] = Ch = \sqrt{\frac{K_w \times C}{K_b}}$$

$$(4) pH = -\log [H^+]$$

$$pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

(2) Hydrolysis of [WA - SB] type salt -

Ex. KCN , $NaCN$, K_2CO_3 , $BaCO_3$, K_3PO_4



➤ **Summary :**

$$(1) K_h = \frac{K_w}{K_a}$$

$$(2) h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}}$$

$$(3) \quad [\text{OH}^-] = \text{Ch} = \sqrt{\frac{K_w \times C}{K_a}} \quad (4) \quad [\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}}$$

$$(5) \quad \text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = 7 + \frac{1}{2} \text{ pK}_a + \frac{1}{2} \log C$$

(3) Hydrolysis of (WA - WB) type salt :

Ex. NH_4CN , CaCO_3 , $(\text{NH}_4)_2\text{CO}_3$, ZnHPO_3

➤ **Summary :**

$$(1) \quad K_h = \frac{K_w}{K_a \times K_b} \quad (2) \quad h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$(3) \quad [\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}} = K_a \cdot h \quad (4) \quad \text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = 7 + \frac{1}{2} \text{ pK}_a - \frac{1}{2} \text{ pK}_b$$

(4) Hydrolysis of [SA – SB] type salt –

Ex. NaCl , BaCl_2 , Na_2SO_4 , KClO_4 etc.

- (i) Hydrolysis of salt of [SA – SB] is not possible
- (ii) Solution is neutral in nature ($\text{pH} = \text{pOH} = 7$)
- (iii) pH of the solution is 7

➤ **BUFFER SOLUTIONS :**

A solution that resists change in pH value upon addition of small amount of strong acid or base (less than 1 %) or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

Types of buffer solutions

- (A) Simple buffer solution
- (B) Mixed buffer solution

➤ **SIMPLE BUFFER SOLUTION :**

A salt of weak acid and weak base in water e.g. $\text{CH}_3\text{COONH}_4$, HCOONH_4 , AgCN , NH_4CN .

Buffer action of simple buffer solution

$$\boxed{\text{pH} = 7 + \frac{1}{2} \text{ pK}_a - \frac{1}{2} \text{ pK}_b}$$

➤ **MIXED BUFFER SOLUTIONS :**

(a) Acidic buffer solution :

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

(b) Basic buffer solution :

A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of NH_4OH and NH_4Cl .

◆ **Condition for maximum buffer action :**

$$[\text{NH}_4\text{OH}] : [\text{NH}_4\text{Cl}]$$

$$1 \quad 1$$

$$\text{pOH} = \text{pK}_b + \log \frac{1}{1}$$

$$\text{pOH} = \text{pK}_b \quad \text{and} \quad \text{pH} = 14 - \text{pK}_b$$

➤ **SOLUBILITY (*s*) AND SOLUBILITY PRODUCT (K_{sp}) :**

This is generally used for sparingly soluble salts. We will be dealing with the solubilities in the following type of solution.

Solubility product (K_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

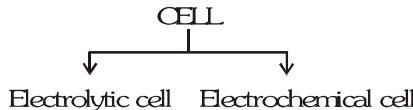
◆ **Simple solubility**

Let the salt is $\text{A}_x \text{B}_y$, in solution in water, let the solubility in $\text{H}_2\text{O} = 's'$ M, then

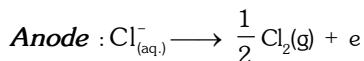
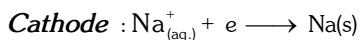
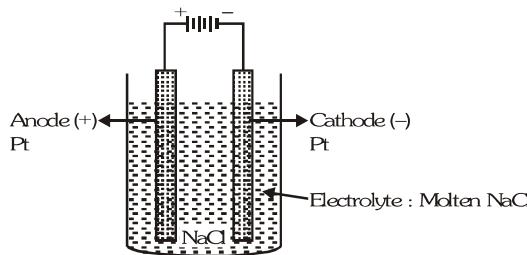


◆ **Condition of precipitation**

- ◆ For precipitation ionic product [IP] should be greater than solubility product k_{sp} .

ELECTRO CHEMISTRY

- Electrolytic cell : Converts electrical energy into chemical energy



- Deposition of material at any electrode follow faraday's law of electrolysis.

Faraday's 1st Law :

$$w = Z it$$

$$w = \frac{M}{n - \text{factor} \times 96500} it$$

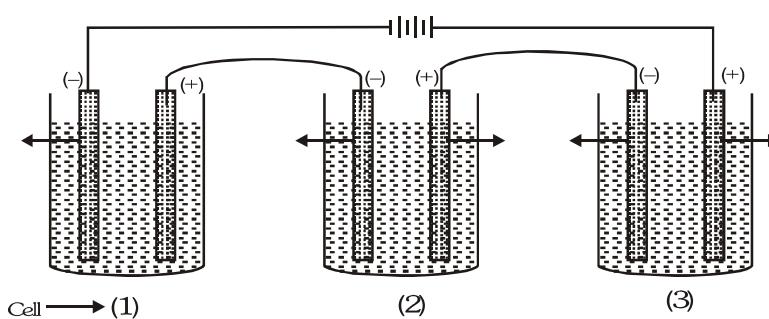
where w = mass deposited (gm)

M = molar mass

i = current (Amp.)

t = time (sec.)

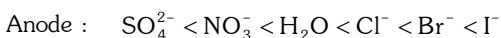
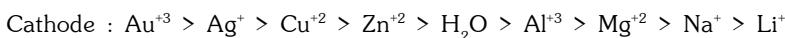
Faraday's second law :



- At any electrode for material deposited.

$$\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3}$$

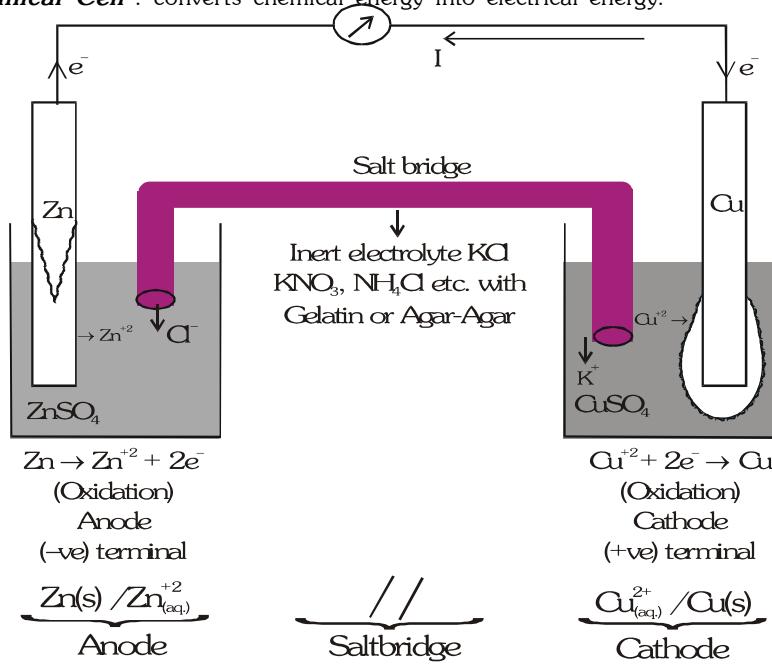
Note : Order of discharge potential.



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PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

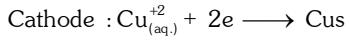
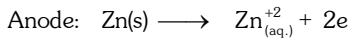
S. No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(i)	Aqueous NaCl	Pt or Graphite	Cl ₂	H ₂
(ii)	Fused NaCl	Pt or Graphite	Cl ₂	Na
(iii)	Aqueous NaOH	Pt or Graphite	O ₂	H ₂
(iv)	Fused NaOH	Pt or Graphite	O ₂	Na
(v)	Aqueous CuSO ₄	Pt or Graphite	O ₂	Cu
(vi)	Dilute HCl	Pt or Graphite	Cl ₂	H ₂
(vii)	Dilute H ₂ SO ₄	Pt or Graphite	O ₂	H ₂
(viii)	Aqueous AgNO ₃	Pt or Graphite	O ₂	Ag

➤ **Electrochemical Cell** : converts chemical energy into electrical energy.



$$\begin{aligned} E_{\text{Cell}} &= SRP_{\text{cathode}} - SRP_{\text{Anode}} \\ &= SRP_{\text{cathode}} + SOP_{\text{at anode}} \end{aligned}$$

Half cell reaction :



➤ **Cell reaction :** $Zn(s) + Cu_{(aq.)}^{+2} \longrightarrow Zn_{(aq.)}^{+2} + Cu(s)$

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

➤ *Nearest equation :*

$$E_{\text{Cell}} = E_{\text{Cell}} - \frac{0.059}{n} \log Q \quad \text{at } 298 \text{ K}$$

➤ Max electrical work done = $nFE = -\Delta G$
 electrical work done = $nFE = -\Delta G$

DIFFERENT TYPE OF ELECTRODES/HALF CELL

Type	Example	Half-cell reaction	Electrode potential (reduction)
Metal - Metal ion	M/M^{n+}	$M^{n+} + ne^- \longrightarrow M(s)$	$E = E + \frac{0.0591}{n} \log [M^{n+}]$
Gas - ion	$Pt / H_2 (P \text{ atm})$ $/ H^+ (XM)$	$H^+ (aq) + e^- \longrightarrow \frac{1}{2} H_2 (P \text{ atm})$	$E = E - 0.0591 \log \frac{\sqrt{P_{H_2}}}{[H^+]}$
Oxidation - reduction	$Pt / Fe^{2+}, Fe^{3+}$	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	$E = E - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$
Metal - insoluble salt Anion	$Ag/AgCl, Cl^-$	$AgCl (s) + e^- \longrightarrow Ag (s) + Cl^-$	$E_{Cl^-/AgCl/Ag} = E_{Cl^-/AgCl/Ag}^0 - 0.0591 \log [Cl^-]$
Calomel electrode	$Cl^- (aq)/Hg/Hg_2Cl_2$	$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^- (aq.)$	$E = E - 0.0591 \log [Cl^-]$

➤ Gibb's Helmhaltz equation :

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]$$

$$\Rightarrow \Delta H = -nFE + nFT \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

JEE-Chemistry Handbook**'THE ELECTROCHEMICAL SERIES'**

<i>Element</i>	<i>Electrode Reduction Reaction</i>	<i>Standard electrode Reduction potential E⁰, Volts</i>
Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	- 3.05
K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	- 2.93
Ba	$\text{Ba}^{+2} + 2\text{e}^- \rightarrow \text{Ba}$	- 2.90
Ca	$\text{Ca}^{+2} + 2\text{e}^- \rightarrow \text{Ca}$	- 2.87
Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	- 2.71
Mg	$\text{Mg}^{+2} + 2\text{e}^- \rightarrow \text{Mg}$	- 2.37
Al	$\text{Al}^{+3} + 3\text{e}^- \rightarrow \text{Al}$	- 1.66
Mn	$\text{Mn}^{+2} + 2\text{e}^- \rightarrow \text{Mn}$	- 1.18
H_2O	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	- 0.828
Zn	$\text{Zn}^{+2} + 2\text{e}^- \rightarrow \text{Zn}$	- 0.76
Cr	$\text{Cr}^{+3} + 3\text{e}^- \rightarrow \text{Cr}$	- 0.74
Fe	$\text{Fe}^{+2} + 2\text{e}^- \rightarrow \text{Fe}$	- 0.44
Cd	$\text{Cd}^{+2} + 2\text{e}^- \rightarrow \text{Cd}$	- 0.40
Ni	$\text{Ni}^{+2} + 2\text{e}^- \rightarrow \text{Ni}$	- 0.25
Sn	$\text{Sn}^{+2} + 2\text{e}^- \rightarrow \text{Sn}$	- 0.14
Pb	$\text{Pb}^{+2} + 2\text{e}^- \rightarrow \text{Pb}$	- 0.13
H_2	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0
Cu	$\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$	+ 0.34
I_2	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+ 0.54
Hg	$\text{Hg}_{2}^{+2} + 2\text{e}^- \rightarrow 2\text{Hg}$	+ 0.79
Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+ 0.80
Hg	$\text{Hg}^{+2} + 2\text{e}^- \rightarrow \text{Hg}$	+ 0.85
Br_2	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+ 1.08
O_2	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+ 1.229
Cl_2	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+ 1.36
Au	$\text{Au}^{+3} + 3\text{e}^- \rightarrow \text{Au}$	+ 1.50
F_2	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+ 2.87

CONDUCTION IN ELECTROLYTES

	<i>Conductance</i>	<i>Specific Conductivity</i>	<i>Molar Conductivity</i>
Symbol Unit	C Ω^{-1}	κ $\Omega^{-1} \text{ cm}^{-1}$	Λ_m $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
Specific	conductance of volume within electrode	conductance of unit volume	conductance of that volume which contain exactly one mole
Change with concentration	decrease with decrease in concentration	Decrease with decrease in concentration	Increase with in decrease in concentration
Formula	$C = \frac{1}{R}$	$k = C$ cell constant	$k = \Lambda_m = K \cdot V$ V = Volume of solution contain 1 mole of electrolyte
Factors	(i) nature of electrolyte (ii) concentration of electrolyte (iii) Type of cell.	(i) nature of electrolyte (ii) concentration of electrolyte	(i) nature of electrolyte (ii) concentration of electrolyte

➤ **KOHLRAUSCH'S LAW :**

$$\Lambda_m^\infty (A_x B_y) = x \lambda_+^\infty + y \lambda_-^\infty$$

$$\Lambda_m^\infty (K_2 SO_4) = 2 \lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty (Na_3 PO_4) = 3 \lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty [Fe_2(SO_4)_3] = 2 \lambda_+^\infty + 3 \lambda_-^\infty$$

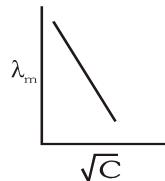
➤ **FORMULA**

$$(1) R = \rho \cdot \frac{\ell}{A}$$

$$(2) \lambda_m = k \cdot \frac{1000}{M}$$

$$(3) \lambda_{eq.} = k \times \frac{1000}{N}$$

$$(4) \text{ for strong electrolyte } \lambda_m = \lambda_{m_\infty} - b \sqrt{C}$$



LIQUID SOLUTION

- **Vapour Pressure :** Pressure of any volatile substance at any given temperature.

$$T \uparrow \Rightarrow V.P. \uparrow$$

Attractive forces $\uparrow \Rightarrow V.P. \downarrow$

- **Raoult's law :**

Non volatile solute and volatile solvent solution.

If $\begin{cases} B = \text{Non volatile solid} \\ P_B = 0 \end{cases}$

$$P_A = P_A^{\circ} X_A$$

- **Colligative Properties :** Properties depends on no. of particles of Non volatile solute in solution.

$$\begin{matrix} \text{No. of particle of} \\ \text{Non volatile solute} \end{matrix} \uparrow \Rightarrow \begin{matrix} \text{Colligative} \\ \text{Properties} \end{matrix} \uparrow$$

- (1) **Relative lowering of V.P. :**

$$\frac{P_A^{\circ} - P_A}{P_A^{\circ}} = i \frac{n_B}{n_A + n_B} \approx i \frac{n_B}{n_A}$$

Where n_B = mole of Non-volatile solute.

i = Vant Hoff's factor.

- (2) **Elevation in B.P. :**

$$\Delta T_b = (T'_b - T_b) = i \cdot k_b \cdot m$$

$$\text{where } K_b = \frac{RT_b^2}{1000 \times \ell_v}$$

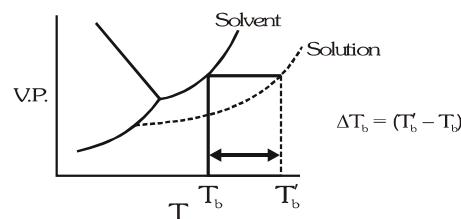
where T_b = B.P. of pure solvent.

ℓ_v = Latent heat of vapourization per gm

K_b = molal elevation constant

M = molar mass

$$\text{where } \ell_v = \left(\frac{\Delta H_{\text{vap}}}{M} \right)$$



- (3) **Depression in F.P.**

$$\Delta T_f = T_f - T'_f = i \cdot k_f \cdot m$$

$$\text{where } k_f = \frac{RT_f^2}{1000 \times \ell_f}$$

T_f = f.p. of pure solvent

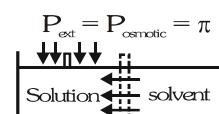
k_f = molal depression constant

ℓ_f = latent heat of fusion per gm.

- (4) **Osmotic pressure :**

$$\pi \propto (P_A^{\circ} - P_A)$$

$$\pi = iC \cdot S.T.$$



where π = osmotic pressure

C = molarity (mole/lit)

$S = R = \text{const.}$ for solution.

Sol.(1) Sol (2)

If $\pi_1 = \pi_2$ Isotonic

If $\pi_1 > \pi_2$ { solⁿ(1) hypertonic
solⁿ(2) hypotonic

Van't Hoff factor for different Cases of solutes undergoing Ionisation and Association :

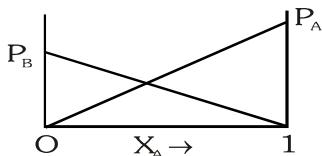
Solute	Example	Ionisation/association (x degree)	y*	van'thoff factor	abnormal mol. wt. (m'_1)
Non-electrolyte	urea-glucose, sucrose etc.	none	1	1	normal mol.wt. (m_1)
Binary electrolyte A^+B^-	NaCl, KCl, HCl CH_3COOH , $FeSO_4$ etc.	$AB \rightleftharpoons A^+ + B^-$	2	$(1 + x)$	$\frac{m_1}{(1 + x)}$
Ternary electrolyte A_2B , AB_3	K_2SO_4 , $BaCl_2$, $K_3[Fe(CN)_6]$, $FeCl_3$	$A_2B \rightleftharpoons 2A^+ + B^{2-}$ $AB_3 \rightleftharpoons A^{3+} + 3B^-$	3 4	$(1+2x)$ $(1+3x)$	$\frac{m_1}{(1 + 2x)}$ $\frac{m_1}{(1 + 3x)}$
Associated Solute	benzoic acid in benzene forming dimer	$2A \rightleftharpoons A_2$ $A \rightleftharpoons \frac{1}{2}A_2$	$\frac{1}{2}$	$\left(1 - \frac{x}{2}\right) = \left(\frac{2-x}{2}\right)$	$\frac{2m_1}{(2-x)}$
	any solute forming polymer A_n	$nA \rightleftharpoons A_n$ $A \rightleftharpoons \frac{1}{n}A_n$	$\frac{1}{n}$	$\left[1 + \left(\frac{1}{n} - 1\right)x\right]$	$\left[\frac{m_1}{1 + \left(\frac{1}{n} - 1\right)x}\right]$
General	one mole of solute giving y mol of products	$A \rightleftharpoons yB$	y	$[1 + (y-1)x]$	$\frac{m_1}{[1 + (y-1)x]}$

* number of products from one mole solute

Raoult's law :

- (1) Volatile binary liquid mix :

Volatile liq.	A	B
Mole fraction	X_A/Y_A	$X_B/Y_A \Rightarrow$ liq/vapour
V.P. of pure liq.	P_A°	P_B°



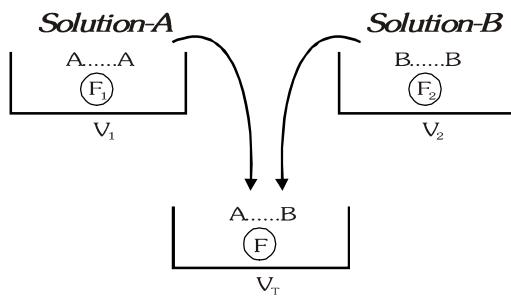
Binary liquid solution :

$$\text{By Raoult's law} \Rightarrow P_T = P_A^\circ X_A + P_B^\circ X_B = P_A + P_B \quad \dots\dots(i)$$

$$\text{By Dalton's law} \Rightarrow P_A = Y_A P_T \quad \dots\dots(ii)$$

$$P_B = Y_B P_T \quad \dots\dots(iii)$$

-
- Ideal and Non-Ideal solution :**



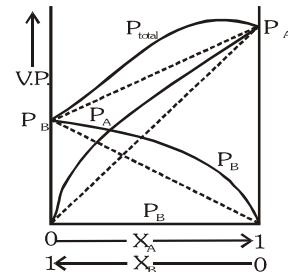
$$\text{Ideal solution : } \begin{cases} F_1 \sim F_2 \sim F \\ V_T = V_1 + V_2 \end{cases} \Rightarrow \Delta H_{\text{solution}} = 0$$

Non-Ideal solution :

- (1)
- Solution showing +ve deviation :**

$$F < F_1 \text{ & } F_2$$

$$V_T > V_1 + V_2 \Rightarrow \Delta H_{\text{solution}} > 0$$

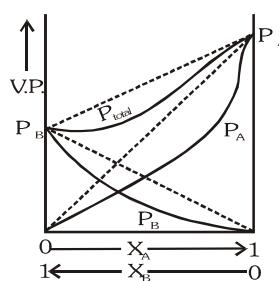


- (2)
- Solution showing -ve deviation :**

$$\Rightarrow F > F_1 \text{ & } F_2$$

$$\Rightarrow V_T < (V_1 + V_2)$$

$$\Rightarrow \Delta H_{\text{solution}} < 0$$



DEVIATION FROM RAOULT'S LAW

<i>Positive deviation ($\Delta H=+ve$)</i>	<i>Negative deviation ($\Delta H=-ve$)</i>	<i>Zero deviation ($\Delta H=0$)</i>
(i) ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(ii) acetone + carbon disulphide	benzene + chloroform	n-hexane + n-heptane
(iii) acetone + benzene	nitric acid + chloroform	ethyl bromide + ethyl iodide
(iv) ethanol + aceton	acetone + aniline	chlorobenzene + bromo benzene
(v) ethanol + water	water + nitric acid	
(vi) carbon tetrachloride chloroform	diethyl ether + chloroform	

➤ **Azeotropic mixtures :**

Some liquids on mixing form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. Azeotropic mixture cannot be separated by fractional distillation.

➤ **Types of Azeotropic mixtures**

(i) **Minimum boiling Azeotropic mixtures**

The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviation. For example (95.5%) + water (4.5%) + water boils at 351.15 K.

(ii) **Maximum boiling Azeotropic mixtures**

The mixture of two liquids whose boiling point are more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.

SOLID STATE

➤ *Various type of Crystals :*

Some Important Characteristics of Various types of Crystals

Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
Binding forces	Electrostatic attraction between ions	Shared electrons	vander Waals or Dipole-dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
Hardness	Hard	Very hard	Soft Graphite	Hard or soft
Brittleness	Brittle	Intermediate	Low	Low
Melting point	High	Very high	Low	Varying from moderate to high
Electrical Conduction	Semi conductor due to crystal imperfections,conductor in fused state	Non-conductor Graphite is good conductor	Bad conductor	Good conductors
Solubility in Polar solvents	Soluble	Insoluble	Soluble as well as insoluble	Good conductors
Heat of Vaporisation (kj mol ⁻¹)	NaCl(s) 170-75	Graphite 718-43	NH ₃ (s) 23.55	Cu(s) 304.59
Heat of fusion (kj mol ⁻¹)	NaCl 28.45	— —	NH ₃ (s) 5.65	Cu(s) 13.016
Example	NaCl, KNO ₃ CsCl, Na ₂ SO ₄ ZnS	Diamond, graphite, Quartz (SiO ₂), SiC	H ₂ O(s), CO ₂ (s), Sulphur, Sugar, Iodine,noble gases	Na, Cu, Ag, Fe, Pt, alloys

THE SEVEN CRYSTAL SYSTEMS

<i>Name of System</i>		<i>Axes</i>	<i>Angles</i>	<i>Bravais Lattices</i>
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred = 3
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Body centred = 2
3.	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive = 1
4.	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred End centred = 4
5.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Primitive, End - centred = 2
6.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive = 1
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Primitive = 1 Total = 14

CUBIC UNIT CELL

<i>Unit cell</i>	<i>Relation between r and a</i>	<i>Packing fraction</i>	<i>Co-ordinatin number</i>	<i>Effective number of particle</i>
Simple cubic Body centred	$r = \frac{a}{2}$	52.4%	6	1
cubic	$r = \frac{a\sqrt{3}}{4}$	68%	8	2
Face centred cubic	$r = \frac{a\sqrt{2}}{4}$	74%	12	4

$$\text{Density : } d = \frac{ZM}{N_A \times a^3} \text{ gm/cm}^3$$

Where Z = effective number of particle

M= molar mass

N_A = Avogadro's number

a = edge length (cm)

Three dimensional close packing :
➤ Hexagonal close packing (HCP) :

Effective number of particle = 6

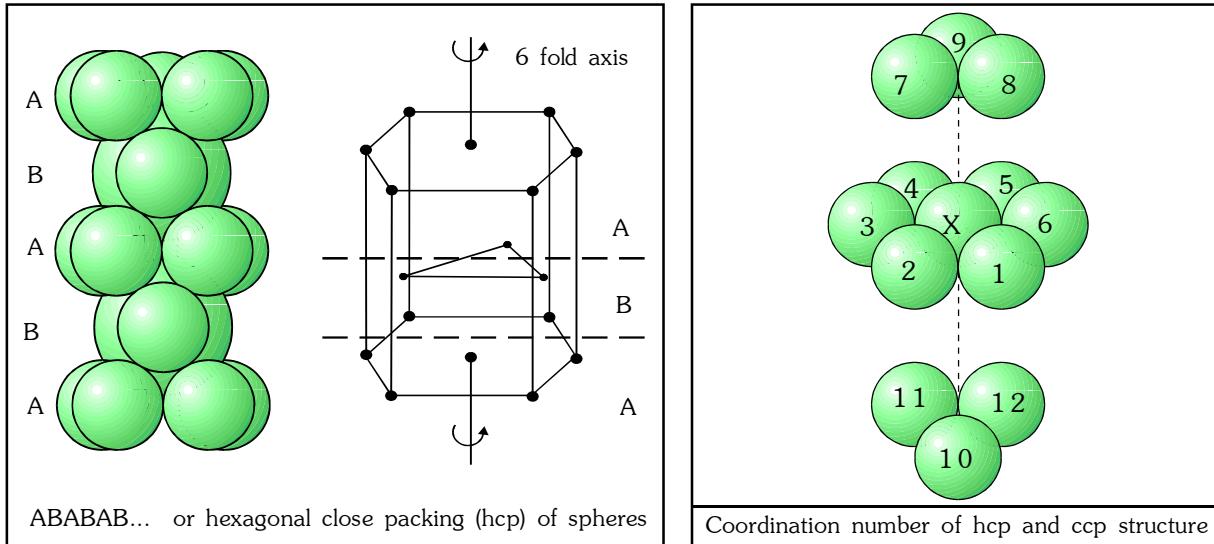
Effective number of octahedral void = 6

Effective number of tetrahedral void = 12

Packing fraction

= 74% ; co-ordination number = 12

$$a = \frac{r}{2}; b = 4 \sqrt{\frac{2}{3}} r$$



➤ **Cubic close packing (CCP) :**

Effective number of particle = 4

Effective number of octahedral void = 4

Effective number of tetrahedral void = 8

Packing fraction = 74% ;

co-ordination number = 12

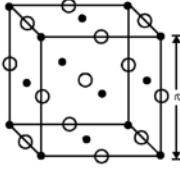
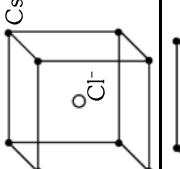
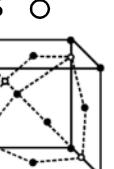
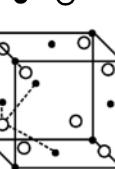
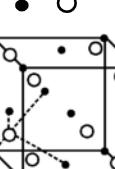
$$\frac{a\sqrt{2}}{4} = r$$

➤ **Different type of voids and their radius ratio :**

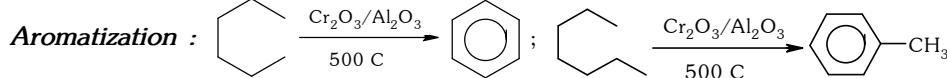
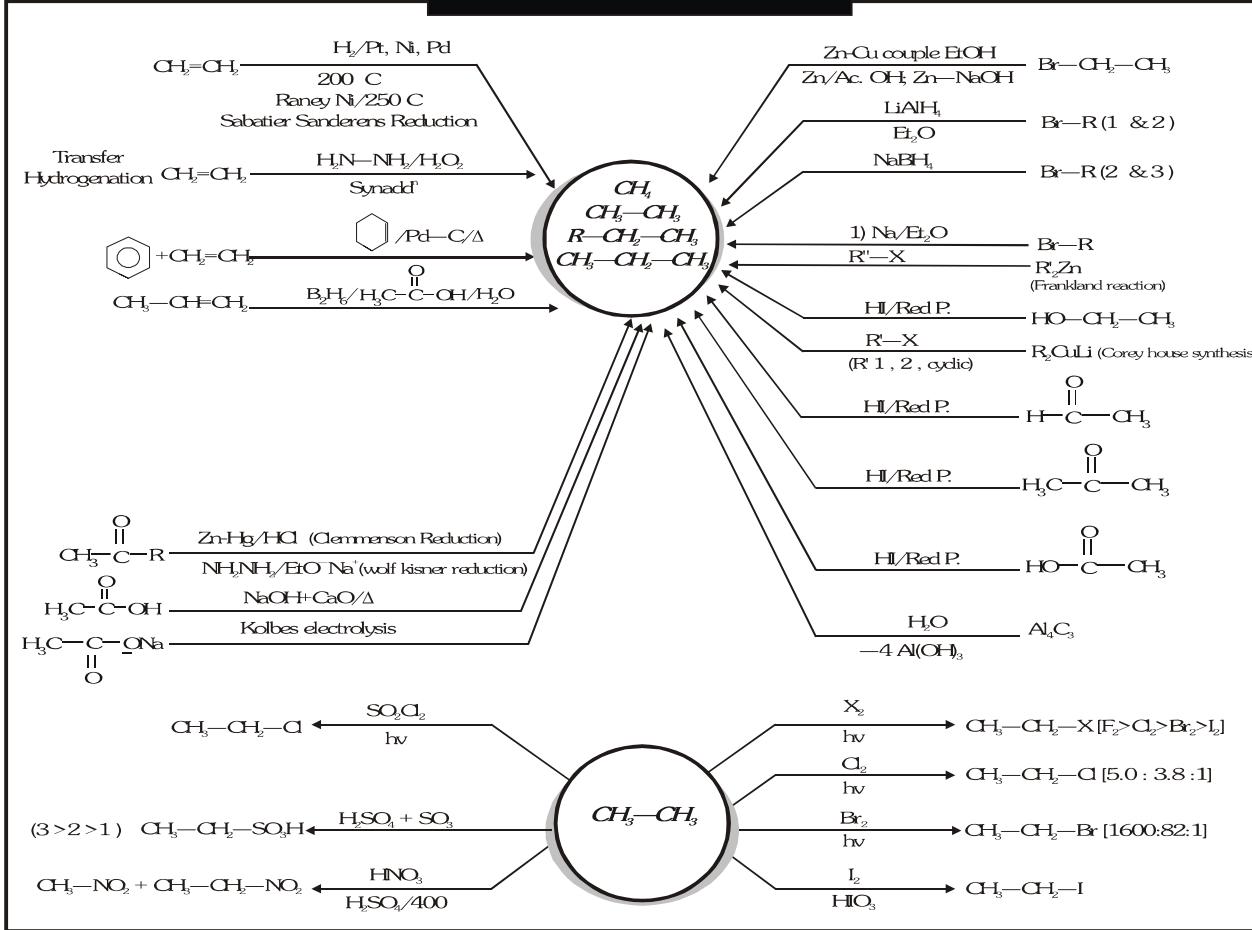
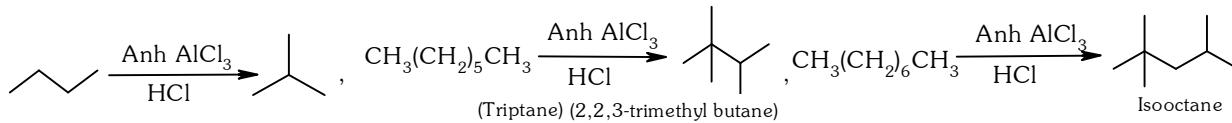
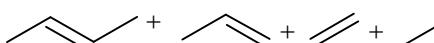
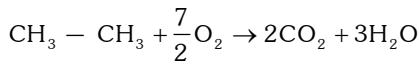
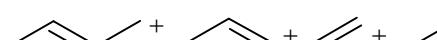
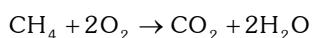
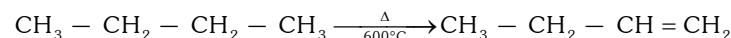
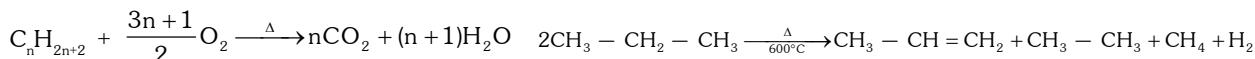
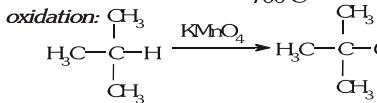
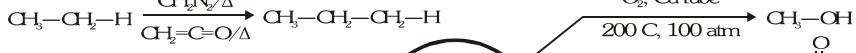
Limiting radius ratio for various types of sites

<i>Limiting radius ratio = r/R</i>	<i>Coordination Number of cation</i>	<i>Structural Arrangement (Geometry of voids)</i>	<i>Example</i>
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO ₂
0.414 - 0.732	4	Square planar	-
0.414 - 0.732	6	Octahedral	NaCl, MgO ₂
0.732 - 1.000	8	Cubic	CsCl

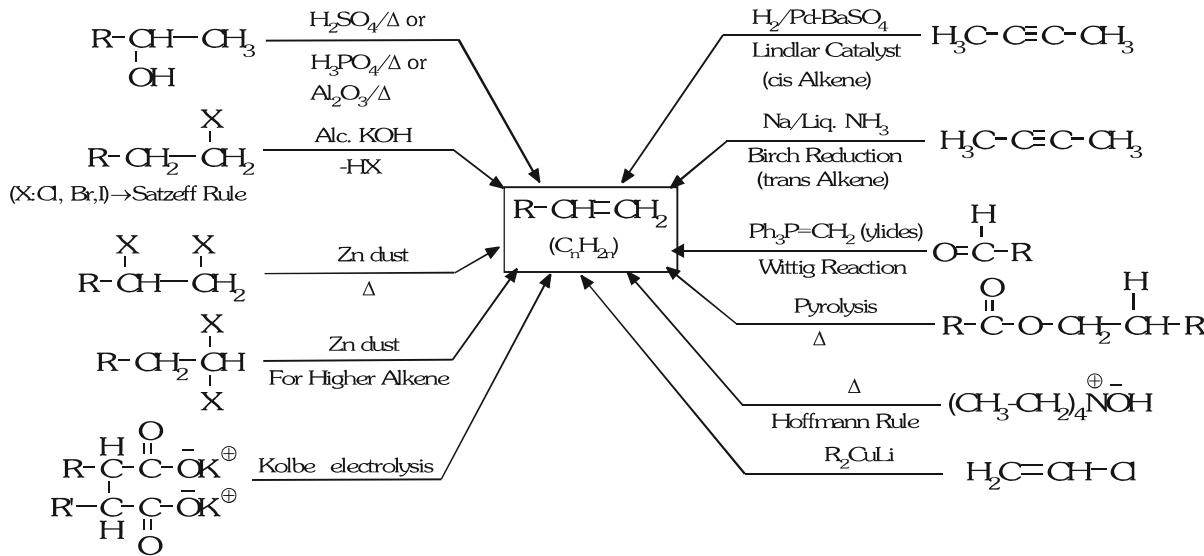
TYPES OF IONIC CRYSTAL

Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.C.	Examples
1. NaCl (1 : 1) (Rock Salt Type)	 Na ⁺ → Every element of C.C.P. Cl ⁻ → At every OHV	6 : 6	4Na ⁺ + 4Cl ⁻ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of II-A (Some exception) AgF, AgCl, AgBr, NH ₄ X
2. CsCl Type (1 : 1)	 B.C.C. Cs ⁺ → at every corner Cl ⁻ → at Body centre or at cubic void	8 : 8	1Cs ⁺ + 1Cl ⁻ 1CsCl (1)	Halides of 'Cs' TiCl, TiBr, CsS
3. Zns Type (1 : 1) (Zinc Blende Type) (Sphalerite)	 C.C.P. Zn ²⁺ → Every element of C.C.P. S ²⁻ → At 50% of THV. or at alternate tetrahedral void	4 : 4	4Zn ²⁺ + 4S ²⁻ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
4. CaF ₂ Type (1 : 2) (Fluorite Type)	 C.C.P. Ca ²⁺ → Every element of C.C.P. F ⁻ → At every THV.	8 : 4	4Ca ²⁺ + 8F ⁻ 4CaF ₂ (4)	BaCl ₂ , BaF ₂ SrCl ₂ , SrF ₂ CaCl ₂ , CaF ₂
5. Na ₂ O Type (2 : 1) (Antiflourine)	 C.C.P. Na ⁺ → At every THV. O ²⁻ → Every element of C.C.P.	4 : 8	8Na ⁺ + 4O ²⁻ 4Na ₂ O (4)	Li ₂ O, Li ₂ S Na ₂ O, Na ₂ S K ₂ O, K ₂ S
6. ZnS Type (1 : 1) (Wurtzite)	 H.C.P. Zn ²⁺ → Every element of H.C.P. S ²⁻ → 50% of THV. or (at alternate THV) of Zns	4 : 4	6Zn ²⁺ + 6S ²⁻ 6ZnS (6)	Same as sphalerite

ALKANE

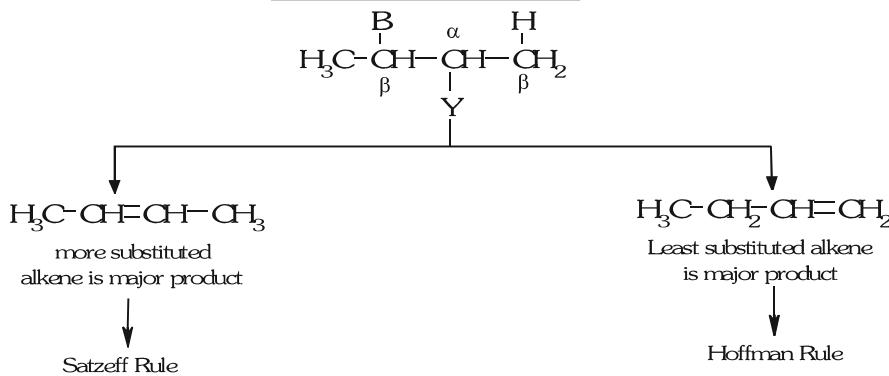
**Isomerization :****Combustion :****Insertion:**

Nutshell Preparation of ALKENE



Elimination Reaction

$E^1, E^2 \& E^{1,2}CB$



(Y) I, Br, Cl, OTs, OBS

in presence of base

$\bar{OH}/Me\bar{O}/Et\bar{O}$
(Alc. KOH)

6:1 (trans to cis)

Y: $OH/Conc. H_2SO_4/\Delta$

: $OH/H_3PO_4/\Delta$

: $OH/Al_2O_3/\Delta$

: $OH/P_2O_5 \text{ or } ZnCl_2/\Delta$

: In presence of bulky base

: When more bulky groups are present around B(O)

: When Y; is $NMe_3^+/OH^-/\Delta$

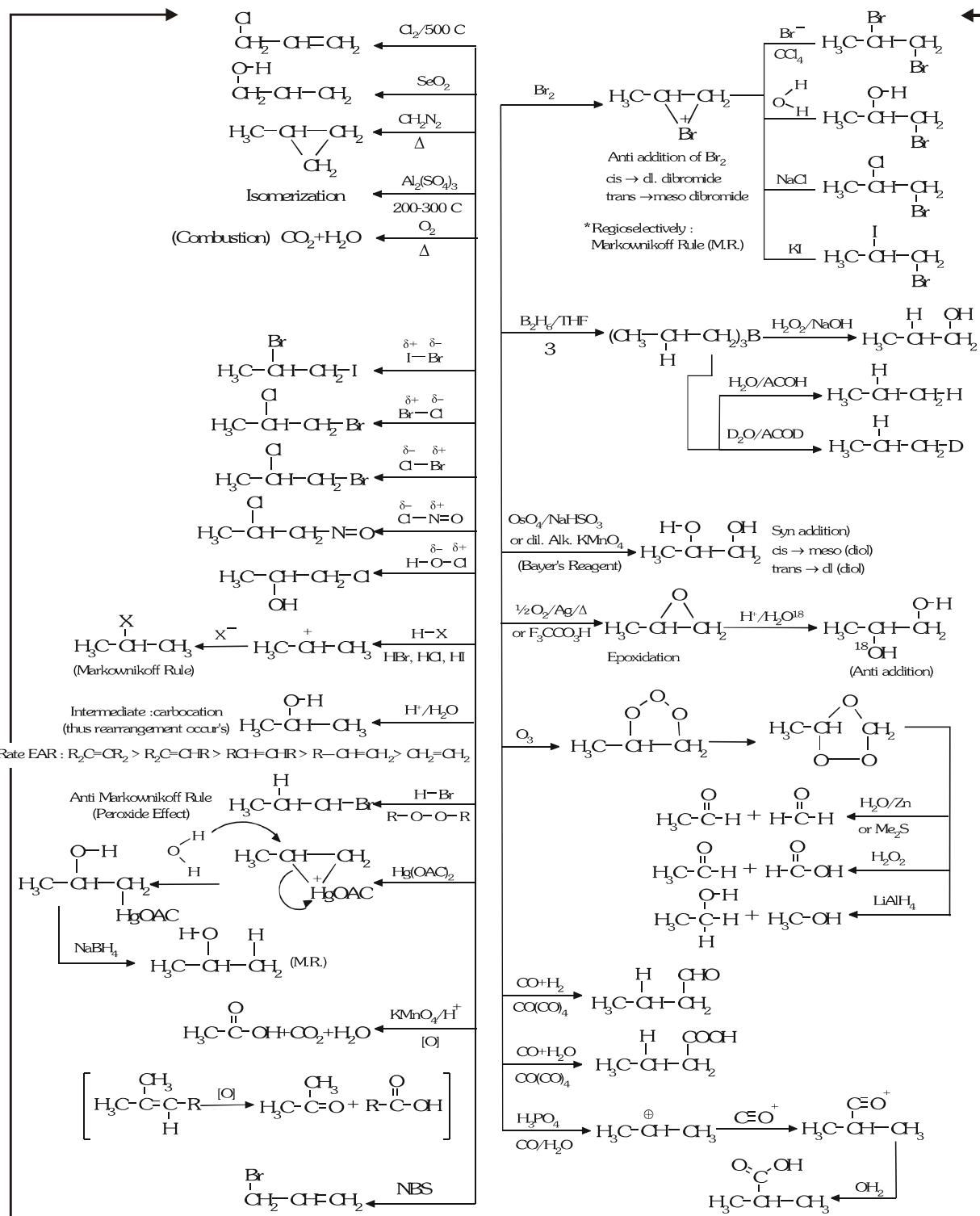
: $SR_2^+/B/\Delta$

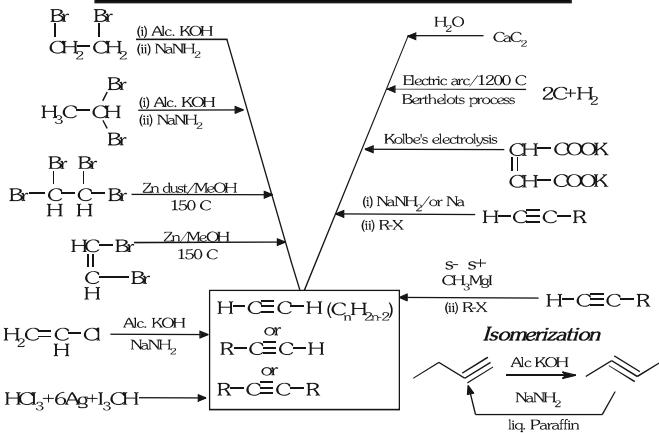
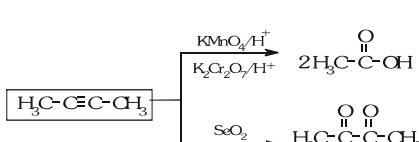
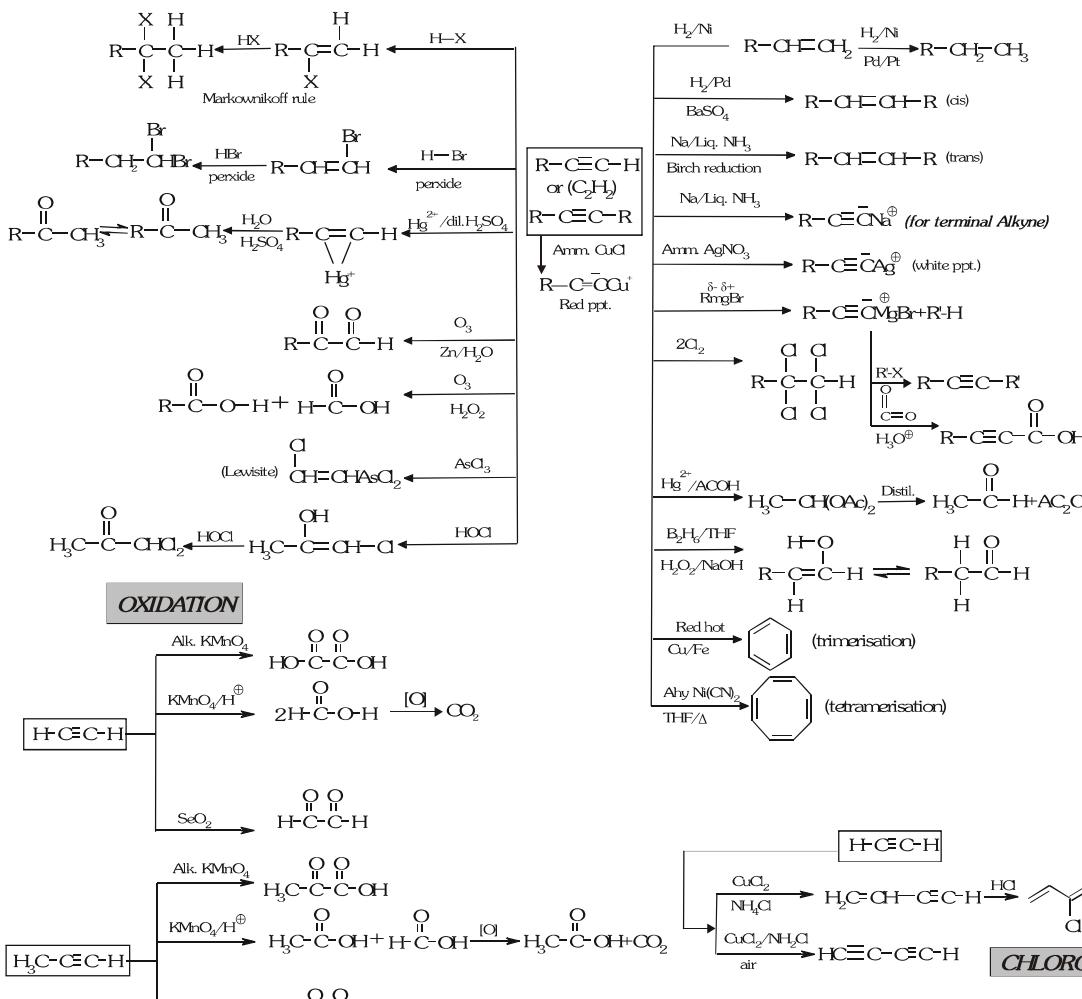
: NR_2^+/Δ

: F / Base

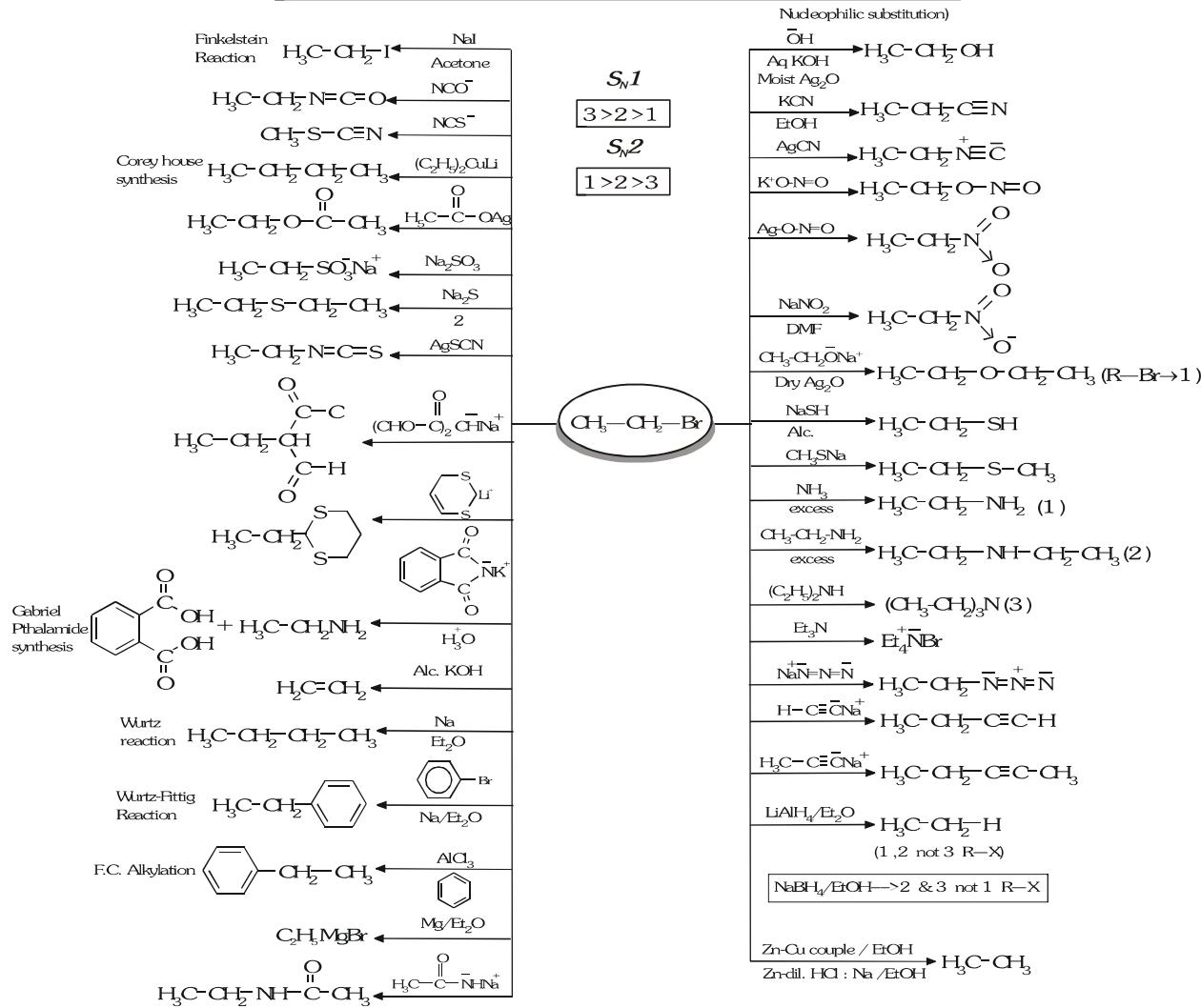
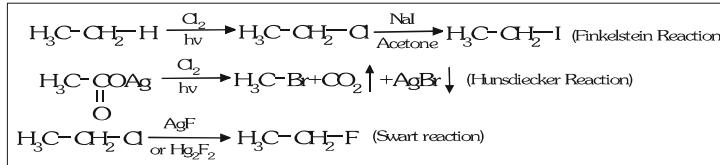
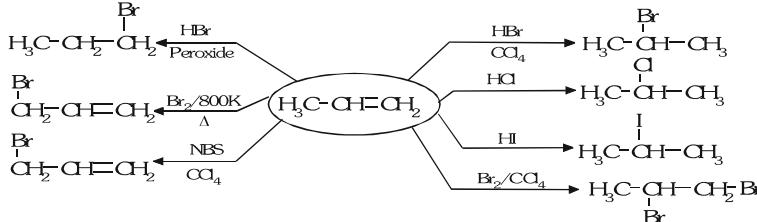
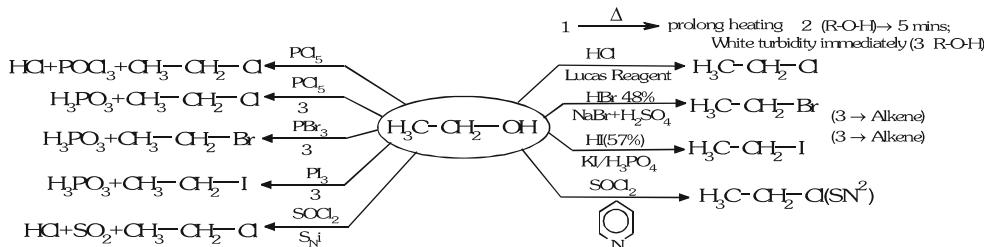
: Pyrolysis of ester

Y: $OH/ThO_2/\Delta$

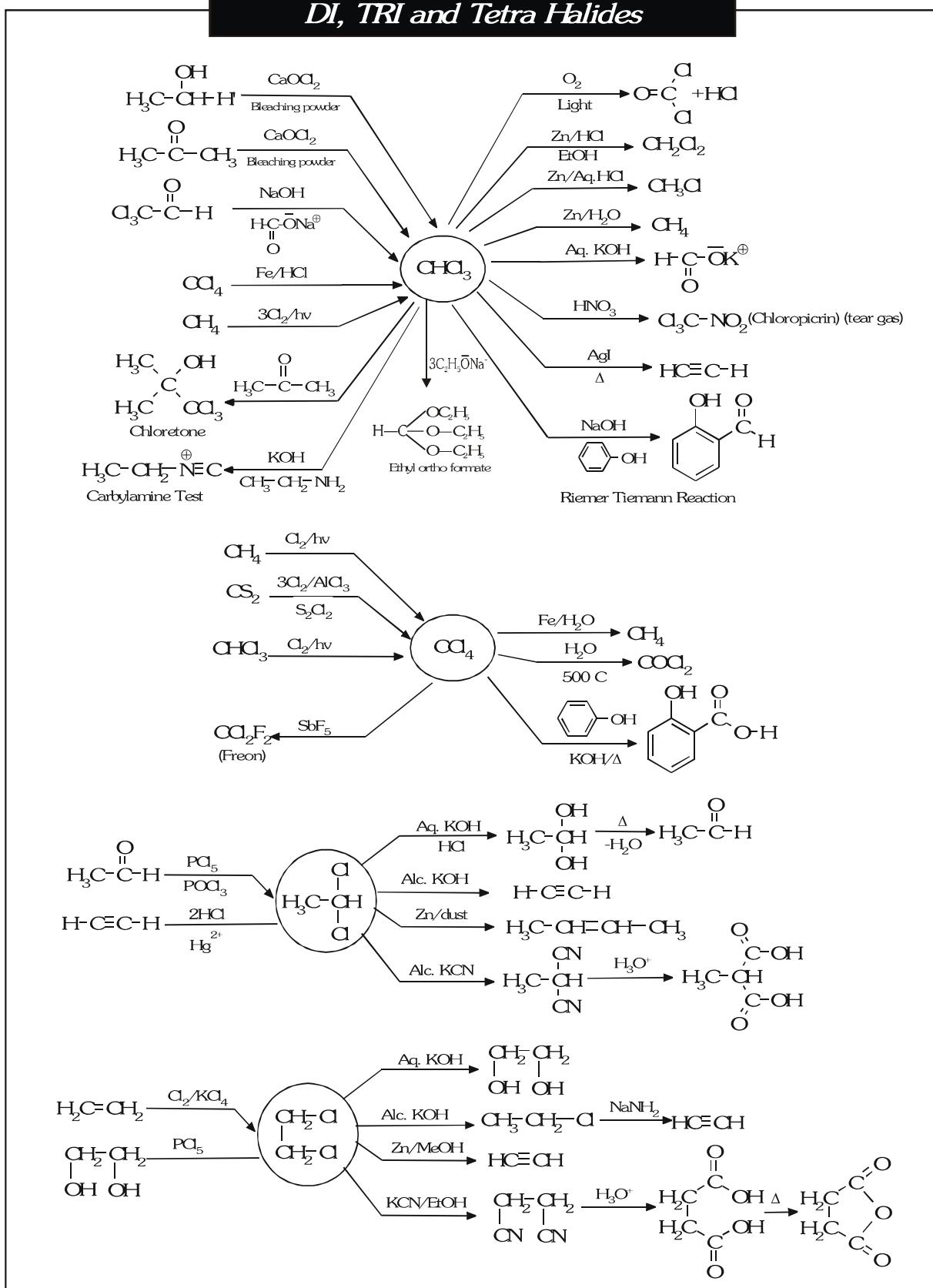
Nutshell reaction of Alkene

Nutshell Preparation of Alkyne**Nutshell reaction of Alkyne**

Nutshell Preparation of ALKYL HALIDE



Nutshell Preparation & Properties of DI, TRI and Tetra Halides



JEE-Chemistry Handbook**Comparison of S_N1 and S_N2**

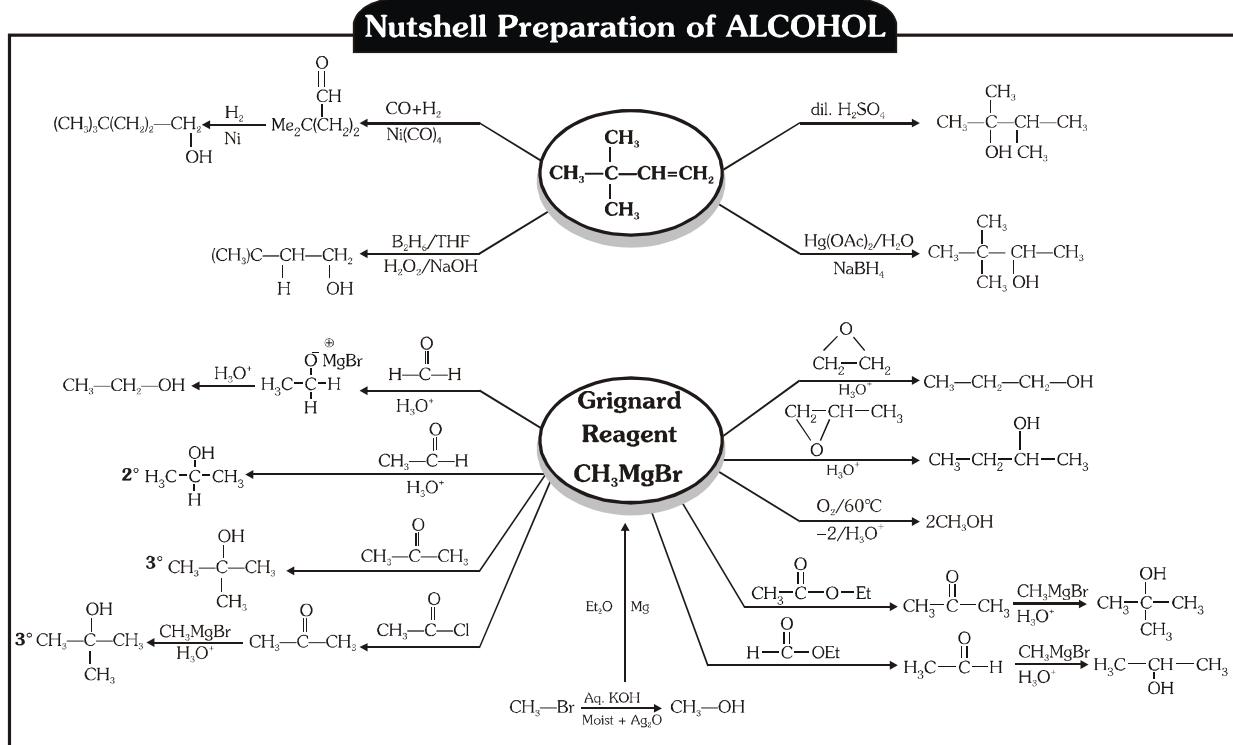
		S_N1	S_N2
A	Kinetics	1 st order	2 nd order
B	Rate	$k[RX]$	$k[RX][Nu:^-]$
C	Stereochemistry	Racemisation	Inversion
D	Substrate	$3 > 2 > 1 > MeX$	$MeX > 1 > 2 > 3$
E	Nucleophile	Not important	Needs Strong Nu
F	Solvent	Good ionizing	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Comparision of $E1$ and $E2$

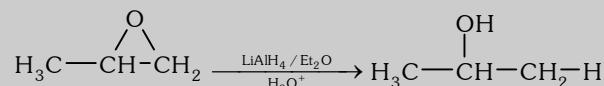
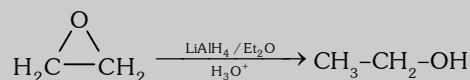
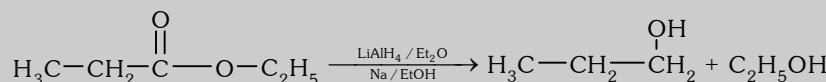
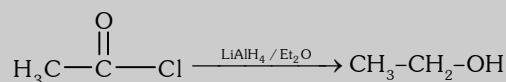
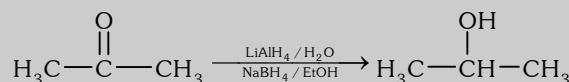
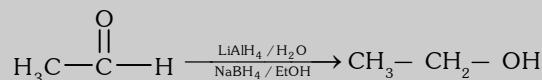
		$E1$	$E2$
A	Kinetics	1 st order	2 nd order
B	Rate	$k[RX]$	$k[RX][B:^-]$
C	Stereochemistry	No special geometry	Anti-periplanar
D	Substrate	$3 > 2 >> 1$	$3 > 2 > 1$
E	Base Strength	Not important	Needs Strong bases
F	Solvent	Good ionizing	Polarity not import
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Summary of S_N1 , S_N2 , $E1$, and $E2$ reactions

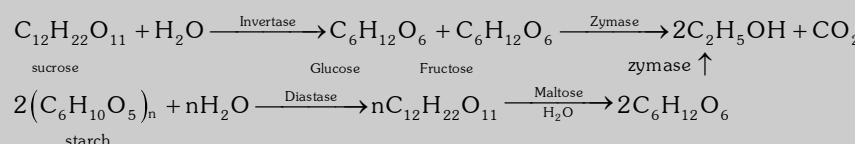
RX	<i>Mechanism</i>	$Nu:^-/B^-$	<i>Solvent</i>	<i>Temp.</i>
1	S_N2	Better $Nu:^-$ $HO:^-$, $C_2H_5O:^-$	Polar aprotic	Low
	E2	Strong & bulky base $(CH_3)_3CO:^-$		High
2	S_N2	$HO:^- C_2H_5O:^-$	Polar aprotic	Low
	E2	$(CH_3)_3CO:^-$		High
	(S_N1)	(Solvent)	Polar aprotic	(Low)
	(E1)	(Solvent)		(High)
3	S_N1	Solvent	Protic	Low
	E1	Solvent	Protic	High

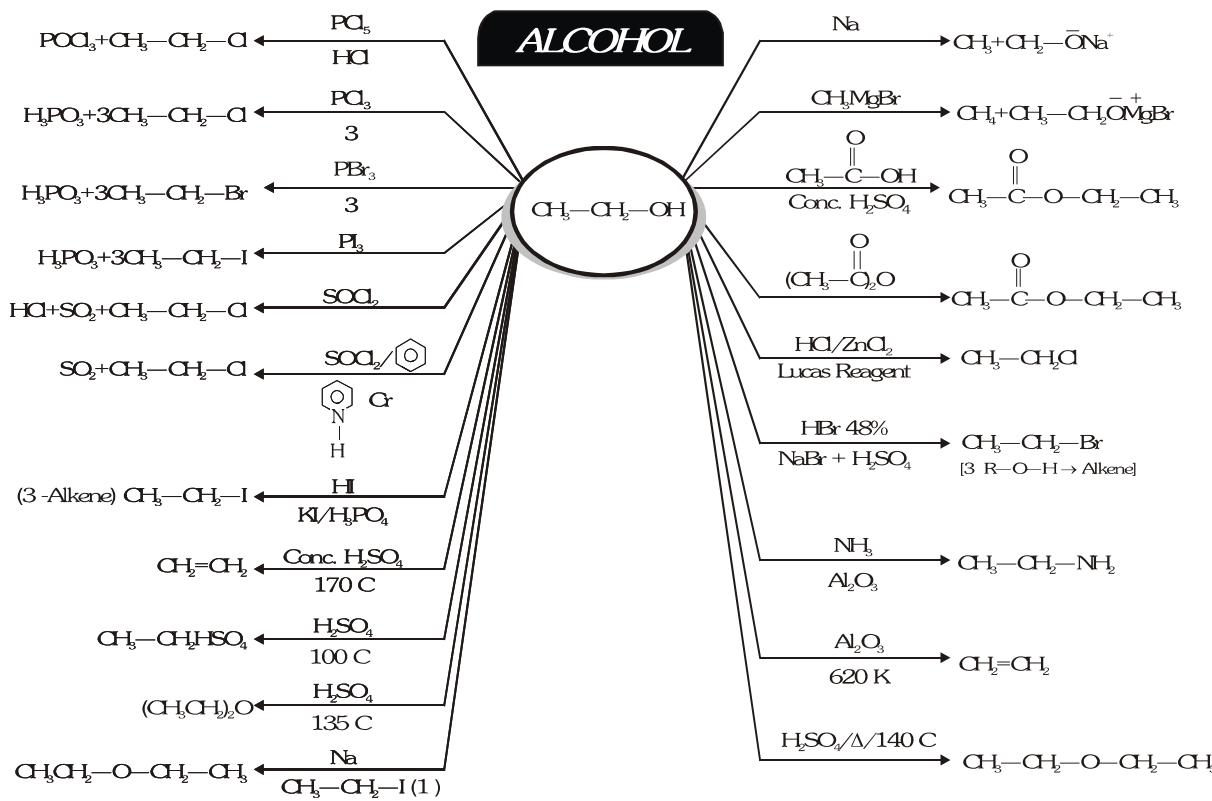


Reduction

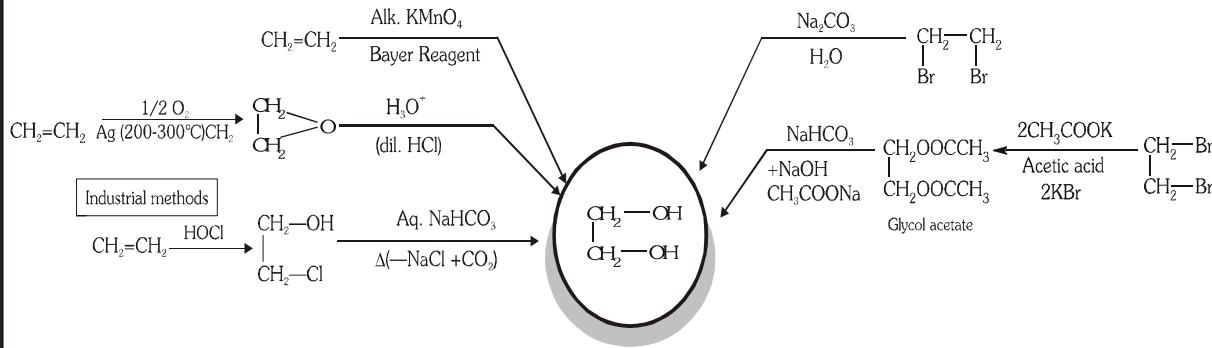


By Fermentation

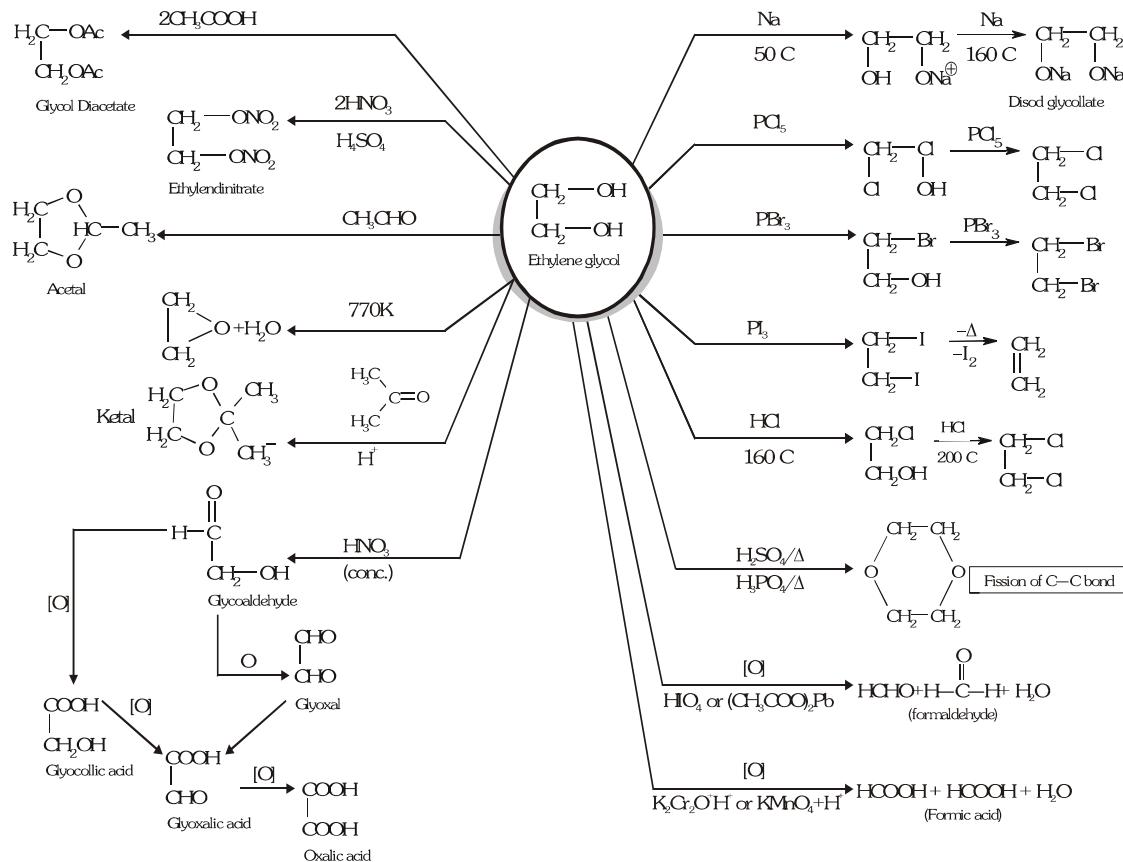


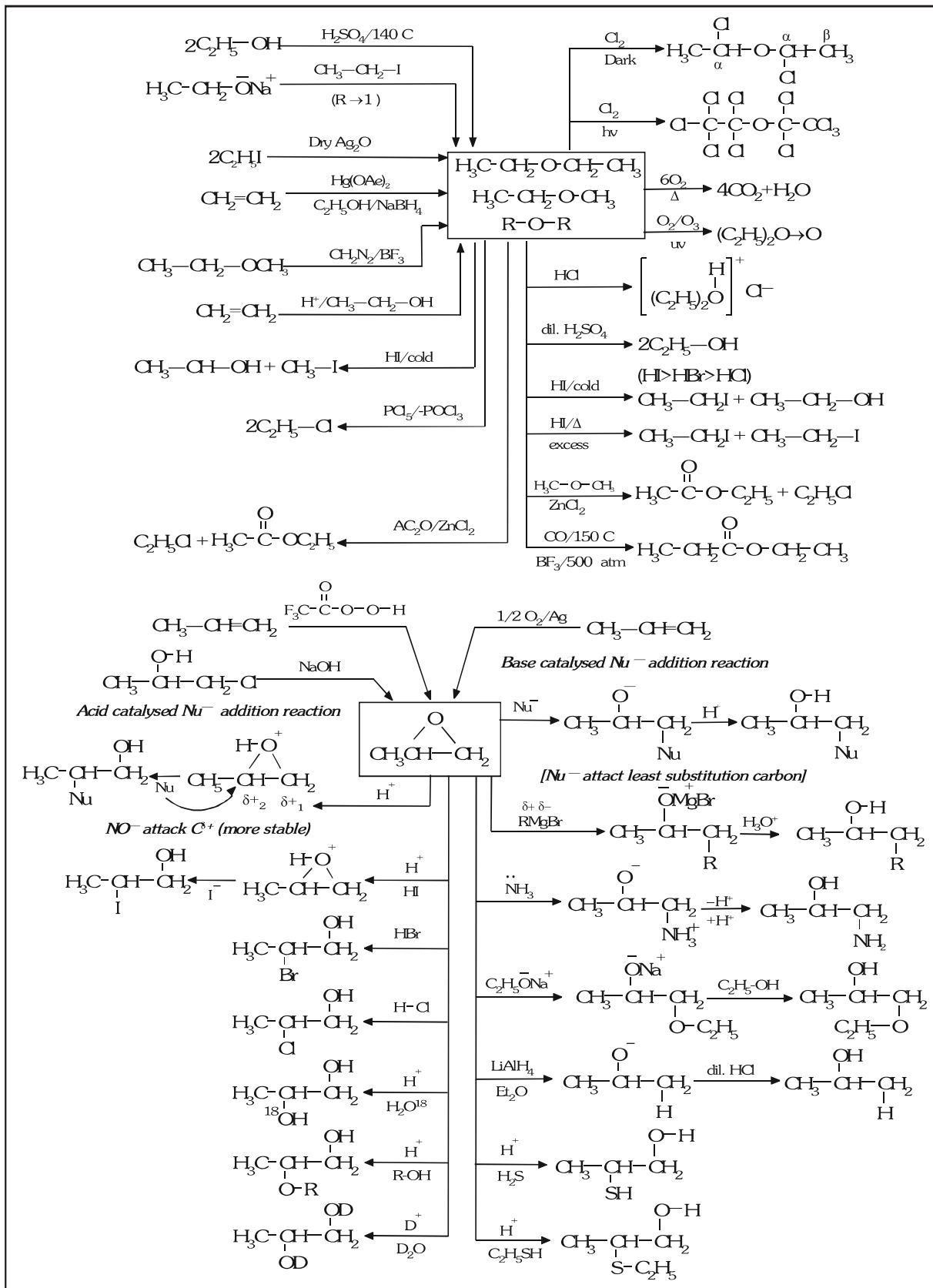
JEE-Chemistry Handbook
'NUTSHELL REVIEW AND PREVIEW OF ALCOHOL REACTIONS'


<i>Reagent</i>	<i>1 Alcohol</i>	<i>2 Alcohol</i>	<i>3 Alcohol</i>
PCC/CH ₂ Cl ₂ PDC/CH ₂ Cl ₂ Jones Reagent H ₂ CrO ₄ /Aq. Acetone	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\overset{\text{OH}}{\underset{\text{H}}{\text{CH}_2}}-\text{CH}_2 \\ \\ \text{1 Alcohol} \end{array}$	$\begin{array}{c} ^{18}\text{OH} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{CH}_2}}-\text{CH}_3 \\ \\ \text{2 Alcohol} \end{array}$	
K ₂ C ₂ O ₇ [⊕] /H [⊕] KMnO ₄ /H ⁺ /OH/Δ	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{CH}_2}}-\text{C}-\text{H} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{CH}_2}}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}-\text{OH}}}+\text{CH}_3-\overset{\text{O}}{\underset{\text{H}}{\text{C}-\text{OH}}} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{OH} \quad \text{CH}_3-\text{C}-\text{OH} \\ \quad \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}-\text{CH}_3}}-\text{CH}_3 \end{array}$	No reaction
Cu/500 C	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{CH}_2}}-\text{C}-\text{H} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{CH}_2}}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}-\text{CH}_3}}-\text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}-\text{CH}_3}}-\text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$ 3 Alcohol
Al(OBu ^t) ₃ Acetone or cyclohexanone	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{CH}_2}}-\text{C}-\text{H} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{CH}_2}}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}-\text{CH}_3}}-\text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}-\text{CH}_3}}-\text{CH}_3 \end{array}$	-
Lucas Reagent HCl/ZnCl ₂	Cloudiness appear upon heating after 30 mins. at normal temp. no. reaction	within five min.	Immediately
<i>Victor Mayer's Test</i>			
P/I ₂	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{I}}{\text{CH}-\text{I}}} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}-\text{I}}} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I} \end{array}$
AgNO ₃	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NO}_2$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{NO}_2}{\text{CH}-\text{NO}_2}} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{NO}_2 \end{array}$	$(\text{CH}_3)_3-\text{NO}_2$
HNO ₂ NaOH	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{\text{N}-\text{OH}}{\text{C}-\text{NO}_2}} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{NO}_2 \\ \text{Nitrolic acid} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{N}\equiv\text{O}}{\text{CH}-\text{NO}_2}} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{NO}_2 \end{array}$	No reaction ↓

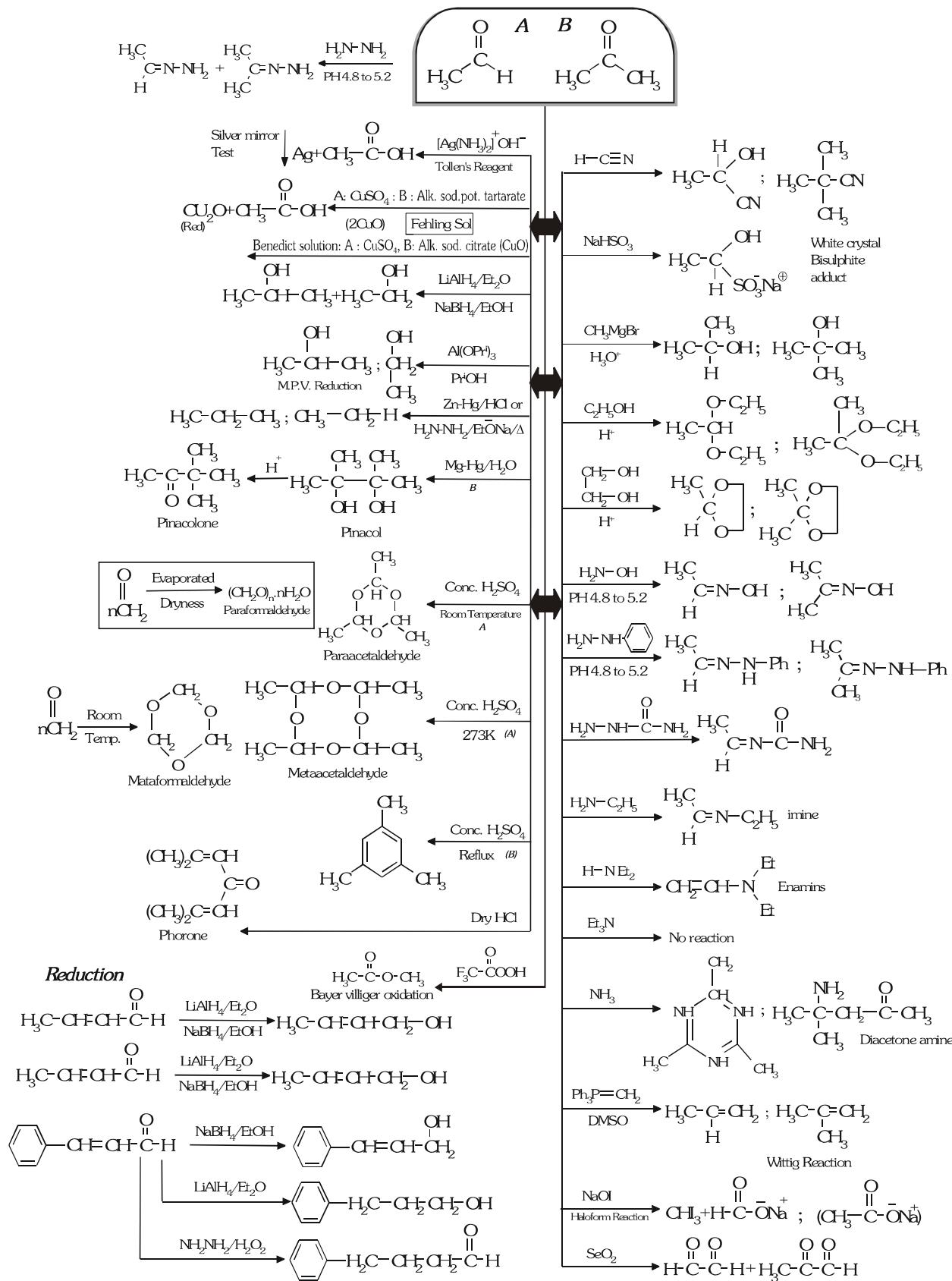
Dihydric Alcohol**Methods of Preparation (Antifreeze Agent)****Chemical Properties**

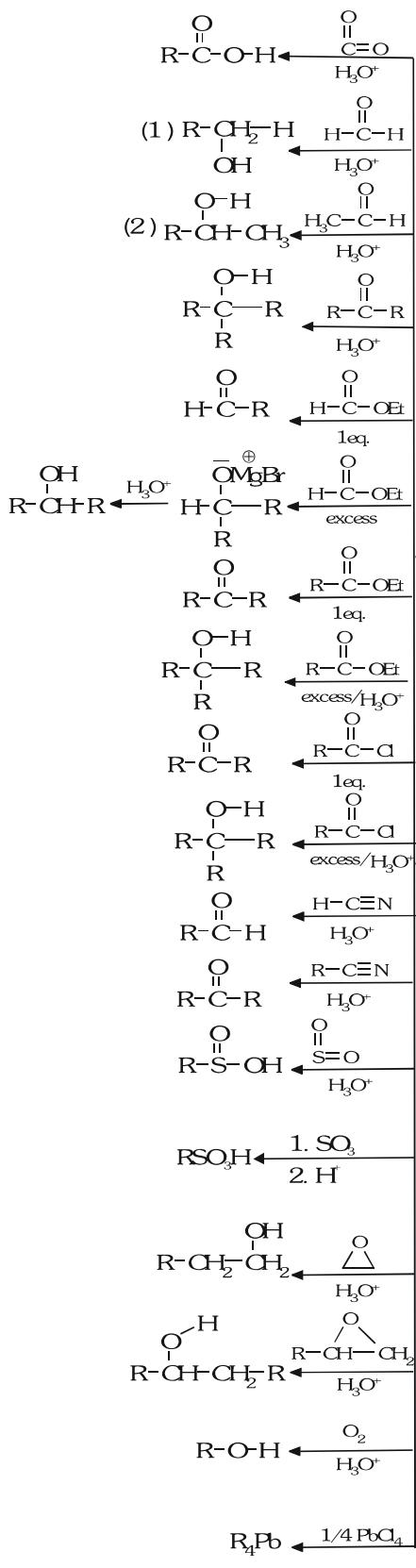
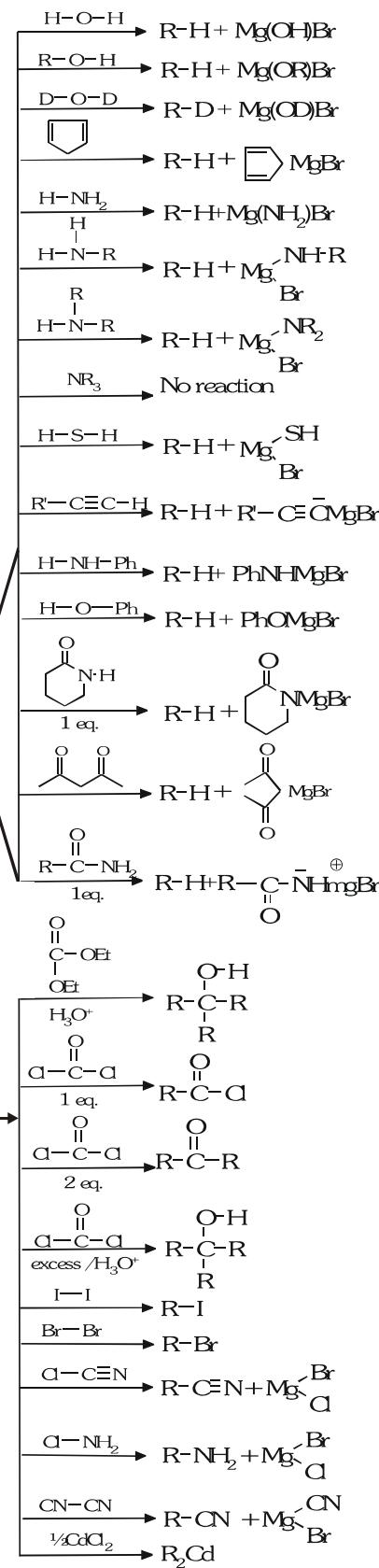
Two 1_o Alcoholic group : one OH group always react completely before other group react



Nutshell review and preview Ether & Epoxides

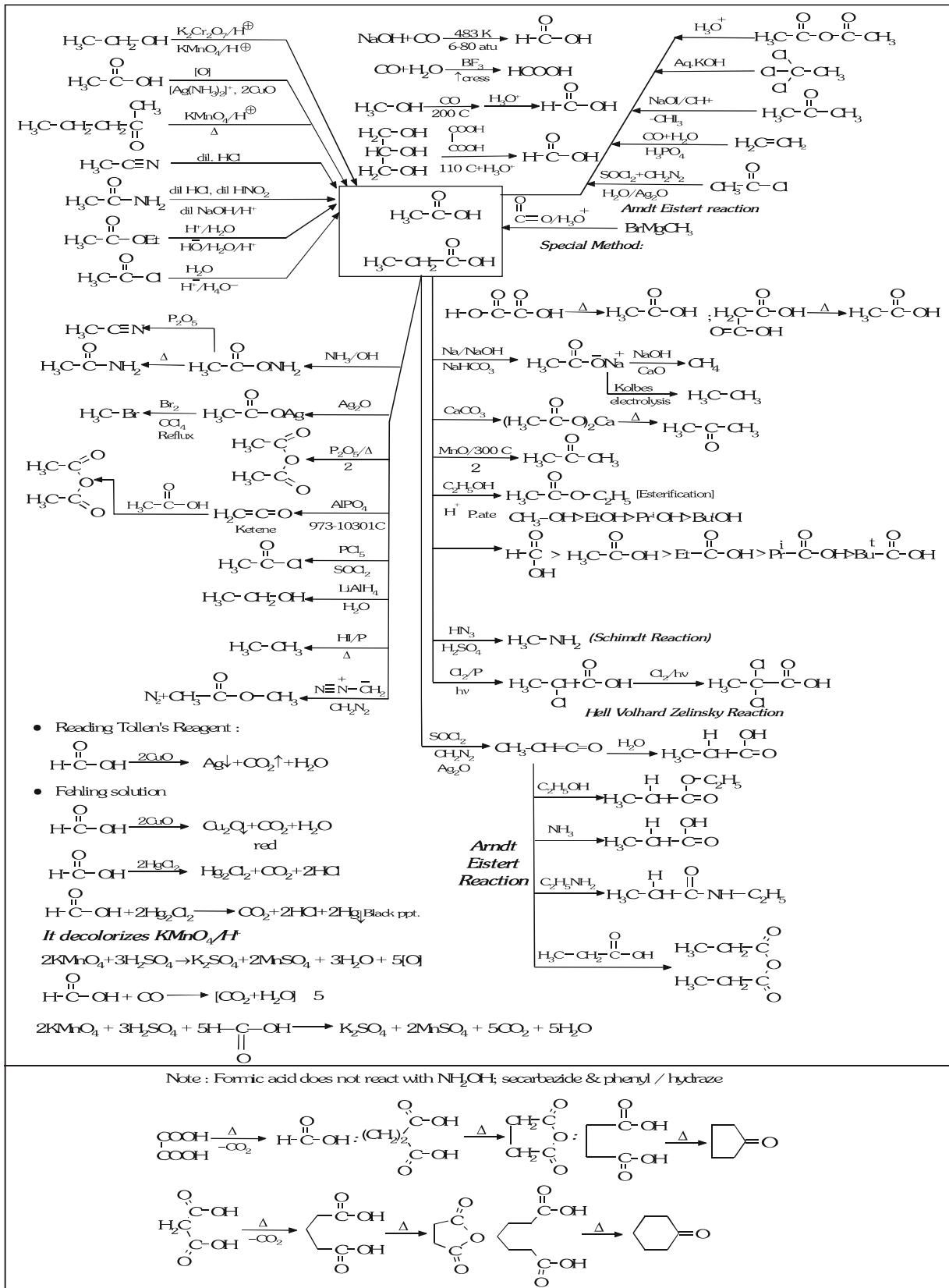
Nutshell preview and review of Carbonyl Reaction

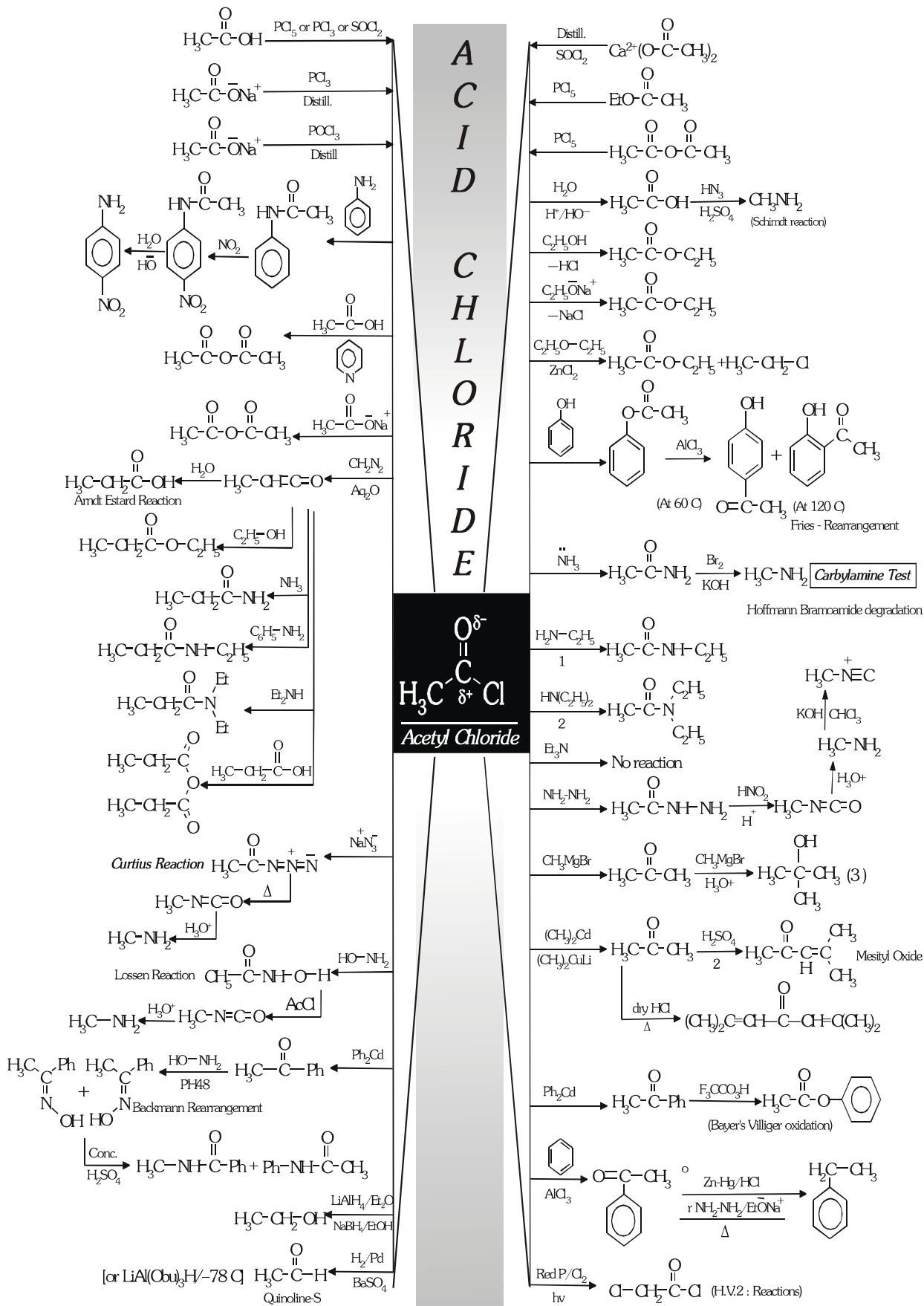


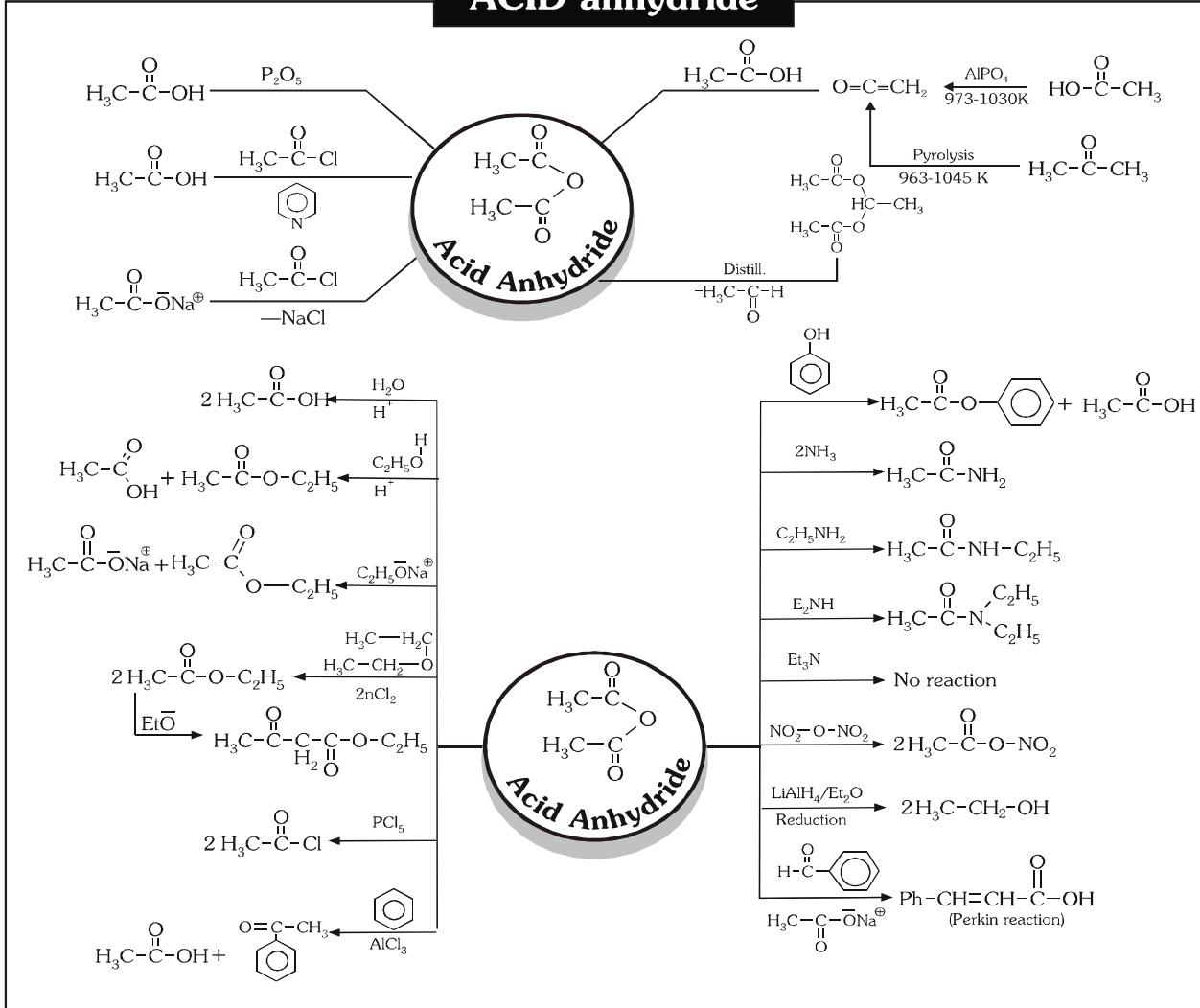
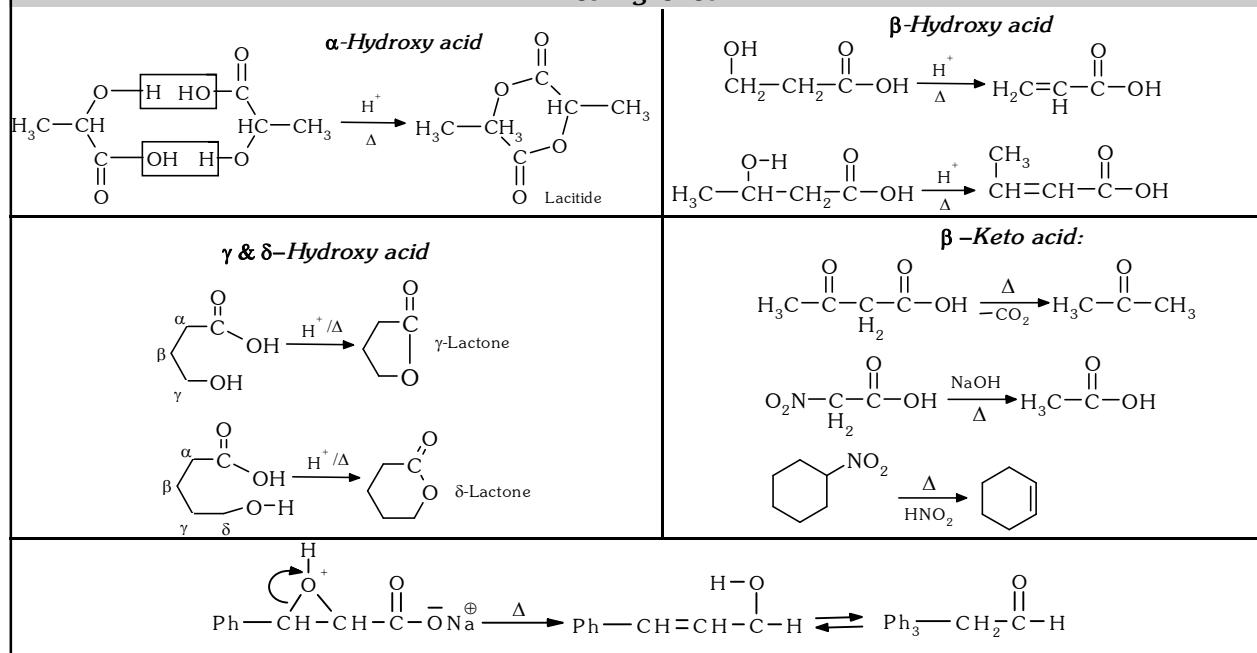
JEE-Chemistry Handbook
As Nucleophile :
GRIGNARD REAGENT

(Active H-containing comp)
GRIGNARD REAGENT as BASE


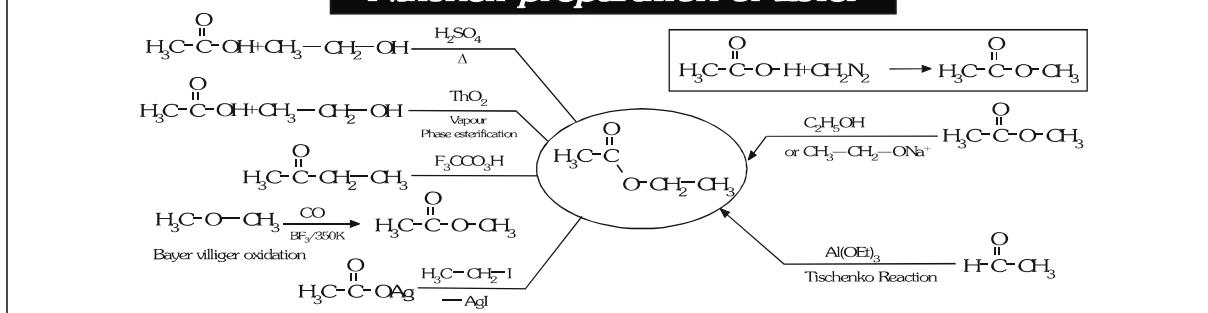
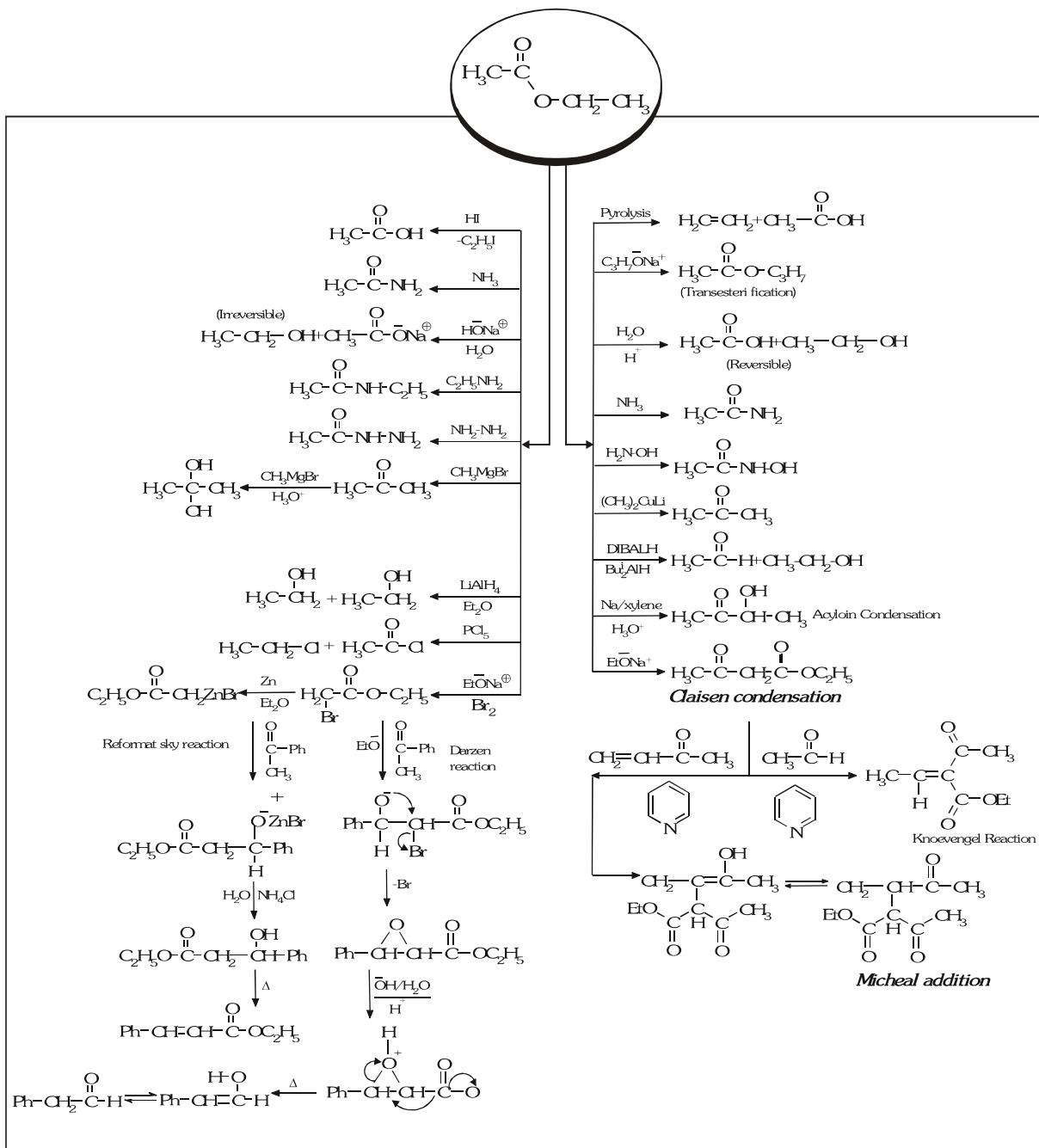
Nutshell preview and review of Carboxylic Acids

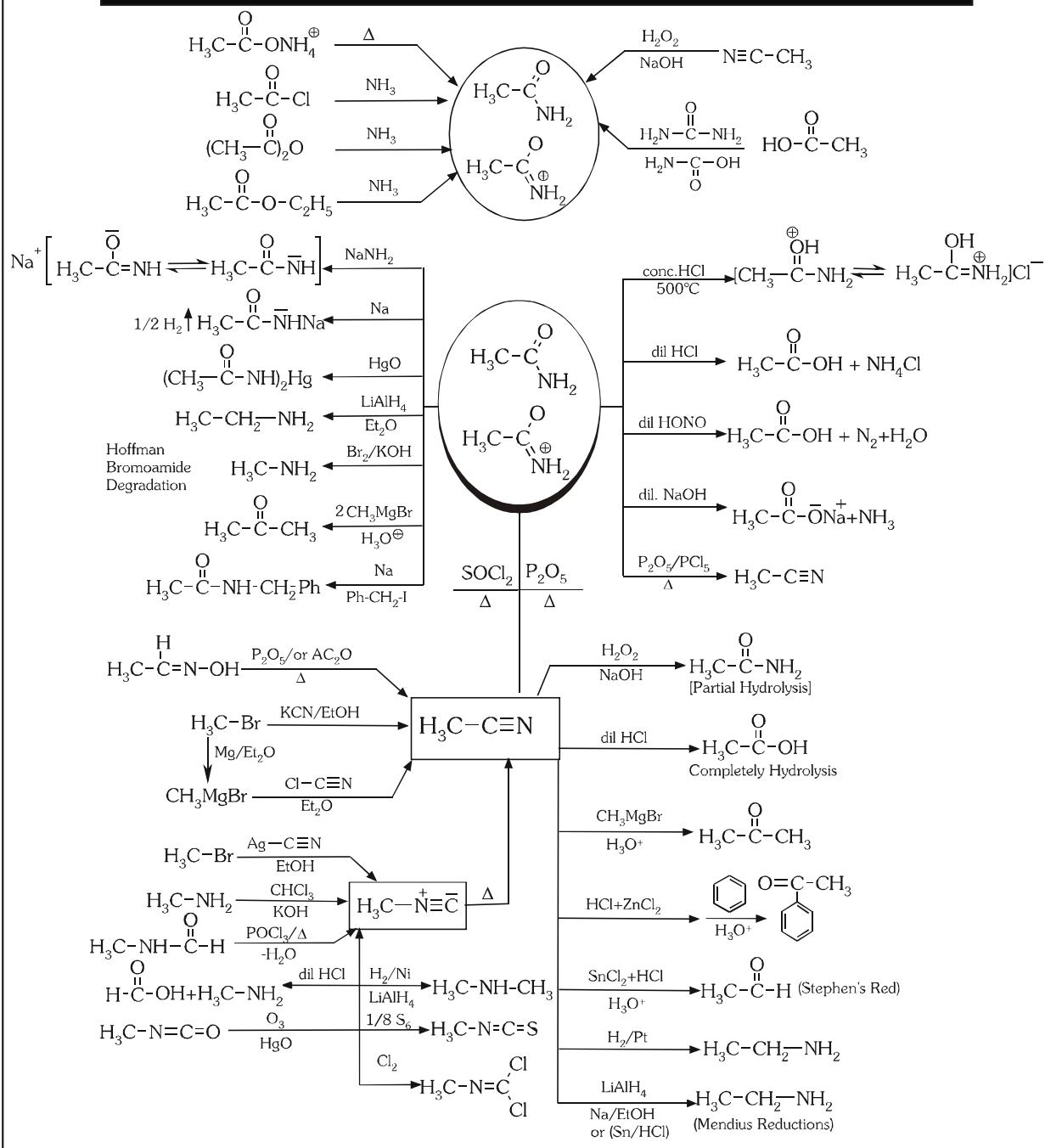
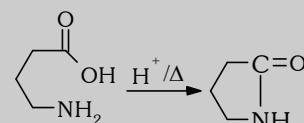
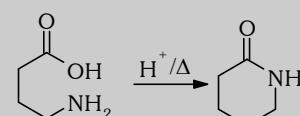
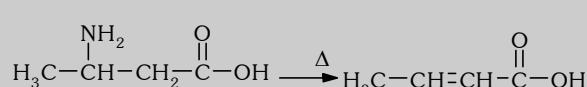
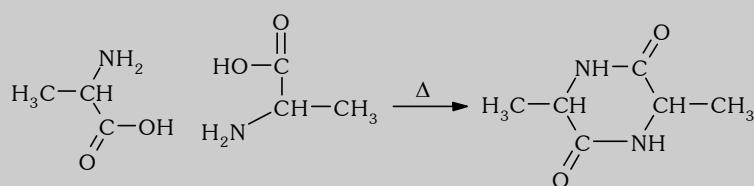
PREPARATION & REACTION

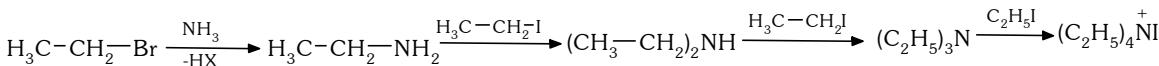




ACID anhydride**Heating effect**

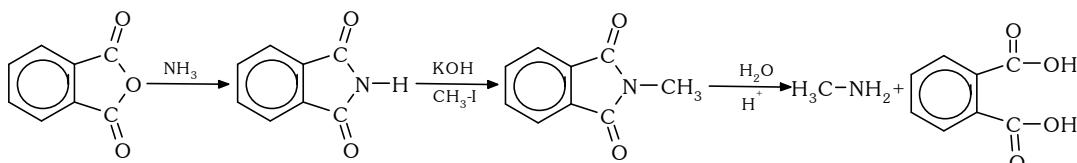
JEE-Chemistry Handbook
Nutshell preparation of Ester

Nutshell chemical properties of Ester


Nutshell preview and review of Amide, Cyanide and Isocyanide**Amino Acid :**

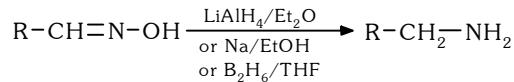
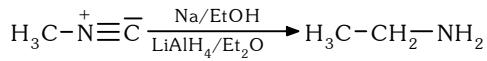
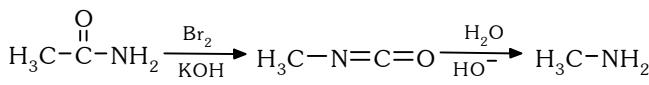
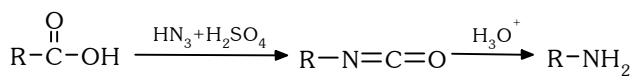
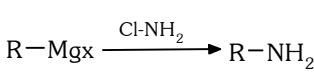
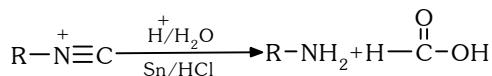
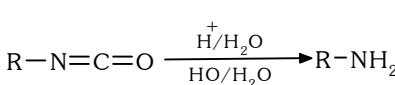
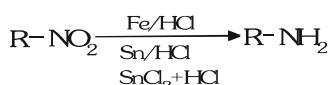
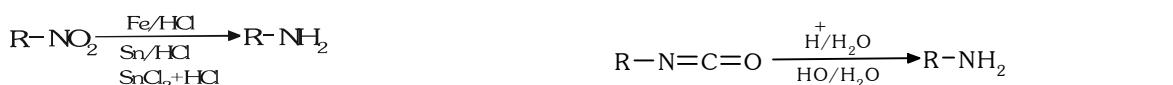
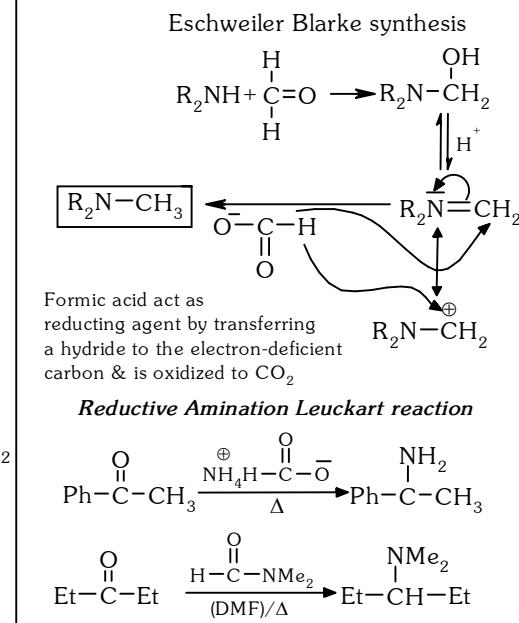
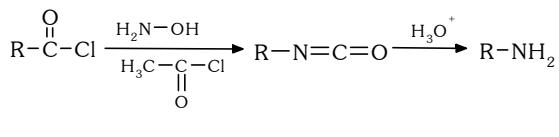
JEE-Chemistry Handbook
METHOD OF PREPARATION OF AMINE
Hoffmann's Ammonolysis


Good yield 1 Amine (If NH_3 1 excess) / Not suitable for Aryl Amine

Reactivity - R-I > R-Br > R-Cl

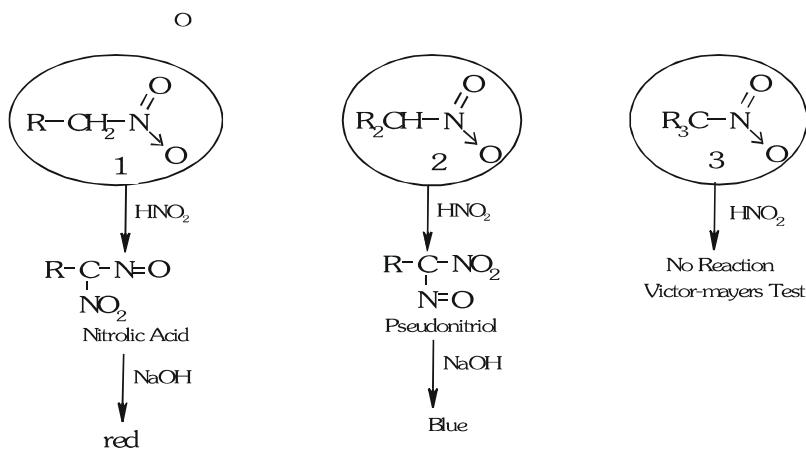
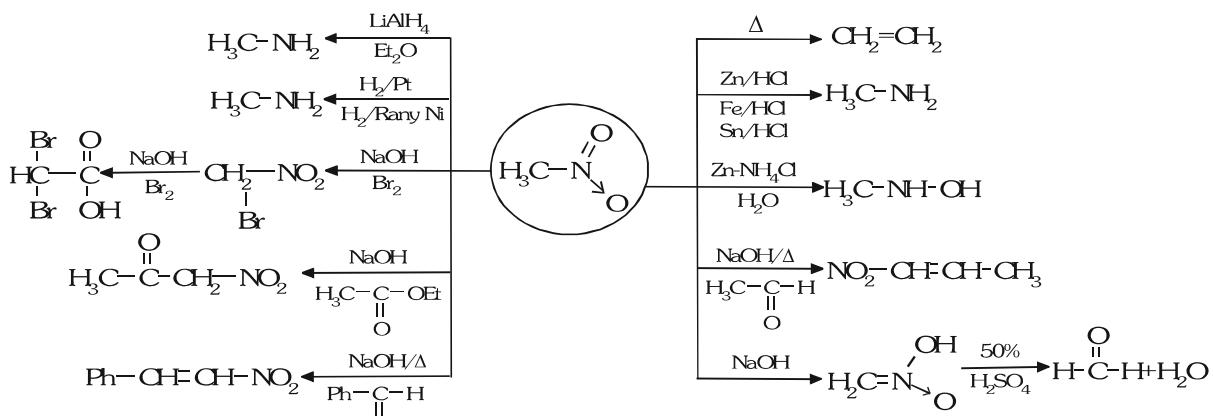
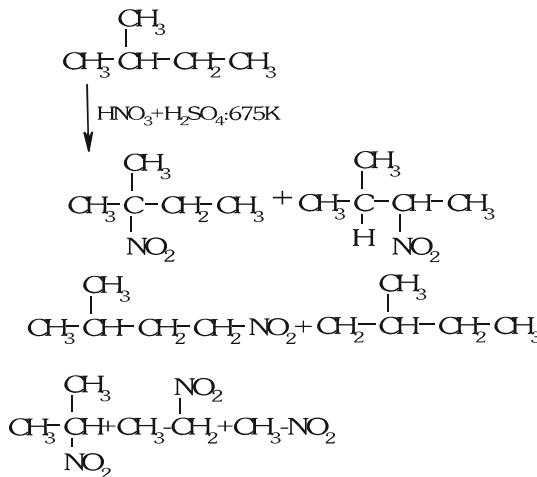
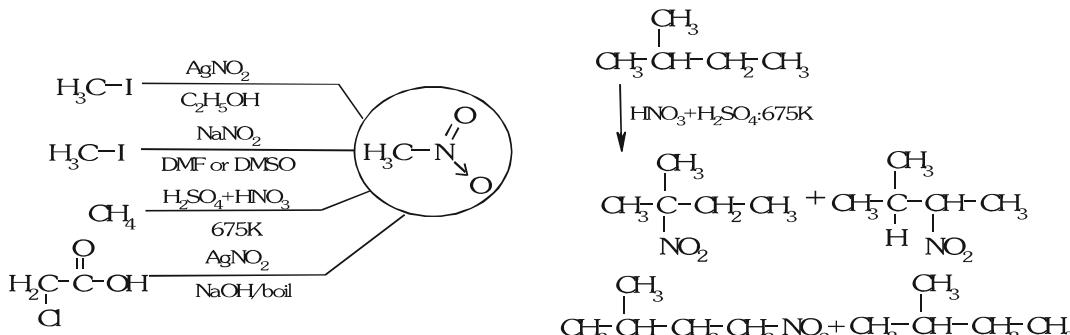
Gabriel / Phthalimide Synthesis :


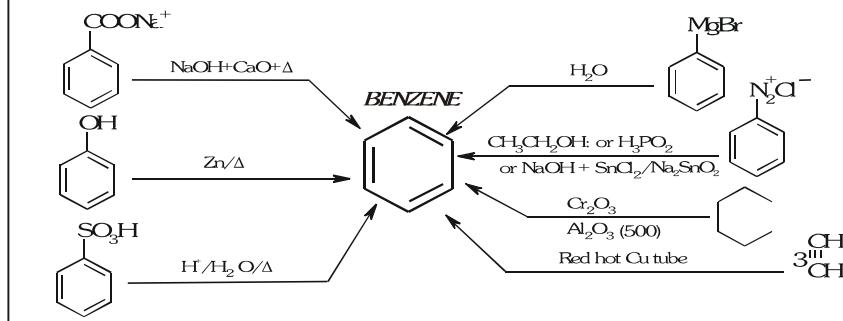
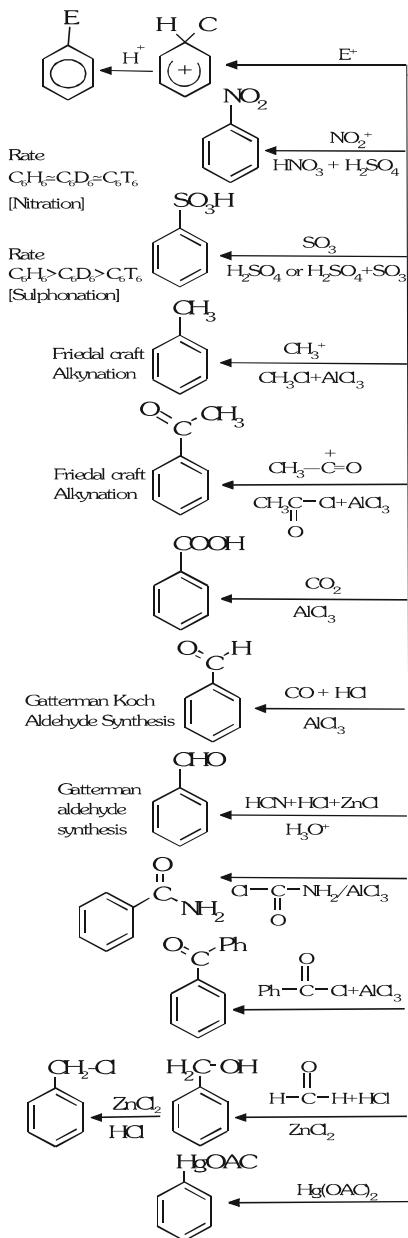
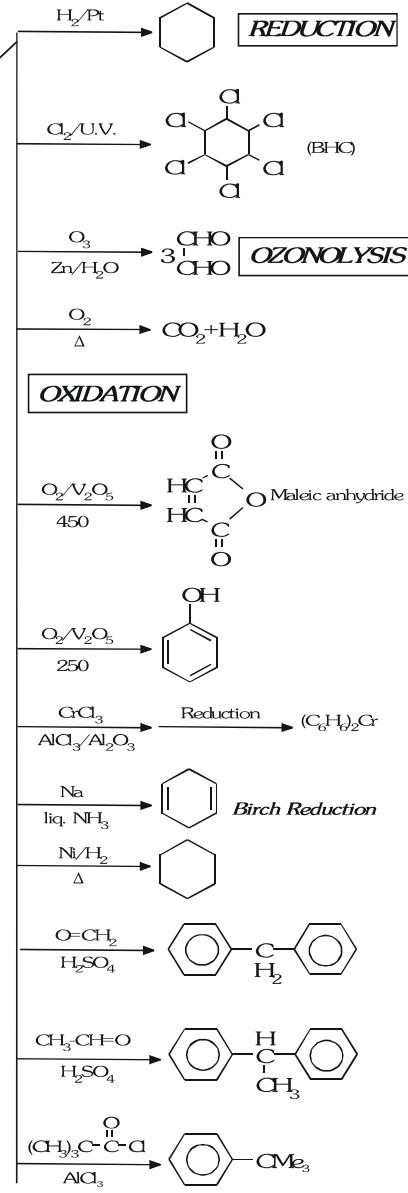
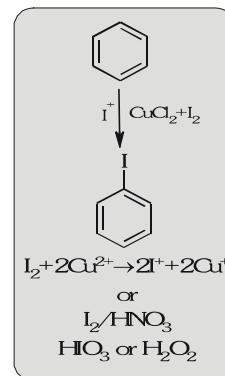
2 & 3 → can't be prepared : Aromatic amine can't prepared

Reduction

Hoffmann Boroamide Degradation :

Schmidt Reaction :

Lossen Reaction


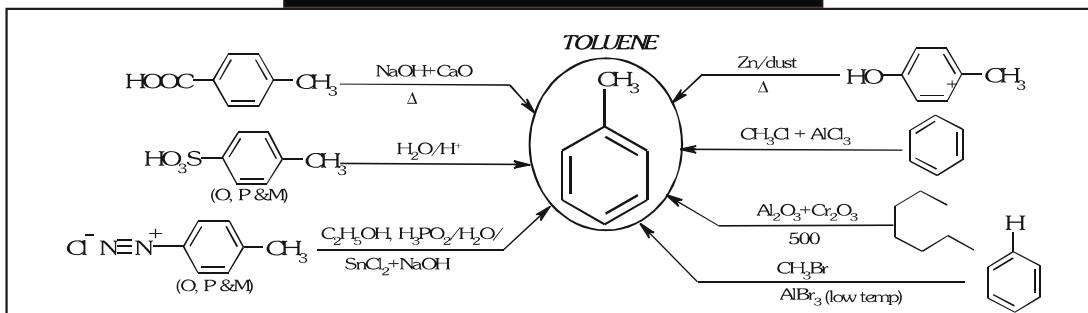
CHEMICAL PROPERTIES OF AMINES

Reagent	$R-\ddot{N}H_2$ (1)	R_2NH (2)	R_3N (3)	
1. HCl	$R-\overset{+}{NH}_3Cl^-$	$R_2\overset{+}{NH}_2Cl^-$	$\overset{+}{R}_3N-\overset{-}{Cl}$ H	
2. CH_3-Br	$R-NH-CH_3$	R_2NH-CH_3	$R_3\overset{+}{N}-CH_3Br^-$	
3. $H_3C-C(=O)-Cl$	$R-NH-C(=O)-CH_3$	$R_2N-C(=O)-CH_3$	No reaction	
4. $(CH_3-C(=O))_2O$	$R-NH-C(=O)-CH_3$	$R_2N-C(=O)-CH_3$	No reaction	
5. $Ph-SO_2Cl$	$R-N(\overset{H}{ })-SO_2-Ph$ <small>soluble</small> $\downarrow NaOH$ $[R-N(SO_2-Ph)Na^+]$	$R_2N(\overset{O}{ })-S-Ph$ $\downarrow O$ $\downarrow NaOH$ <small>Insoluble</small>	No reaction	
6. Carbylamine Test $CHCl_3/KOH$ ($:CCl_3$)	$R-\overset{+}{N}\equiv C^-$	No reaction	No reaction	
7. $HNO=O /H^+$	$R-OH + N_2 + HCl$	$R_2N-N=O$	$R_3\overset{+}{N}-\overset{-}{HON}=O$	
8. Hoffmann Mustard Oil Test				
1. $\begin{matrix} S \\ \\ C=S \end{matrix}$ $\Delta/HgCl_2$	$R-NH-C(=S)SH$ $R-N=C=S + HgS$	$R_2N-C(=S)SH$ No reaction	- No reaction	$\xrightarrow{KOH} \left(\begin{matrix} S \\ \\ C=S \end{matrix} \right)_2$ $\xrightarrow{HCl} Ph-N=C=S + Ph-NH_2$
2. Hoffmann Test $\begin{matrix} COOEt \\ \\ COOEt \end{matrix}$	$\begin{matrix} CONH-R \\ \\ CONH-R \\ Oxamide (solid) \end{matrix}$	$\begin{matrix} O=C-NR_2 \\ \\ COOEt \\ Oxamic ester (liquid) \end{matrix}$	No reaction	$O=C-NH-Ph$ $O=C-NH-Ph$
$R'MgX$	$R'-H + R-NHMgBr$	$R''H + R_2NMgBr$	No reaction	$R'H + PhNHMgBr$
			No reaction	
$O=C\begin{matrix} Cl \\ \\ Cl \end{matrix}$	$(RNH)_2C=O$	$(R_2N)_2C=O$	No reaction	$Ph-N=C=O$
$Ph-N=C=O$	$Ph-\overset{O}{ }-NH-C-NH-R$	$Ph-\overset{O}{ }-NH-C(\overset{R}{ })-N-R$	No reaction	$Ph-\overset{O}{ }-NH-C-NH-Ph$
Oxidation	$R-CH_2-NH_2$	R_2NH	R_3N	
$KMnO_4$	$R-CH=NH \xrightarrow{H_3O^+} RCHO$	R_2N-NR_2	No reaction	
H_2SO_5	$R-CH_2-NH-OH$ $R-C(=O)-N(OH)R$	R_2N-O-H	$R_3N=O$	
$KMnO_4$	$R_2CH-NH_2 : \\ R_2C=NH \xrightarrow{H_3O^+} R_2C=O$			
H_2SO_5		$R_3C-\overset{KMnO_4}{\longrightarrow} R_3C-\overset{+}{NH}_2$		

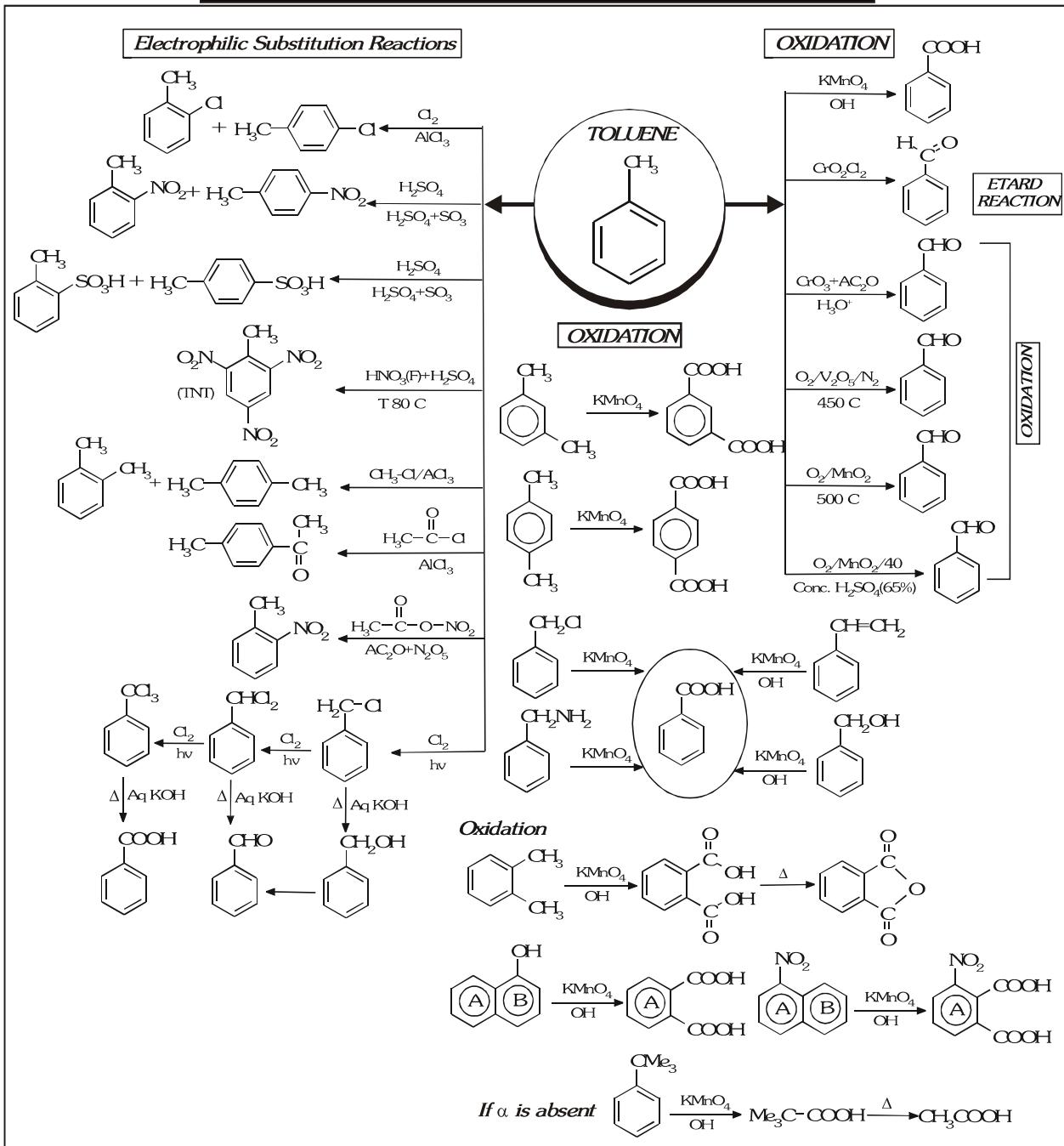
Nutshell preview and review of Nitro and Nitrite


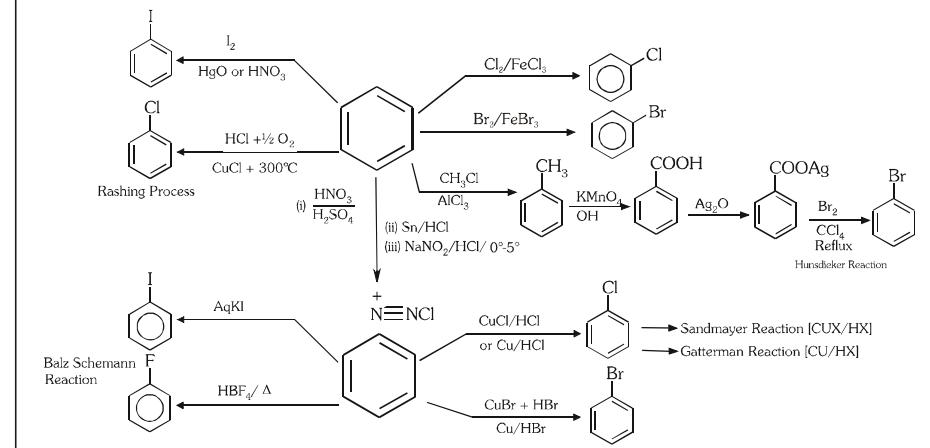
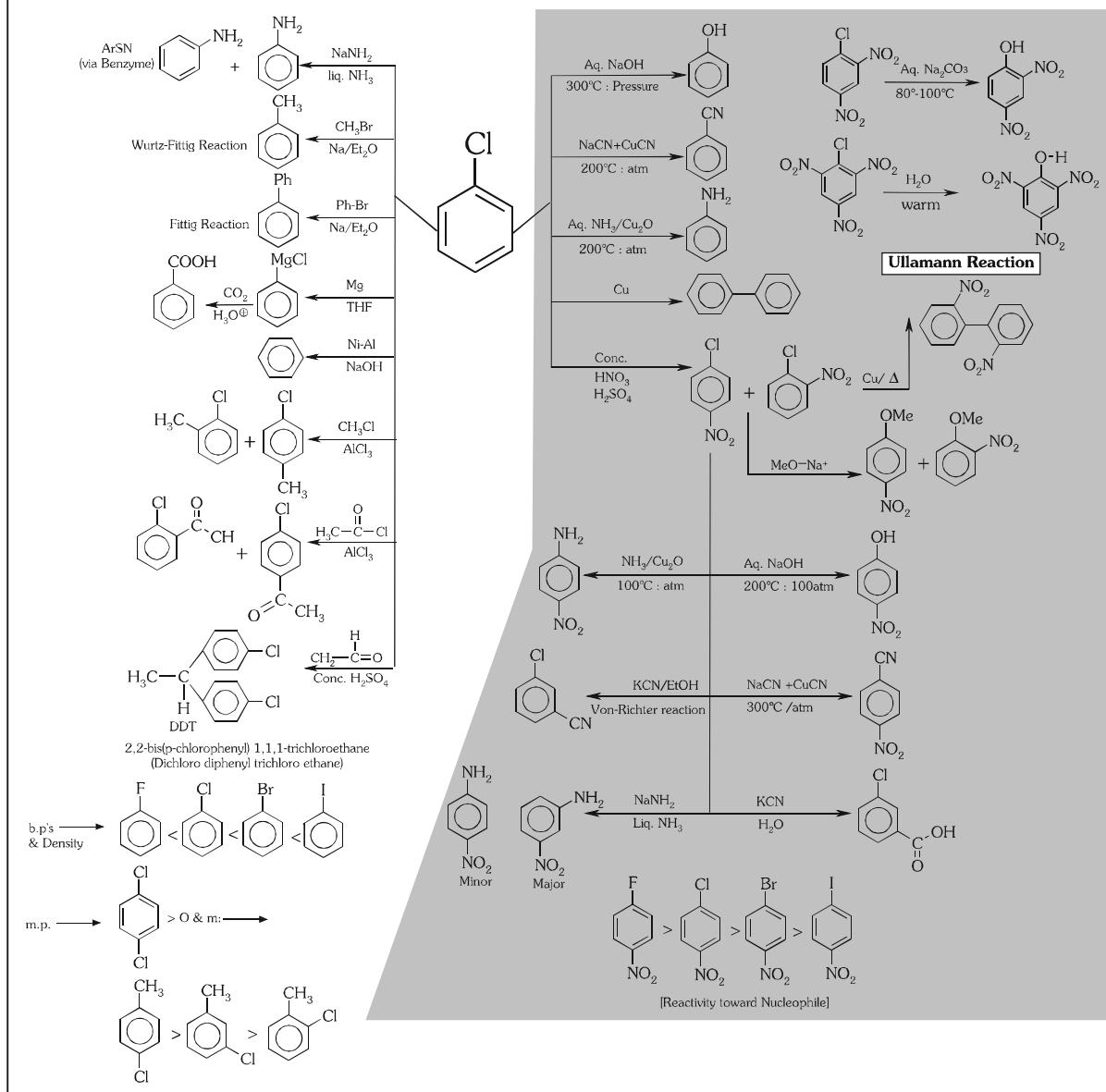
Nutshell Preparation of Benzene**Nutshell Review and Preview of Benzene Reactions****Electrophilic Substitution Reactions****BENZENE**

Nutshell Preparation of Toluene

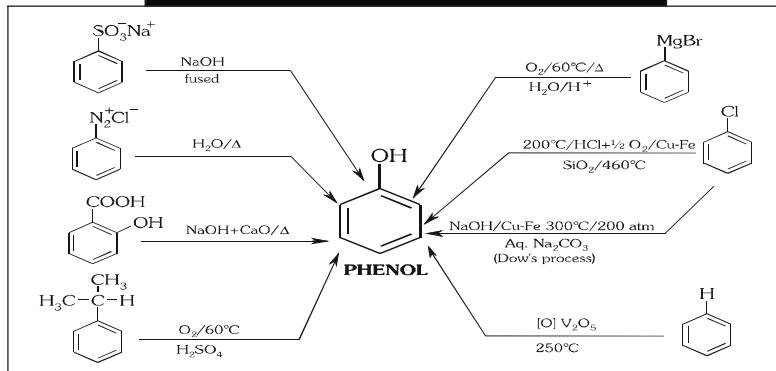


Nutshell Review and Preview of Toluene Reactions

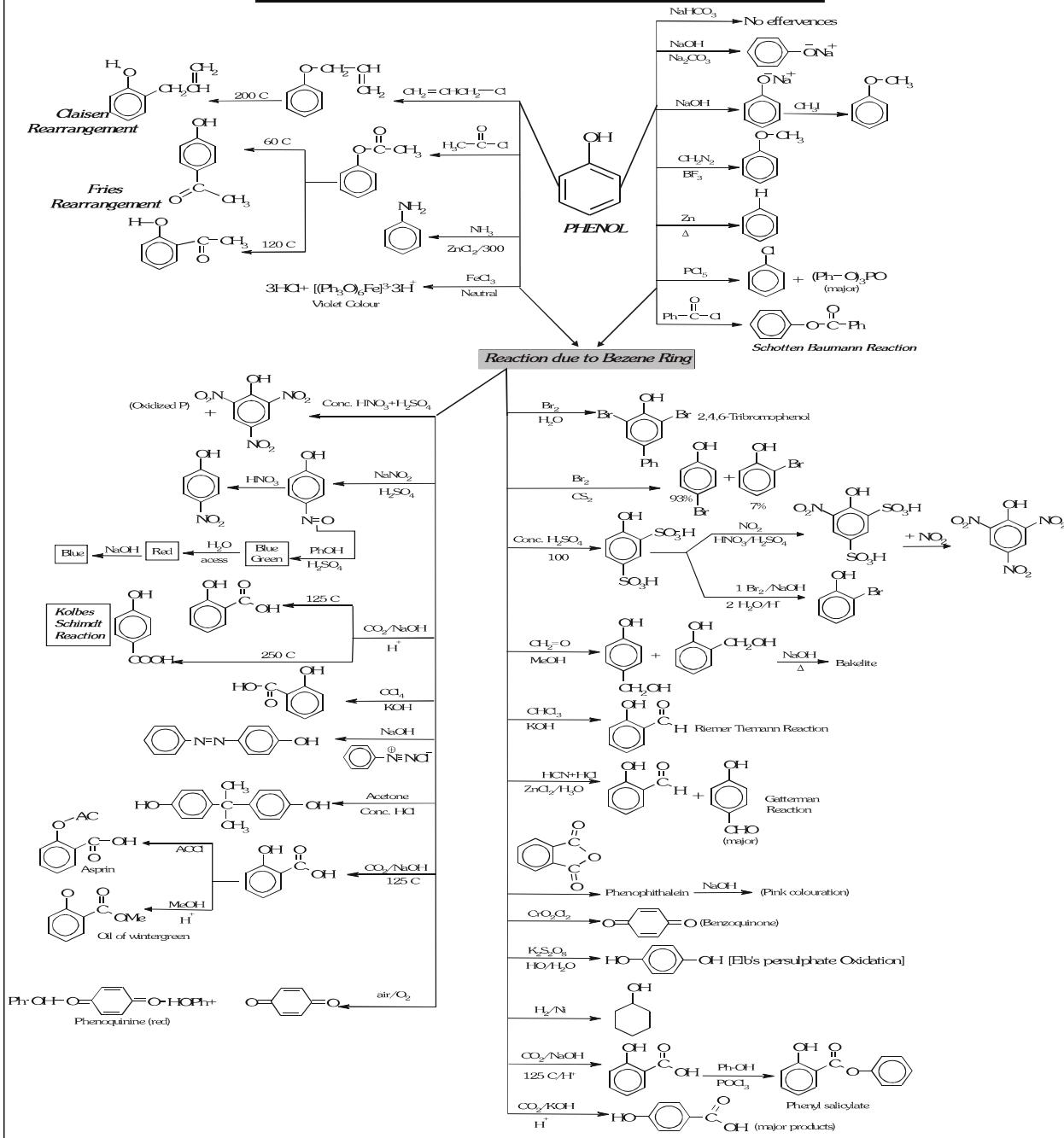


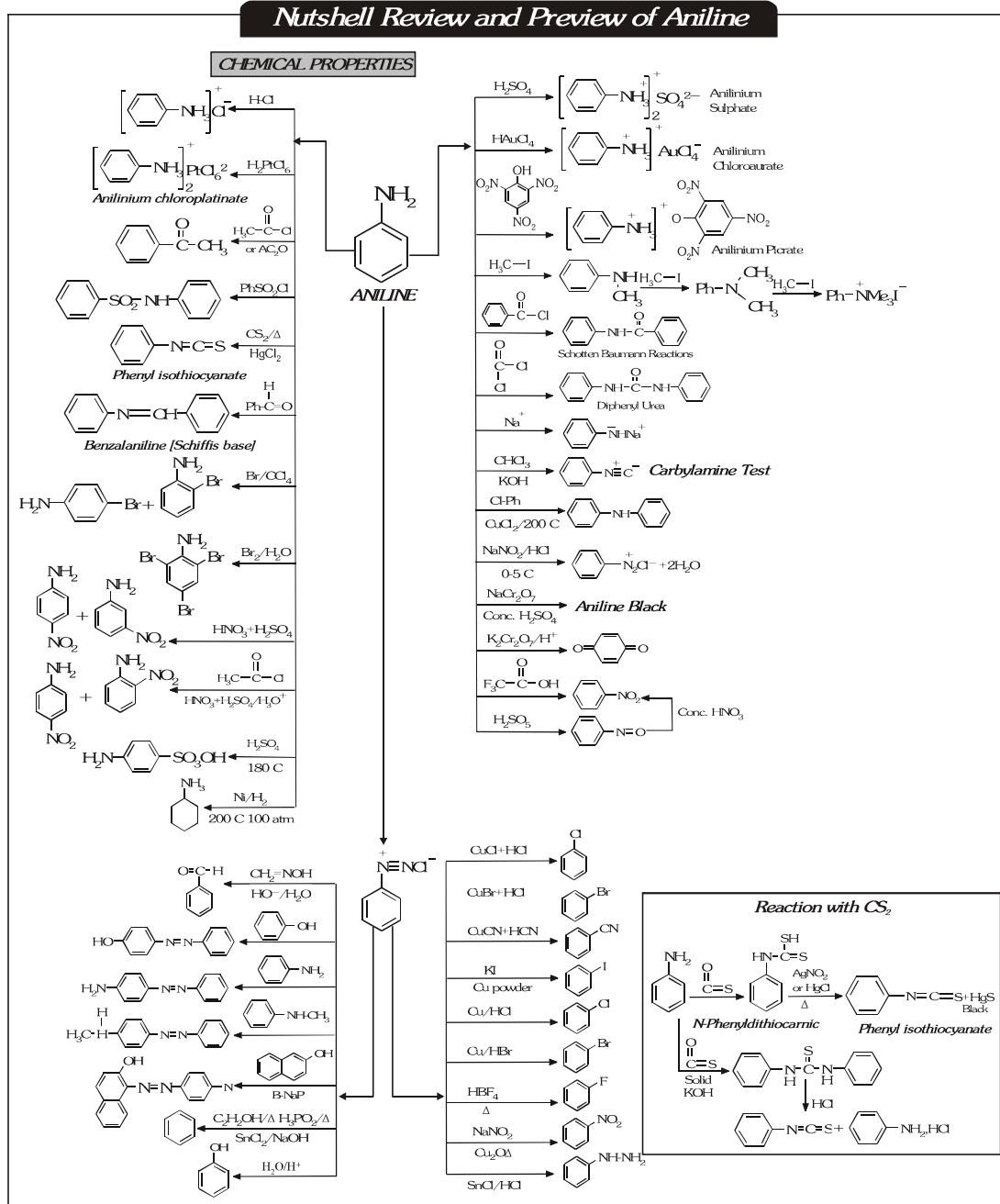
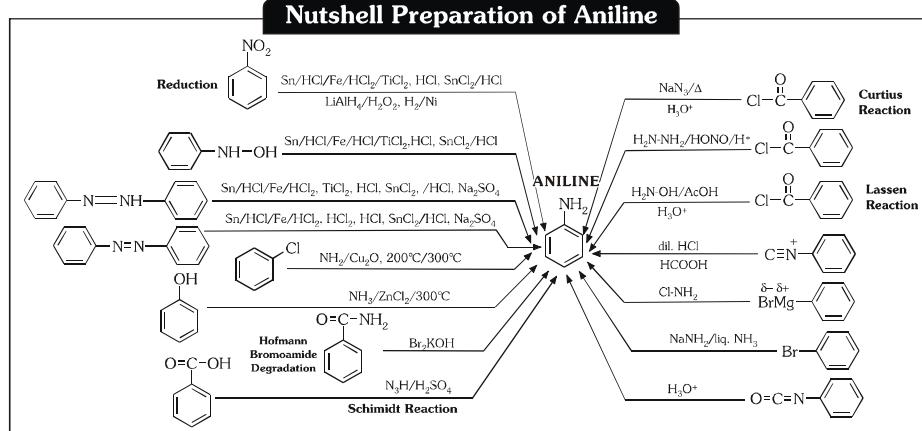
Nut Shell preparation 'Aromatic Halogen Compound'**Nutshell review and Preview of Aromatic Halogen Reactions**

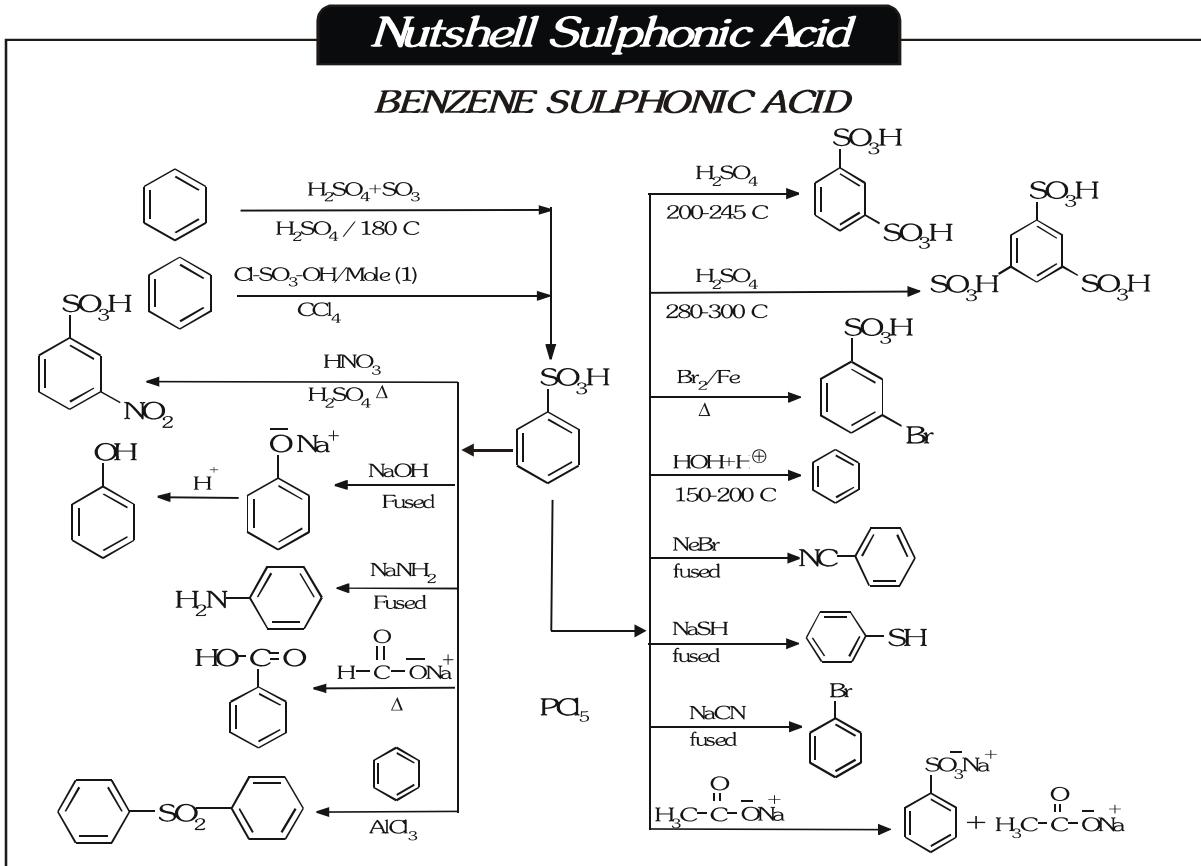
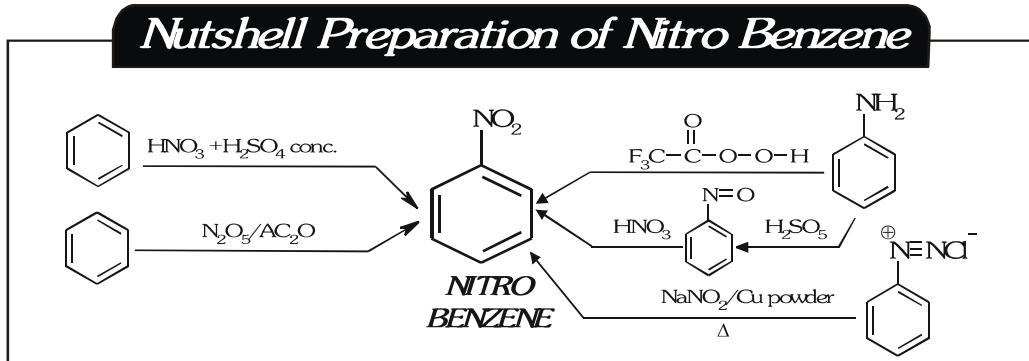
Nutshell Preparation of Phenol

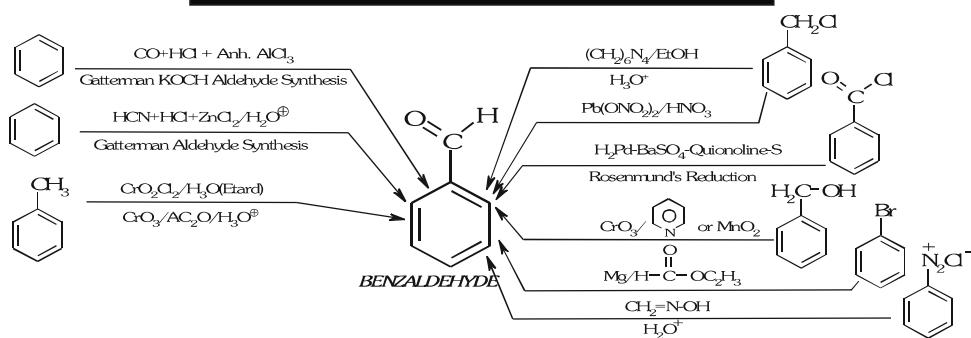
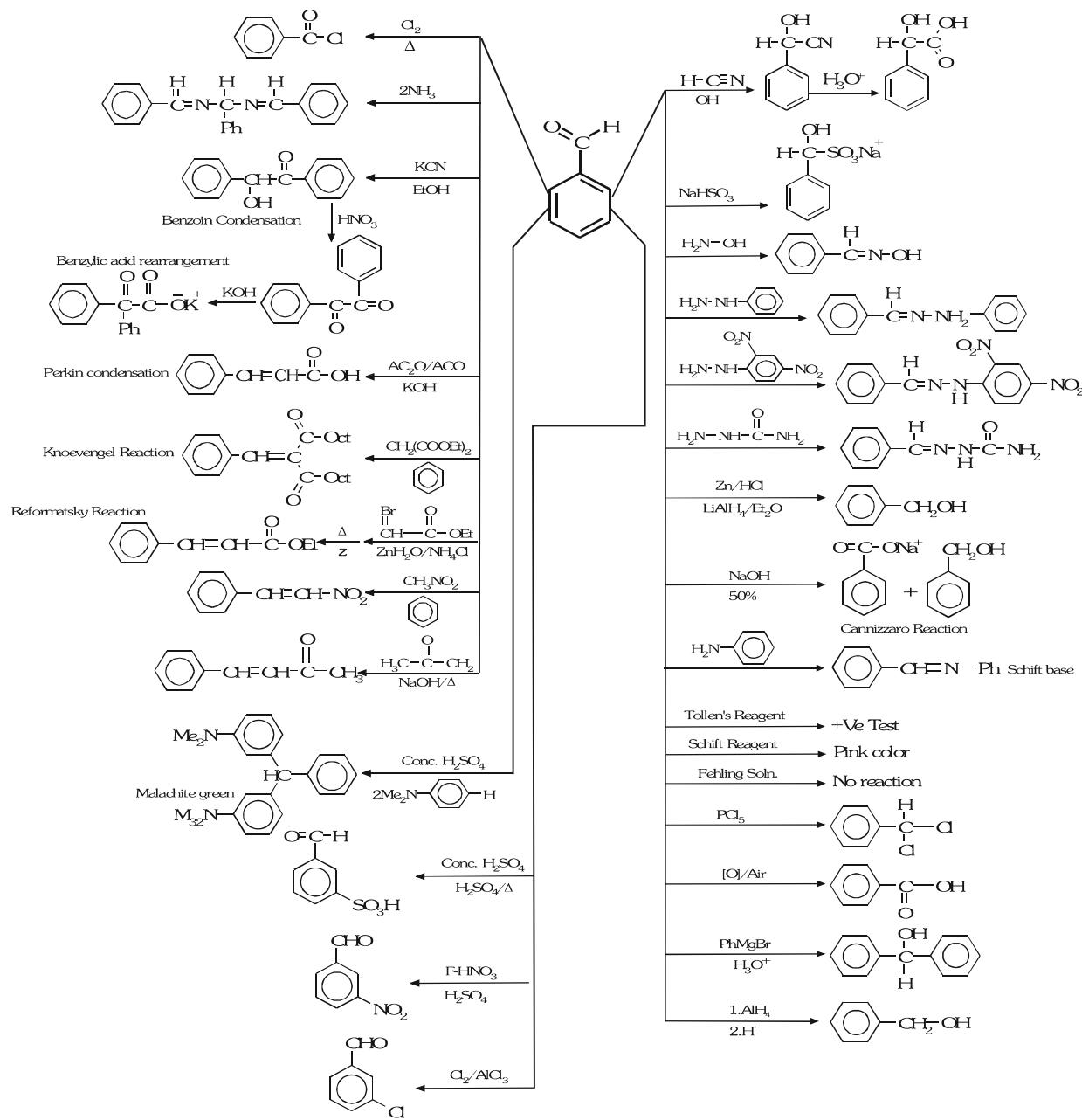


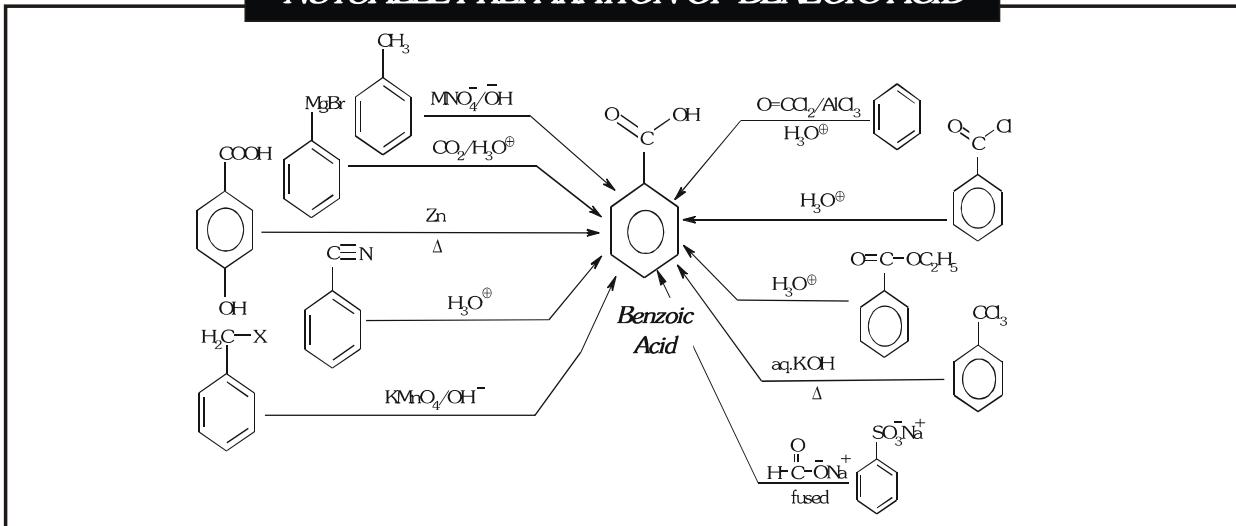
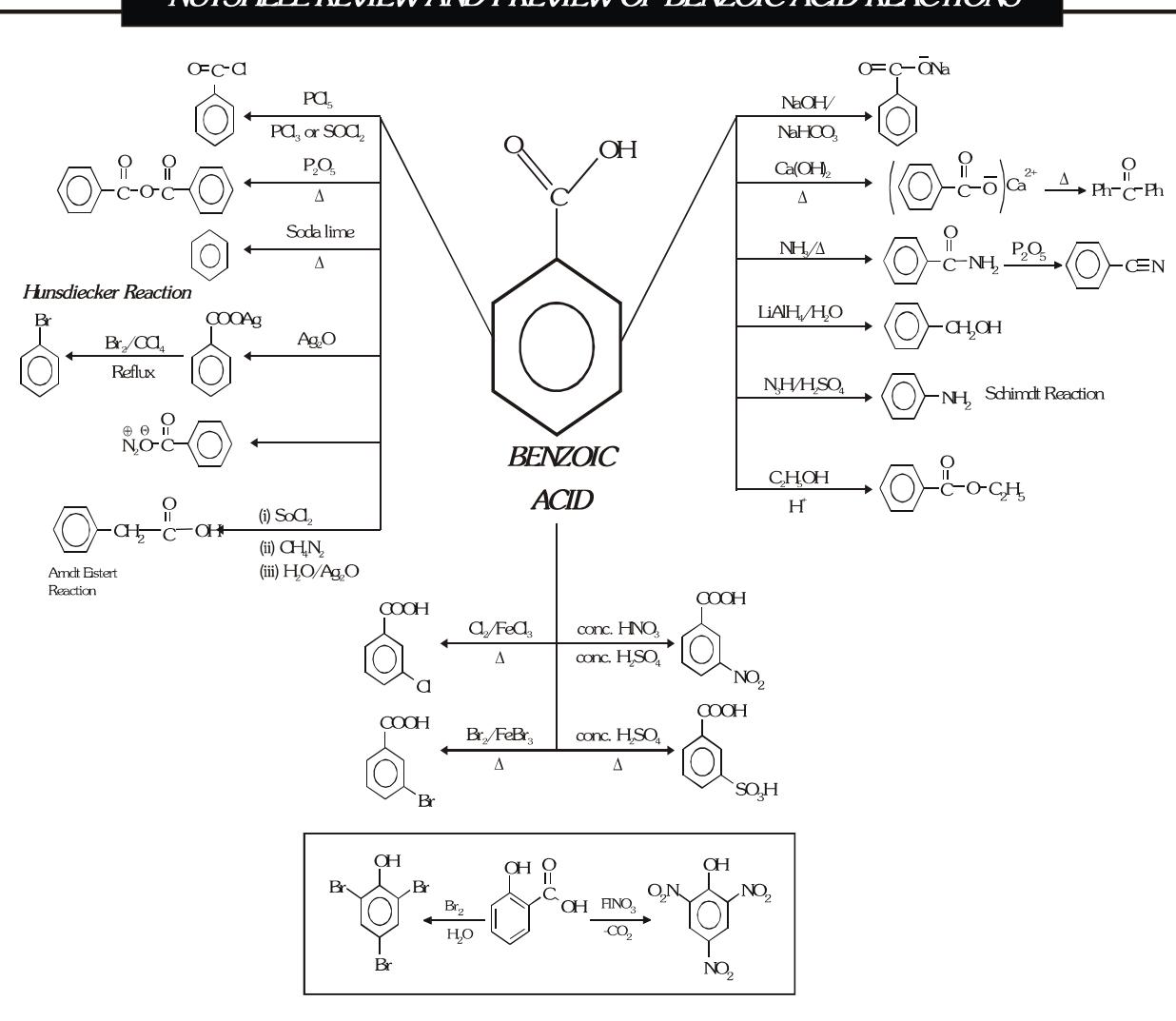
Nutshell Review and Preview Phenol Reactions

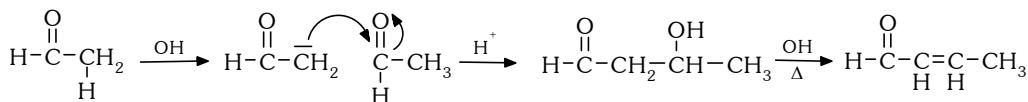
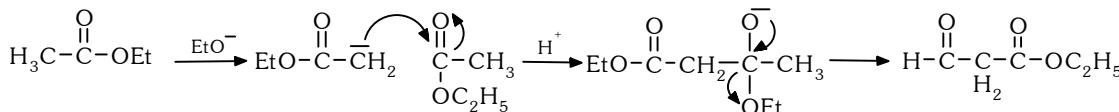
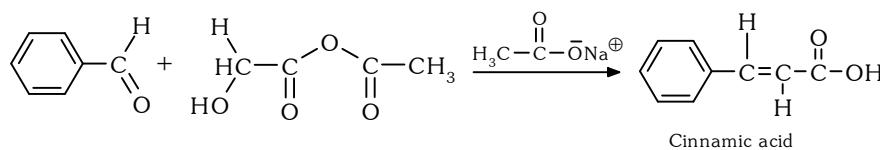
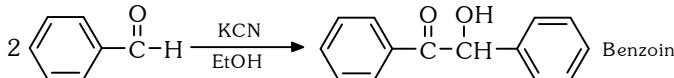
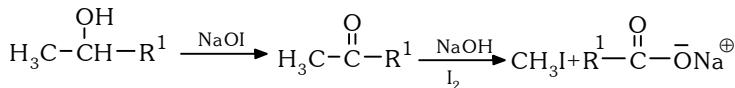
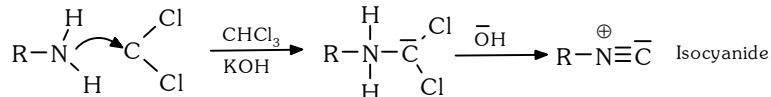
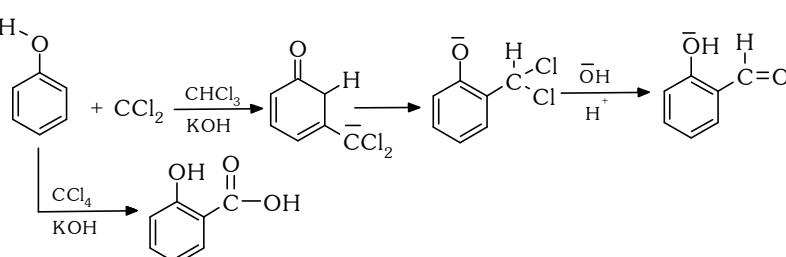
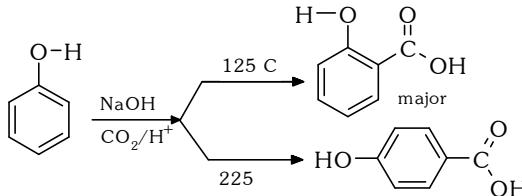


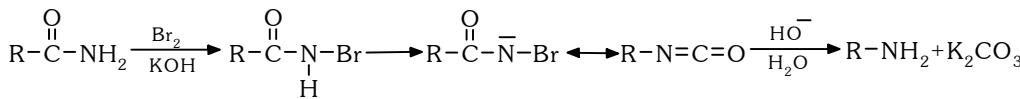
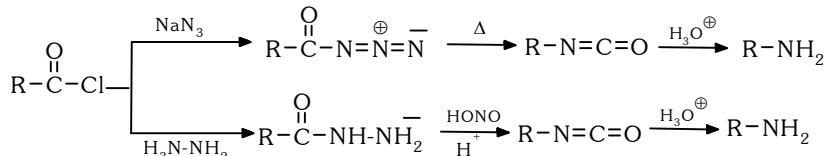
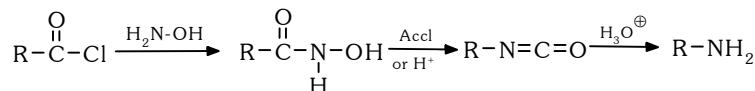
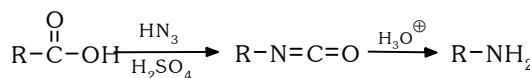
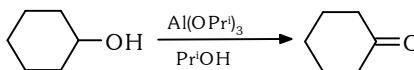
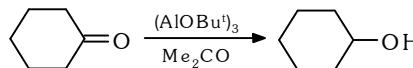
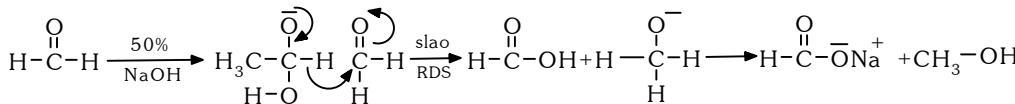
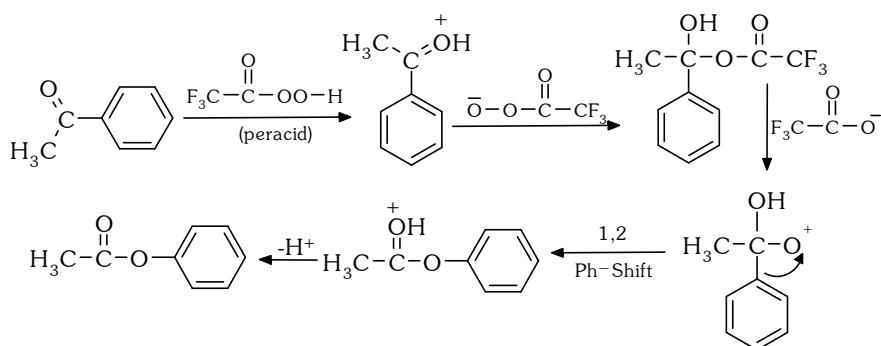
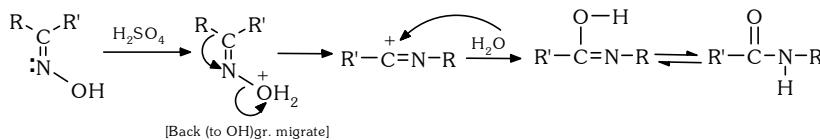




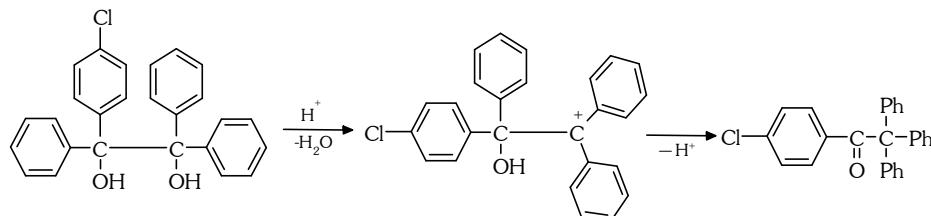
Nutshell Preparation of Benzaldehyde**Nutshell Review and Review of Benzaldehyde Reactions**

JEE-Chemistry Handbook**NUTSHELL PREPARATION OF BENZOIC ACID****NUTSHELL REVIEW AND PREVIEW OF BENZOIC ACID REACTIONS**

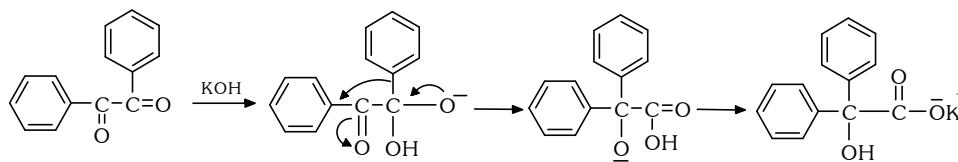
NUTSHELL REVIEW & PREVIEW OF**ORGANIC NAME REACTIONS**• **Aldol Condensation**• **Claisen Condensation**• **Perkin Condensation**• **Benzoin Condensation**• **Wittig Reaction**• **Haloform Reaction**• **Carbylamine Test**• **Reimer Tiemann Reaction**• **Kobe's Schmidt Reaction**

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Hofmann Bromoamide Degradation

Curtius Reaction

Lossen Reaction

Schimdt Reaction

Meerwein Ponndorfverly reduction

Oppeneuer Oxidation

Cannizzaro reaction

Bayer villiger oxidation

Beckmann Rearrangement


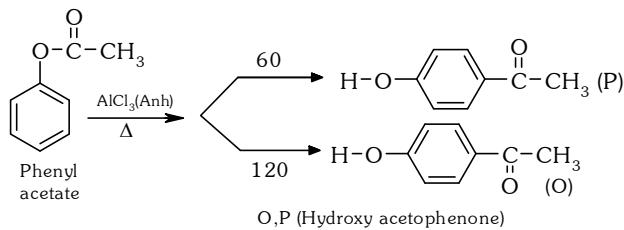
• *Pinacol Pincolone rearrangement*



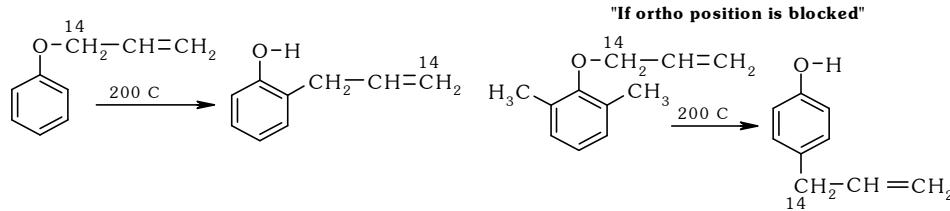
• *Benzilylic acid rearrangement*



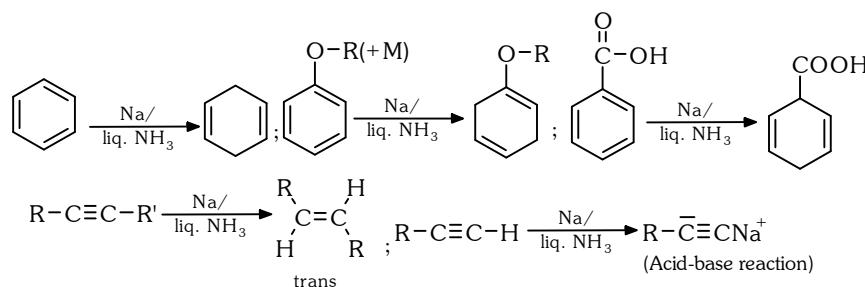
• *Fries Rearrangement*



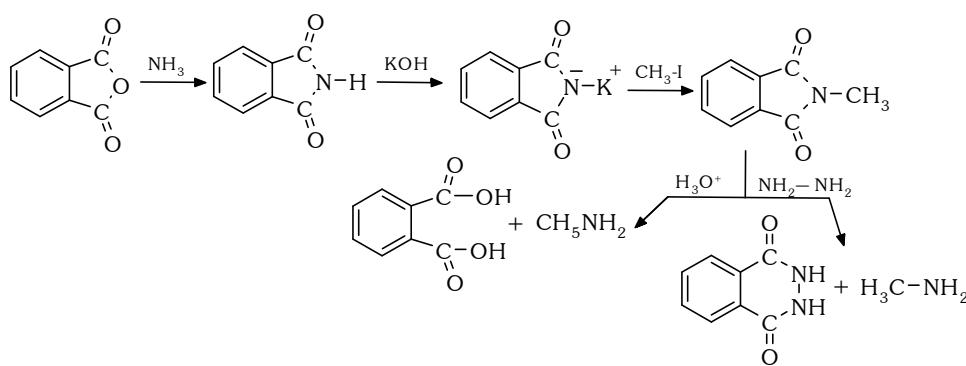
• *Claisen Rearrangement*



• *Birch Reduction*



• *Gabriel Synthesis*



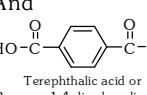
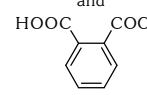
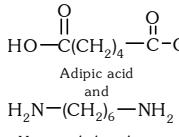
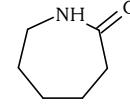
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Name	Reactant	Reagent	Product
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl	Alkane
Coupling Reaction		NaOH (phenol) HCl (Aniline)	Azo Dyne (Detection of OH or NH ₂ gr)
Diazotization		NaNO ₂ + HCl 0 - 5 C	
Diels Alder Reaction			cyclic addition product
Etard reaction		CrO ₂ Cl ₂ /CS ₂	
Fittig Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation		Anhydrous AlCl ₃	Alkyl Benzene
Friedel Craft acylation		Anhydrous AlCl ₃	Acyl Benzene
Gattermann aldehyde synthesis	C ₆ H ₆	HCN + HCl + ZnCl ₂ /H ₃ O ⁺	Benzaldehyde
Gattermann-Koch reaction	C ₆ H ₆ (CO + HCl)	anhy AlCl ₃	Benzaldehyde
Hell-Volhard-Zelinsky reaction	carboxylic acid having α-hydrogen atom	Br ₂ / red P	α- halogenated carboxylic acid
Hoffmann mustard oil reaction	primary aliphatic amine + CS ₂	HgCl ₂ /Δ	CH ₃ CH ₂ -N=C=S + HgS (black)
Hunsdiecker reaction	Ag salt of carboxylic acid	Br ₂ /CCl ₄ , 80 C	alkyl or aryl bromide
Kolbe electrolytic reaction	alkali metal salt of carboxylic acid	electrolysis	alkane, alkene and alkyne
Meerwein - Ponndorf	Ketone	[(CH ₃) ₂ CHO] ₃ Al + (CH ₃) ₂ CHOH	Secondary alcohol
Mendius reaction	alkyl or aryl cyanide	Na/C ₂ H ₅ OH	primary amine
Rosenmund reduction	acid chloride	H ₂ , Pd/BaSO ₄ , S, boiling xylene	aldehyde
Sabatier-Senderens reaction	Unsaturated hydrocarbon	Raney Ni/H ₂ , 200 – 300 C	Alkane
Sandmeyer reaction		CuCl/HCl or CuBr/HBr or CuCN/KCN, heat	halo or cyanobenzene
Gattermann Reaction	C ₆ H ₅ N ₂ ⁺ Cl ⁻	Cu/Hx(HBr)/HBr/HBr	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	NaOH + C ₆ H ₅ COCl	
Stephen reaction	alkyl cyanide	SnCl ₂ /HCl	Aldehyde
Ullmann reaction	Iodobenzene	Cu (heat)	Diphenyl
Williamson synthesis	alkyl halide	sodium alkoxide or sodium phenoxide	ether
Wurtz-Fittig reaction	alkyl halide + aryl halide	Na/dry ether	alkyl benzene

ADDITION POLYMERS

S. No	Name of Polymer	Abbreviation	Starting Materials	Nature of Polymer	Properties	Applications
I. Polyolefins						
1.	Polyethylene or Polyethene		$\text{CH}_2=\text{CH}_2$	Low density homopolymer (branched chain growth)	Transparent, moderate tensile strength, high toughness	Packing material bags, insulation for electrical wires and cables. Buckets, tubes, house ware pipes, bottles and toys
2.	Polypropylene or Polypropene Herculon	or or	$\text{CH}_3\text{CH}=\text{CH}_2$	Homopolymer, linear, chain growth	Harder and stronger than polyethene	Packing of textiles and foods, liners for bags, heat shrinkage wraps, carpet fibres, ropes, automobile mouldings, stronger pipes and bottles.
3.	Polystyrene or Styron		$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	Homopolymer, linear, chain growth	Transparent	Plastic toys, household wares, radio and television bodies, refrigerator linings.
II. Polydienes						
1.	Neoprene		$\text{H}_2\text{C}=\text{CH}-\overset{\text{Cl}}{\underset{ }{\text{C}}}-\text{CH}_2$ Chloroprene or 2-Chloro-1,3-butadiene	Homopolymer, chain growth	Rubber like, a superior resistant to aerial oxidation, and oils, gasoline etc.	Horses shoe heels, stoppers.
2	Buna S (Styrene- Butadiene, Rubber)	SBR or GRS	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ 1,3-butadiene and $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ Styrene	Copolymer, chain growth	Rubber like, a superior resistant to aerial oxidation, and oils, gasoline etc.	Manufacturer of tyres, rubber soles, water proof shoes.
III. Polyacrylates						
1.	Polymethylmethacrylate (Flexiglass Lucite, Acrylic or Perspex)	PMMA	$\text{H}_2\text{C}=\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{COOCH}_3$	Homopolymer	Hard, transparent, excellent light transmission. Optical clarity better than glass, takes up colours.	Lenses, light covers, light shades, signboards, transparent domes, skylights, air craft windows, dentures and plastic jewellery.
2.	Polyethylacrylate		$\text{H}_2\text{C}=\text{CH}-\text{COOC}_2\text{H}_5$	Homopolymer	Tough, rubber like product.	
3.	Polyacrylonitrile or Orlon	PAN	$\text{CH}_2=\text{CH}-\text{CN}$	Homopolymer	Hard, horny and high melting materials.	Orion, acrilon used for making clothes, carpets, blankets and preparation of other polymers.
IV. Polyhalofins						
1.	Polyvinyl chloride	PVC	$\text{CH}_2=\text{CH}-\text{Cl}$	Homopolymer, chain growth	Pliable (easily moulded)	(i) Plasticised with polyester polymers used in rain coats, hand bags, shower curtains, fabrics, shoe soles, vinyl flooring (ii) Good electrical insulator, (iii) Hose pipes.
2.	Polytetrafluoroethylene, or Teflon	PTFE	$\text{F}_2\text{C}=\text{CF}_2$	Homopolymer	Flexible and inert to solvents, boiling acids even aqua regia, stable upto 598 K	(ii) For nonstick utensils coating (ii) Making gaskets, pump packings, valves, seals, non lubricated bearings.
3.	Polymonochlorotrifluor o-ethylene	PCTFE	$\text{ClFC}=\text{CF}_2$		Less resistant to heat and chemicals due to presence of chlorine atoms.	Similar to those of Teflon.

JEE-Chemistry Handbook**CONDENSATION POLYMERS**

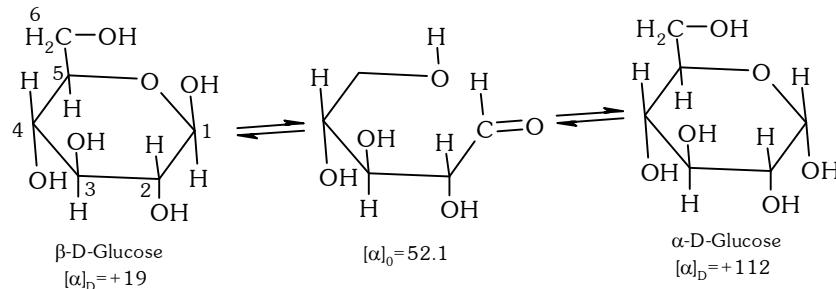
S. No	Name of Polymer	Abbre- viation	Starting Materials	Nature of Polymer	Properties	Applications
I. Polyesters						
1.	Terylene or Dacron or Mylar		HO—CH ₂ —CH ₂ —OH Ethylene glycol or Ethane-1,2-diol And  Terephthalic acid or Benzene-1,4-dicarboxylic acid	Copolymer, step growth, linear	Fibre crease resistant, low moisture content, not damaged by pests like moths.	For wash and wear fabrics, tyre cords, sea belts and sails.
2.	Glyptal or Alkyl resin		HO—CH ₂ —CH ₂ —OH Ethylene glycol and  Phthalic acid or Benzene-1,2-dicarboxylic acid	Copolymer, linear step growth	Thermoplastic, dissolves in suitable solvents and solutions, on evaporation leaves a tough but not flexible film.	Paints and lacquers.
II. Polyamides						
1.	Nylon-6,6		 Adipic acid and H ₂ N—(CH ₂) ₆ —NH ₂ Hexamethylenediamine	Copolymer, linear, step growth		
2	Nylon-6,10		H ₂ N(CH ₂) ₆ NH ₂ Hexamethylene diamine and HOOC(CH ₂) ₈ COOH Sebacic acid	Copolymer, linear, step growth	High tensile strength, abrasions resistant, somewhat elastic	(i) Textile fabrics, carpets, bristles for brushes. (ii) Substitute of metals in bearings (iii) Gears elastic hosiery. Mountaineering ropes, tyre cords, fabrics.
3.	Nylon-6 or Perlon L		 Caprolactum	Homopolymer, linear		Mountaineering ropes, tyre cords, fabrics.
Formaldehyde resins						
1.	Phenolformaldehyde resin or Bakelite		Phenol and formaldehyde	Copolymer, step growth		(i) with low degree polymerization for binding glue, wood, varnishes, lacquers. (ii) With high degree polymerisation for combs, for mica table tops, fountain pen barrels, electrical goods (switches and plugs), gramophone records.
2.	Melamine formaldehyde resin		Melamine and formaldehyde	Copolymer, step growth	Tough, rubber like product.	Non-breakable and non-plastic crockery.

CARBOHYDRATES

- Polyhydroxy aldehyde or Ketone (cyclic hemiacetal / or hemiacetal or acetal or ketal)
 - Monosaccharide ($C_nH_{2n}O_n$) : single unit, can't be hydrolysed : Glucose; fructose (by glycosidic linkage)
- Sucrose $\xrightarrow{H_3O^+}$ Glucose + Fructose; maltose $\xrightarrow{H_3O^+}$ 2 Glucose unit
- Lactose $\xrightarrow{H_3O^+}$ Glucose + Galactose
- Polysaccharide : Contain more than monosaccharide units
($C_6H_{10}O_5)_n$: Starch & cellulose.

TYPE OF SUGAR		
Give Test	Reducing	Non Reducing
1. Tollen's Reagent	+ve test	-ve test
2. Fehling Reagent	+ve test	-ve test
3. Benedict Test	+ve test	-ve test
4. Mutarotation	Yes	No
5. Functional Unit	$\begin{array}{c} \alpha \\ \\ -C-C=O / -C-C-O- \\ \\ OH \end{array}$ <p>Hemiacetal</p> <p>Hemiketal</p> <p>Acetal</p> <p>Ketal</p>	
6. Example	All monosaccharide Glucose; fructose, mannose, galactose, Dissaccharide : maltose; lactose	Dissaccharide : Sucrose Polysaccharide : starch cellulose

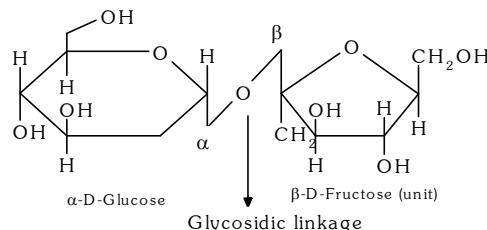
- Mutarotation:** When either form is placed in solution it slowly form the other via open chain aldehyde form & gradual change in specific rotation until specific value is reached.



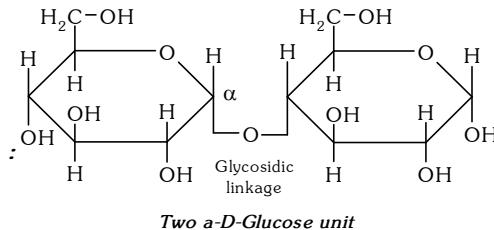
- Anomer's :** Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new-symmetric carbon is referred to as Anomeric carbon.
- Epimer's :** Distereomer's which differ in conformation at one chiral carbon [maltose & glucose (epimers carbon is C₂)]

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- Sucrose :**

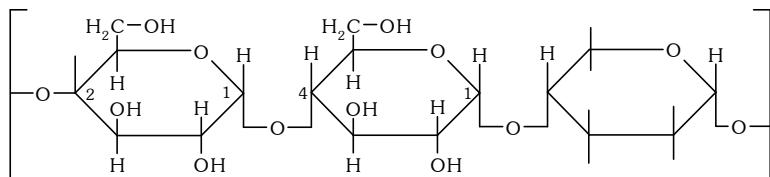


- Maltose**



- Starch :** (Amylose & Amylopectin)

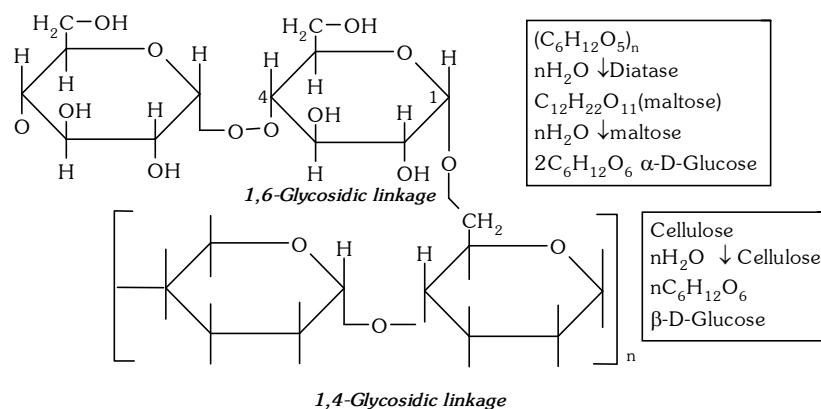
- Amylose : (Straight Chain) :**



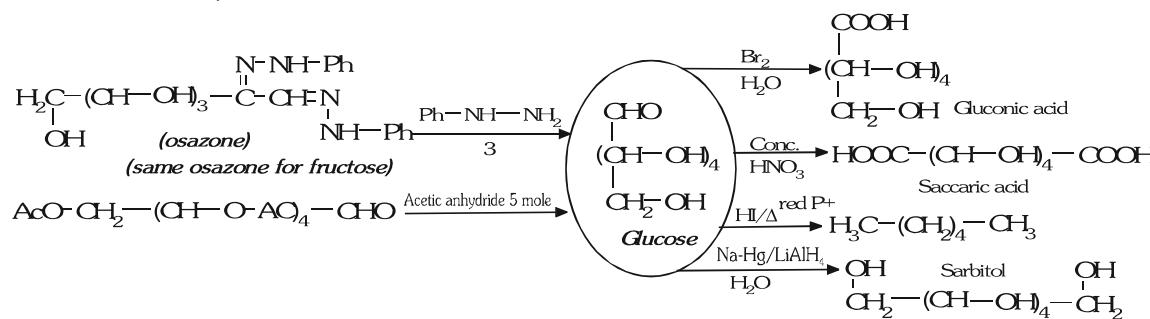
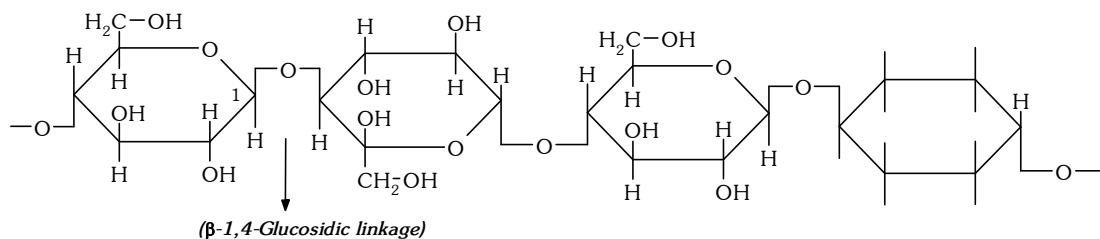
(α-1,4 Glycosidic linkage)

(i) Soluble in H_2O & give blue colour with I_2 (ii) 10 to 20%

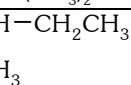
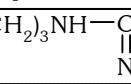
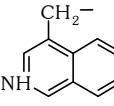
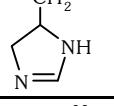
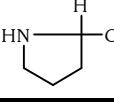
- Amylopectin (Branch chain) : ($C_6H_{12}O_5)_n$**



- Cellulose :** (Straight chain β -D-Glucose unit)



AMINO ACIDS

S.No.	Name of amino acid	Structure of R	Three letter symbol
1.	Glycine	-H	Gly
2	Alanine	-CH ₃	Ala
3.	Valine	-CH(CH ₃) ₂	Val
4.	Leucine	-CHCH(CH ₃) ₂	Leu
5.	Isoleucine		Ile
6.	Arginine		Arg
7.	Lysine	-(CH ₂) ₄ NH ₂	Lys
8.	Glutamic acid	-CH ₂ CH ₂ COOH	Glu
9.	Aspartic acid	-CH ₂ COOH	Asp
10.	Glutamine	-CH ₂ CH ₂ CONH ₂	Gln
11.	Asparagine	-CH ₂ CONH ₂	Asn
12.	Threonine	-CHOH.CH ₃	Thr
13.	Serine	-CH ₂ OH	Ser
14.	Cysteine	-CH ₂ SH	Cys
15.	Methionine	-CH ₂ CH ₂ SCH ₃	Met
16.	Phenylalanine	-CH ₂ C ₆ H ₅	Phe
17.	Tyrosine	-CH ₂ C ₆ H ₄ OH (p)	Tyr
18.	Tryptophan		Trp
19.	Histidine		His
20.	Proline		Pro

ISOELECTRONIC POINT

- In electric field these ions will migrate towards the electrodes of opposite charge (+ve ions towards cathode and -ve ions towards anode). At a certain pH the dipolar ion exists as neutral ion and does not migrate to either electrodes. This pH is known as isoelectric point of amino acids. For neutral amino acids.

PEPTIDES

- Condensation products of two or more molecules of α -amino acids is called peptides.
- Peptide Linkage** : Linkage which unites the α -amino acid molecules together is called peptide linkage. It is $-\text{CO}-\text{NH}-$ linkage.

STRUCTURE OF PROTEINS

- Primary structure** : The sequence in which various amino acids are arranged in a protein is known as the primary structure of a protein. The number, sequence and identity of amino acids in a protein constitute primary structure of a protein.
- Secondary structure** : The coiling of the long strings of amino acids in a protein is its secondary structure. The α -helix is a common secondary structure. In α -helix, the peptide chain coils and the turns of the coil are held together by hydrogen bonds. Another type of secondary structure is possible in which the protein chains are stretched out. It is a β -pleated sheet structure.
- Tertiary structure** : The folding and binding of α -helix into more complex shapes illustrates the tertiary structure of proteins. At normal pH and temperature, each protein will take the energetically most stable shape. This shape is specific to a given amino acids which form proteins.
- Quaternary protein structure** results when several protein molecules are bonded together to form a still larger units.

COLOUR TESTS

- Biuret Test** : Proteins give a violet or blue colour with 10% NaOH solution and a drop of very dilute copper sulphate. The test is due to $-\text{CO}-\text{NH}-$ group and is given by all compounds containing this group.
- Millon's Test** : Millon's reagent is a solution of mercuric and mercurous nitrate in nitric acid. Protein, when warmed with Millon's reagent, gives a white precipitate which changes to red.

ALKALI METALS

- **Physical properties :** General electronic configuration ns^1 .

General oxidation state +1.

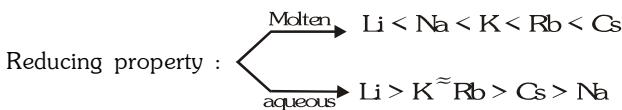
Atomic/Ionic size Li < Na < K < Rb > Cs.

Density Li < K < Na < Rb < Cs

Ionisation energy Li > Na > K > Rb > Cs

Flame colour	Li	Na	K	Rb	Cs
	Crimsen red	Golden yellow	Pale violet	Reddish violet	Blue

Basic nature increase down to the group

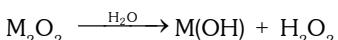
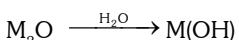


- **Chemical properties :**

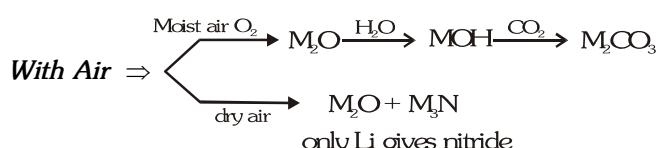
With O₂ ⇒ Lithium forms normal oxide [Li₂O]

Sodium forms peroxide (Na₂O₂)

K, Rb,Cs forms superoxide KO₂,RbO₂, CsO₂



With Water ⇒ M + H₂O → MOH + H₂



With NH₃ ⇒ : M + (X + Y) NH₃ → [Na(NH₃)_X]⁺ + [e(NH₃)_Y]⁻
ammoniated e⁻

Paramagnetic, blue colour excess of metal dimagnetic and copper bronze colour.

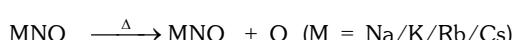
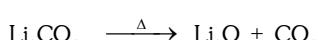
on standing Li + NH₃ → Li₂NH (Lithamide)

M(Na/K/Rb/Cs) + NH₃ → MNH₂ (amide)

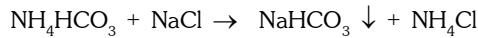
With Halides ⇒ M + X₂ → MX

K, Rb, Cs forms poly halide due to large size

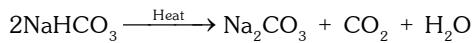
Carbonates : Only Li₂CO₃ decomposes



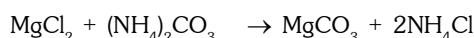
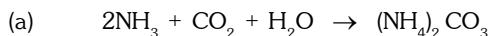
- Na_2CO_3 does not impart any colour to the flame but NaCl does because the thermal ionization of Na_2CO_3 does not take place at the temperature of flame of the burner.
- In **Solvay's process**, CO_2 gas is passed through saturated brine (NaCl) solution when sparingly soluble NaHCO_3 separates out.



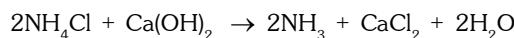
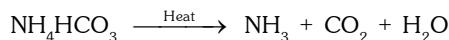
The NaHCO_3 formed above is calcined to form Na_2CO_3



- The reactions taking place at different stages during the manufacture of Na_2CO_3 by Solvay process are given as under :



(b) Ammonia recovery tower



(c) Calcination of NaHCO_3



(i) **Efflorescence :**

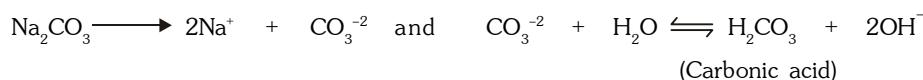
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ when exposed to air it gives out nine out of ten H_2O molecules.



(Monohydrate)

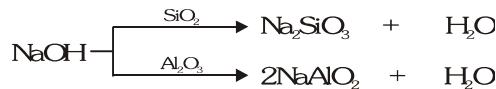
This process is called efflorescence. Hence washing soda losses weight on exposure to air.

(ii) **Hydrolysis :** Aqueous solution of Na_2CO_3 is alkaline in nature due to anionic hydrolysis.



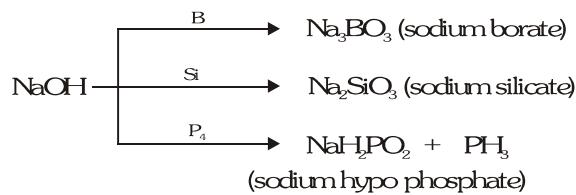
(e) **Uses**

- (i) For making fusion mixture ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$)
- (ii) In the manufacture of glass, caustic soda, soap powders etc.
- (iii) In laundries and softening of water.
- (iv) NaOH is **strong base**

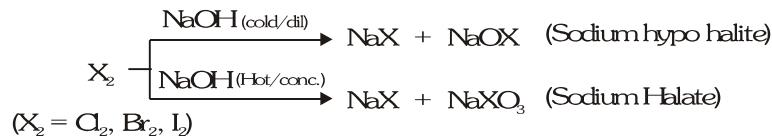


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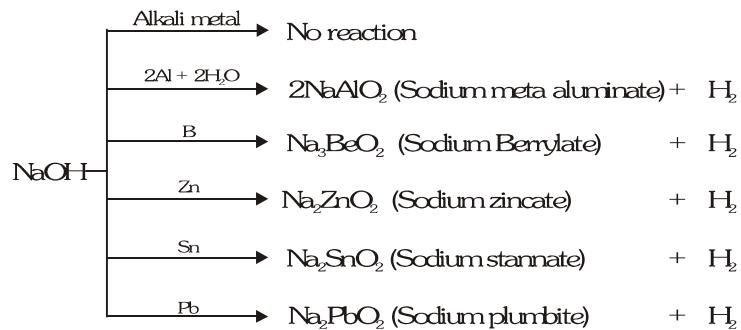
(iv) **Reaction with non metals :** no reaction with H₂, N₂ and C



(v) **Reaction with halogens**



(vi) **Reaction with Metal :**



ALKALINE EARTH METALS

- **Physical properties** : General electronic configuration ns^2 .

General oxidation state +2.

Atomic/Ionic size Be < Mg < Ca < Sr < Ba

Ionisation energy Be > Mg > Ca > Sr > Ba

Flame colour **Ca - Brick red** **Sr - Crimson red**

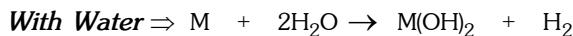
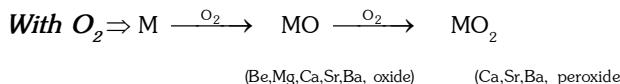
Ba - Apple green

Basic nature increase down to the group

Reducing property : Order of reducing property in aqueous and gaseous medium is

$Be^{+2} < Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$

- Chemical properties :



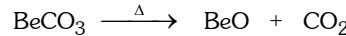
With Air ⇒ In moist air, except Be all the elements converts into carbonates.

In dry air Be and Mg gives nitride and oxide both while other gives only oxides.

With NH₃ ⇒ : Only Ca, Sr and Ba gives blue solution of ammoniated electron.

Carbonates :

- (i) Except BeCO₃, all the carbonates are stable towards heat



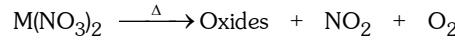
- (ii) Order of decreasing stability -



Nitrates :

- (i) Alkaline earth metals forms M(NO₃)₂ type nitrates. (M –Alkaline earth metal).

- (ii) All alkaline metals nitrates on heating gives oxides and NO₂ + O₂



- **SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM**

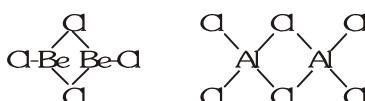
- (a) Both lithium and magnesium are harder and lighter than other elements in the respective groups.
- (b) Lithium and magnesium react slowly with cold water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, Li₃N and Mg₃N₂.
- (c) The oxides, Li₂O and MgO do not combine with excess oxygen to give a peroxide or a superoxide.
- (d) The carbonates of lithium and magnesium decompose easily on heating to form the oxide and CO₂. Solid bicarbonates are not formed by lithium and magnesium.

JEE-Chemistry Handbook

- (e) Both LiCl and MgCl₂ are soluble in ethanol.
- (f) Both LiCl and MgCl₂ are deliquescent and crystallise from aqueous solution as hydrates, LiCl·2H₂O and MgCl₂·8H₂O.

➤ **DIAGONAL SIMILARITY BETWEEN BERYLLIUM AND ALUMINIUM** : In many of its properties, beryllium resembles aluminium. Thus –

- (a) The two elements have same electronegativity and their charge/ radius ratios.
- (b) Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalis to form soluble complexes, beryllates [Be(OH)₄]²⁻ and aluminates, [Al(OH)₄]⁻.
- (c) The chlorides of both beryllium and aluminium



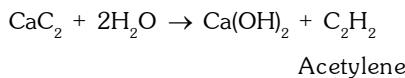
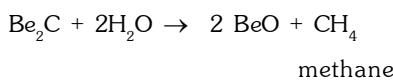
have bridged chloride structures in vapour phase.

- (d) Salts of these metals form hydrated ions, Ex. [Be(OH₂)₄]²⁺ and [Al(OH₂)₆]³⁺ in aqueous solutions. Due to similar charge/ radius ratios of beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as BeF₄²⁻ and [Be(C₂O₄)₂]²⁻ and aluminium forms octahedral complexes like AlF₆³⁻ and [Al(C₂O₄)₃]³⁻.

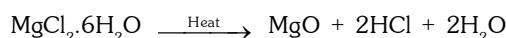
- Among alkaline earth metals, Be and Mg do not impart any characteristic colour to the flame due to more ionization energies.
- The stability of the carbonates of alkaline earth metals increases in the order.



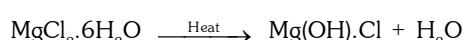
- Be₂C on treatment with H₂O forms CH₄ while CaC₂ forms C₂H₂.



- BeCl₂ in the vapour phase above 900°C is monomeric ; below 900°C in the vapour exists as a mixture of monomer BeCl₂ and dimer Be₂Cl₄, in the solid state, has a polymeric structure and when dissolved in a coordinating solvent it exists as a monomer.
- Anhydrous MgCl₂ cannot be prepared by the simple heating of hydrated magnesium chloride MgCl₂·6H₂O, as it gets hydrolysed to magnesium oxide.

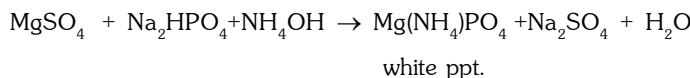


- Out of the oxides of group 2 elements only BeO is extremely hard, non volatile, has high melting point and it is amphoteric.
- **Anhydrous magnesium chloride** (MgCl₂) cannot be prepared by heating MgCl₂·6H₂O. since on heating MgCl₂·6H₂O undergoes hydrolysis with the evolution of HCl gas.



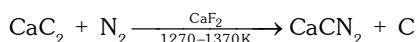
➤ Analytical detection of Mg :

- (i) Charcoal cavity test. On heating on a charcoal cavity with one drop of $\text{Co}(\text{NO}_3)_2$, a pink colour is imparted to the residue $\text{CoO} \cdot \text{MgO}$.
- (ii) The salt solution when mixed with NH_4Cl and NH_4OH and finally treated with soluble phosphates forms a white precipitate of magnesium ammonium phosphate.



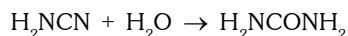
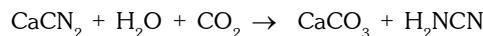
➤ Hydrolith (CaH_2) is calcium hydride.

➤ Calcium cyanamide (CaCN_2) is prepared by heating a mixture of CaC_2 in an atmosphere of N_2 at 1270–1370K with CaF_2 .

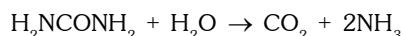


Its trade name is Nitrolim.

➤ Calcium cyanamide (CaCN_2) is a slow acting manure and is preferred to soluble compounds like NaNO_3 or $(\text{NH}_4)_2\text{SO}_4$ since it confers fertility of a permanent nature. It is a nitrogenous fertiliser and undergoes a series of changes giving cyanamide, urea, NH_3 and finally the nitrates which are assimilable by plants.



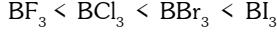
Urea



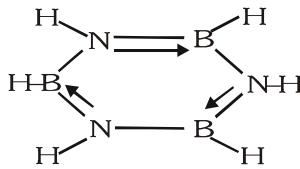
BORON FAMILY

- B_2O_3 and $\text{B}(\text{OH})_3$ are acidic, Al_2O_3 and $\text{Al}(\text{OH})_3$; Ga_2O_3 and $\text{Ga}(\text{OH})_3$ are amphoteric while In_2O_3 and $\text{In}(\text{OH})_3$ are basic. Thus, on moving down the group, there is gradual change from acidic to amphoteric and then to basic character of the oxide and hydroxides of the elements.

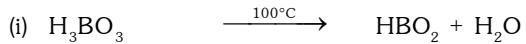
- The relative Lewis acidic strength of trihalides of boron increase in the order.



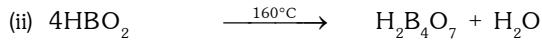
- Borazine or Borazole or inorganic benzene is $\text{B}_3\text{N}_3\text{H}_6$.



- Action of heat on orthoboric acid



Orthoboric acid Metaboric acid



Metaboric acid Tetraboric acid

- Above 160 C, it swells up giving frothy mass and finally forms boron trioxide, B_2O_3 .

- Some important ores of Boron are given as under.

(i) Boric acid, H_3BO_3

(ii) Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

(iii) Colemanite, $\text{Ca}_2\text{B}_4\text{O}_{11} \cdot 5\text{H}_2\text{O}$

- Some important minerals of aluminium are given as under.

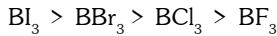
(i) Corundum, Al_2O_3

(ii) Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

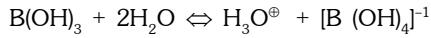
(iii) Cryolite, Na_3AlF_6

(iv) Felspar, KAlSi_3O_8

- Melting and boiling points of halides of boron decrease in the order

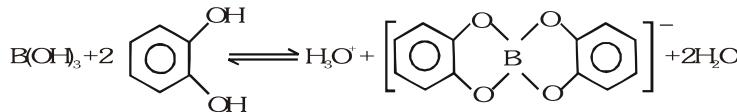


- Boric acid is a weak monobasic acid



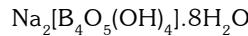
$$\text{pKa} = 9.25$$

- It is difficult to titrate boric acid against NaOH solutions and the end point cannot be located correctly. However, it can be successfully titrated in the presence of polyhydroxy alcohols (e.g. Glycerol, marinital, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.

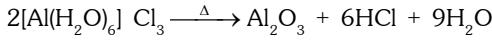


Boron is complex by these compounds. These complex ions cannot interact with H^+ ions as boron atom has already acquired its maximum covalency of four. Consequently, boric acid in presence of polyhydroxy alcohols can be titrated against NaOH to a definite end point.

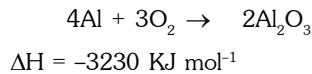
- **Borax**, which is normally written as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, contains tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ comprising BO_4 and BO_3 units. Thus, borax should have been formulated as



- **Aluminium trifluoride** (AlF_3) is different from other trihalides of Al in being insoluble and nonvolatile. In AlF_3 , the coordination number of Al is six, in AlCl_3 the coordination number of Al changes from 6 to 4 as it melts while in AlBr_3 and AlI_3 the coordination number remains four. In AlF_3 each Al is surrounded by a distorted octahedron of 6F atoms and 1 : 3 stoichiometry is achieved by the sharing of corner fluorine atoms between two octahedra.
- **Aluminium chloride** (AlCl_3) in the pure and anhydrous state is a white solid but commercial samples are yellowish due to the impurity of FeCl_3 .
- **Anhydrous AlCl_3** , in the crystalline state possesses a closely packed layer structure with six coordinated aluminium octahedral arrangement.
- **Anhydrous AlCl_3** has a very high affinity for water. On treating AlCl_3 with water the Cl^- ions go outside the coordination sphere to form $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ with enthalpy of solution -330 KJ mol^{-1} . Due to this strong Al – O linkage hydrate cannot be dehydrated on heating to form AlCl_3 .



- **Aluminium chloride**, is a polymeric solid which exists as a dimer Al_2Cl_6 between 200–400 C and then monomer up to 800 C.
- **Thermite welding**, Aluminium has got a very high affinity for oxygen.



It, therefore, displaces metals less electropositive than itself from oxides. The large amount of heat produced is used in welding rails or heavy machinery without removing them from their position. This is called thermite welding or Gold Schmidt's aluminothermic process. In this process, a mixture of Ferric oxide (3 parts) and aluminium powder (1 part) called thermite is used.

- **Pseudo alums** are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.

- (i) $\text{MnSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (ii) $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

They are not isomorphous with true alums.

- **Extraction of Aluminium.** Al is usually extracted from Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. First, bauxite is purified from the impurities (Red bauxite contains Fe_2O_3 as impurity while white bauxite contains silica as impurity). Red bauxite can be purified by Baeyer's process or Hall's process while white bauxite is purified by Serpeck's process.
- **Baeyer's process,** involves the roasting of the ore to convert FeO to Fe_2O_3 and then digested at 423K with conc. NaOH solution for a few hours when Al_2O_3 gets dissolved to give a solution of $[\text{Al}(\text{OH})_4]^{-1}$. The basic oxide impurities such as Fe_2O_3 are not affected.



Aluminate ion

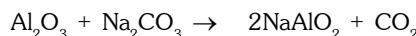
Fe_2O_3 left undissolved is filtered off. The treatment of $\text{Al}(\text{OH})_4^{-1}$ solution with a weak acid precipitate pure $\text{Al}(\text{OH})_3$.



(White ppt.)

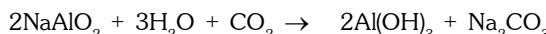
The $\text{Al}(\text{OH})_3$ precipitate is removed by filtration and ignited to get alumina, Al_2O_3 .

- **Hall's process,** Involves the fusion of the ore with Na_2CO_3 when soluble sodium meta aluminate, NaAlO_2 is produced. This is extracted with water when Fe_2O_3 is left as a residue.

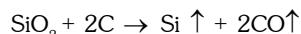


Sodium meta aluminate

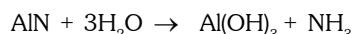
The water extract is heated upto 333K and CO_2 is passed through it. $\text{Al}(\text{OH})_3$ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_3 .



- **Serpeck's process** involves the heating of bauxite with coke in a current of N_2 at 2075K. The SiO_2 present in the ore is reduced to silicon which volatilizes off and alumina gives aluminium nitride. This can be hydrolysed to $\text{Al}(\text{OH})_3$ which on fusion gives alumina.

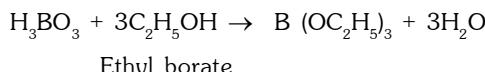


Aluminium nitride

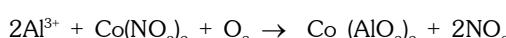


Electrolysis of Al_2O_3 to from aluminium. Pure alumina is dissolved in fused cryolite, Na_3AlF_6 at 1225 K by current of 100 amperes and 6 – 7 volts to get Al. The Al obtained is purified by Hooke's process.

- **Boron nitride (BN),** has a structure similar to that of graphite.
- Green edged flame test for borate (BO_3^{3-}) ion. A mixture of $\text{C}_2\text{H}_5\text{OH}$ and BO_3^{3-} salt with conc. H_2SO_4 burns with green edge flame due to the formation of ethyl borate.



- **Charcoal cavity test for aluminium.** On heating with Na_2CO_3 and a drop of cobalt nitrate solution a blue coloured residue to **cobalt metaaluminate** (Thenard's blue) is obtained.



Blue residue

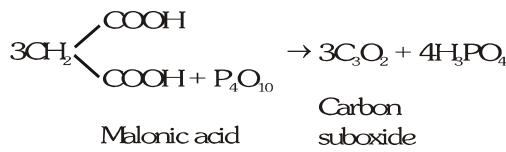
CARBON FAMILY

- **Inert pair effect** the reluctance of ns electrons to take part in bond formation is called inert pair effect. This effect is more pronounced in heavier elements and that too for 13, 14 and 15 group. It results in the decrease in oxidation state by 2 units. For examples, Tl is more stable in oxidation state + 1 than the oxidation state +3.
- Gold dissolves in aqua regia forming $\text{H}[\text{AuCl}_4]$ while Pt dissolves forming $\text{H}_2[\text{PtCl}_6]$.
- CO_2 is a gas while SiO_2 is a solid at room temperature.
- Trimethylamine $(\text{CH}_3)_3\text{N}$ is pyramidal while Trisilylamine $\text{N}(\text{SiH}_3)_3$ is planar due to back bonding.
- SiCl_4 is a Lewis acid but CCl_4 is not because carbon cannot expand its octet due to the absence of vacant d-orbitals.
- White Lead is chemically $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ and Red lead is Pb_3O_4 .
- Silicones are polymeric organosilicon compounds containing Si–O–Si linkage. They have high thermal stability of Si–O–Si chains and are also called high temperature polymers.
- **General formula** : $(\text{R}_2\text{SiO})_n$. Where R = $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_6\text{H}_5$
- **Catenation** is the unique tendency of 14 group elements to form long chains of different sizes and shapes. The tendency to show catenation is directly related to the strength of bond. The bond energies of 14 group elements decrease as under :

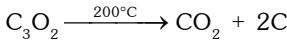
	C–C	Si–Si	Ge–Ge	Sn–Sn	Pb–Pb
<i>Bond energy (KJ mole⁻¹)</i>	348	222	167	155	–

This is the reason why carbon forms many chains, Si, a few and Ge and Sn form practically no chains.

- **Carbon suboxide** (C_3O_2) is an foul smelling gas which can be prepared by the dehydration of malonic acid with P_4O_{10} .



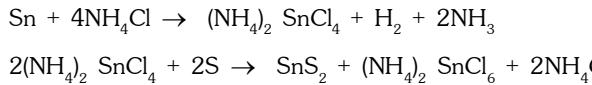
On heating upto 200 C, it decomposes into CO_2 and carbon.



The molecule is thought to have a linear structure.



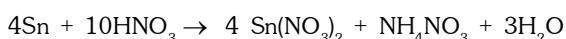
- Silicon polymers or silicones are polymeric organosilicon compounds containing Si – O – Si linkages. Their general formula is $(\text{R}_2\text{SiO})_x$. They may be linear, cyclic or cross linked polymers.
- **Mosaic gold** (SnS_2). Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold. It is prepared by heating mixture of tin filings, sulphur and NH_4Cl in a retort.



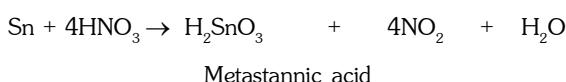
➤ **Tin Cry.** Tin metal when bent produces a cracking noise due to rubbing of metal crystals over one another.

➤ **Action of conc. HNO_3 on tin**

(a) Dilute HNO_3



(b) Hot conc. HNO_3



➤ **Red lead (Pb_3O_4)** is considered to be mixture of lead monoxide and lead dioxide and it is written as $(\text{PbO}_2 \cdot 2\text{PbO})$.

➤ **Lead dioxide (PbO_2)**. It is a brown powder obtained by the treatment of red lead with HNO_3 .



It is used as an active material of the positive plate in storage cells and finds use in match industry as an oxidizing agent.

➤ **The main ores of lead are**

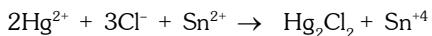
(i) Glena, PbS

(ii) Cerrusite, PbCO_3

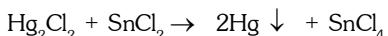
(iii) Anglesite, PbSO_4

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ on heating undergoes to form its basic chloride $\text{Sn}(\text{OH})\text{Cl}$. The anhydrous salt, therefore, be obtained by heating the hydrated salt.

➤ Stannous chloride reduces mercuric chloride (HgCl_2) to a white precipitate of mercurous chloride (Hg_2Cl_2) which finally turns to metallic mercury (dark grey or black).



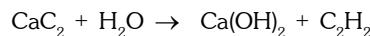
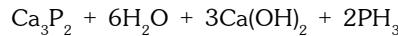
Mercurous chloride



Black

NITROGEN FAMILY

- **Holme's signals.** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2 . The mixture burns with a bright luminous flame and it acts as a signal for approaching ships.



- **The strength and solubilities of oxyacids of 15 group elements are given as under.**

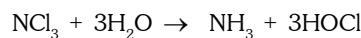
HNO_3	H_3PO_4	H_3AsO_4	H_3SbO_4	H_3BiO_3
Strong (Soluble)	Weak (Soluble)	Weaker (Soluble)	Amphoteric (Insoluble)	Basic (Insoluble)

- Acidity of oxides and the solubility of 15 group oxides decreases from N to Bi. For example, N_2O_3 , N_2O_5 , P_4O_6 , P_4O_{10} , As_4O_6 and As_4O_{10} are acidic and dissolve water forming acids. Sb_4O_6 and Sb_4O_{10} are weakly acidic and insoluble in water. Bi_2O_3 is a basic oxide and is insoluble in water.

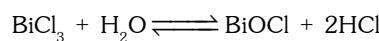
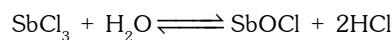
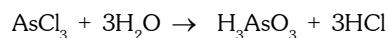
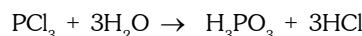
- The oxoacids of phosphorus are given as under :

Formula	Name of acid No.	Oxidation of phosphorus	Comments about acidic nature
H_3PO_2	Hypophosphorus acid	+ 1	Weak, monobasic strong reducing agent.
H_3PO_3	Phosphorus acid reducing agent.	+ 3	Dibasic acid, strong
$\text{H}_4\text{P}_2\text{O}_6$	Hypophosphoric acid	+ 4	Tetrabasic
H_3PO_4	Orthophosphoric acid	+ 5	Tribasic
$\text{H}_4\text{P}_2\text{O}_7$	Pyrophosphoric acid	+ 5	Tetrabasic
HPO_3	Metaphosphoric acid	+ 5	Monobasic

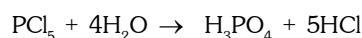
- NCl_3 is hydrolysed with H_2O to NH_3 and HOCl .



- PCl_3 is hydrolysed with water to form phosphorus acid, H_3PO_3 .



- PCl_5 on hydrolysis forms phosphoric acid, H_3PO_4 .

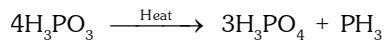


- With Nessler's reagent K_2HgI_4 , ammonium salts give a reddish brown ppt. of Million's base $\text{HgO} \cdot \text{Hg}(\text{NH}_2)_2$

- Phosphorescence is the glowing of white phosphorus in the dark.
- Some main point of difference between white phosphorus and red phosphorus are given as under.

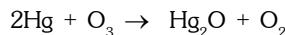
Property	White phosphorus	Red phosphorus
(i) Physical state	Pale yellow soft solid, Can be cut with knife. White when freshly cut.	Red Phosphorus Dark and brittle powder
(ii) Odour	Garlic	Odourless
(iii) Density	1.8 g/cm ³	2.1 g/cm ³
(iv) Solubility	Soluble in CS ₂	Insoluble
(v) Ignition temp.	303K (melts under water at 317K)	533 K (does not melt but sublimes)
(vi) With hot caustic soda	Dissolves and PH ₃ is evolved	No action

- **Smoke screens**, involve the use of calcium phosphide, Ca₃P₂. The PH₃ gas obtained from Ca₃P₂ catches fire to give the needed smoke.
- **Phosphatic slag or Thomas slag or Basic slag** is obtained as a biproduct in the manufacture of steel and is probably a double salt of tricalcium phosphate and calcium silicate.
- On heating, phosphorus acid, H₃PO₃ decomposes into phosphine (PH₃) and phosphoric acid (H₃PO₄).



OXYGEN FAMILY

- Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.



As a result of it, mercury loses its meniscus and starts sticking to the glass.

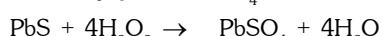
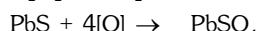
- The bleaching action of ozone and H_2O_2 is permanent and is due to oxidation while that of SO_2 is temporary and is due to reduction.

- Temporary hardness of water is due to the presence of bicarbonates of Ca and Mg and Permanent hardness is due to the presence of sulphates and chlorides of Ca and Mg.

- Calgon is a trade name given to sodium polymetaphosphate $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$. It is generally employed for softening of hard water.

- $10\text{V H}_2\text{O}_2$ means that one mole of that H_2O_2 at N.T.P. evolves 10ml. of oxygen gas.

- H_2O_2 is used to restore the colour of old lead paintings which have been blackened due to the formation of PbS by the action of H_2S present in the air.

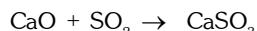


Black White

- Antichlor action of H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl .

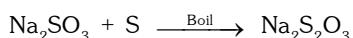


- SO_2 gas is dried by bubbling the mixture through conc. H_2SO_4 . It is not dried over quick lime (CaO) as it reacts with it to form calcium sulphite.

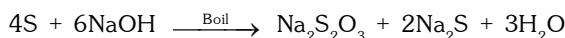


- **Sodium thiosulphate** $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is prepared by the following methods :

- (a) By boiling sodium sulphite with sulphur.



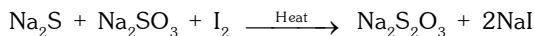
- (b) By boiling sulphur with NaOH



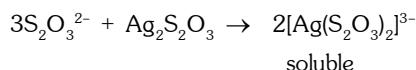
- (c) By passing SO_2 into Na_2S solution.



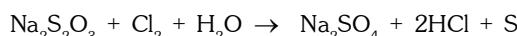
- (d) By spring's reaction



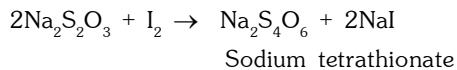
- **Concentrated $\text{Na}_2\text{S}_2\text{O}_3$** does not give a white ppt. with AgNO_3 . This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.



- **Sodium thiosulphate** is oxidized by Cl_2 to sodium sulphate.

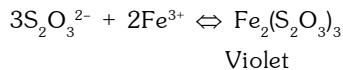


- **Sodium thiosulphate** is oxidized to sodium tetrathionate $\text{Na}_2\text{S}_4\text{O}_6$ by I_2

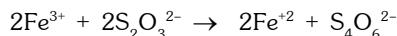


This reaction forms the basis of iodometric estimation of $\text{Cr}_2\text{O}_7^{2-}$ and Cu^{2+} salts.

- **Sodium thiosulphate** reacts with FeCl_3 solution to form a violet coloured solution of ferric thiosulphate.



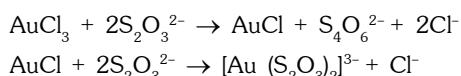
The violet colour disappears quickly due to the reduction of ferric chloride by $\text{S}_2\text{O}_3^{2-}$ ions,



- **Sodium thiosulphate** reduces cupric salts to cuprous salts.



- Sodium thiosulphate reduces auric salts to aurous salt.



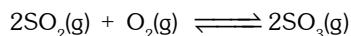
- **Neutral oxides** are those which are neutral towards litmus e.g., carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O) and nitric oxide (NO).

- Ozone is heavier than air and is slightly soluble in water but is more soluble in turpentine oil, glacial acetic acid and CCl_4 .

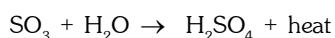
- H_2S gas is dried by passing over CaCl_2 or P_2O_5 .

- **Sulphur trioxides** (SO_3) is a white crystalline solid with melting point 290K and boiling point 318K.

- SO_3 is prepared by the direct oxidation of SO_2 with atmospheric oxygen in presence of finally divided Pt or V_2O_5 at a pressure of 2atm. and temperature 700K.

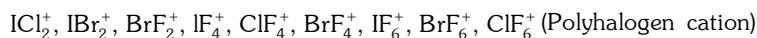
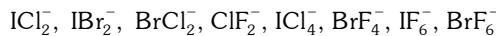


- SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.



HALOGEN FAMILY

- Some of the example of polyhalides are :



- Pseudo halides are uninegative groups which show certain characteristics of halide ions. For example Cyanide (CN^-), Cyanate (OCN^-), Thiocyanate (SCN^-), Selencyanate (SeCN^-), Azide (N_3^-), Aziothio carbonate (SCSN_3^-) and isocyanate (ONC^-).

- The electron affinity values (in KJ mol⁻¹) for 17 group element are given below :

F	Cl	Br	I
333	349	325	296

- The bond energies (in KJ mol⁻¹) for halogens are :

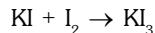
F ₂	Cl ₂	Br ₂	I ₂
158.8	242.6	192.8	151.1

- AgF is soluble in water while AgCl, AgBr and AgI are insoluble.

Test for chlorine :

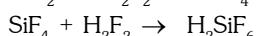
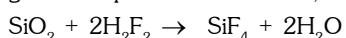
- It is a greenish yellow gas with irritating smell.
- It turns starch iodide paper blue.
- It bleaches litmus paper and indigo solution.

- Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI_3 .



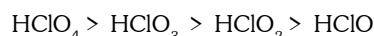
The solution behaves as a simple mixture of KI and I_2 .

- **Action of silica and glass.** Strong solution of HF attacks glass readily forming silicon fluoride which gives complex fluosilicic acid, H_2SiF_6 with excess HF.



This is called etching of glass.

- The acidic strength of the oxoacids of halogen decreases in the following order.



The chlorine oxyanion in which the central atoms has highest oxidation number will have maximum number of oxygen atoms for participation in the extension of the π -bond. Thereby the charge on the ion is delocalized which greatly stabilizes the ion and thus decreases its tendency to accept a proton i.e., causes the ion to be very weak base with the result that the strength of the acid increases.

- The acidity of oxoacids of different halogens having the same oxidation number decreases with the increases in atomic numbers of the halogen


SOME REAGENTS OR MIXTURES

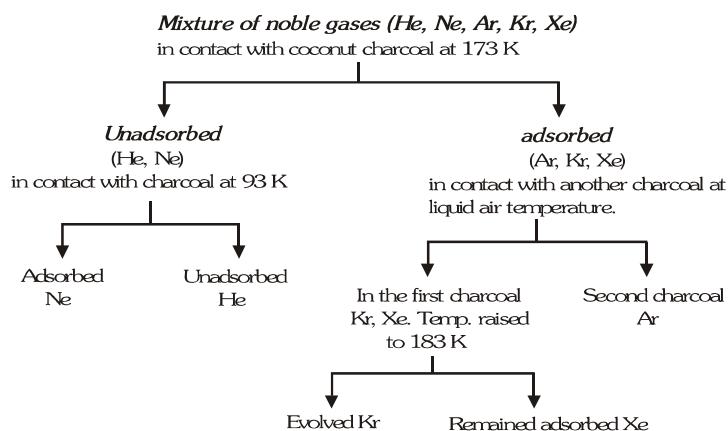
- **Lithophone** : A mixture of $\text{ZnS} + \text{BaSO}_4$ used as white paint.
- **Nitrolgium** : Calcium cyanamide + graphite used as fertilizer.

NOBEL GAS

- The most important source of noble gases is atmosphere in which they are present in following proportions by volume and mass:

<i>Element</i>	<i>Percentage by volume</i>	<i>Percentage by mass</i>
He	0.0006	0.000037
Ne	0.0015	0.001
Ar	0.932	1.285
Kr	0.0001	0.00028
Xe	0.00001	0.00004

- Helium is present to the extent of 2% in natural gas found in the united states and Canada.
- Helium is also present in the minerals of radioactive elements uranium and thorium *Ex.* clevite, uranite, thorianite, monazite, pitchblende etc.
- The sixth member of the zero group was discovered in 1900 by Dorn as one of the disintegration products of radium and was named radon or nitron.
- In Dewar's method, the separation of noble gases are summarized below

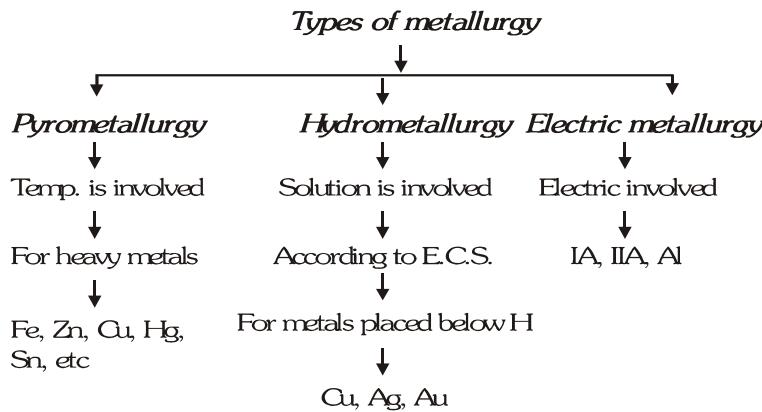


- The viscosity of He is extremely low, about $1/100^{\text{th}}$ of hydrogen gas.

METALLURGY

➤ Bunch of process to extract metal from their respective ore

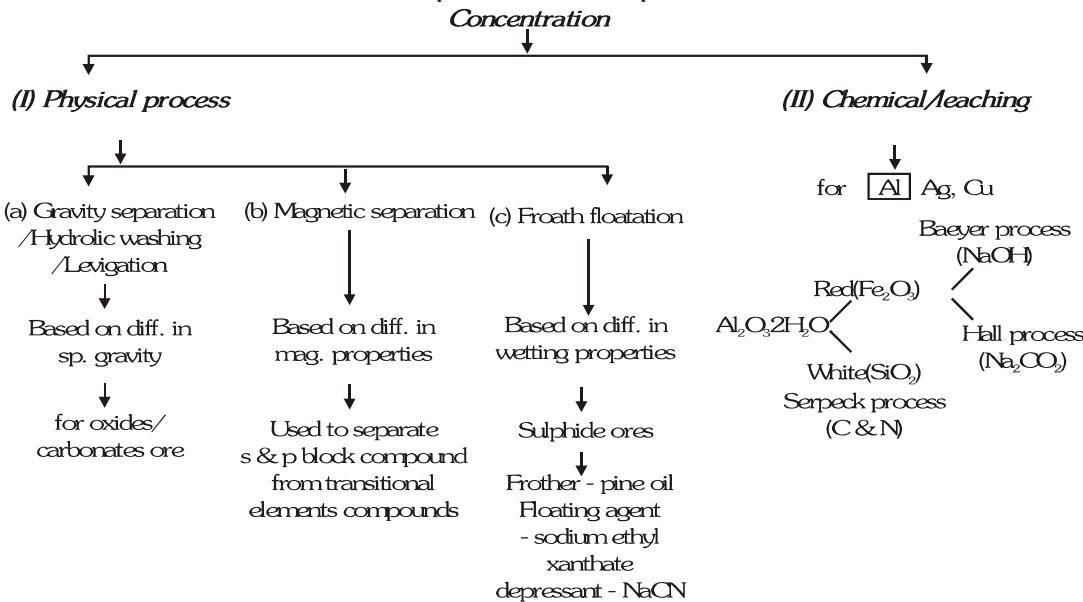
Ore : Minerals from which metal can be extracted economically :



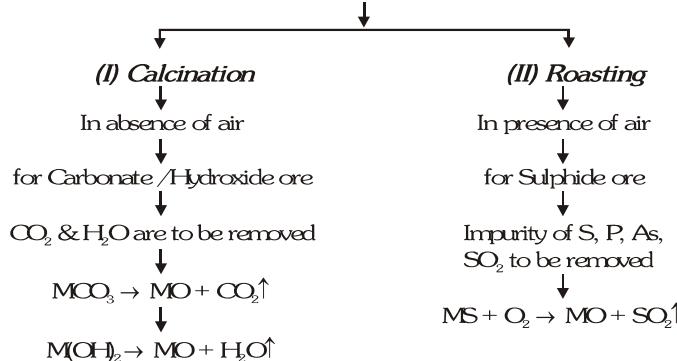
Metallurgical process :

1. **Mining** : Ore obtain in big lumps (less reactive)
2. **Crushing/grinding/pulverization** : big lumps convert into powder (more reactive)
3. **Concentration** : To remove matrix/gangue from ore

To increase the concentration of ore particle in ore sample.



Ag, Au, are concentrated by cyanide process.

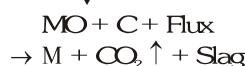
(4) Calcination & Roasting

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5. **Reduction** : To obtain metal (95 to 98%) from metal oxide.

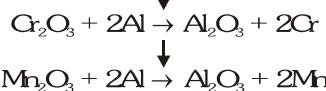
(I) Chemical reduction

(a) by C (smelting)



(b) by Al

(Thermite process)



Flux - substance to convert non-fusible impurities to fusible one.

Flux

Acidic flux

Removes basic impurities
Non-metallic oxide (SiO_2)

Basic flux

Removes acidic impurities
Metallic oxide (CaO)

Imp. point – At high temp. C is reducing agent.

– At low temp. CO is reducing agent.

(II) Self reduction

For Cu, Pb

For sulphide ore only

(III) Metal displacement reduction

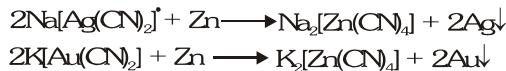
Metal placed below H in E.C.S.

Ag, Au, Cu

(i) Cyano complex



(ii) Reduction to free metal



(IV) Electrolytic reduction

For IA, IIA, Al

Electrolysis of molten sol.

(i) Extraction of Al (Hall-Herault)

– Al can be extracted from Al_2O_3

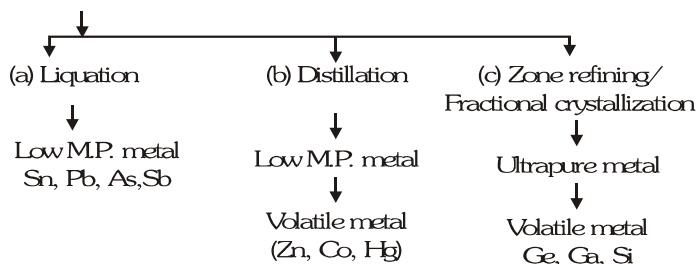
– To decrease fusion temp. of Al_2O_3 , Na_3AlF_6 & CaF_2 is to be added

– Na_3AlF_6 & CaF_2 (Neutral flux) increase the conductivity & reduce the fusion temp.

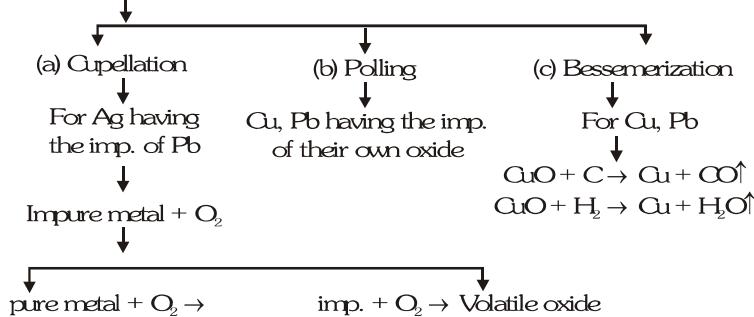
- (ii) Extraction of Na (Down cell process)
- Na can be extracted from NaCl
 - Neutral flux (CaCl_2) to be added to decrease the fusion temp. of NaCl
 - Neutral flux - substance used to increase the conductivity of NaCl
 - decrease the fusion temp. of ionic compounds of (IA, IIA, Al) which is more than the melting point of metal.

Refining : To obtain metal (99.98%)

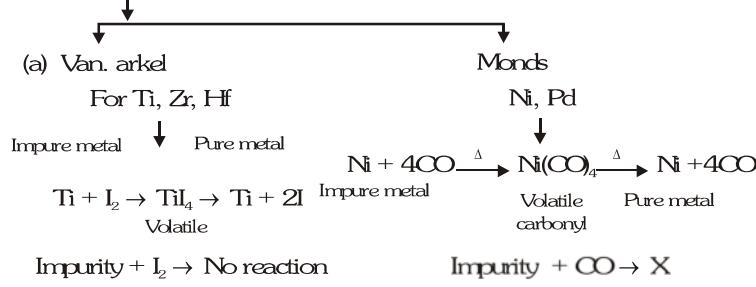
(I) Physical Process



(II) Chemical Process



(III) Thermal decomposition



(IV) Electrolytic refining

Anode - made up of impure metal

Cathode - pure metal deposited

Impurity deposited below anode as anode mud

Thermodynamics principle of metallurgy

- The graphical representation of Gibbs energy was first used by H.I.T. Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram such diagrams help us in predicting the feasibility of thermal reduction of an ore.
- The criterion of feasibility is that at a given temperature, Gibbs energy of reaction must be negative.
- At high temperature 'C' is the best reducing agent.
- At low temperature 'CO' is the best reducing agent.
- In blast furnace reduction takes place at low temperature i.e. why CO is the reducing agent.

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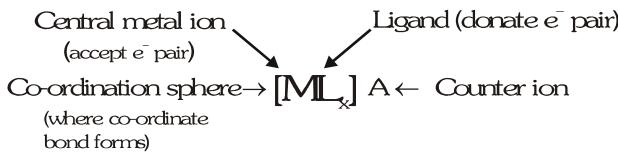
A summary of the occurrence and Extraction of some Metals is presented in the following table :

Metal	Occurrence	Common method of extraction	Refining	Remarks
Aluminium E = -1.66	1. Bauxite, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten $\text{Na}_3\text{AlF}_6 + \text{CaF}_2$	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required
Iron E = -0.44	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 3. Limonite, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ 4. Siderite, FeCO_3	Reduction of the oxide with CO and coke in Blast furnace	Bessemerization (impurites has more affinity for O_2 as compare to Fe)	Temperature approaching 2170K is required
Copper E = -0.34	1. Copper pyrites, CuFeS_2 2. Copper glance, Cu_2S 3. Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ 4. Cuprite, Cu_2O 5. Azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Roasting of sulphide partially and reduction	(i) Polling (ii) Electrolytic method.	It is self reduction in a specially designed converted. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc E = -0.76	1. Zinc blende or Sphalerite, ZnS 2. Calamine, ZnCO_3 3. Zincite, ZnO	Roasting of sulphide ore or calcination of ZnCO_3 followed by reduction with coke	The metal may be purified by fractional distillation	For ZnO , carbon is better reducing agent than Cu and Zn is obtain in vapours form $\text{ZnO} + \text{C} \xrightarrow{1673\text{K}} \text{Zn} + \text{CO}$
Mg E = -2.36	1. Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 2. Magnesite, MgCO_3	Electrolysis of fused MgCl_2 with KCl	-	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is heated in the excess current of dry HCl gas to produce anhydrous MgCl_2
Sn E = -0.14	1. Cassiterite, SnO_2 (Tin stone)	Reduction of the SnO_2 with carbon. $\text{SnO}_2 + 2\text{C} \rightarrow \text{Sn} + 2\text{CO}$	Polling and Liquidation	Ore contain impurity of wolframite, $\text{FeWO}_4 + \text{MnWO}_4$ (magnetic substance)
Pb E = -0.13	1. Galena, PbS	Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon $\text{PbS} + 2\text{PbO} \rightarrow 3\text{Pb} + \text{SO}_2$ $\text{PbO} + \text{C} \rightarrow \text{Pb} + \text{CO}$	Liquidation & electrolytic method.	-
Ag E = 0.80	1. Argentite- Ag_2S , native Silver	Hydro metallurgy $\text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{NaAg}(\text{CN})_2 + \text{N}_2\text{S}$ $2\text{NaAg}(\text{CN})_2 + \text{Zn} \rightarrow \text{Na}_2\text{Zn}(\text{CN})_4 + 2\text{Ag}$	Cuplation & electrolytic method	In hydro metallurgy Ag obtain in the form of dark amorphous ppt.
Au E = 1.40	Native ore	1. Amalgamation. 2.Cynide process	Cuplation & electrolysis method.	In hydro metallurgy Au obtain in the form of dark amorphous ppt.

COORDINATION CHEMISTRY

- Addition compound Double salt → completely furnish into their constituents ions
 Complex compound → Do not furnish completely

Representation of complex compound



- Co-ordination number (property of metal = no. of e^- pair accept by metal ion).
- Denticity (property of ligand) = no. of e^- pair donate by ligand
- Polydentate ligand forms rings with central metal ion, ring is known as chelate ring & ligand are called chelating ligand.
- Ligand which have two donor sites (atoms) but at a time only one site (atom) donates are known as ambidentate ligand. They are



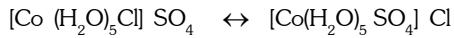
Ex. CN^- can coordinate through either the nitrogen or the carbon atom to a central metal ion.

- Ligands which have two or more than two donor sites but sometimes in complex formation they do not use all donor sites this type of ligands are called flexidentate ligand.

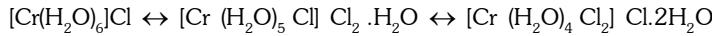
Ex. SO_4^{2-} , CO_3^{2-} .

- **Structural isomerism :**

- (i) **Ionisation isomerism :** Counter ion as a ligand & ligand act as counter ion.



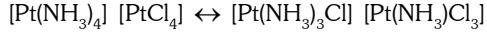
- (ii) **Hydrate isomersim :** Number of water molecule inside & outside the co-ordinate sphere are different.



- (iv) **Linkage :** when ambidentate ligand is present in co-ordination sphere.



- (iv) **Co-ordination isomerism :** In cationic anionic complex when ligand/metal ion interchange



- **Stereo isomerism :**

- (i) **Geometrical isomerism :**

C.N. = 4

- Tetrahedral does not show

- Square planar $M_{a_2b_2}$, M_{a_2bc} , M_{abcd} , $M_{(AB)_2}$, $M_{(AB)_2ab}$. Show geometrical isomerism.

C.N. = 6

- M_{abcdef} have 15 geometrical isomerism.
- Ma_3b_3 have 2 geometrical isomerism [fac-Mer]
- (ii) **Optical isomerism :** (does not have plane of symmetry)

C.N. = 4

- (i) Tetrahedral M_{abcd} is optically active
- (ii) Generally square planar is not optically active but in some case depend on ligand.

C.N. = 6

- (i) M_{abcdef} optically active.
- (ii) $M_{(AA)_2b_2}$ cis is optically active but trans does not.
- (iii) $M_{(AA)_3}$ optically active.

Theories of co-ordination compound :(i) **Werner theory -**

- (a) Oxidation state of central metal ion is called primary valency satisfies by anions, represent by dotted line.
- (b) Co-ordination number of central metal ion is called secondary valency satisfies by neutral molecule or anions, represent by solid line.

(ii) **Sidwik EAN Rule :**

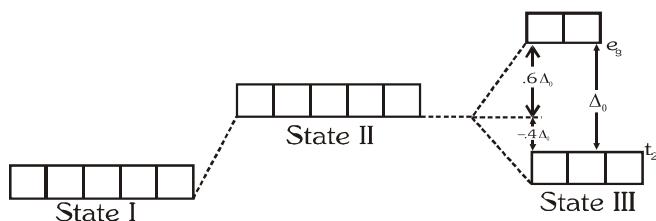
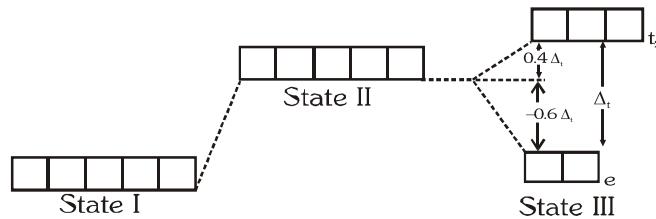
EAN = atomic number (Z) of the metal - oxidation state of metal ion + number of electrons gained from the donor atoms of the ligands.

(iii) **Valence bond theory :**

- (i) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- (ii) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **Outer orbital complexes** respectively.
- (iii) If inner 'd' orbitals are involved in hybridisation, then it is through only the pairing of unpaired electrons in the 'd' orbitals of metal ion.
- (iv) Then such type of complexes will be **diamagnetic** or **less paramagnetic** and will be called as **Low spin complexes**.
- (v) All outer orbital complexes have **paramagnetic** nature and they are called as **High spin complexes**.

(iv) **Crystal Field Theory :**

In the electric field of these negative charges, the five d orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

In octahedral**In tetrahedral**

Orbitals which have same energy in a subshell are known as degenerate orbitals.

➤ ***Crystal field stabilisation energy (CFSE):***

(i) For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{e_g})]\Delta_0$ + Paring energy (P.E.)

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{e_g} = number of electron in e_g orbitals

(ii) For tetrahedral CFSE = $[-0.6(n_e) + 0.4(n_{t_2})]\Delta_t$ + Paring energy (P.E.)

where n_{t_g} = number of electron in t_g orbitals

n_e = number of electron in e orbitals

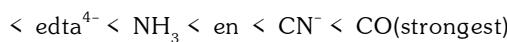
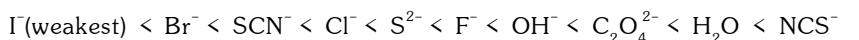
➤ ***Factor affecting splitting***

- (i) Strength of ligand
- (ii) Oxidation state of central metal ion
- (iii) Transition series (d-series)
- (iv) Geometry (number of ligands).

➤ ***Strength of ligand depends upon :***

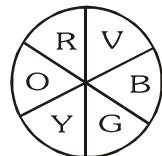
- (i) good σ donor (ii) good π acceptor (iii) high negative charge (iv) Small in size

➤ ***Series which shows the relative strength of ligands***



➤ ***Paramagnetism*** $\mu = \sqrt{n(n+2)} B.M.$

➤ ***Complementary colour relationship :***



For example complementary colour of red is green.

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d-BLOCK

- The f-block elements differ from those of d-blocks elements in that they have unstable electroconfiguration in the outer shells in comparison to that of d-blocks element.

d-block elements electronic configuration

$$(n-1)d^{1-10} \cdot ns^{1-2}$$

Most common oxidation state +2

- The colour in d-block elements is due to d-excitation while in f-block element, it is due to f-f transitions.
 - They show variable oxidation state due to less energy difference between ns and (n-1) d sub shell.
 - Most of the d-block compounds act as catalyst due to their variable oxidation state or complex formation tendency or adsorption on their surface. Example :

contact process = V_2O_5

Ostwald process = Pt/Rh

$$\text{Haber process} = \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}$$

Zeigter Natta = $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$

Phenton reagent = $\text{FeSO}_4 + \text{H}_2\text{O}_2$

Hydrogenation of Alkene = Ni/Pd

Decomposition of KClO_3 = MnO_2

Wilkinson catalyst = RhCl + PPh₃

- ## ➤ Action of heat on copper sulphate



Bluish green

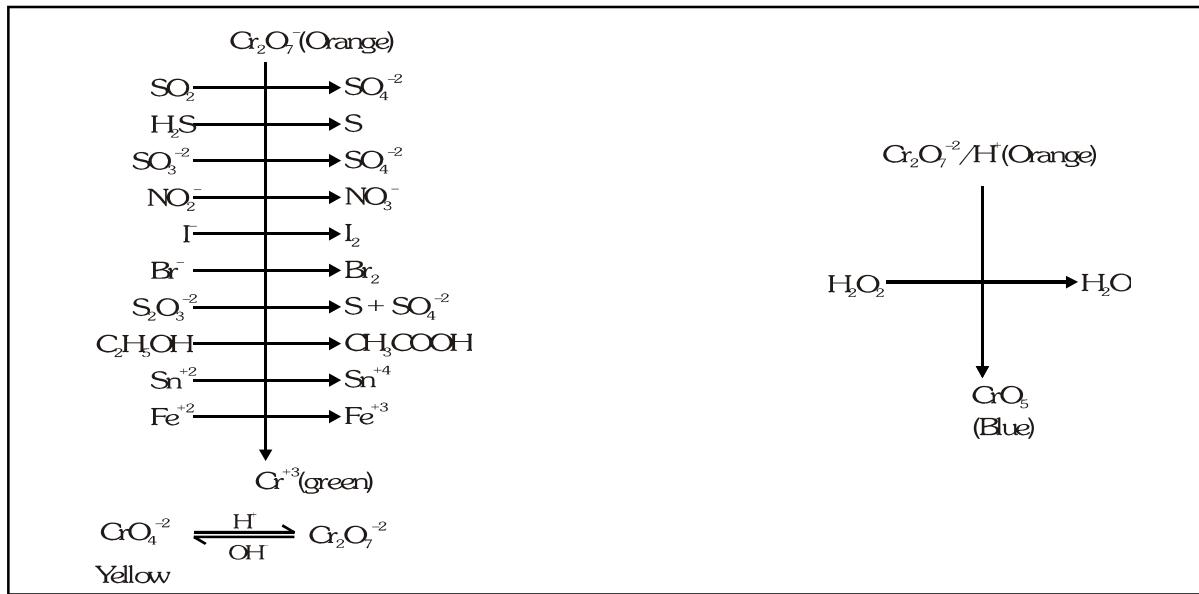
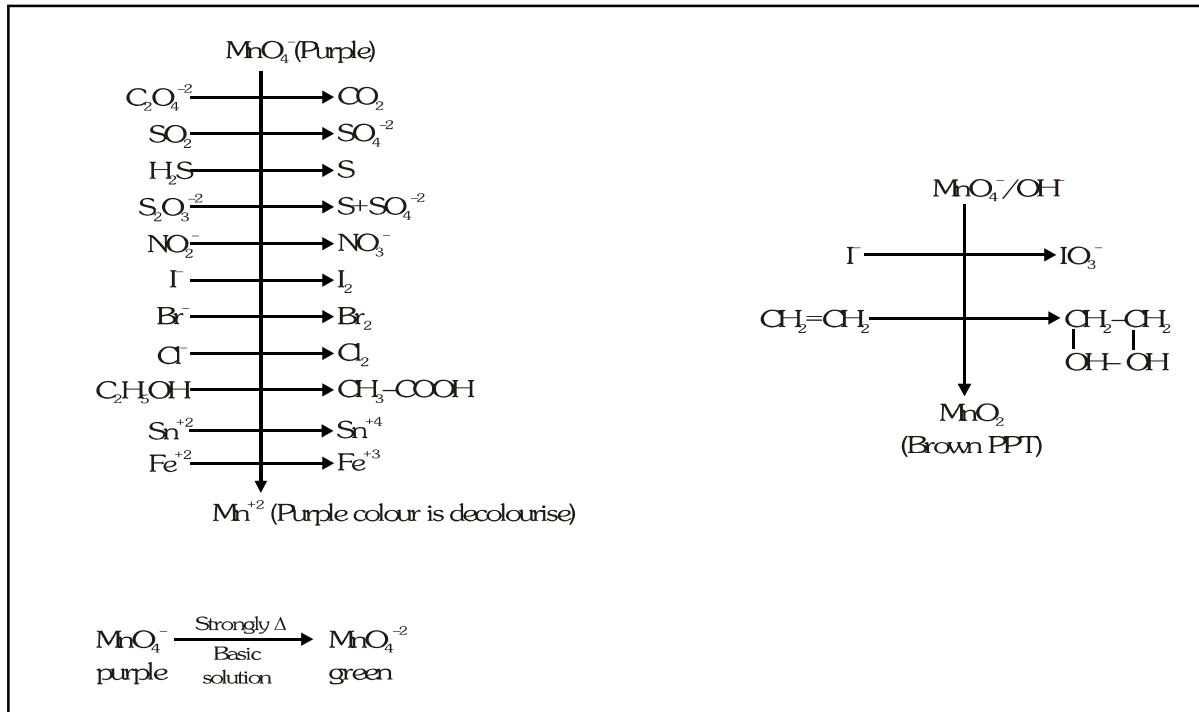
White

- ***Chemical volcano.*** When crystals of red coloured ammonium dichromate are heated, a violent action takes place accompanied by flashes of light and nitrogen is liberated leaving behind a dark green residue of chromium sesquioxide (Cr_2O_3)



Ammonium dichromate

Chromium sesquioxide

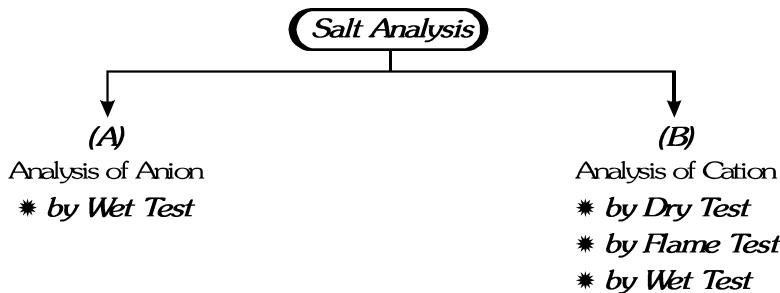
➤ Reactions of $\text{Cr}_2\text{O}_7^{2-}$:➤ Reaction of MnO_4^- 

SALT ANALYSIS

Definition :

The branch of chemical analysis which aims to find out the constituents of a mixture of compound is known as Qualitative Analysis.

The identification of a substances usually involves its conversion into a new substance possessing characteristic properties with the help of one or more substance of known composition. The substance which is used to bring about such change is called a Reagent.



GROUP 'A' RADICALS : (*Decomposition by dil.HCl/dil.H₂SO₄*)

(1) RADICALS DETECTED WITH DILUTE HCl/DILUTE H₂SO₄

(I) CARBONATE (CO₃²⁻)

All carbonates except those of alkali metals and ammonium are insoluble in H₂O.

(i) Dilute HCl

With dilute HCl, it decomposes with effervescences due to the evolution of carbon dioxide.



The gas produces white turbidity with lime water, Ca(OH)₂ or baryta water, Ba(OH)₂.



White turbidity

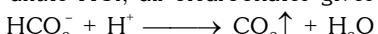


Soluble

(II) BICARBONATE (HCO₃⁻)

Dilute HCl

With dilute HCl, all bicarbonates gives effervescences due to the evolution of CO₂.



The gas gives white turbidity with lime water or baryta water.



White turbidity

(III) SULPHIDE (S²⁻)

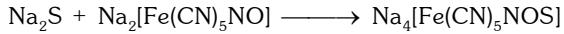
(i) Dilute HCl or Dilute H₂SO₄



Yellow ppt

(ii) Sodium Nitroprusside Solution

With sodium nitroprusside solution, ionic sulphide gives a purple colour in alkaline medium.



Purple colour

No reaction occurs with solutions of hydrogen sulphide or free gas. If however, filter paper moistened with a solution of the reagent is made alkaline with sodium hydroxide or ammonia solution, a purple colouration is produced with free hydrogen sulphide also.

(IV) SULPHITE (SO_3^{2-})

Only the sulphites of alkali metals and ammonium are soluble in water.

Dilute HCl or Dilute H_2SO_4

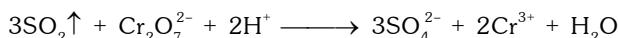
Dilute HCl or H_2SO_4 decomposes sulphites with the evolution of sulphur dioxide.



The gas can be identified

(a) By suffocating odour of burning sulphur.

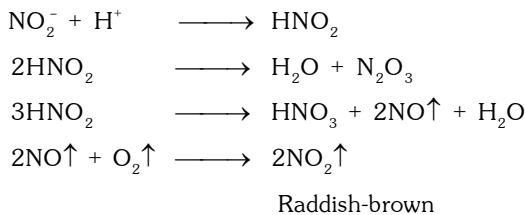
(b) By green colour formation, when passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution.



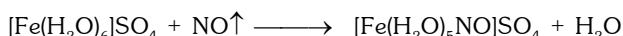
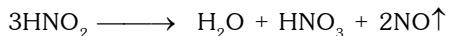
Green colour

(V) NITRITE (NO_2^-)

All other nitrites except AgNO_2 (sparingly soluble) are soluble in H_2O .

(i) Dilute HCl**(ii) Brown ring test**

When the nitrite solution is added carefully to a concentrated solution of iron (II) sulphate acidified with dilute acetic or dilute sulphuric acid, a brown ring appears due to the formation of $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ at the junction of the two liquids. If the addition has not been made slowly and cautiously, a brown colouration results.



Brown ring

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(2) RADICALS DETECTED WITH CONCENTRATED H_2SO_4

(I) CHLORIDE (Cl^-)

(i) Concentrated H_2SO_4

With concentrated H_2SO_4 , chlorides gives vapours of HCl.



Vapour evolved

- (a) Turns blue litmus paper red
- (b) Gives white fumes of NH_4Cl when a glass rod moistened with aqueous ammonia solution is brought close to the mouth of test tube.

(ii) Chromyl Chloride Test

When a mixture containing chloride ion is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4 , deep orange-red fumes of chromyl chloride (CrO_2Cl_2) are formed.



Orange-red
fumes

When chromyl chloride vapours are passed into sodium hydroxide solution, a yellow solution of sodium chromate is formed, which when treated with lead acetate gives yellow precipitate of lead chromate.



Yellow solution



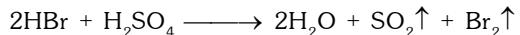
Yellow ppt

This test is given by ionic chlorides only. Chlorides of Hg^{2+} , Hg_2^{2+} , Pb^{2+} , Ag^+ , Sn^{4+} and Sb^{3+} do not respond to chromyl chloride test due to their covalent character, which allows them to ionise only slightly.

(II) BROMIDE (Br^-)

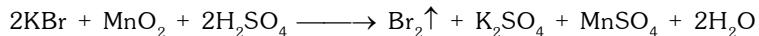
(i) Concentrated H_2SO_4

If concentrated sulphuric acid is poured in a bromide solution, first a reddish-brown solution is formed, later reddish-brown vapours of bromine accompany the hydrogen bromide.



Reddish-brown

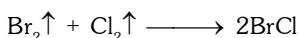
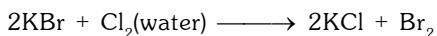
(ii) Manganese dioxide and Concentrated Sulphuric Acid



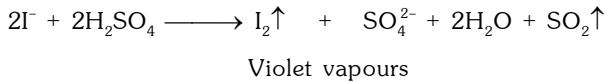
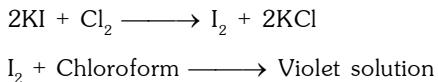
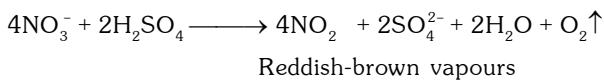
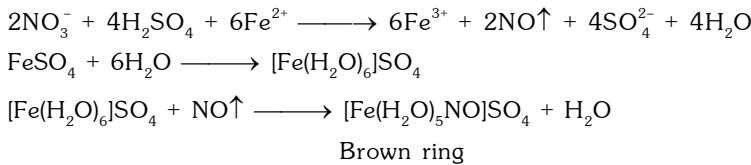
Reddish-brown

(iii) Chlorine Water

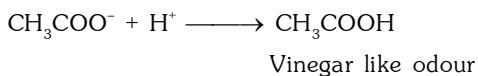
When chlorine water is added to a solution of bromide, free bromine is liberated which colours the solution orange-red. If CS_2 , $CHCl_3$ or CCl_4 is added to the solution and the liquid shaken, the bromine dissolves in the organic solvent and after allowing to stand forms a reddish-brown solution below the colourless aqueous layer.



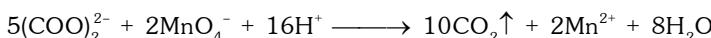
Pale yellow solution

(III) IODIDE (I)**(i) Concentrated H_2SO_4** **(ii) Chlorine Water****(IV) NITRATE (NO_3^-)****(i) Concentrated H_2SO_4** **(ii) Brown Ring Test****(V) ACETATE (CH_3COO^-)****Dilute Sulphuric Acid**

On adding a small quantity of dilute H_2SO_4 to the acetate salt, acetic acid is produced, which can be easily recognized by its vinegar-like odour

**(VI) OXALATE ($C_2O_4^{2-}$)****Potassium Permanganate Solution**

Potassium permanganate solution gets decolourized when warmed in acid solution with an oxalate salt to 60 C. Many other organic compounds also effect the bleaching of permanganate but if the evolved carbon dioxide is tested by the lime water reaction, the test becomes specific for oxalates.

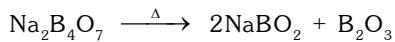
**GROUP 'B' RADICALS****SULPHATE (SO_4^{2-})**

Sulphates of barium, strontium and lead are practically insoluble in water, those of calcium and mercury(II) are slightly soluble and most of the remaining metallic sulphates are soluble.

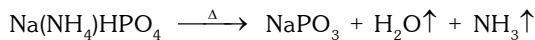
Barium Chloride Solution

On adding $BaCl_2$ solution to a sulphate salt solution, a white precipitate of barium sulphate ($BaSO_4$) insoluble in warm dilute hydrochloric acid and in dilute nitric acid but moderately soluble in boiling concentrated hydrochloric acid is formed.



ANALYSIS OF CATIONS**(1) Dry Tests****Borax Bead Test :**

Copper (II) metaborate

Microcosmic Salt Bead Test

transparent bead



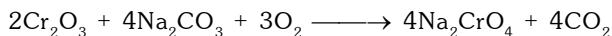
(blue bead)

Sodium Carbonate Bead Test

The sodium carbonate bead is prepared by fusing a small quantity of sodium carbonate on a platinum wire loop in the Bunsen flame; a white, opaque bead is produced. If this is moistened, dipped into a little KNO_3 and then into a small quantity of a manganese salt (for example) and the whole heated in the oxidising flame, a green bead of sodium manganate (Na_2MnO_4) is formed.



A yellow bead is obtained with chromium salt due to formation of sodium chromate (Na_2CrO_4)

**(2) Flame Tests**

Paste of the salt and con. HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed; salts, particularly of group V(Ba^{2+} , Ca^{2+} , Sr^{2+}), are identified by colours of the flame and summarised in table.

<i>Colour</i>	<i>Cation</i>
Golden yellow	Na^+
Violet (Lilac)	K^+
Carmine-red	Li^+
Brick-red	Ca^{2+}
Apple-green	Ba^{2+} , Mo^{2+}
Green	Cu^{2+} , (BO_3^{3-}) , Tl^{3+}
Crimson-red	Sr^{2+}

(3) Qualitative Analysis of Cation mixtures :

Group	Group Reagent	Cations	ppt/colour							
I	Dil. HCl	Ag ⁺ , Hg ₂ ²⁺ , Pb ²⁺	AgCl Hg ₂ Cl ₂ White PbCl ₂							
II	IIA dil. HCl/H ₂ S	Pb ²⁺ , Cu ²⁺ , Bi ³⁺ , Hg ²⁺ , Cd ²⁺	PbS ↓ Black	CuS, ↓ Black	Bi ₂ S ₃ , ↓ Brown	HgS, ↓ Black	CdS ↓ Yellow			
	IIIB dil. HCl/H ₂ S	As ³⁺ , As ⁵⁺ , Sb ³⁺ , Sb ⁵⁺ , Sn ²⁺ , Sn ⁴⁺	As ₂ S ₃ ↓ Yellow	As ₂ S ₅ ↓ Yellow	Sb ₂ S ₃ ↓ Orange	Sb ₂ S ₅ ↓ Orange	SnS ↓ Brown	SnS ₂ ↓ Yellow		
III	NH ₄ Cl/NH ₄ OH	Al ³⁺ , Cr ³⁺ , Fe ³⁺	Al(OH) ₃ ↓ White	Cr(OH) ₃ ↓ Green	Fe(OH) ₃ ↓ Brown					
IV	NH ₄ Cl/NH ₄ OH/ H ₂ S	Ni ²⁺ , Co ²⁺ , Mn ²⁺ , Zn ²⁺	NiS ↓ Black	CoS ↓ Black	MnS ↓ Pink/Buff/Skin	ZnS ↓ Dirty white				
V	NH ₄ Cl/NH ₄ OH/ (NH ₄) ₂ CO ₃	Ba ²⁺ , Sr ²⁺ , Ca ²⁺	BaCO ₃ ↓ White	SrCO ₃ ↓ White	CaCO ₃ ↓ White					
VI	No common group reagent	Na ⁺ , Mg ²⁺ , K ⁺	No common ppt							
Zero	No common group reagent	NH_4^+	No common ppt (Generally identify by Nessler's reagent)							

PREPARATION OF ORIGINAL SOLUTION

Transparent, aqueous solution of salt is known as original solution and it is prepared by dissolving salt/mixture in suitable solvent. To prepare original solution, following solvents are used strictly in the order given below:

- | | |
|------------------|----------------|
| (i) Cold Water | (ii) Hot water |
| (iii) Dilute HCl | (iv) Conc. HCl |

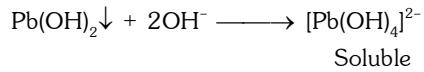
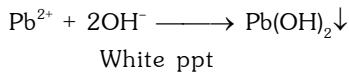
(A) Group I (Pb²⁺, Ag⁺, Hg₂²⁺) RADICALS :

On adding dilute HCl to the salt solution if white precipitate is obtained, it indicates the presence of Pb²⁺, Ag⁺ or Hg₂²⁺ ion in the solution.

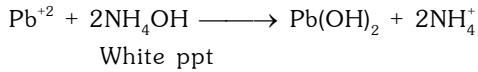
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1 LEAD (II)

(i) Sodium Hydroxide Solution

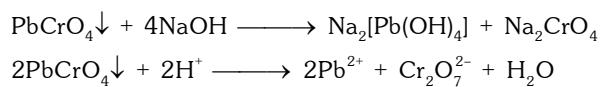
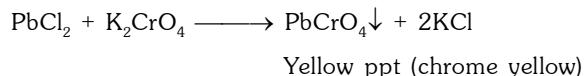


(ii) Ammonia Solution



(iii) Potassium Chromate Solution

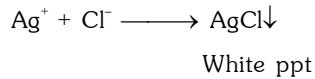
PbCl_2 is soluble in hot water and gives a yellow precipitate with K_2CrO_4 . The precipitate obtained is insoluble in acetic acid but soluble in NaOH and nitric acid.



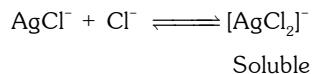
2. SILVER (I)

(i) Dilute Hydrochloric Acid

With dilute hydrochloric acid (or soluble chlorides), a white precipitate of silver chloride is formed.



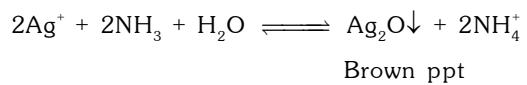
With concentrated hydrochloric acid precipitation does not occur. After decanting the liquid from over the precipitate. It can be dissolved in concentrated hydrochloric acid, when a dichloroargentate(I) complex is formed.



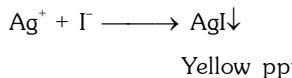
On dilution with water, the equilibrium shifts back to the left and the precipitate reappears. Dilute ammonia solution dissolves the precipitate to form the diamineargentate(I) complex ion.

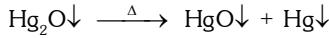
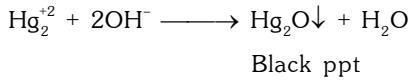
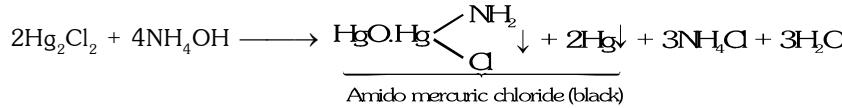
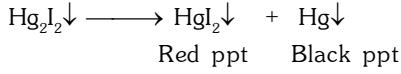
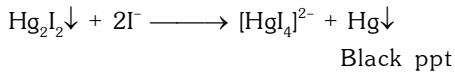
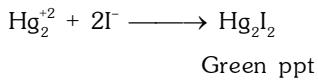
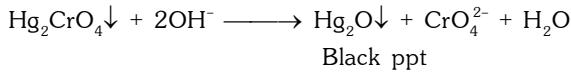


(ii) Ammonia solution



(iii) Potassium Iodide Solution

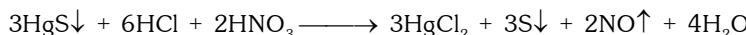
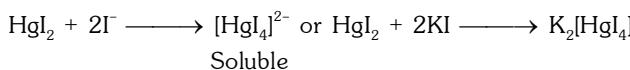
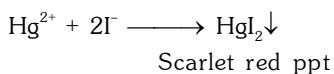
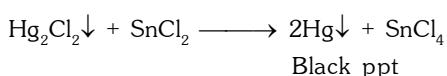
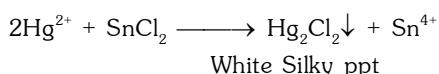
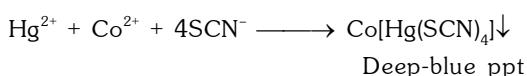


3. MERCURY (I)**(i) Sodium Hydroxide Solution****(ii) Ammonia Solution****(iii) Potassium Iodide Solution****(iv) Potassium Chromate Solution****(B) Group II A (Pb^{2+} , Hg^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+}) RADICALS :**

The precipitates of group IIA are insoluble in yellow ammonium sulphide.

1. MERCURY (II)

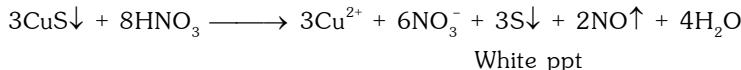
HgS precipitated dissolves in aqua regia forming undissociated HgCl_2 .

**(i) Potassium Iodide Solution****(ii) Tin(II) Chloride Solution****(iii) Cobalt(II) Thiocyanate Test**

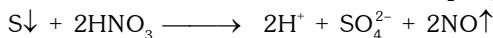
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2. COPPER (II)

Hot, concentrated nitric acid dissolves copper(II) sulphide, leaving behind sulphur as a white precipitate.

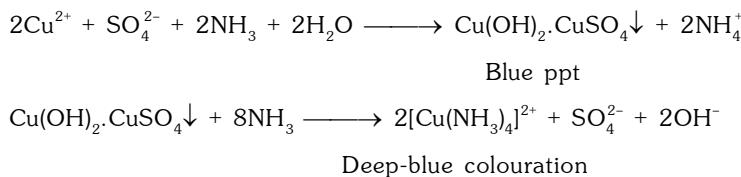


When boiled for long sulphur is oxidised to H_2SO_4 and a clear blue solution is obtained.

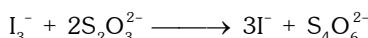
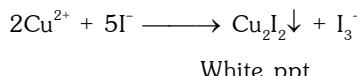


(i) Ammonia Solution

When ammonia solution is added to solution of Cu^{2+} , a blue precipitate of a basic copper sulphate is obtained, which is soluble in excess reagent giving deep-blue colouration of tetraamminecopper(II) sulphate.

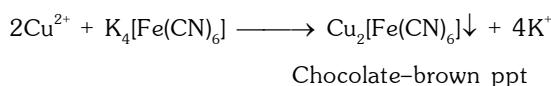


(ii) Potassium Iodide

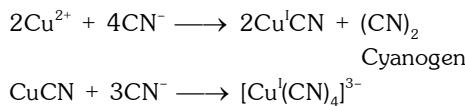


(iii) Potassium Hexacyanoferrate(II) solution

Cu^{2+} ions give chocolate-brown precipitate with $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution.



(iv) Test by NaCN & KCN



3. BISMUTH (III)

(i) Sodium Hydroxide

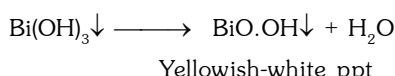
With NaOH solution, Bi^{3+} give a white precipitate of bismuth(III) hydroxide.



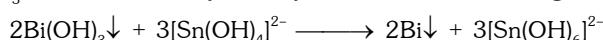
The precipitate is soluble in acids.



When boiled, the precipitate loses water and turns yellowish-white.

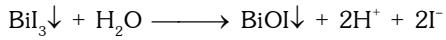
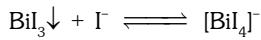


$\text{Bi}(\text{OH})_3$ when reduced by tetrahydroxostannate(II) ions give black precipitate of bismuth metal.

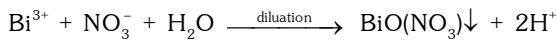


(ii) Potassium Iodide

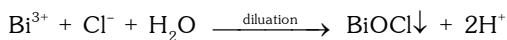
Black ppt



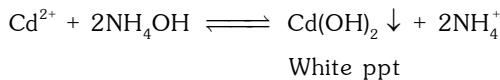
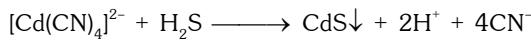
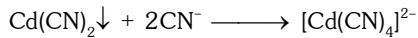
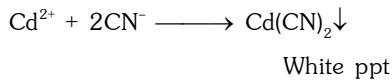
Orange ppt

(iii) Water

White ppt



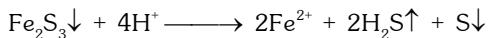
White ppt

4. CADMIUM (II)**(i) Ammonium Hydroxide****(ii) Potassium Cyanide**

The marked difference in the stabilities of the copper and cadmium tetracyanato complexes serves as the basis for the separation of Cu^{2+} and Cd^{2+} ions.

(C) Group III (Fe^{3+} , Al^{3+} , Cr^{3+})**1. IRON (III)****(i) Ammonium Sulphide Solution**

Black ppt

**(ii) Sodium Hydroxide Solution**

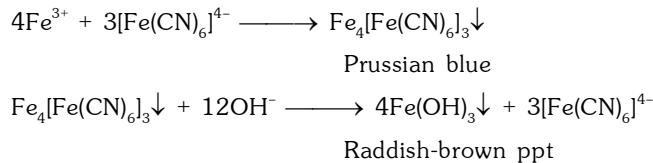
With sodium hydroxide solution, a reddish-brown precipitate of iron(III) hydroxide, insoluble in excess of the reagent (distinction from aluminium and chromium) is obtained.



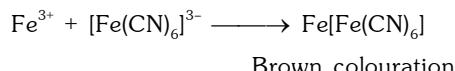
Reddish-brown ppt

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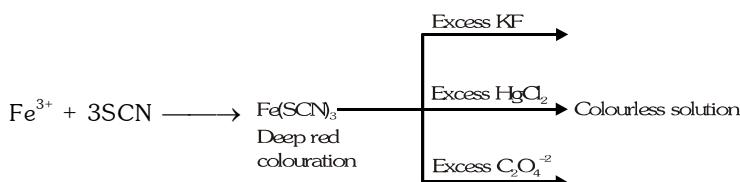
(iii) Potassium Hexacyanoferrate(II)



(iv) Potassium Hexacyanoferrate(III)

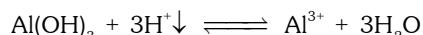
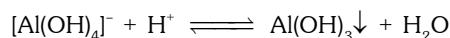
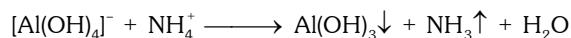
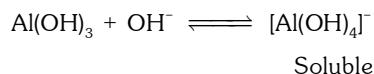
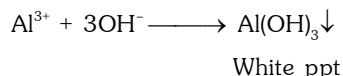


(v) Ammonium Thiocyanate Solution



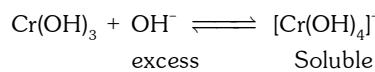
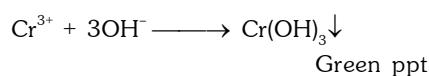
2. ALUMINIUM (III)

Sodium Hydroxide Solution

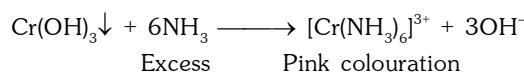
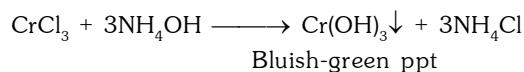


3. CHROMIUM (III)

(i) Sodium Hydroxide Solution

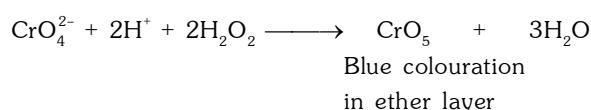


(ii) Ammonia Solution

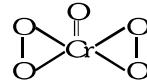


(iii) Chromium Pentoxide (Chromium Peroxide, Peroxochromic Acid) Test

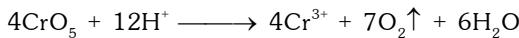
On acidifying the solution with dilute sulphuric acid, adding few drops of ether or amyl alcohol to the mixture and finally adding some hydrogen peroxide, blue colouration is formed, which can be extracted into the organic phase by gently shaking. During the reaction, chromium pentoxide is formed.



Chromium pentoxide has the following structure :



Because of the two peroxide groups, the compound is often called chromium peroxide. The name peroxochromic acid is less appropriate, because the compound does not contain hydrogen at all. In aqueous solution, the blue colour fades rapidly, because chromium pentoxide decomposes to chromium(III) and oxygen.



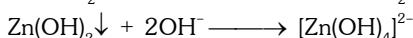
(D) Group IV (Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+})

1. ZINC (II)

(i) Sodium Hydroxide Solution



White gelatinous ppt



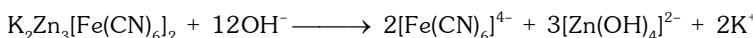
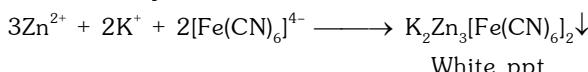
(ii) Ammonia Solution



White ppt



(iii) Potassium Hexacyanoferrate(II)



(iv) Ammonium tetrathiocyanatomercurate(II)

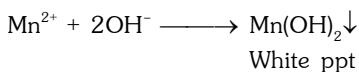


White ppt

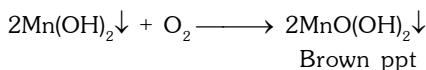
2. MANGANESE (II)

(i) Sodium Hydroxide Solution

With sodium hydroxide solution, an initially white precipitate of manganese(II) hydroxide is obtained.

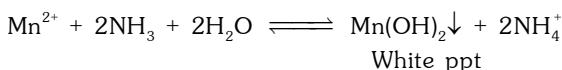


The precipitate is insoluble in excess reagent. It rapidly oxidizes on exposure to air, becoming brown, when hydrated manganese dioxide, $\text{MnO}(\text{OH})_2$, is formed.



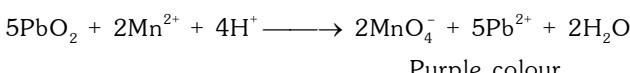
(ii) Ammonia Solution

With NH_3 solution, Mn^{2+} gives a white precipitate of manganese (II) hydroxide.



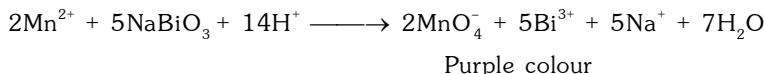
The precipitate is soluble in ammonium salts, when the reaction proceeds towards the left.

(iii) Lead dioxide and Concentrated Nitric Acid



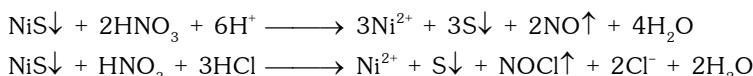
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(iv) Sodium Bismuthate (NaBiO_3) Solution

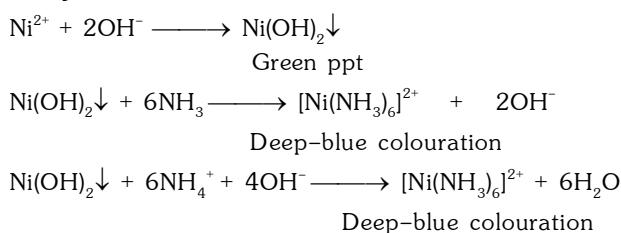


3. NICKEL (II)

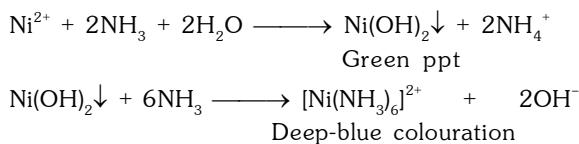
The black precipitate of NiS(II) is insoluble in cold dilute HCl and in acetic acid but dissolves in hot concentrated nitric acid and in aqua regia with the separation of sulphur.



(i) Sodium Hydroxide Solution



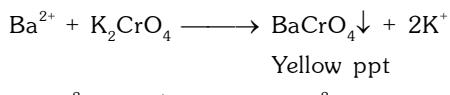
(ii) Ammonia Solution



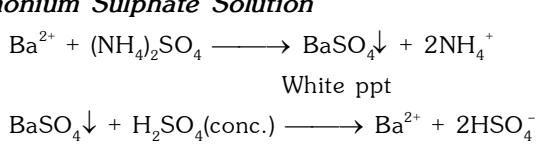
(E) Group V (Ba^{2+} , Sr^{2+} , Ca^{2+})

1. BARIUM (II)

(i) Potassium Chromate Solution



(ii) Ammonium Sulphate Solution



(iii) Ammonium Oxalate Solution

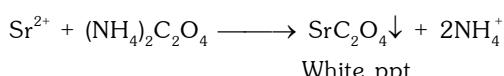


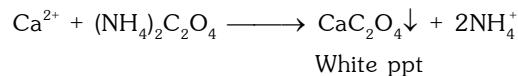
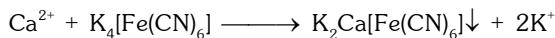
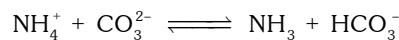
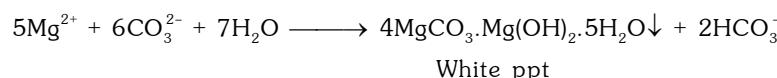
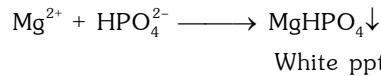
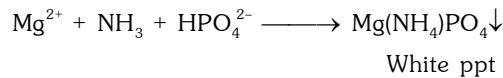
2. STRONTIUM (II)

(i) Ammonium Sulphate Solution



(ii) Ammonium Oxalate Solution

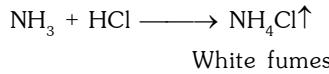


3. CALCIUM (II)**(i) Ammonium Oxalate Solution****(ii) Potassium Hexacyanoferrate(II) Solution****(F) Group VI (Na^+ , K^+ , Mg^{2+})****1. MAGNESIUM (II)****(i) Ammonia Solution****(ii) Ammonium Carbonate Solution****(iii) Disodium hydrogen phosphate Solution****(G) Group Zero (NH_4^+)****1. AMMONIUM (NH_4^+)****(i) Sodium Hydroxide Solution**

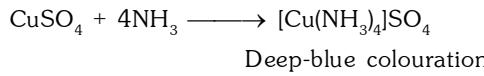
All ammonium salts on heating with alkali (NaOH) gives smell of NH_3 .



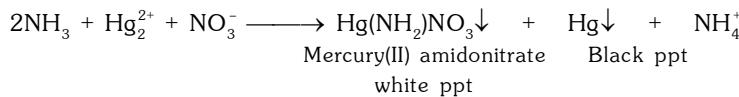
- (a) The gas evolved can be detected by its smell.
- (b) Gas evolved gives white fumes of NH_4Cl with HCl .



- (c) Paper soaked in CuSO_4 solution, becomes deep-blue by NH_3 due to the complex formation.

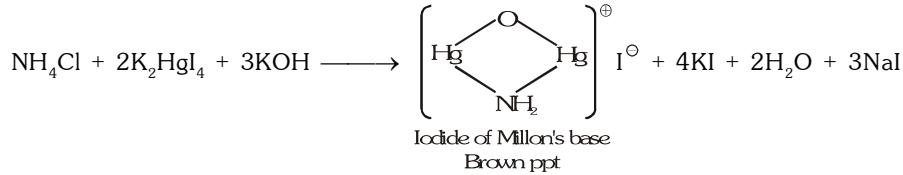


- (d) Gas can be identified by its ability to turn filter paper moistened with mercury(I) nitrate solution black.

**(ii) Nessler's Reagent**

With Nessler's reagent (an alkaline solution of potassium tetraiodomercurate(II), ammonium salts form a brown precipitate or brown or yellow colouration is produced depending on the amount of NH_4^+ ions present in the solution. The precipitate is a basic mercury(II) amido-iodine.

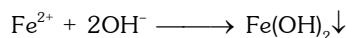
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This test can detect even traces of NH_3 present in a sample.

IRON (II)

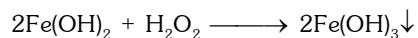
(i) **Sodium Hydroxide Solution**



White ppt

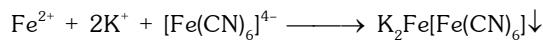


Reddish-brown ppt



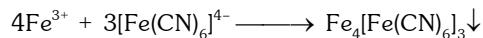
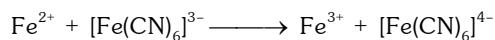
Reddish-brown ppt

(ii) **Potassium Hexacyanoferrate (II) Solution**



White ppt

(iii) **Potassium Hexacyanoferrate(III) Solution**



Prussian blue

(iv) **Ammonium thiocyanate Solution**

With ammonium thiocyanate solution, no colouration is obtained with pure iron(II) salts (distinction from (III) ions)

(v) **Dimethylglyoxime Reagent**

With dimethylglyoxime reagent soluble red iron(II) dimethyl glyoxime is obtained in ammoniacal solution. Iron(III) salts give no colouration, but nickel, cobalt and large quantities of copper salts interfere and must be absent.

Important Notes

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