

Index

SBG STUDY
CHEMISTRY
SHORT
NOTES

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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** i

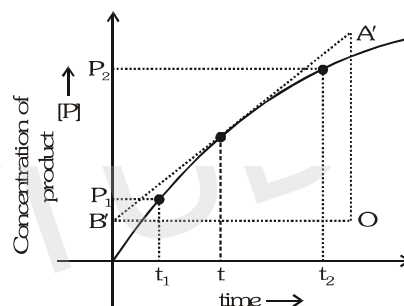
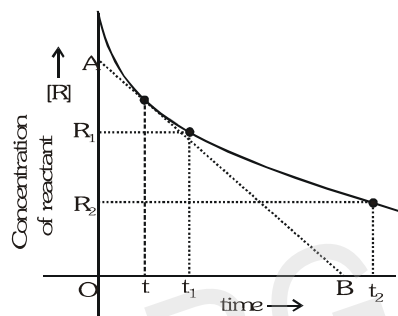


➤ **Instantaneous rate** $i - \frac{1}{a} \left(\frac{d[A]}{dt} \right) = -\frac{1}{b} \left(\frac{d[B]}{dt} \right) = \frac{1}{c} \left(\frac{d[C]}{dt} \right) = \frac{1}{d} \left(\frac{d[D]}{dt} \right)$

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

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

(Graphical method for determining rate :



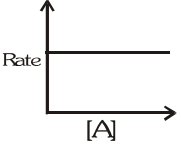
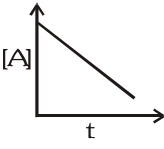
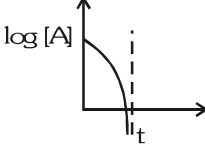
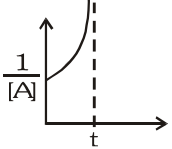
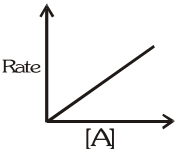
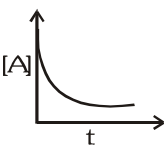
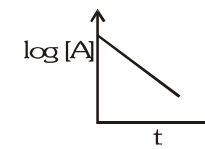
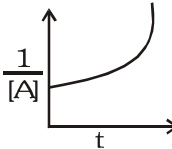
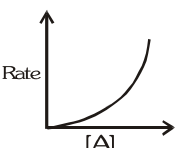
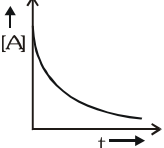
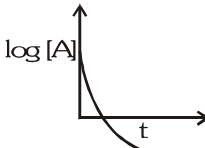
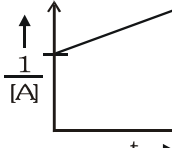
$$\text{Avg. Rate} = - \left(\frac{[R]_2 - [R]_1}{t_2 - t_1} \right) = \frac{([P]_2 - [P]_1)}{t_2 - t_1}$$

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

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

Order	Zero	1st	2nd	nth
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 ($t_{1/2}$)	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$	$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{[A]_0^{n-1}} \right]$
($t_{3/4}$)	$t_{3/4} = 1.5 t_{1/2}$	$t_{3/4} = 2 t_{1/2}$	$t_{3/4} = 3 t_{1/2}$	$t_{3/4} = (2^{n-1} + 1) t_{1/2}$

➤ **Graphs of various order**

Order	Rate vs [A]	[A] vs t	log [A] vs t	$\frac{1}{[A]}$ vs t
Zero order				
First order				
Second order				

Where

 $[A]_0$ \ initial concentration $[A]$ \ concentration at time t $t_{1/2}$ \ time taken for initial concentration of reactant to decrease by 50% $t_{3/4}$ \ time taken for initial concentration of reactant to decrease by 75%➤ **Monitoring Kinetics Experimentally i**

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

e.g. (i) Total pressure on a gaseous reaction.

(ii) Volume of a reagent (Acidoc, Basoc, oxodoc, redoxoc, etc.)

(iii) Volume of a gaseous mixture (V)

(iv) Optical rotation (R)

For a Reaction -

	A_n	\longrightarrow	nB	
$t = 0$	c		0	c_0 \ conc. at $t = 0$
$t = t$	$c - x$		nx	c_t \ conc. at $t = t$
$t = \infty$	0		nc	c_∞ \ conc. at $t = \infty$

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_∞
$k = \frac{1}{t} \ln \frac{X_0}{X_0 - x}$	$k = \frac{1}{t} \ln \frac{(n-1)X_0}{nX_0 - X_t}$	$k = \frac{1}{t} \ln \frac{(n-1)X_\infty}{n(X_\infty - X_t)}$	$k = \frac{1}{t} \ln \left(\frac{X_\infty - X_0}{X_\infty - X_t} \right)$

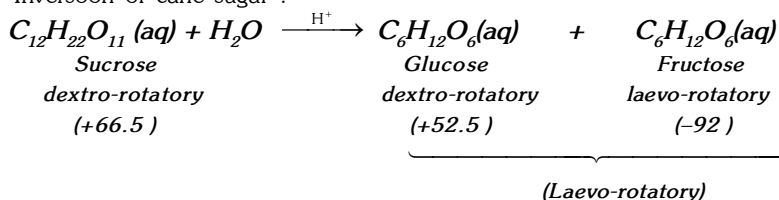
where

x \ amount of reactant reacted on time 't'.

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

➤ **Examples i (For Monitoring Kinetics Experimently)**

(o) Inversion of cane sugar :



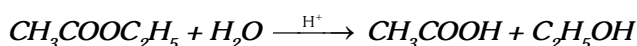
$$k = \frac{2.303}{t} \log \left(\frac{r_{\infty} - r_0}{r_{\infty} - r_t} \right)$$

r_0 = rotation at time, $t = 0$

r_t = rotation at time, $t = t$

r_{∞} = rotation at time, $t = \infty$

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



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

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

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

◆ $t_{1/2}$ is independent of initial concentration.

◆ In equal time interval, reaction finishes by equal amount.

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

◆ 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 i**

• $t_{1/2}$ 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 at $t = \frac{[A]_0}{k}$

➤ **Temperature dependence i**

- Arrhenius equation : $k = A.e^{-E_a/RT}$

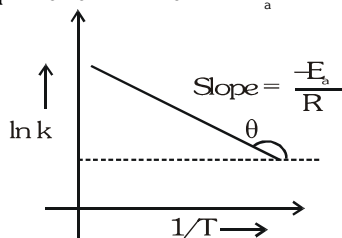
- E_a = minimum energy over and above the avg. energy of reactant which must be possessed by reacting molecule for collision to be successful.

- A = frequency factor - proportional to number of collisions per unit volume per second.

- $e^{-E_a/RT}$ = Fraction of collision on 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 i Graphical determination of E_a

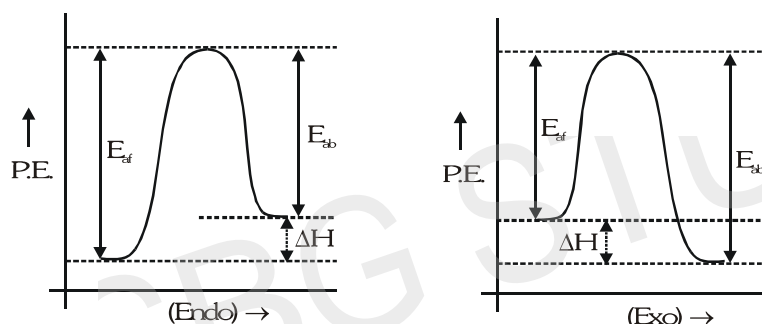


Temperature coefficient $\frac{k_{T+10}}{k_T}$

By default $T = 298 \text{ K}$

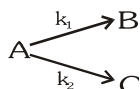
Variation of rate constant with temperature $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

➤ **Endothermic and exothermic reactions i**



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

➤ **Parallel reaction i**



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

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

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

(ov) % 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 i**

Rate law $\rightarrow \text{rate} = k [A]^m [B]^n$

Pseudo rate law :

rate = $k_1 [A]^m$

[B] assumed constant on two cases :

(o) B on large excess (oo) \rightarrow CATALYST

NUCLEAR CHEMISTRY

➤ **All nuclear reactions are first order i**

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

First order

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

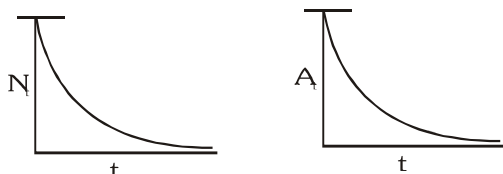
$\lambda \rightarrow$ Decay constant

$N_0 \rightarrow$ Initial nucleus

$N_t \rightarrow$ Nucleus at 't'

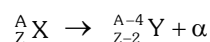
$$\text{Activity} = A = \frac{-dN_t}{dt} = \lambda N_t ; \text{Nucleus/sec.}$$

$A_t =$ Rate of decay



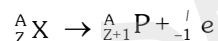
$$t_{1/2} = \frac{\ln 2}{\lambda}$$

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



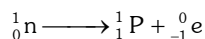
To \downarrow size of large nucleus

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



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

Nuclear change on β decay



➤ **γ -decay** i

Photons from excited nucleus after α - or β - decay

No effect on n/p ratio

High energy γ radiation.

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

➤ **Parallel decay** i

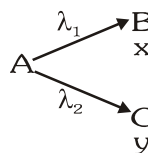
$$t = 0 \quad N_0$$

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

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

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

$\lambda \rightarrow$ No dependence on temp.



THERMODYNAMICS

➤ THERMODYNAMICS i

- ◆ 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 i

State variable whose value depends upon size of system.

Examples - mass, volume, charge, mole etc.

➤ Intensive state variable i

State variable whose value does not depend upon size of system.

Examples - concentration, density, temperature etc.

➤ Path variable i

- ◆ **Heat i** Mode of energy transfer between system and surrounding due to temperature difference.
- ◆ **Work i** Mode of energy transfer between system and surrounding due to difference on 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 -

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

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

- (v) If two states 1 and 2 are connected by n paths involving q and w , 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 (non-state functions) but their sum is a state function (ΔU).

- ◆ **Enthalpy** is 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 an 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 -

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

For Isobaric change -

$$\Delta H = \Delta U + P \Delta V \quad \dots \dots \dots (ii)$$

For Isochoric change -

$$\Delta H = \Delta U + V(\Delta P) \quad \dots \dots \dots (iii)$$

For a differential change

$$dH = dU + PdV + VdP \quad \dots \dots \dots (iv)$$

- **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.

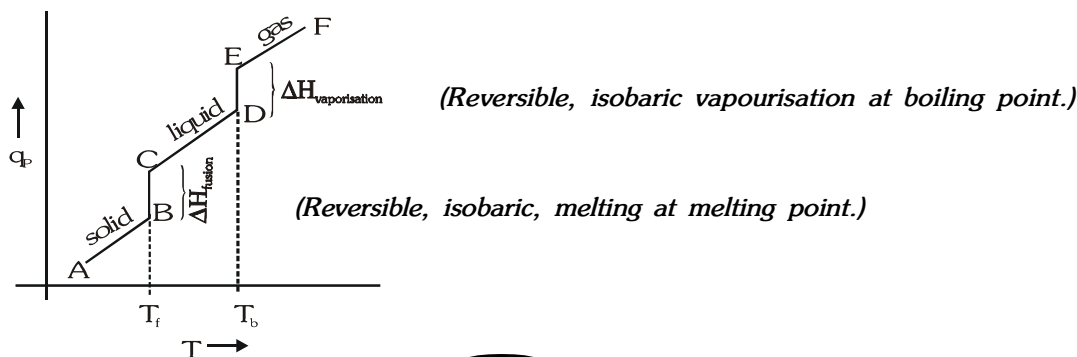
- ◆ **Relationship between ΔH and ΔU for phase transitions.**

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

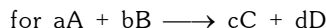
For sublimation $\Delta H_{\text{sublimation}} = \Delta U_{\text{sublimation}} + RT$

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

- ◆ **Heating curve at constant pressure**



- ◆ **Enthalpy of reaction ($\Delta_r H$)** i 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.



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

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

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

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

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

- ◆ **The stoichiometric coefficient of solids and liquids is 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 $P = 1 \text{ bar}$.

Standard enthalpy, internal energy change for reaction.

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

SECOND LAW

- **Spontaneous process** i

- A process which takes place on its own without an external help.
- Spontaneous process \equiv Irreversible process \equiv Natural process.

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

$$\Delta S_{\text{universe}} > 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

- S is a state function. S is measure of disorder of system.

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

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

- (o) Entropy change for ideal gas process :

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

- (oo) Entropy change for system on phase transition :

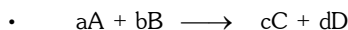
$$\Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T_b}$$

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

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

(ooo) 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 are obtained by third law.

(B) Entropy change on surrounding :

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

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

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

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

$$\Delta S_{\text{system}} = -\Delta S_{\text{surr.}}$$

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

$$\Delta S_{\text{total}} \geq 0$$

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

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

(oo) $\left. \begin{array}{l} \text{If Solid} \longrightarrow \text{liquid} \\ \text{liquid} \longrightarrow \text{gas} \end{array} \right\} \Delta_r S > 0$

(ooo) If cyclohexane taken place $\Delta_r S < 0$.

➤ **Gibb's function i $G = H - TS$**

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

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

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

(A) Change on ΔG for phase transition :

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

(oo) For irreversible phase transitions $\Delta G_{P,T} = \Delta H_{P,T} - T\Delta S_{P,T}$

(B) Change on ΔG for chemical reaction :



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

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

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \quad \dots\dots(ooo)$$

Where, $Q \equiv$ Reaction quotient

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

At equilibrium :

- $\Delta G = 0 \quad \text{G}_{\text{product}} = \text{G}_{\text{reactant}}$
- $\Delta G = -RT \ln K_{\text{eq.}}$
- At equilibrium the system Gibbs's function is at maximum value.

➤ **Difference between $\Delta_r G$ and $\Delta_r G^\circ$:**

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

$\Delta_r G$ = change in Gibbs'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 equation.
- (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 i**

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

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

IDEAL GAS PROCESSES i

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

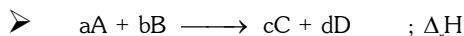
V_2 = Final volume
 P_2 = Final pressure

V_1 = Initial volume
 P_1 = Initial 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 mixture of reacting ideal gases at constant Temperature :
 $\Delta_r H = \Delta_r U + (\Delta n_g) RT.$
- **Exothermic Reaction**
 $H_p > H_R$ $U_p > U_R$
 $\Delta_r H > 0$
 $\Delta_r U > 0$
- **Endothermic Reaction**
 $H_p < H_R$ $U_p < U_R$
 $\Delta_r H < 0$
 $\Delta_r U < 0$
- **Reversible Phase Transition**
 Isothermal and Isobaric
Example
 (a) Melting or Freezing at MP
 (b) Vaporisation or condensation at B.P.
 (c) Sublimation at sublimation point.
 (d) Interconversion of allotropic forms at Transition temperature.
- $S_g \gg S_l > S_s$; $V_g \gg V_l > V_s$;
 $V_g \gg V_l < V_s$ (Water) ; $H_g \gg H_l > H_s$;
 $U_g \gg U_l > U_s$; $\Delta H_{sub} \gg \Delta H_{vap} > \Delta H_{fus}.$
 At same Pressure and Temperature
 $\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus}.$
- For reversible phase transition.
 $W = - P_{ext} [\Delta V]$
 $\Delta S_{trans.} = \frac{\Delta H_{trans}}{T_{trans}}$
 $q = \Delta H_{trans}$
 $\Delta U_{trans} = \Delta H_{trans} + w$
- $\Delta_r H = \sum V_p H (\text{product}) - \sum V_R H (\text{Reactant})$
 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**
 (a) $\Delta_r H = \sum V_p \Delta H_f (P) - \sum V_R \Delta H_f (R)$
 (b) $\Delta_r H = \sum V_R \Delta H_{comb.} (R) - \sum V_p \Delta H_{comb.} (P)$
 (c) $\Delta_r H = \sum \Delta H_{atomisation} (R) - \sum \Delta H_{atomisation} (P)$
- ΔH_f (Element in solid state) = 0.
 $\Delta H_f (CO_2, g) = \Delta H_{comb.} (C, \text{graph.})$

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



$\Delta_r H$ = change on 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 os functoon of P, T.

$$P \uparrow \quad \backslash \quad G \uparrow$$

$$T \uparrow \quad \backslash \quad G \downarrow$$

➤ $\Delta H_f (H^+, aq) = 0$
 $\Delta G_f (H^+, aq) = 0$
 $E_{H_2 | H^+}^\circ = 0$
 $S_m (H^+, aq) = 0$] By conventoon

➤ $q = \int ms dt$

$$= \int nC_m dt$$

$$= \int C dt$$

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

specofoc molar Total
heat heat heat
capacoty capacoty capacoty

➤ For strong Acod and strong base

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

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

➤ If acod or base os weak

$$\Delta H_{neutr.} = - 57.1 + \Delta H_{ionosatoon} \quad \backslash \quad + ve$$

➤ Heat evolved on SA + SB tottratoon = (no. of eqv. dñmotong reagent) 57.1 kJ

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

➤ $\Delta_r H$ (Actual) - $\Delta_r H$ (theoretocal) = $[\sum V_p RE (P) - \sum V_R RE (R)]$

□ $\Delta H_{hydratoon} [CuSO_4, s]$

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

➤ **Enthalpy of atomisation :**

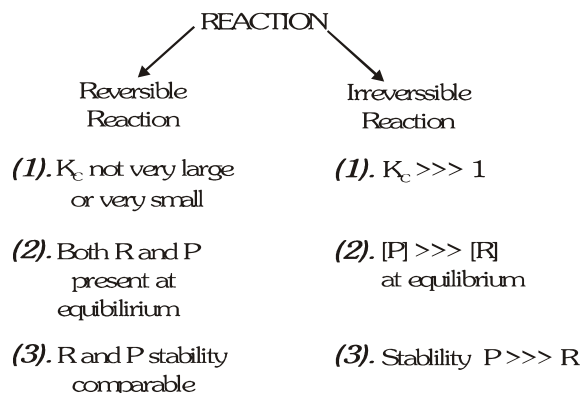
$$\Delta H_{atomosatoon} (O_2, g) = BE (O = O)$$

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

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

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

CHEMICAL EQUILIBRIUM



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

➤ **For gaseous reactions.**

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

$$K_p > K_c \quad \text{of} \quad \Delta n_g > 0$$

$$K_p < K_c \quad \text{of} \quad \Delta n_g < 0$$

$$K_p = K_c \quad \text{of} \quad \Delta n_g = 0$$

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

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

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

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

➤ For pure solids & pure liquids (solvent) :

Active mass = 1 [Conventionally]

Activity = 1 [thermodynamically]

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

➤ **Reaction Quotient (Q_c / Q_p)**

(o) Used to find direction of reaction mixture -dF/dx.

(oo) $Q < K_c$ or $Q_p < K_p$ \ FWD.

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

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

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

➤ If

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

or

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

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**

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

$n, P, m, V \rightarrow$ mols, partial pressure, mass, partial volume of reactant respectively.

% dissociation = % reactant converted to product $\times 100 \alpha$

$\alpha \leq 1$ [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 :

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

• $M_{avg.}$ & VD_{mix} as a function of mixture composition.

• For mixture of reacting gas $M_{avg.}$ changes & becomes constant at equilibrium.

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

➤
$$\frac{(VD)_o}{(VD)_f} = \frac{M_o}{M_f} = \frac{n_f}{n_o} = \frac{P}{P}$$

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

• On going FWD.

If $\Delta n_g > 0$



If $\Delta n_g < 0$



If $\Delta n_g = 0$ $P, n, M_{avg.}, VD = \text{Constant}$

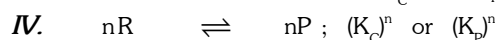
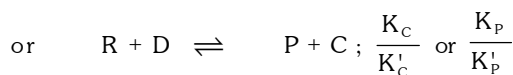
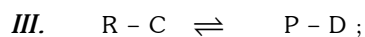
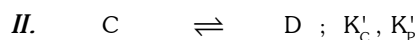
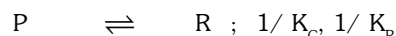
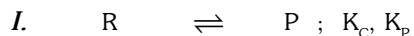
➤ For a reaction with $\Delta n_g \neq 0$

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 :



➤ **Relative Humidity (R.H.)**

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

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

If $RH \geq 100\%$ \ Saturated air sample

➤ **Le chatelier Principle**

Case I : [R] increased \ Forward shift

[P] increased \ Backward shift

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

Case II : Total P increased (or V decreased)

If $\Delta n_g > 0$ \ backward

If $\Delta n_g < 0$ \ forward

If $\Delta n_g = 0$ \ no effect

Case III : V Increased

\ Same effect as P decreased

If $\Delta n_g > 0$ \ forward

If $\Delta n_g < 0$ \ backward

If $\Delta n_g = 0$ \ no effect

Case IV : T Increased

If $\Delta_r H > 0$ \ forward

If $\Delta_r H < 0$ \ backward

T decreased

If $\Delta_r H > 0$ \ backward

If $\Delta_r H < 0$ \ 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.

\ No effect

Case VII : Adding inert gas at constant Pressure

\ Same effect as Pressure decrease or volume increase

➤ **Thermodynamics state of Equilibrium :**

$G_{\text{mix}} \rightarrow$ Mixture

$\Delta_r G \rightarrow 0$

$\sum \nu_p G_p = \sum \nu_r G_r$

} at P, T constant

If $\Delta_r G < 0$ \ $\sum \nu_p G_p < \sum \nu_r G_r$

(Reactoon shofts forward to attaan equolobroum.

$$\text{If } \Delta_r G > 0 \quad \sum V_P G_P > \sum V_R G_R$$

(Reactoon shofts backward to attaan equolobroum.

$$\text{If } \Delta_r G = 0 \quad \text{Equolobroum state}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln(Q)$$

$\Delta_r G^\circ$ = Standard Gobbs energy of reactoon (when all Reactants & Products are on standard states)

➤ **Standard State**

Gas → Ideal gas

$$\text{Actovoty} = \text{Partoal pressure} = 1 \text{ bar} \approx 1 \text{ atm.}$$

Solute → Ideal solutoon

$$\text{Actovoty} = \text{concentratioon} = 1M$$

Solid/Liquid → Pure actovoty = 1

□ Q contaons actovoty of specoes o.e., partoal presson bar (or atm) for gas
molaroty for solute os unoty for solod or loquod.

□ At equolobroum $\Delta_r G = 0$ & $Q = K_{eq}$

$$\Delta_r G = -RT \ln k_{eq}$$

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

□ For gaseous homogeneous reactoon,

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

For homogeneous reactoon on solutoon phase

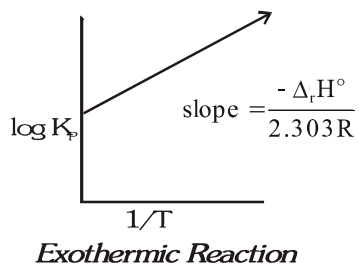
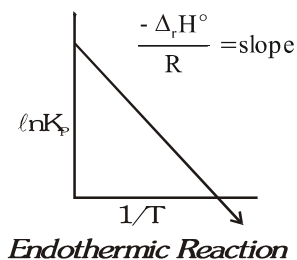
$$\Delta_r G = -RT \ln K_c$$

□ BP, M.P. & Sublomatoon poont all oncrease on oncrease pressure

Exception – M.P. of H_2O decrease on oncreaseing 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 i

1. **Strong electrolyte i** 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 , $\text{Ba}(\text{OH})_2$, CsOH , RbOH

(c) All Salts $\rightarrow \text{NaCl}$, KCl , CuSO_4 ,

2. **Weak electrolytes i** 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 , $\text{B}(\text{OH})_3$

(b) Weak base $\rightarrow \text{NH}_4\text{OH}$, $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$

➤ ACIDS BASES AND SALTS i

Arrhenius concept i

Arrhenius Acid i Substance which gives H^+ 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 i Any substance which releases OH^- (hydroxyl) ion in water (OH^- donor).

◆ First group elements (except Li) form strong bases

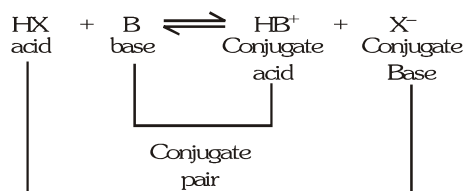
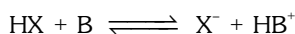
➤ Bronsted - Lowry concept i (Conjugate acid - base concept) (Protonic concept)

Acid i substances which donate H^+ are Bronsted Lowry acids (H^+ donor)

Base i substances which accept H^+ are Bronsted Lowry bases (H^+ acceptor)

➤ Conjugate acid - base pairs i

In a typical acid base reaction



Ex i

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^-		

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

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

Acid \rightarrow e^- pair acceptor

Ex. Electron deficient molecules : $BF_3, AlCl_3$
Cations : H^+, Fe^{2+}, Na^+
Molecules with vacant orbitals : SiF_4, PF_3

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

Base \rightarrow (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 i**

According to Arrhenius concept

$H_2O \rightleftharpoons H^+ + OH^-$ so, ionic product of water, $K_w = [H^+][OH^-] = 10^{-14}$ at 25 (exp.)

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

K_w increases with increase in temperature.

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

$pH = 7 = pOH$	(neutral)	} at 25°C
$pH < 7$ or $pOH > 7$	(acidic)	
$pH > 7$ or $pOH < 7$	(Basic)	

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

➤ **Degree of dissociation of water i**

$$H_2O \rightleftharpoons H^+ + OH^- \quad \alpha = \frac{\text{no. of moles dissociated}}{\text{Total no. of moles initially taken}}$$

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

➤ **Absolute dissociation constant of water i**

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$\text{So, } pK_a = pK_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

❑ **ACIDITY AND pH SCALE i**

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 Sørensen known as pH scale.

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

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

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

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 i

(a) Strong acid solution i

(o) If concentration is greater than 10M.

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

so $[H^+] =$ normality of strong acid solution

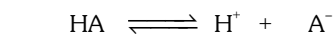
(oo) If concentration is less than 10M

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

So $[H^+] =$ normality of strong acid + H^+ ions coming from water on presence of this strong acid

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

- 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 = 0 C 0 0

t_{eq} C(1 - α) Cα Cα

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha^2}{1 - \alpha}$$

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%)

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

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

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

- 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 10M, then contribution from the water can be neglected, or not then we have to take $[H]$ from the water also.

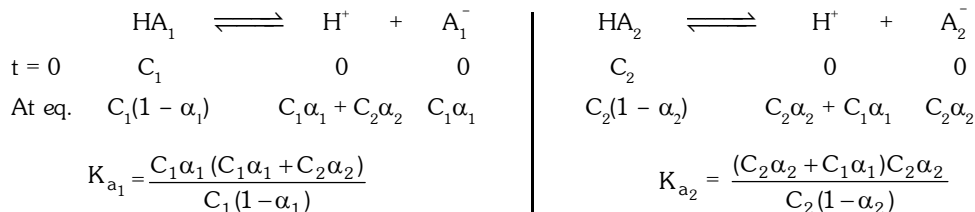
➤ Relative strength of weak acids and bases i

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 i

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



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

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

$$[\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} + \frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} \quad \left([\text{H}^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}} \right)$$

- ◆ If the dissociation constant of one of the acids 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 i

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

In an aqueous solution, following equilibrium exists.

If

α_1 = degree of ionization of H_2A on presence of H_2A

K_{a_1} = first ionization constant of H_2A

α_2 = degree of ionization of HA^- on presence of H_2A

K_{a_2} = second ionization constant of H_2A

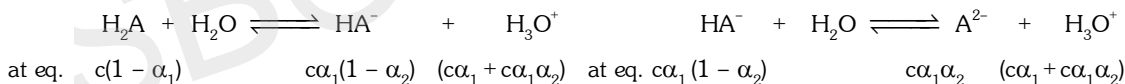
I step



$$(K_{eq_1}) [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = K_{a_1}$$

$$\begin{aligned} \therefore K_{a_1} &= \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1 - \alpha_2)]}{c(1 - \alpha_1)} \\ &= \frac{[c\alpha_1(1 + \alpha_2)][\alpha_1(1 - \alpha_2)]}{1 - \alpha_1} \quad \dots\dots (o) \end{aligned}$$

II step



$$(K_{eq_2}) [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]} = K_{a_2}$$

$$\begin{aligned} K_{a_2} &= \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2]}{c\alpha_1(1 - \alpha_2)} \\ &= \frac{[c\alpha_1(1 + \alpha_2)]\alpha_2}{1 - \alpha_2} \quad \dots\dots (oo) \end{aligned}$$

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 (o) and

(oo) 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 $[\text{H}_3\text{O}^+] < 10^{-6}$ M, the contribution of H_3O^+ from water should be added.
- ◆ If the total $[\text{H}_3\text{O}^+] > 10^{-6}$ M, then $[\text{H}_3\text{O}^+]$ contribution from water can be ignored.

Using this $[\text{H}_3\text{O}^+]$, pH of the solution can be calculated.

Approximation i

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

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

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

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

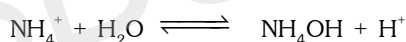
- ◆ Hence, for a diprotic acid (or a polyprotic acid) $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} \ll K_{a_1}$

➤ **SALTS i**

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

Classification of salts i**(1) Simple salts****(2) Normal salt i** (o) Acid salts (oo) Basic salts**(3) Double salts****(4) Complex salts****(5) Mixed salts**➤ **TYPES OF SALT HYDROLYSIS i****(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 i**

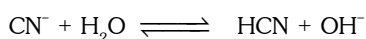
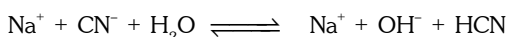
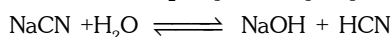
$$(1) K_h = \frac{K_w}{K_b} \quad (2) h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}$$

$$(3) [H^+] = Ch = \sqrt{\frac{K_w \times C}{K_b}} \quad (4) pH = -\log [H^+]$$

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

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

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

➤ **Summary i**

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

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

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

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

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

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

➤ **Summary i**

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

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

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

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

Ex. NaCl , BaCl_2 , Na_2SO_4 , KClO_4 etc.

(o) Hydrolysis of salt of [SA - SB] is not possible

(oo) Solution is neutral in nature ($\text{pH} = \text{pOH} = 7$)

(ooo) pH of the solution is 7

➤ **BUFFER SOLUTIONS i**

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 i**

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

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

➤ **MIXED BUFFER SOLUTIONS :**

(a) Acidic buffer solution i

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

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

(b) Basic buffer solution i

A basic buffer solution consists of a mixture of 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 i

$$\frac{[\text{NH}_4\text{OH}]}{1} : \frac{[\text{NH}_4\text{Cl}]}{1}$$

$$\text{pOH} = \text{p}K_b + \log \frac{1}{1}$$

$$\text{pOH} = \text{p}K_b \quad \text{and} \quad \text{pH} = 14 - \text{p}K_b$$

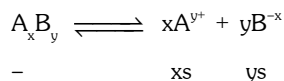
➤ SOLUBILITY (s) AND SOLUBILITY PRODUCT (K_{sp}) i

This is generally used for sparingly soluble salts. We will be dealing with the solubilities on 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 be A_xB_y , on solution in water, let the solubility be 's' M, then

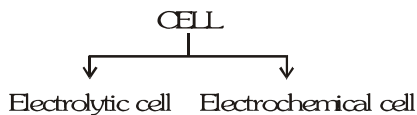


$$- \quad \quad \quad xs \quad \quad ys \quad \quad \therefore K_{sp} = (xs)^x (ys)^y = x^x \cdot y^y \cdot (s)^{x+y}$$

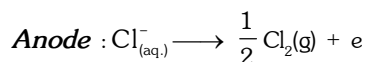
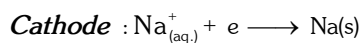
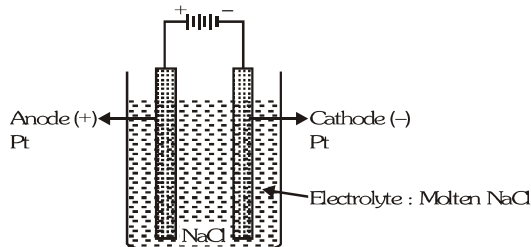
◆ Condition of precipitation

- ◆ For precipitation ion 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 follows Faraday's law of electrolysis.**

Faraday's 1st Law :

$$w = Z \cdot i \cdot t$$

$$w = \frac{M}{n \cdot \text{factor} \times 96500} \cdot i \cdot t$$

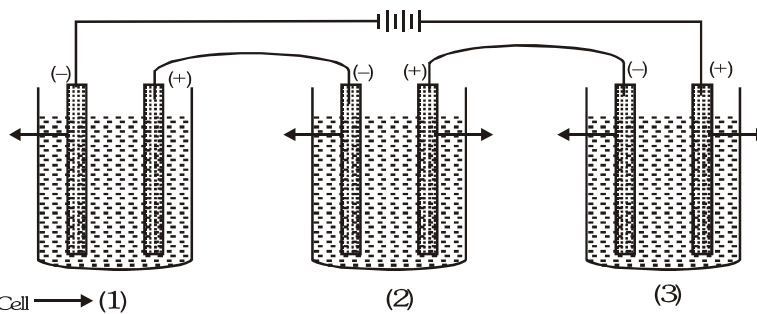
where w = mass deposited (gm)

M = molar mass

i = current (Amp.)

t = time (sec.)

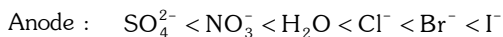
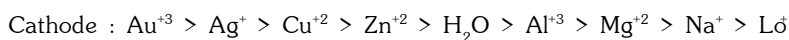
Faraday's second law :



- At any electrode, the material deposited.

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

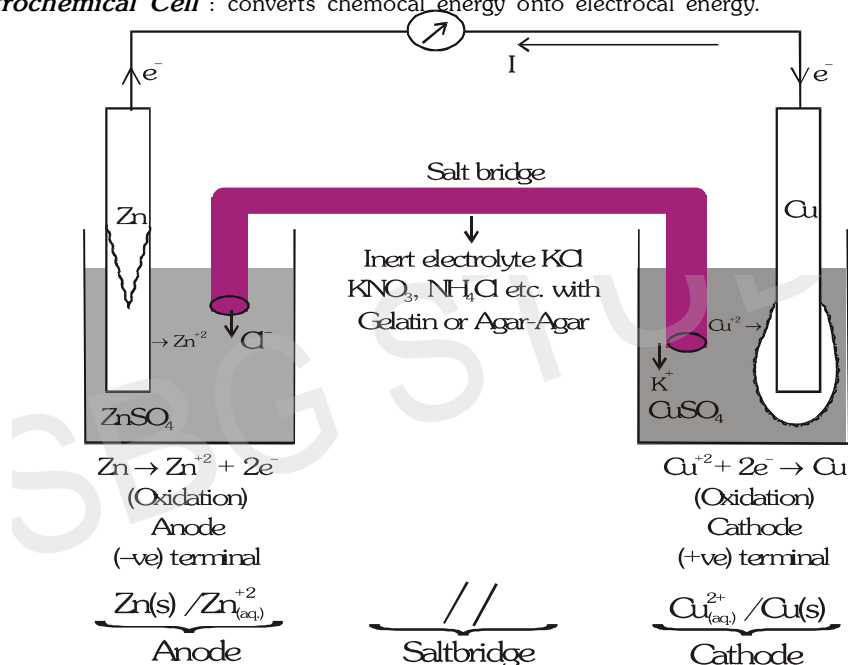
Note : Order of discharge potential.



PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

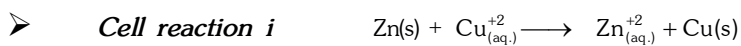
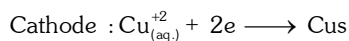
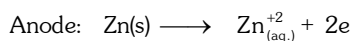
S. No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(o)	Aqueous NaCl	Pt or Graphite	Cl_2	H_2
(oo)	Fused NaCl	Pt or Graphite	Cl_2	Na
(ooo)	Aqueous NaOH	Pt or Graphite	$\frac{1}{2}\text{O}_2$	H_2
(ov)	Fused NaOH	Pt or Graphite	O_2	Na
(v)	Aqueous CuSO_4	Pt or Graphite	O_2	Cu
(vo)	Dilute HCl	Pt or Graphite	Cl_2	H_2
(voo)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(vooo)	Aqueous AgNO_3	Pt or Graphite	O_2	Ag

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



➤
$$E_{\text{Cell}} = \text{SRP}_{\text{cathode}} - \text{SRP}_{\text{Anode}}$$

$$= \text{SRP}_{\text{cathode}} + \text{SOP}_{\text{at anode}}$$

Half cell reaction i


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

➤ **Nearest equation i**

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

➤ Max electrocal work done = $nFE = -\Delta G$
electrocal 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+}	$M^{n+} + ne^{-} \longrightarrow M(s)$	$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$
Gas - ion	$Pt / H_2 (P \text{ atm})$ $/ H^{+} (XM)$	$H^{+} (aq) + e^{-}$ $\longrightarrow \frac{1}{2} H_2 (P \text{ atm})$	$E = E^{\circ} - 0.0591 \log \frac{\sqrt{P_{H_2}}}{[H^{+}]}$
Oxidation - reduction	$Pt / Fe^{2+}, Fe^{3+}$	$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$	$E = E^{\circ} - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$
Metal - insoluble salt Anion	$Ag/AgCl, Cl^{-}$	$AgCl (s) + e^{-}$ $\longrightarrow Ag (s) + Cl^{-}$	$E_{Cl^{-}/AgCl/Ag} = E_{Cl^{-}/AgCl/Ag}^{\circ} - 0.0591 \log [Cl^{-}]$
Calomel electrode	$Cl^{-}(aq)/Hg/Hg_2Cl_2$	$Hg_2Cl_2(s) + 2e^{-}$ $\longrightarrow 2Hg(l) + 2Cl^{-}(aq.)$	$E = E^{\circ} - 0.0591 \log [Cl^{-}]$

➤ Gobb's Helmholtz equatoon :

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

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

'THE ELECTROCHEMICAL SERIES'

<i>Element</i>	<i>Electrode Reduction Reaction</i>	<i>Standard electrode Reduction potential E^0, Volts</i>
Lo	$\text{Lo}^+ + e^- \rightarrow \text{Lo}$	- 3.05
K	$\text{K}^+ + e^- \rightarrow \text{K}$	- 2.93
Ba	$\text{Ba}^{+2} + 2e^- \rightarrow \text{Ba}$	- 2.90
Ca	$\text{Ca}^{+2} + 2e^- \rightarrow \text{Ca}$	- 2.87
Na	$\text{Na}^+ + e^- \rightarrow \text{Na}$	- 2.71
Mg	$\text{Mg}^{+2} + 2e^- \rightarrow \text{Mg}$	- 2.37
Al	$\text{Al}^{+3} + 3e^- \rightarrow \text{Al}$	- 1.66
Mn	$\text{Mn}^{+2} + 2e^- \rightarrow \text{Mn}$	- 1.18
H_2O	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	- 0.828
Zn	$\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn}$	- 0.76
Cr	$\text{Cr}^{+3} + 3e^- \rightarrow \text{Cr}$	- 0.74
Fe	$\text{Fe}^{+2} + 2e^- \rightarrow \text{Fe}$	- 0.44
Cd	$\text{Cd}^{+2} + 2e^- \rightarrow \text{Cd}$	- 0.40
No	$\text{No}^{+2} + 2e^- \rightarrow \text{No}$	- 0.25
Sn	$\text{Sn}^{+2} + 2e^- \rightarrow \text{Sn}$	- 0.14
Pb	$\text{Pb}^{+2} + 2e^- \rightarrow \text{Pb}$	- 0.13
H_2	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0
Cu	$\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}$	+ 0.34
I_2	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+ 0.54
Hg	$\text{Hg}_2^{+2} + 2e^- \rightarrow 2\text{Hg}$	+ 0.79
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+ 0.80
Hg	$\text{Hg}^{+2} + 2e^- \rightarrow \text{Hg}$	+ 0.85
Br_2	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+ 1.08
O_2	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	+ 1.229
Cl_2	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+ 1.36
Au	$\text{Au}^{+3} + 3e^- \rightarrow \text{Au}$	+ 1.50
F_2	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+ 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 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
Specifoc	conductance of volume within electrode	conductance of unit volume	conductance of that volume which contains exactly one mole
Change with concentration	decrease with decrease on concentration	Decrease with decrease on concentration	Increase with decrease on concentration
Formula	$C = \frac{1}{R}$	$\kappa = C \times \text{cell constant}$	$\kappa = \Lambda_m \times \frac{1}{V}$ $V = \text{Volume of solution containing 1 mole of electrolyte}$
Factors	(o) nature of electrolyte (oo) concentration of electrolyte (ooo) Type of cell.	(o) nature of electrolyte (oo) concentration of electrolyte	(o) nature of electrolyte (oo) concentration of electrolyte

➤ **KOHLRAUSEH'S LAW :**

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

$$\Lambda_m^\infty (K_2SO_4) = 2\lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty (Na_3PO_4) = 3\lambda_+^\infty + \lambda_-^\infty$$

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

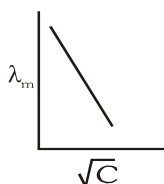
➤ **FORMULA**

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

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

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

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



LIQUID SOLUTION

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

$$T \uparrow \quad V.P. \uparrow$$

$$\text{Attractive forces} \uparrow \quad V.P. \downarrow$$

- **Raoult's law**

Non volatile solute and volatile solvent solution.

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

$$P_A = P_A^\circ X_A$$

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

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

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

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

Where n_B = mole of Non-volatile solute.

ϕ = Vant Hoff's factor.

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

$$\Delta T_b = (T'_b - T_b) = \phi K_b m$$

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

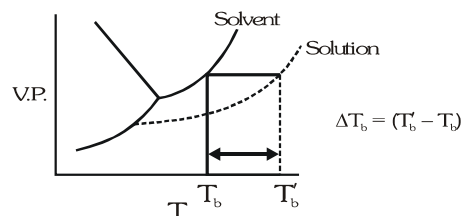
where T_b = B.P. of pure solvent.

ℓ_v = Latent heat of vaporization per gm

K_b = molal elevation constant

M = molar mass

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



(3) **Depression on F.P.**

$$\Delta T_f = T_f - T'_f = \phi K_f m$$

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

T_f = f.p. of pure solvent

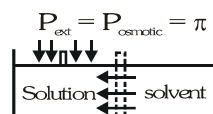
K_f = molal depression constant

ℓ_f = latent heat of fusion per gm.

(4) **Osmotic pressure**

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

$$\pi = \phi C \cdot S.T.$$



where π = osmotic pressure

C = molarity (mole/lit)

S = R = const. for solution.

Sol.(1) Sol (2)
If $\pi_1 = \pi_2$ Isotonic

If $\pi_1 > \pi_2$ $\left\{ \begin{array}{l} \text{sol}^n(1) \text{ hypertonic} \\ \text{sol}^n(2) \text{ hypotonic} \end{array} \right.$

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

Solute	Example	Ionisation/association (α 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 ₃ COOH, FeSO ₄ etc.	$AB \xrightleftharpoons[1-x]{\quad} \underset{x}{A^+} + \underset{x}{B^-}$	2	(1 + α)	$\frac{m_1}{(1 + \alpha)}$
Ternary electrolyte A_2B, AB_3	K ₂ SO ₄ , BaCl ₂ , K ₃ [Fe(CN) ₆], FeCl ₃	$A_2B \xrightleftharpoons[1-x]{\quad} \underset{2x}{2A^+} + \underset{x}{B^{2-}}$ $AB_3 \xrightleftharpoons[1-x]{\quad} \underset{x}{A^{3+}} + \underset{3x}{3B^-}$	3 4	(1+2 α) (1+3 α)	$\frac{m_1}{(1 + 2\alpha)}$ $\frac{m_1}{(1 + 3\alpha)}$
Associated Solute	benzoic acid on benzene forming dimer any solute forming polymer A_n	$2A \xrightleftharpoons{\quad} A_2$ $A \xrightleftharpoons[(1-x)]{\quad} \frac{1}{2} A_2$ $nA \xrightleftharpoons{\quad} A_n$ $A \xrightleftharpoons[(1-x)]{\quad} \frac{1}{n} A_n$	$\frac{1}{2}$ $\frac{1}{n}$	$\left(1 - \frac{\alpha}{2}\right) = \left(\frac{2-\alpha}{2}\right)$ $\left[1 + \left(\frac{1}{n} - 1\right)\alpha\right]$	$\frac{2m_1}{(2 - \alpha)}$ $\left[\frac{m_1}{1 + \left(\frac{1}{n} - 1\right)\alpha} \right]$
General	one mole of solute giving y mol of products	$A \xrightleftharpoons{\quad} yB$	y	[1+(y-1) α]	$\frac{m_1}{[1 + (y - 1)\alpha]}$

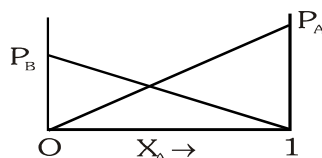
* number of products from one mole solute

Raoult's law i

(1) Volatile binary liquid mix :

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

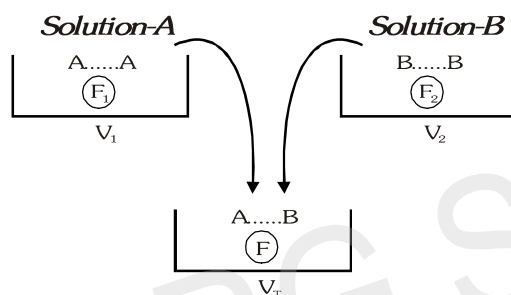
Binary liquid solution :



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

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

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

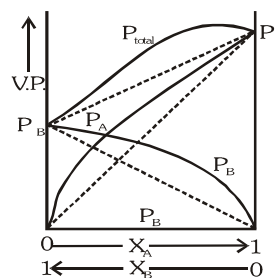
➤ **Ideal and Non-Ideal solution i**

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

Non-Ideal solution i(1) **Solution showing +ve deviation i**

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

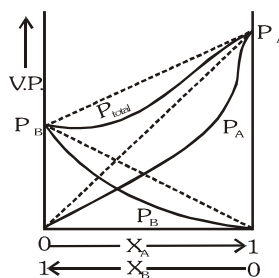
$$V_T > V_1 + V_2 \quad \Delta H_{\text{solution}} > 0$$

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

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

$$V_T < (V_1 + V_2)$$

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



DEVIATION FROM RAOULT'S LAW

Positive deviation ($\Delta H = +ve$)	Negative deviation ($\Delta H = -ve$)	Zero deviation ($\Delta H = 0$)
(o) ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(oo) acetone + carbon disulphide	benzene + chloroform	hexane + n-heptane
(ooo) acetone + benzene	nitroic acid + chloroform	ethyl alcohol + ethyl iodide
(ov) ethanol + acetone	acetone + aniline	chlorobenzene + bromobenzene
(v) ethanol + water	water + nitroic acid	
(vo) carbon tetrachloride + chloroform	diethyl ether + chloroform	

➤ **Azeotropic mixtures i**

Some liquids on mixing form azeotropes which are a 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 is 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	Positively charged cations are in a "sea or pond" of electrons.
Bonding forces	Electrostatic attraction between ions	Shared electrons	van der Waals or Dipole-dipole	Electrostatic attraction between positively charged cations 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 Conductance	Semi-conductor due to crystal imperfections, conductor on 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	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Promotive, Face-centred, Body centred = 3
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Promotive, Body centred = 2
3.	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Promotive = 1
4.	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Promotive, Face-centred, Body centred End centred = 4
5.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$; $\beta \neq 90^\circ$	Promotive, End - centred = 2
6.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Promotive = 1
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Promotive = 1 Total = 14

CUBIC UNIT CELL

<i>Unit cell</i>	<i>Relation between r and a</i>	<i>Packing fraction</i>	<i>Co-ordination number</i>	<i>Effective number of particle</i>
Simple cubic	$r = \frac{a}{2}$	52.4%	6	1
Body centred 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

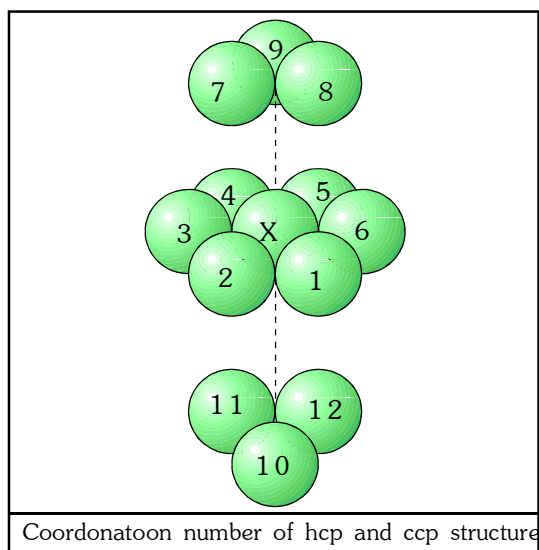
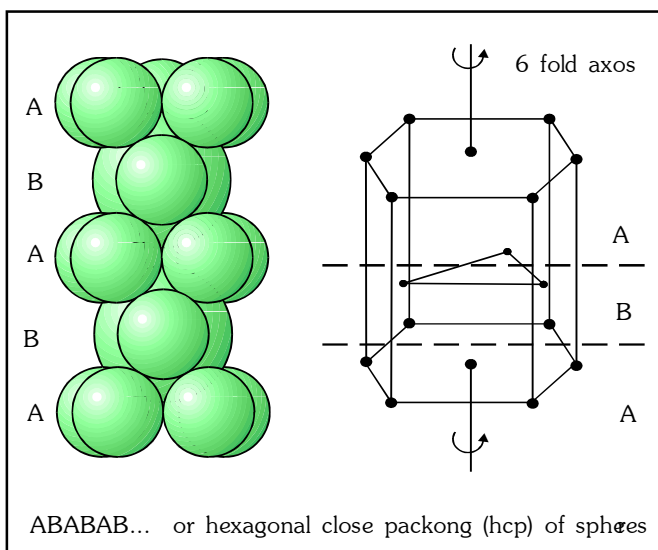
Effective number of octahedral void = 6

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) i**

Effective number of particles = 4

Effective number of octahedral void = 4

Effective number of tetrahedral void = 8

Packing fraction = 74% ;

Coordination number = 12

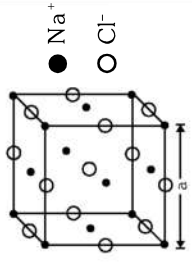
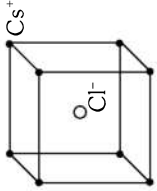
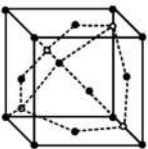
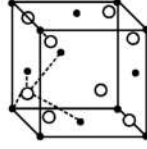
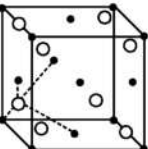
$$\frac{a\sqrt{2}}{4} = r$$

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

Limiting radius ratio for various types of sites

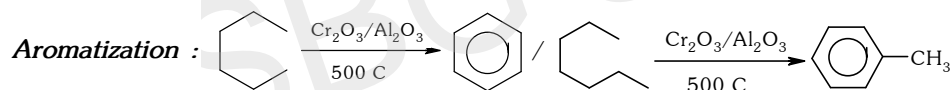
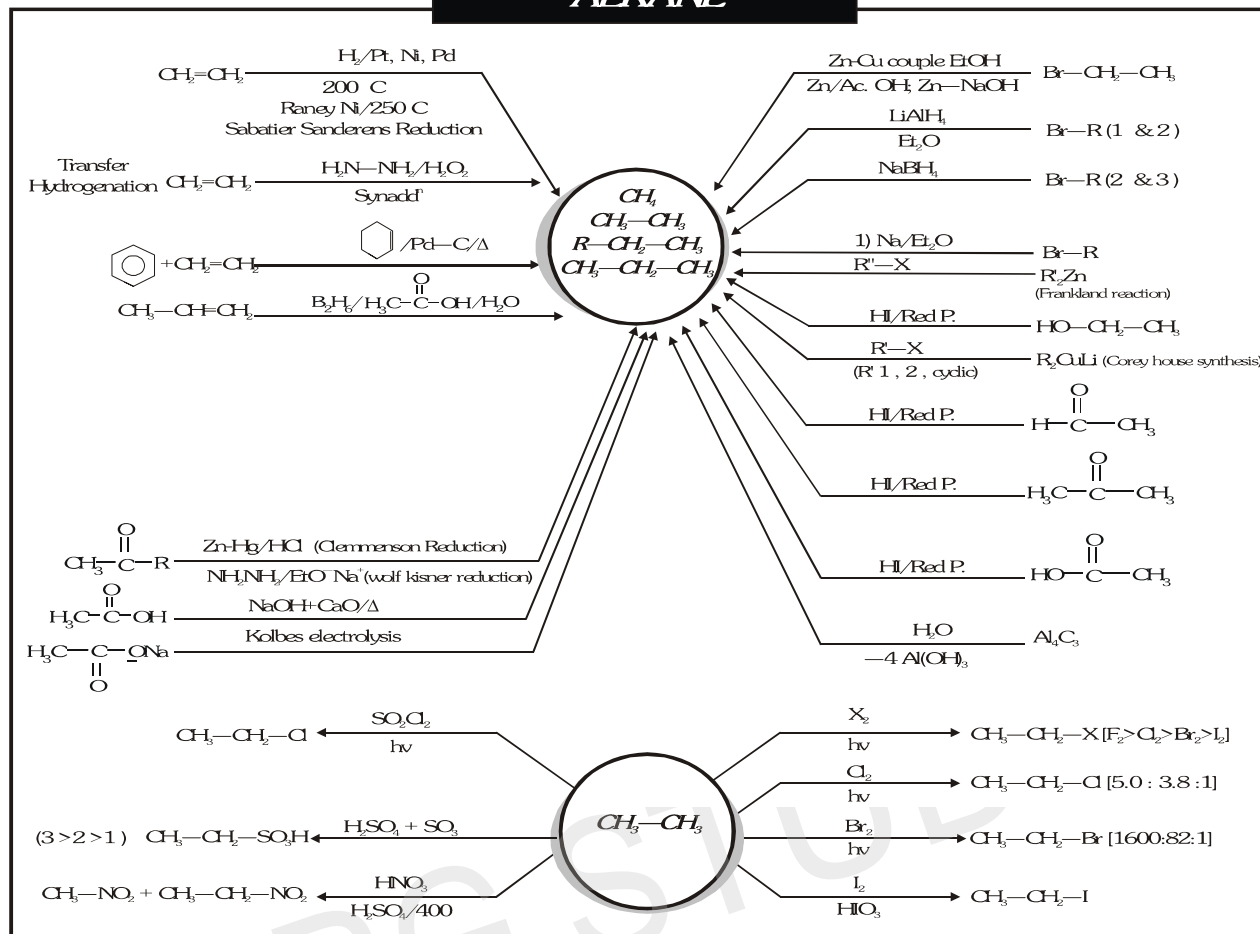
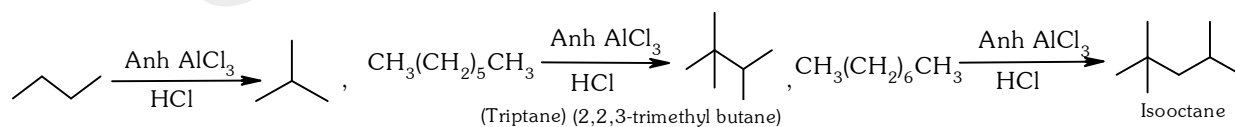
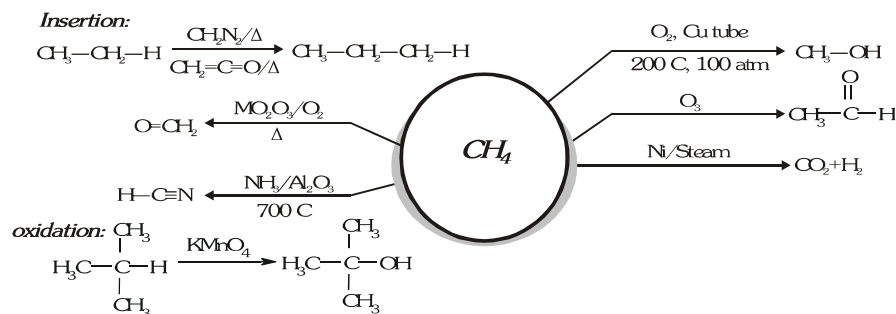
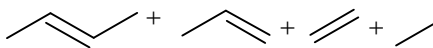
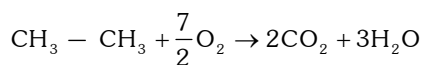
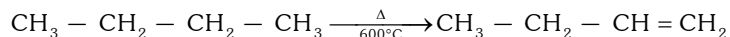
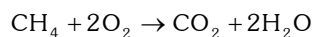
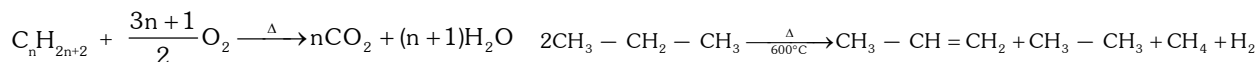
Limiting radius ratio = r/R	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SnO_2
0.414 - 0.732	4	Square planar	–
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl

TYPES OF IONIC CRYSTAL

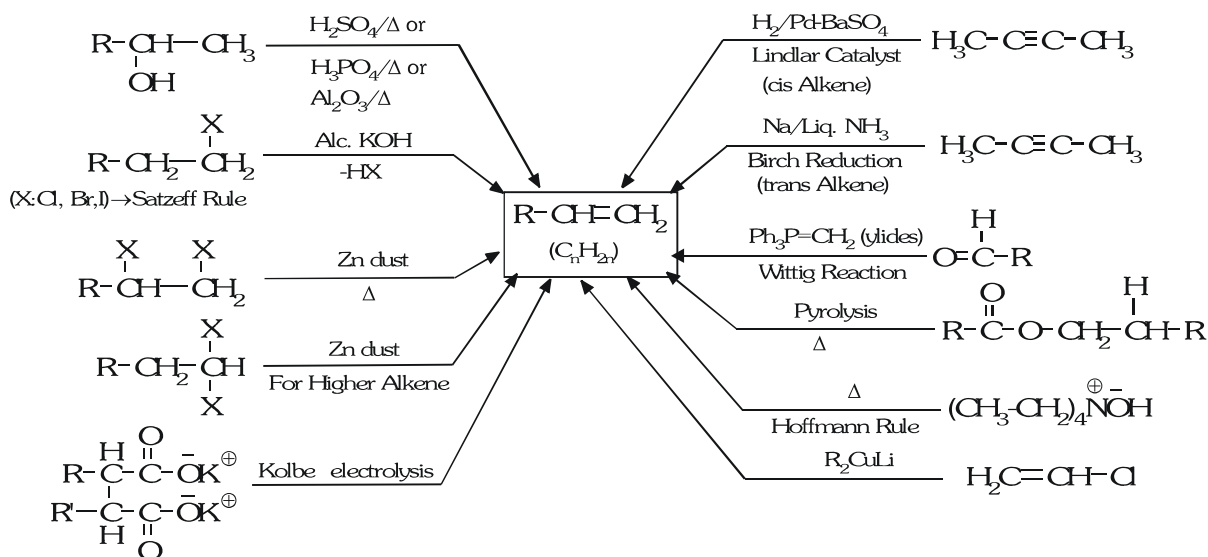
Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.C.	Examples	
1. NaCl (1 : 1) (Rock Salt Type)	$\begin{array}{c} \text{Na}^+ \rightarrow \text{Every element of C.C.P.} \\ \text{C.C.P.} \swarrow \searrow \\ \text{Cl}^- \rightarrow \text{At every THV} \end{array}$	6 : 6	$4\text{Na}^+ + 4\text{Cl}^-$ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of II-A (Some exception) AgF, AgCl, AgBr, NH_4X	
2. CsCl Type (1 : 1)	$\begin{array}{c} \text{Cs}^+ \rightarrow \text{at every corner} \\ \text{B.C.C.} \swarrow \searrow \\ \text{Cl}^- \rightarrow \text{at Body centre or at cubic void} \end{array}$	8 : 8	$1\text{Cs}^+ + 1\text{Cl}^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CaS	
3. ZnS Type (1 : 1) (Zinc Blende Type) (Sphalerite)	$\begin{array}{c} \text{Zn}^{+2} \rightarrow \text{Every element of C.C.P.} \\ \text{C.C.P.} \swarrow \searrow \\ \text{S}^{2-} \rightarrow \text{At 50\% of THV. or at alternate tetrahedral void} \end{array}$	4 : 4	$4\text{Zn}^{+2} + 4\text{S}^{2-}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI	
4. CaF_2 Type (1 : 2) (Fluorite Type)	$\begin{array}{c} \text{Ca}^{+2} \rightarrow \text{Every element of C.C.P.} \\ \text{C.C.P.} \swarrow \searrow \\ \text{F}^- \rightarrow \text{At every THV.} \end{array}$	$4\text{Ca}^{+2}, 8\text{F}^-$ 8 : 4	$4\text{Ca}^{+2} + 8\text{F}^-$ 4CaF_2 (4)	BaCl_2 , BaF_2 SrCl_2 , SrF_2 CaCl_2 , CaF_2	
5. Na_2O Type (2 : 1) (Antifluorine)	$\begin{array}{c} \text{Na}^+ \rightarrow \text{At every THV.} \\ \text{C.C.P.} \swarrow \searrow \\ \text{O}^{2-} \rightarrow \text{Every element of C.C.P.} \end{array}$	$8\text{Na}^+, 4\text{O}^{2-}$ 4 : 8	$8\text{Na}^+ + 4\text{O}^{2-}$ $4\text{Na}_2\text{O}$ (4)	Li_2O , Li_2S Na_2O , Na_2S K_2O , K_2S	
6. ZnS Type (1 : 1) (Wurtzite) another geometry of ZnS	$\begin{array}{c} \text{Zn}^{+2} \rightarrow \text{Every element of H.C.P.} \\ \text{H.C.P.} \swarrow \searrow \\ \text{S}^{2-} \rightarrow 50\% \text{ of THV. or (at alternate THV)} \end{array}$	4 : 4	$6\text{Zn}^{+2} + 6\text{S}^{2-}$ 6ZnS (6)	Same as sphalerite	

ल

ALKANE

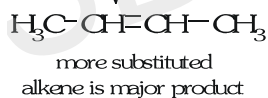
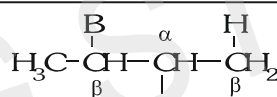
**Iomerization :****Combustion :**

Nutshell Preparation of ALKENE

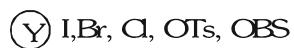


Elimination Reaction

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



Saytzeff Rule



in presence of base



(Alc. KOH)

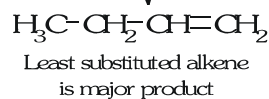
6:1 (trans to cis)

Y: OH/Conc. H_2SO_4/Δ

: OH/ H_3PO_4/Δ

: OH/ Al_2O_3/Δ

: OH/ P_2O_5 or $ZnCl_2/\Delta$



Hoffman Rule

: In presence of bulky base

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

: When y; is $N^+Me_3/OH^-/\Delta$

: $SR_2^+/B^-/\Delta$

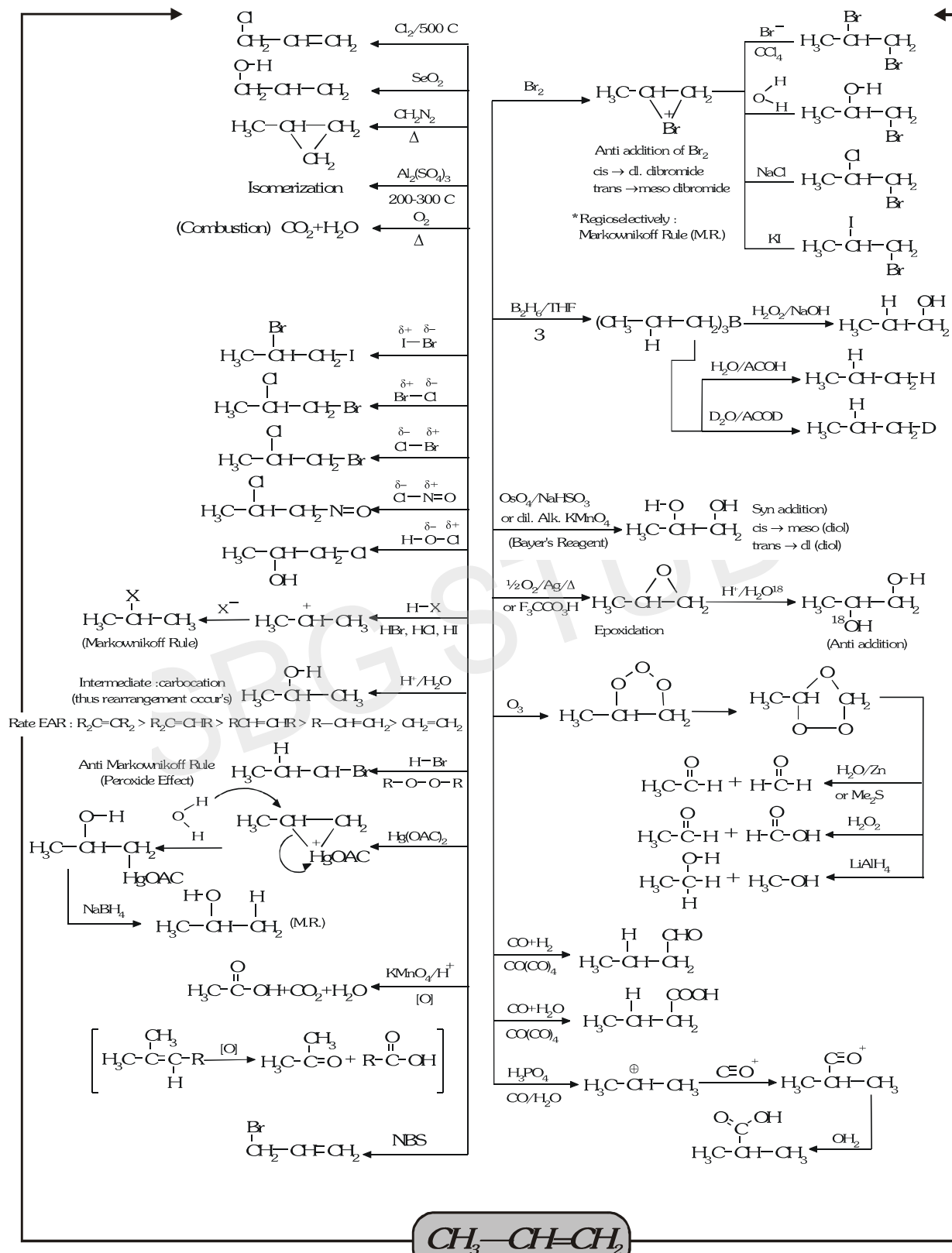
: $NR_2^+/O^-/\Delta$

: F / Base

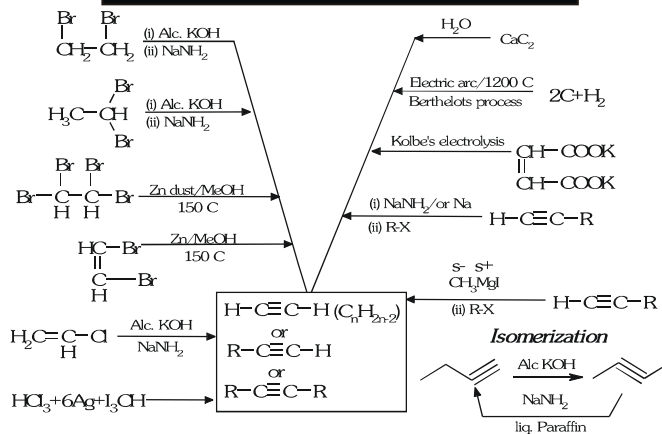
: Pyrolysis of ester

Y: OH/ ThO_2/Δ

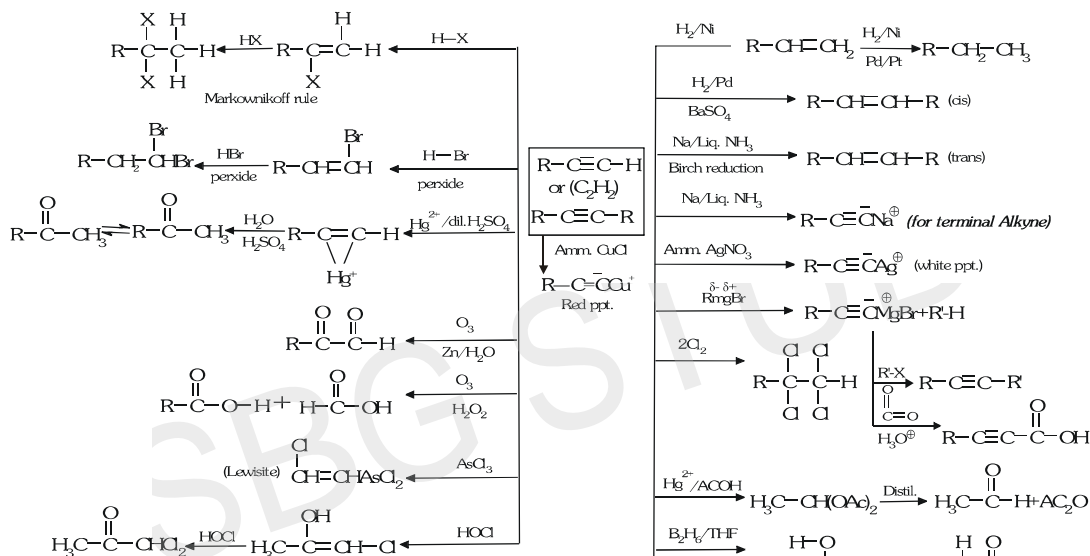
Nut hell reaction of Alkene



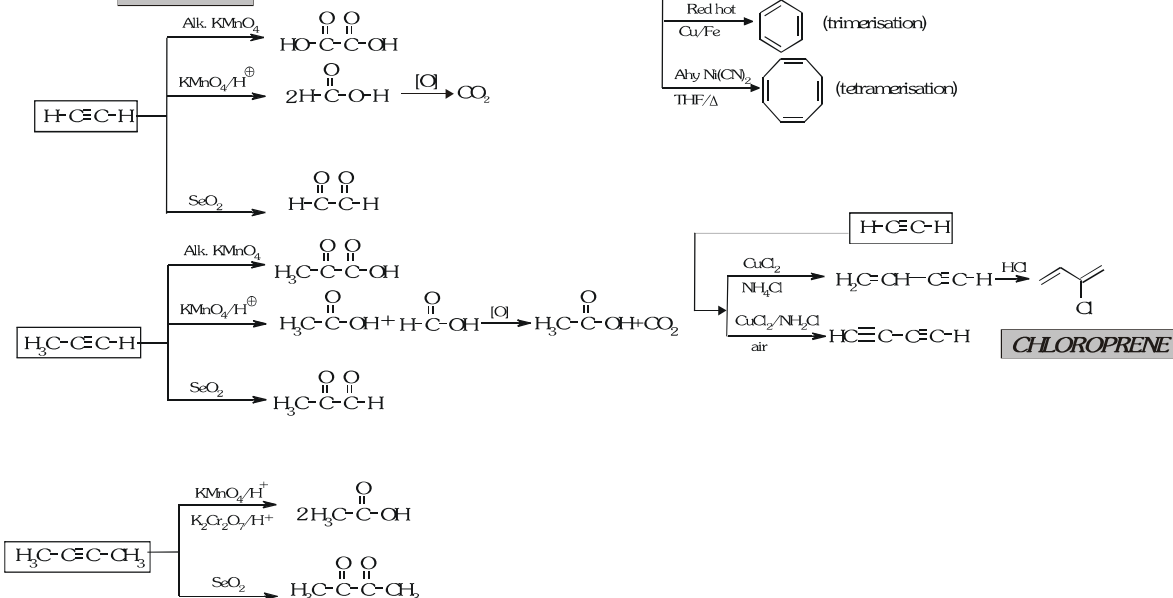
Nutshell Preparation of Alkyne



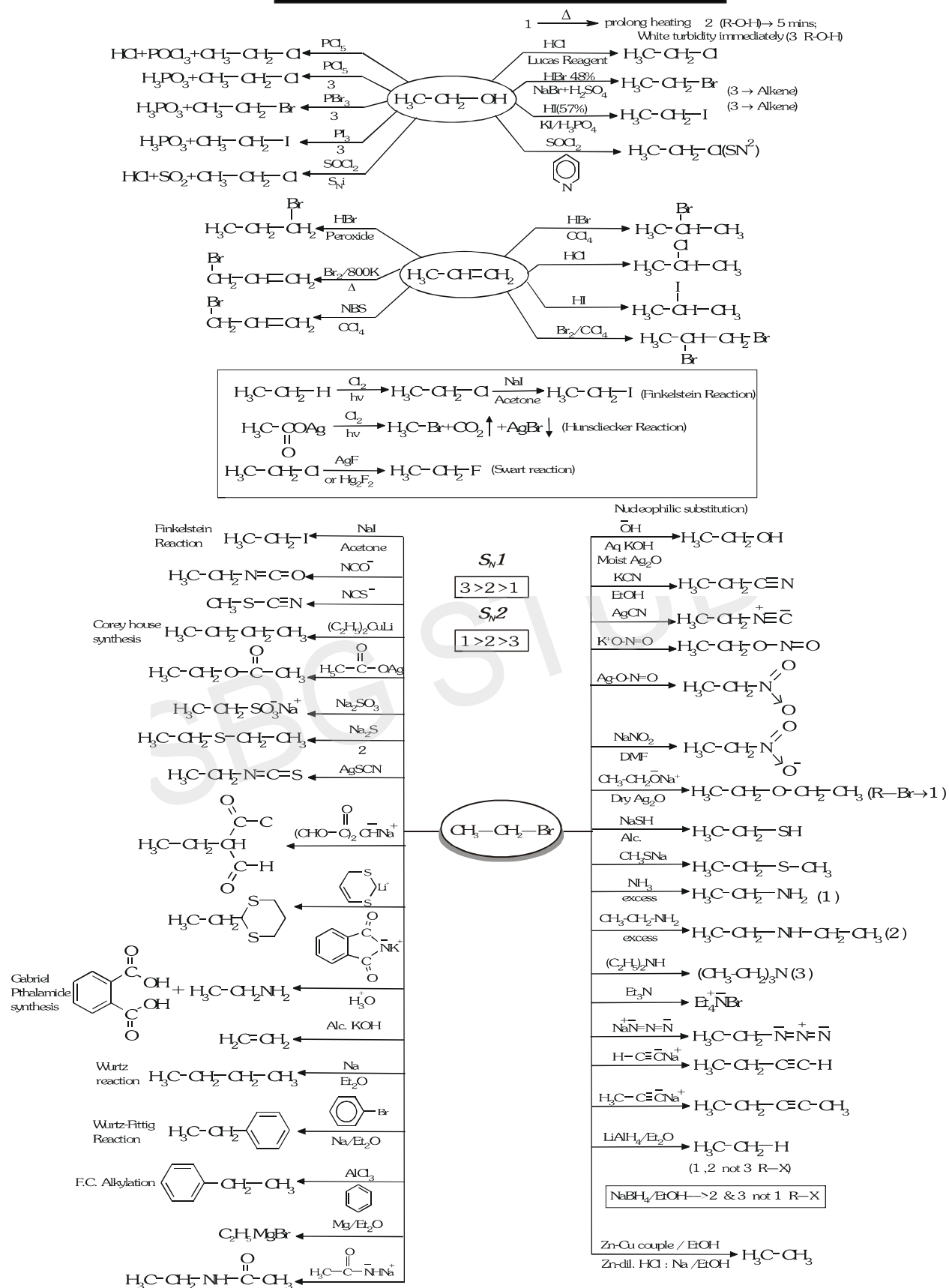
Nutshell reaction of Alkyne



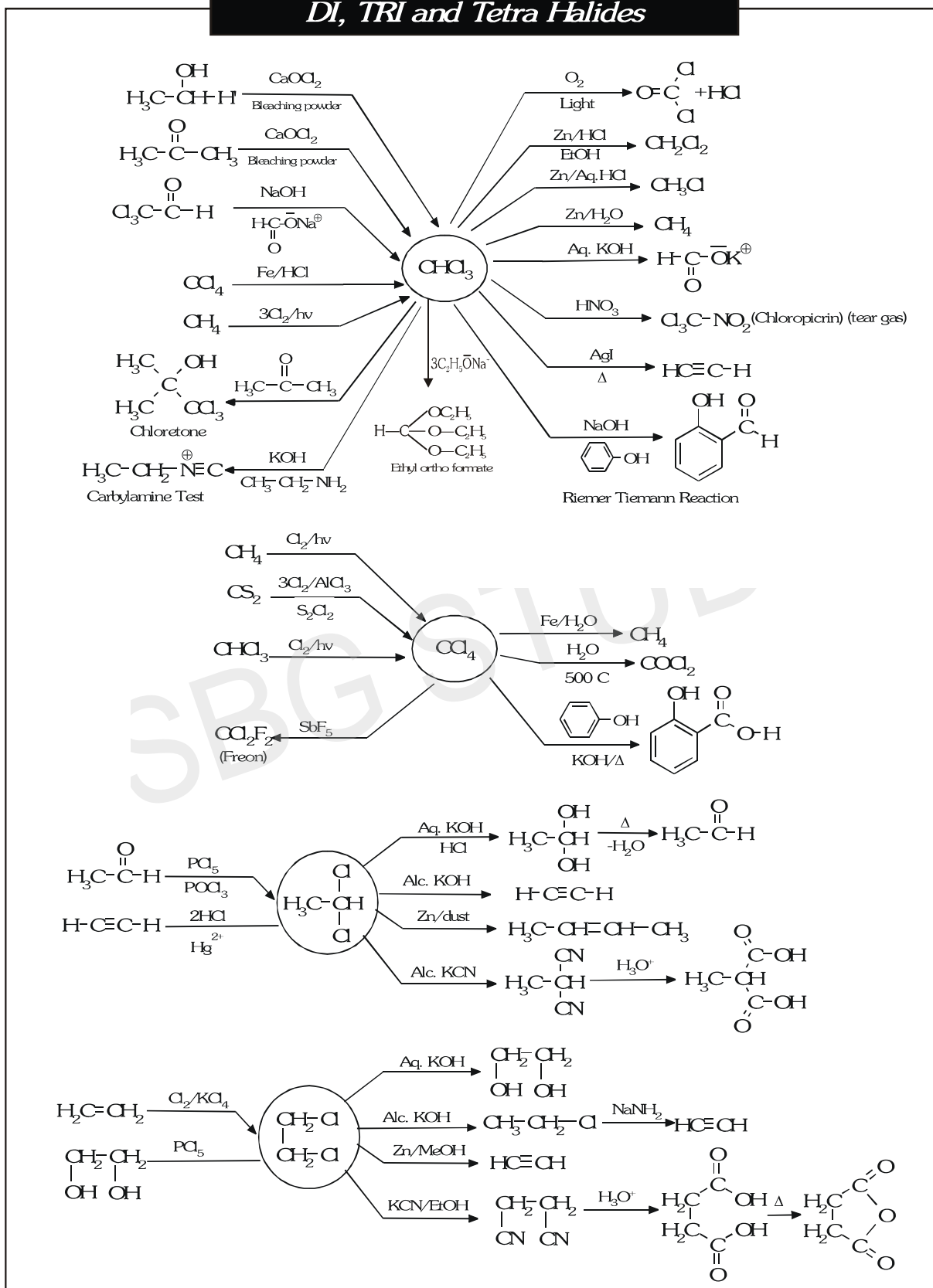
OXIDATION



Nutshell Preparation of ALKYL HALIDE



Nutshell Preparation & Properties of DI, TRI and Tetra Halides



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

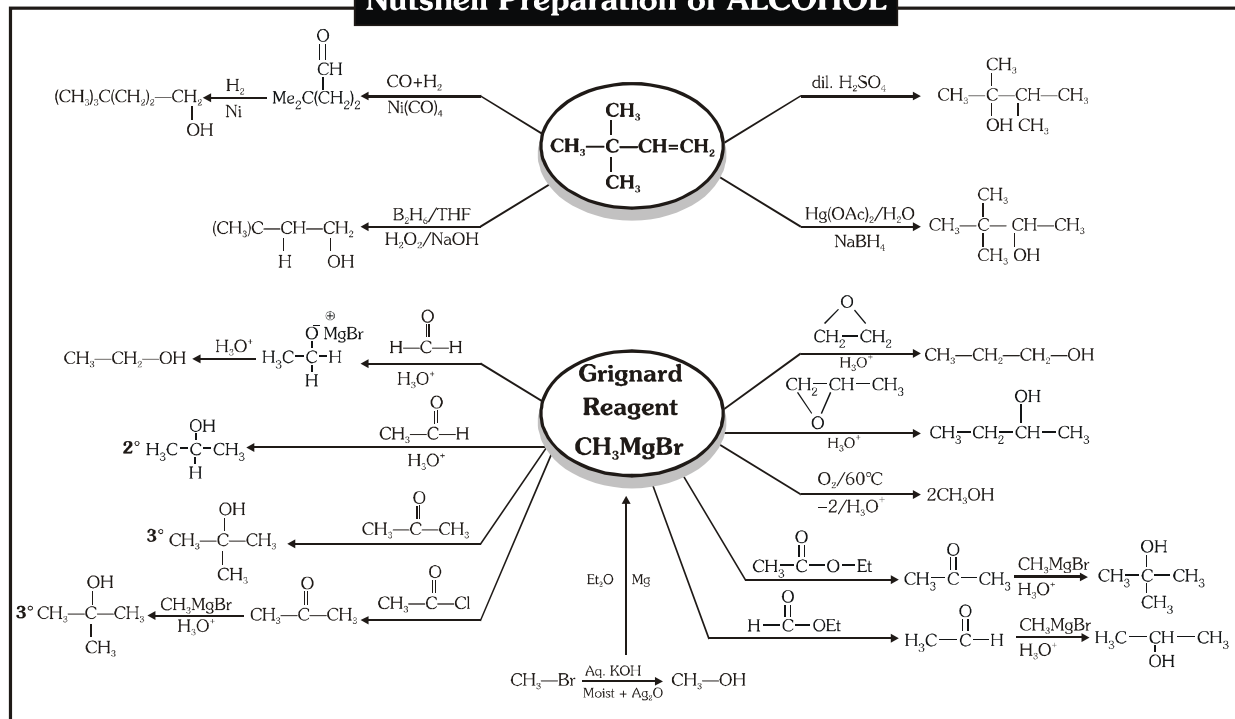
Comparison of $E1$ and $E2$

		$E1$	$E2$
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

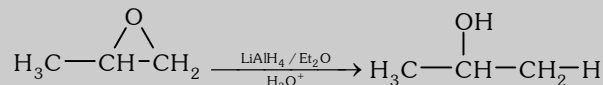
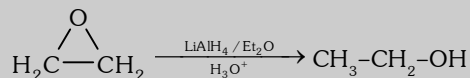
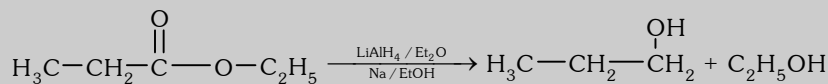
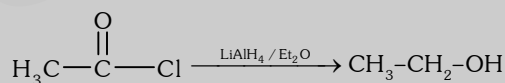
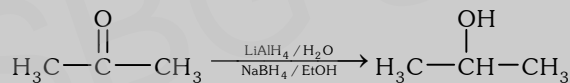
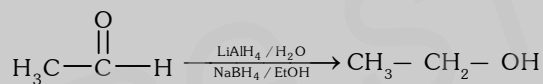
Summary of S_N1 , S_N2 , $E1$, and $E2$ reaction

RX	Mechanism	$Nu:]^-/B:]^-$	Solvent	Temp.
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

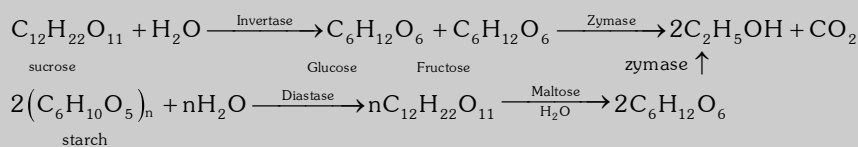
Nutshell Preparation of ALCOHOL

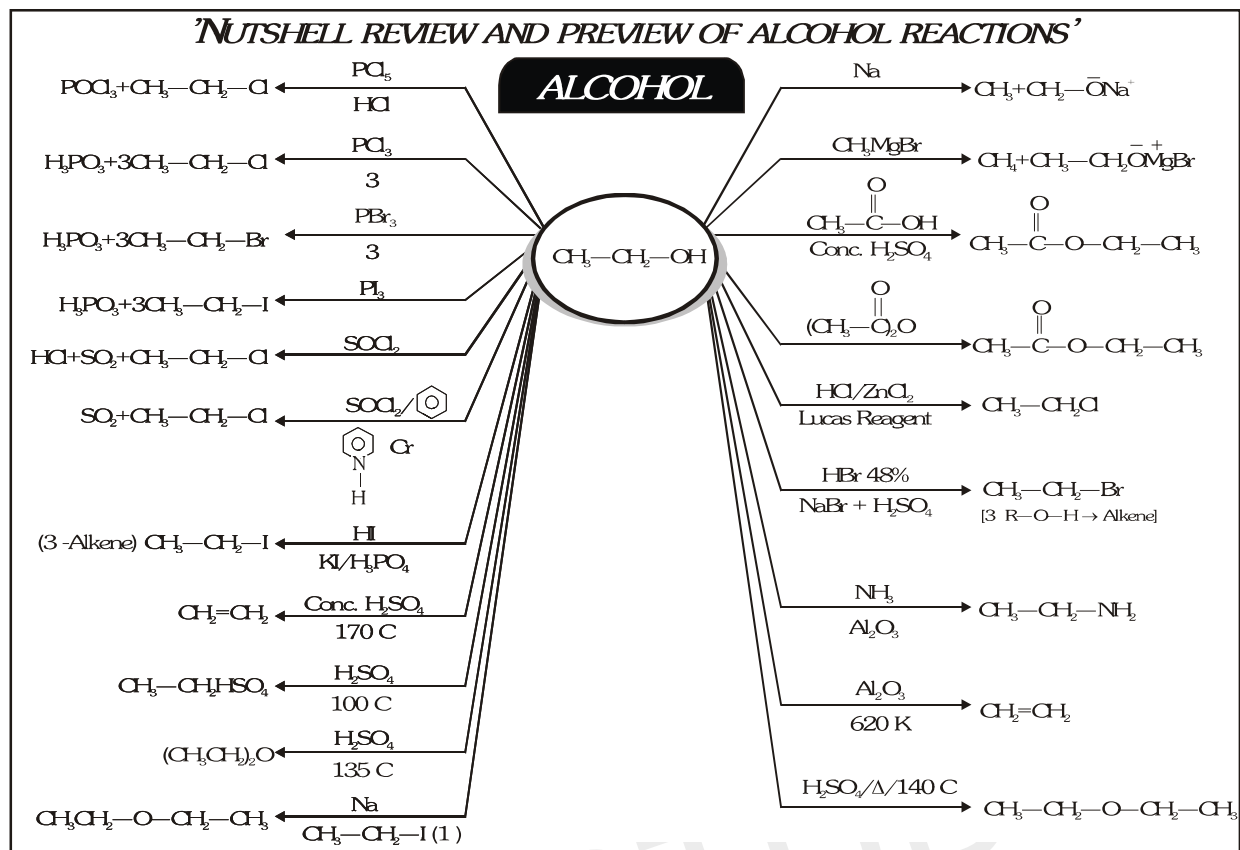


• Reduction



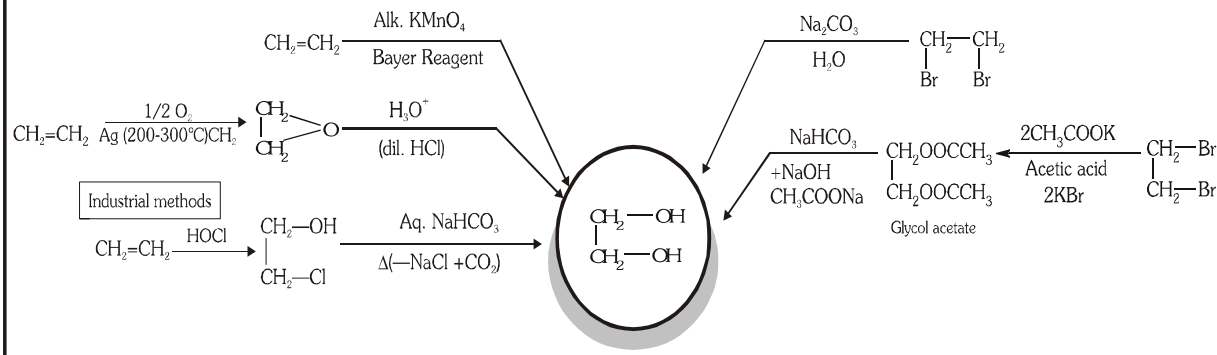
• By Fermentation



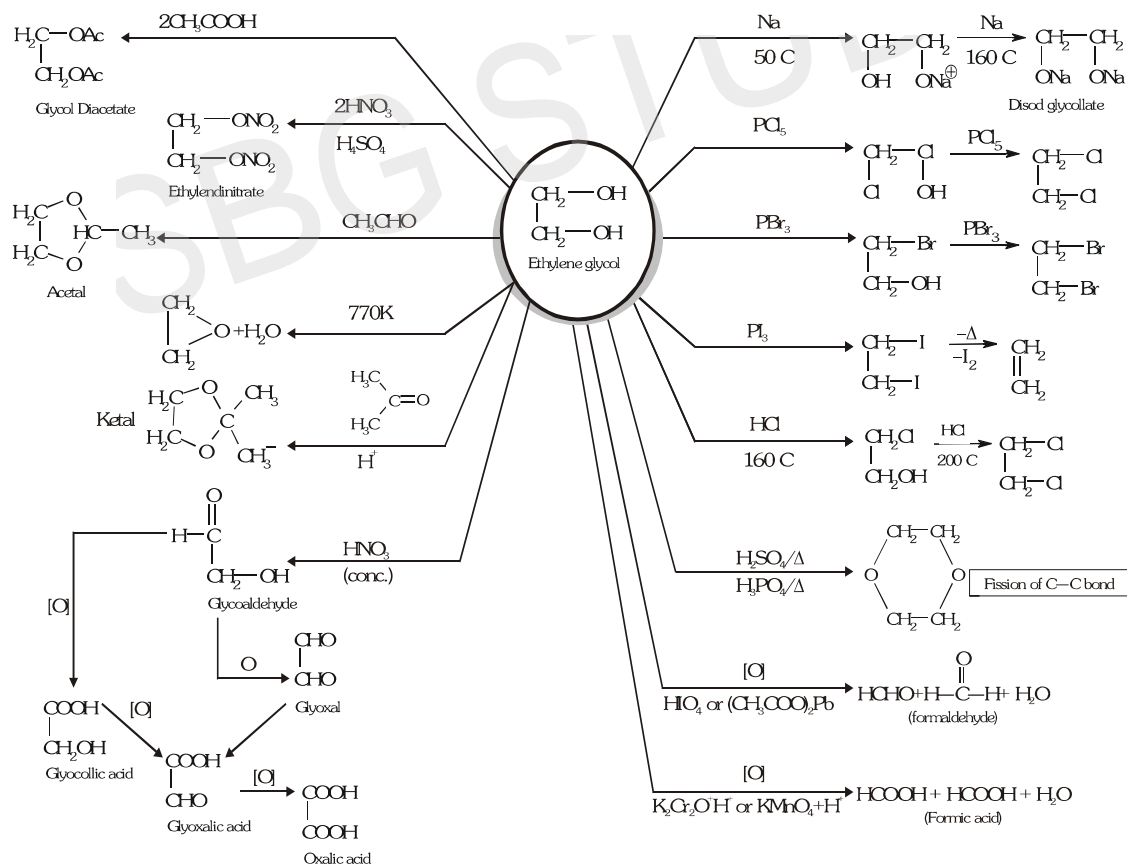


Reagent	$\begin{array}{c} \text{OH} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\ \text{1 Alcohol} \end{array}$	$\begin{array}{c} ^{18}\text{OH} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \text{2 Alcohol} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \\ \text{3 Alcohol} \end{array}$
PCC/CH ₂ Cl ₂ PDC/CH ₂ Cl ₂ Jones Reagent H ₂ CrO ₄ /Aq. Acetone	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{O} .8 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \end{array}$	No reaction
$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ $\text{KMnO}_4/\text{H}^+/\text{OH}^-/\Delta$	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \quad \text{O} .8 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{OH} + \text{CH}_3-\text{C}-\text{OH} \end{array}$	
Cu/500 C	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}=\text{CH}_2 \end{array}$
$\text{Al}(\text{O}i\text{Bu})_3$ Acetone or cyclohexanone	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \end{array}$	-
Lucas Reagent HCl/ZnCl ₂	Cloudiness appear upon heating after 30 mins. at normal temp. no. reaction	within five min.	Immediately
Victor Mayer' Test			
P/I ₂	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{I} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{I} \\ \\ \text{CH}_3 \end{array}$
AgNO ₃	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NO}_2$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{NO}_2 \end{array}$	$(\text{CH}_3)_3-\text{NO}_2$
HNO ₂ NaOH	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{NO}_2 \\ \\ \text{N}-\text{OH} \\ \text{Nitrolic acid} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{NO}_2 \\ \\ \text{N}=\text{O} \end{array}$	No reaction ↓

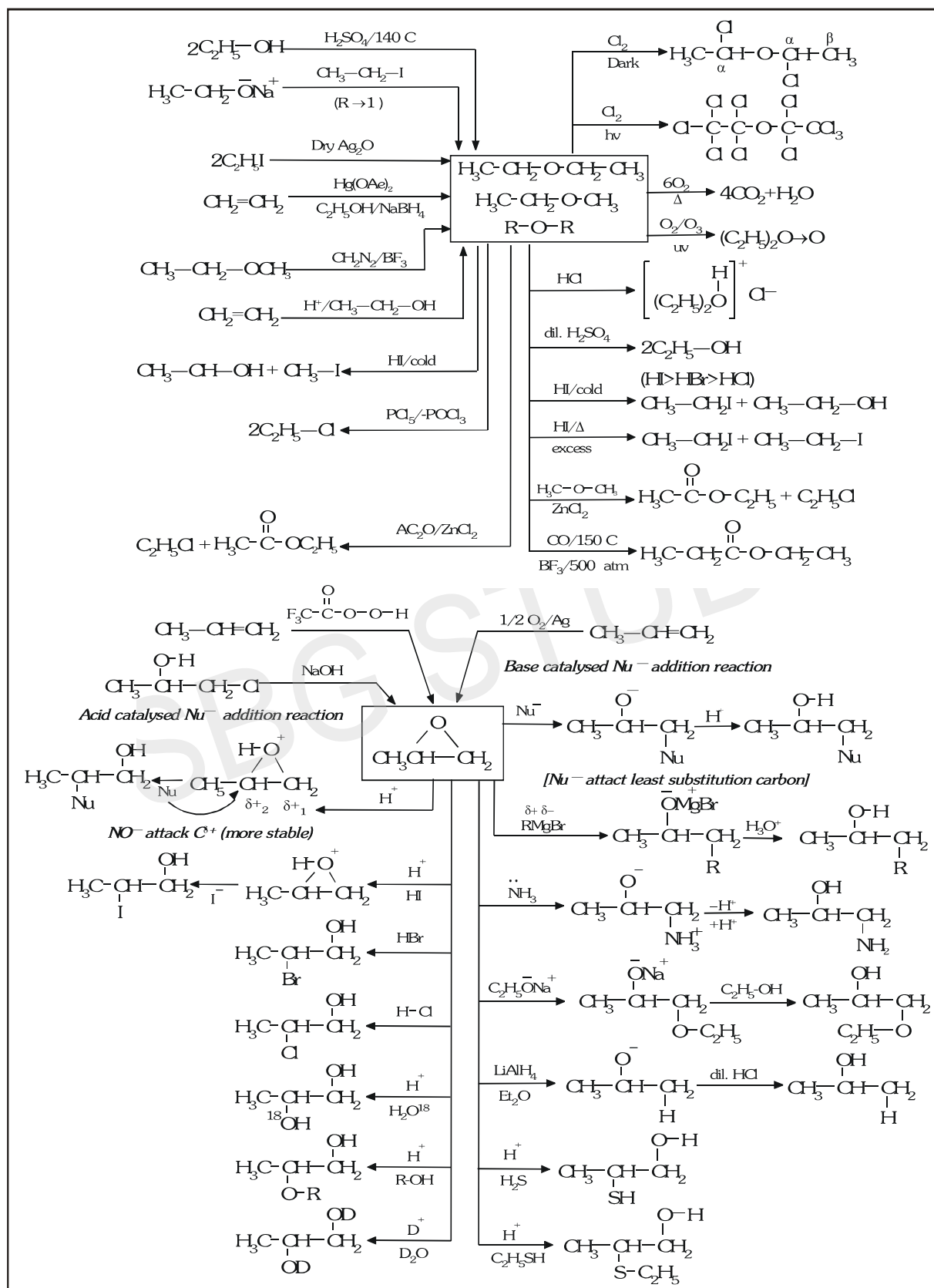
Methods of Preparation (Antifreeze Agent)



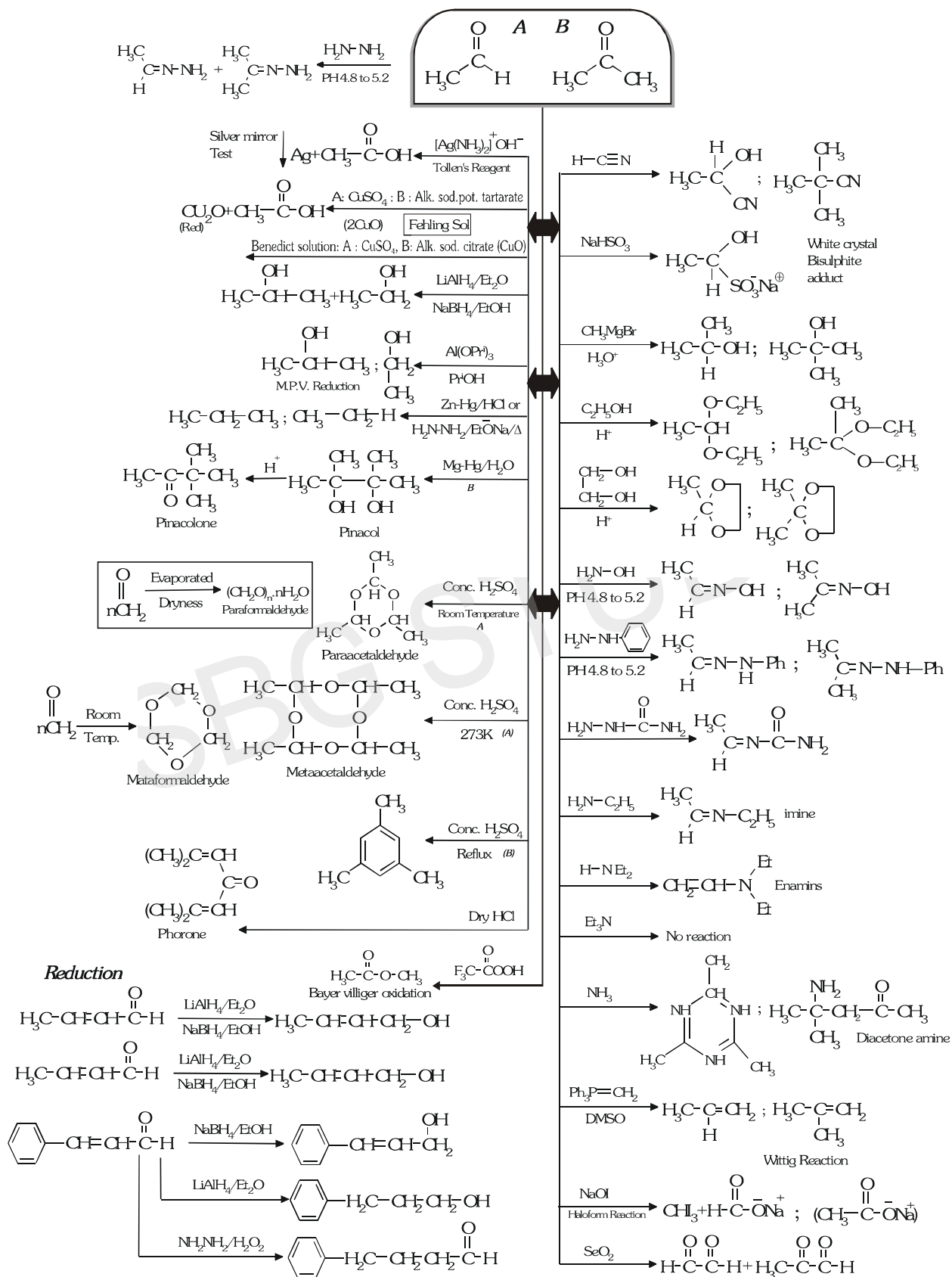
Two 1° Alcoholic group : one OH group always react completely before other group react



Nutshell review and preview Ether & Epoxides

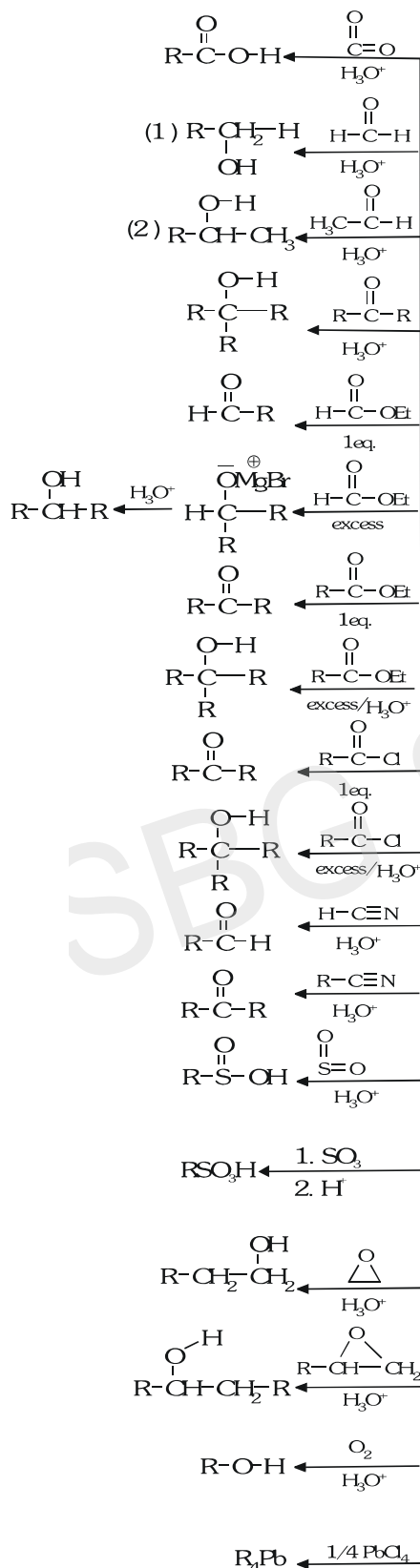


Nutshell preview and review of Carbonyl Reaction



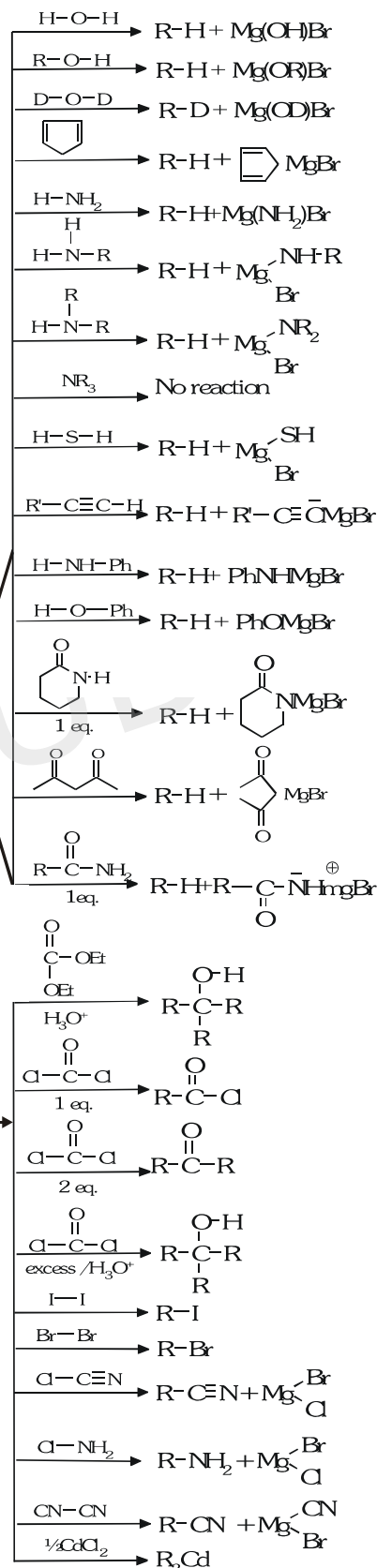
As Nucleophile :

GRIGNARD -REAGENT



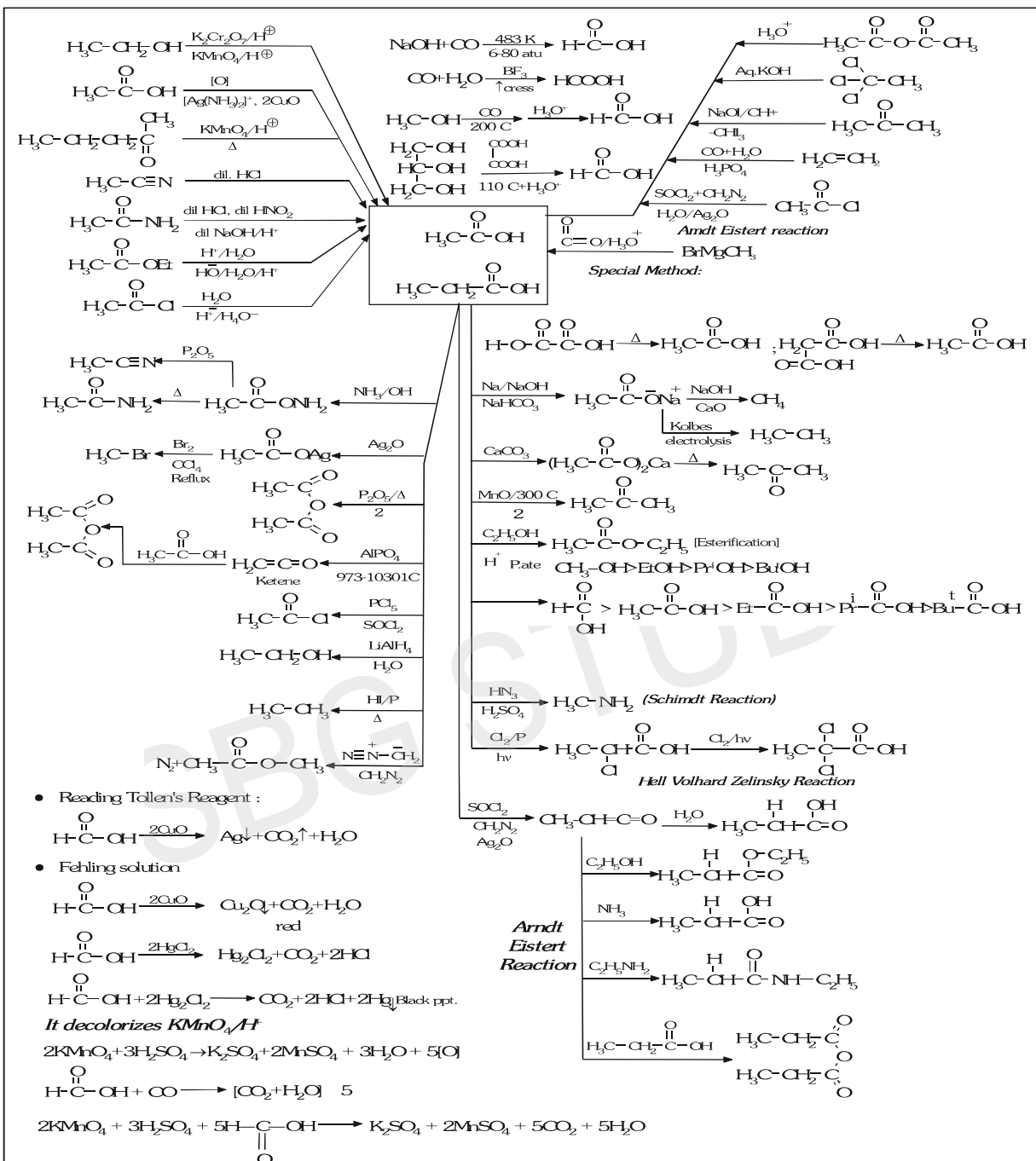
(Active H-containing comp)

GRIGNARD REAGENT as BASE

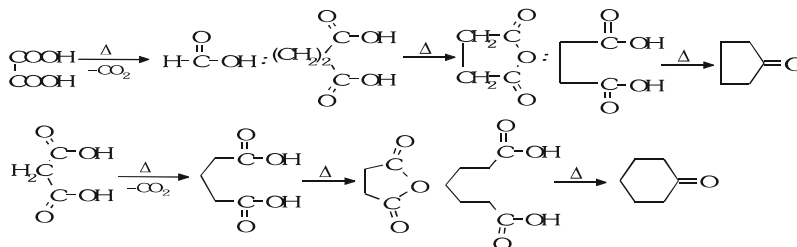


Nut hell preview and review of Carboxylic Acid

PREPARATION & REACTION

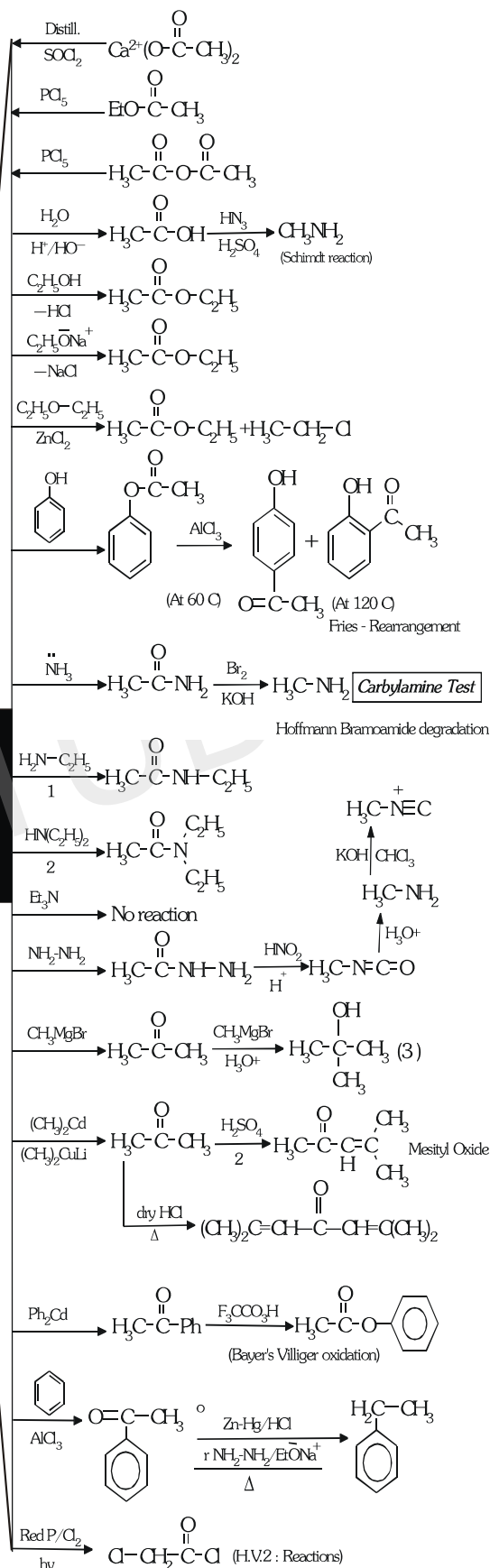


Note : Formic acid does not react with NH_2OH ; secarbazide & phenyl / hydrazide

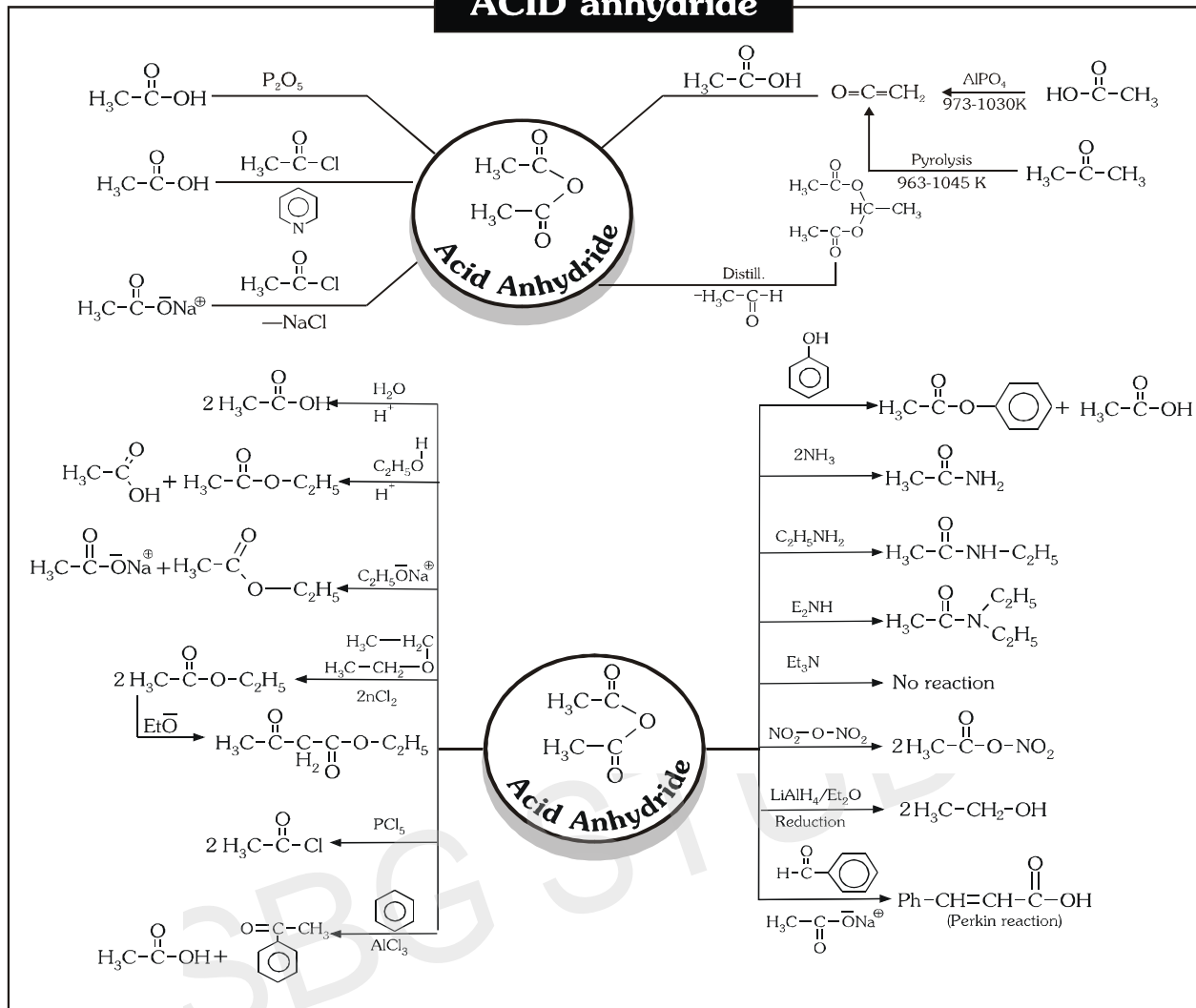


$$\begin{array}{c} \text{O}^{\delta-} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{Cl} \\ \delta+ \end{array}$$

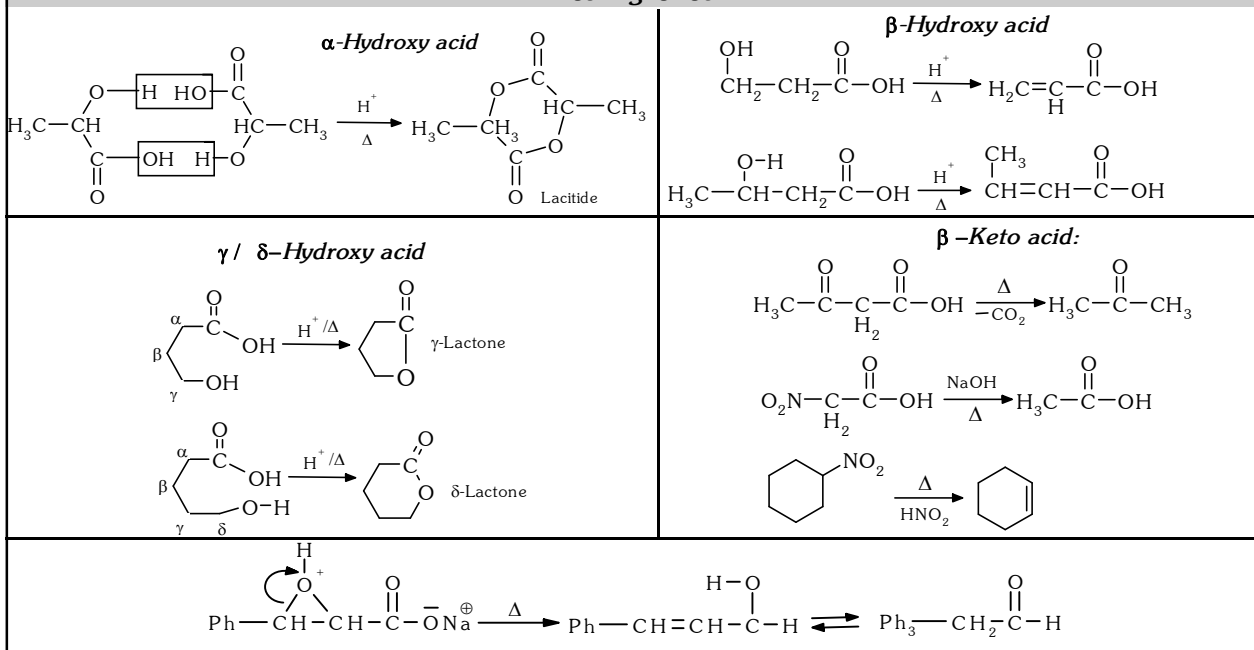
Acetyl Chloride



ACID anhydride



Heating effect



Nutshell preparation of Ester

$\text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{OH} + \text{H}_3-\text{CH}_2-\text{CH}_2-\text{OH} \xrightarrow[\Delta]{\text{H}_2\text{SO}_4}$

$\text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{OH} + \text{H}_3-\text{CH}_2-\text{CH}_2-\text{OH} \xrightarrow{\text{ThO}_2}$

$\text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{F}_3\text{COO}_3\text{H}}$

$\text{H}_3\text{C}-\text{O}-\text{CH}_3 \xrightarrow[\text{BF}_3/350\text{K}]{\text{CO}}$

$\text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{OAg} \xrightarrow[\text{-AgI}]{\text{H}_3\text{C}-\text{CH}_2-\text{I}}$

Bayer villiger oxidation

$\text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_3$

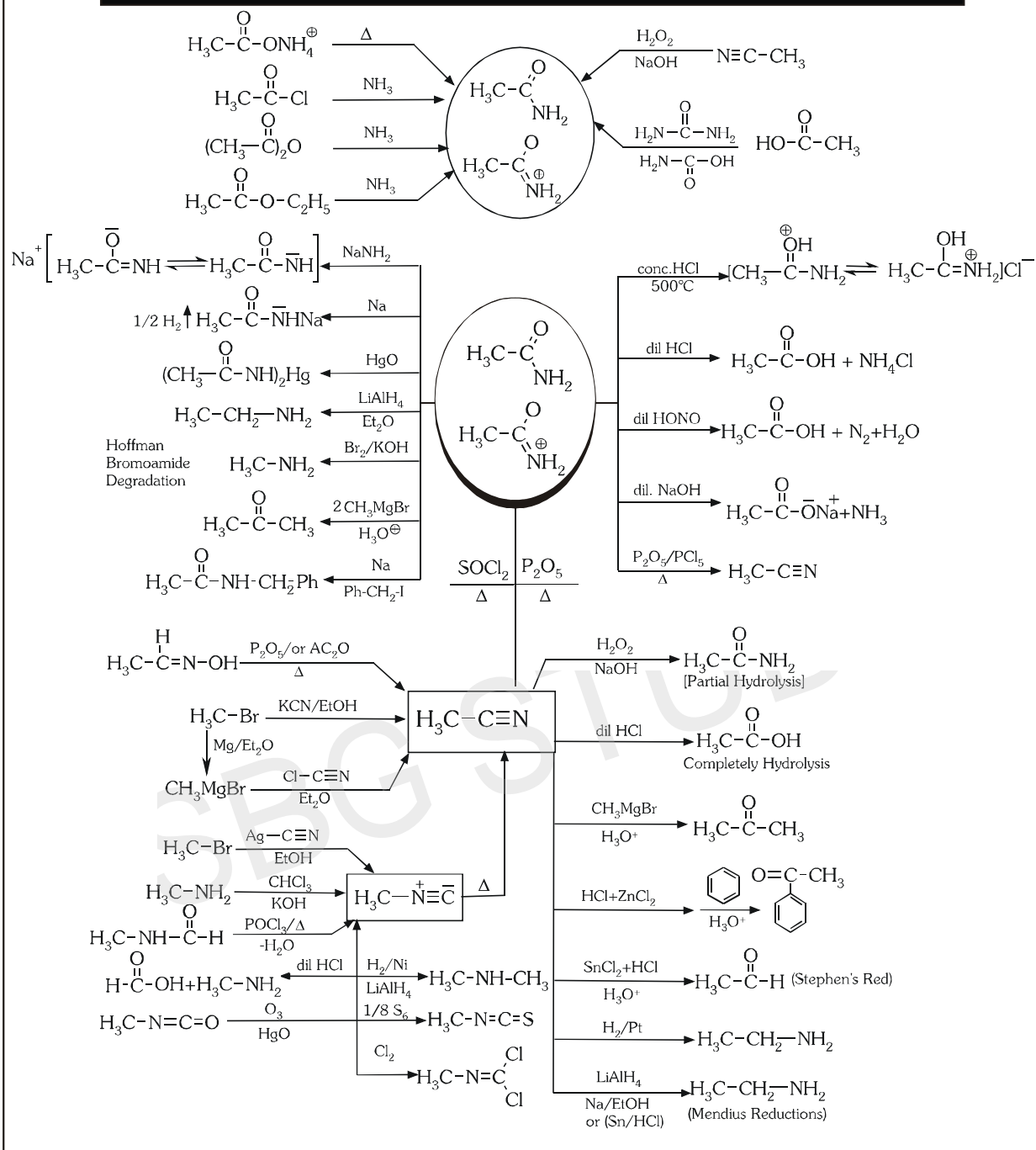
$\text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{H} + \text{H}_2\text{N}-\text{CH}_2-\text{N}_2 \rightarrow \text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{CH}_3$

$\text{C}_2\text{H}_5\text{OH}$ or $\text{CH}_3-\text{CH}_2-\text{ONa}^+$ $\rightarrow \text{H}_3\text{C}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{CH}_3$

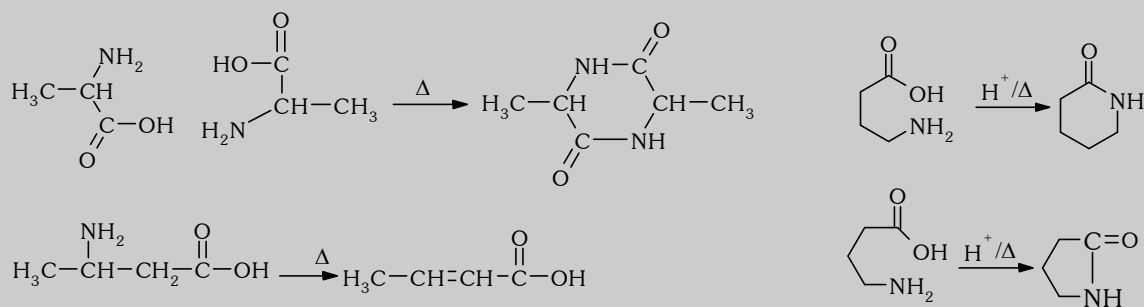
$\text{Al}(\text{OEt})_3$ Tischenko Reaction $\rightarrow \text{H}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_3$

[illegible]

Nutshell preview and review of Amide, Cyanide and Isocyanide

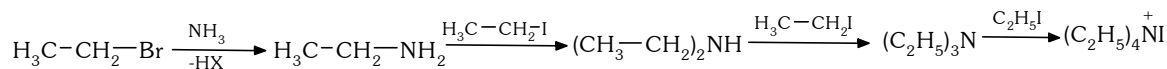


Amino Acid :



METHOD OF PREPARATION OF AMINE

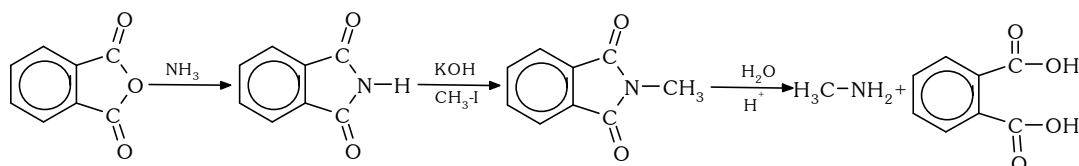
Hoffmann's Ammonolysis



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

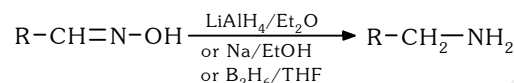
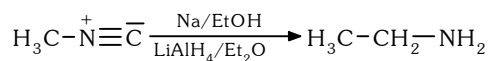
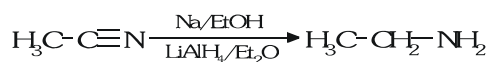
Reactivity - $\text{R-I} > \text{R-Br} > \text{R-Cl}$

Gabriel / Phthalimide Synthesis :

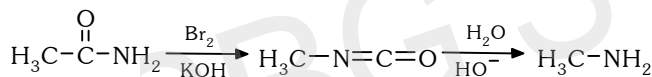


2 & 3 → can't be prepared : Aromatic amine can't be prepared

Reduction



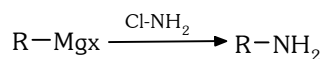
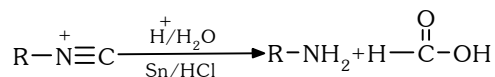
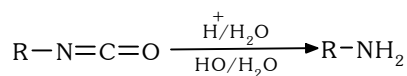
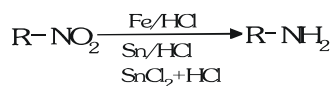
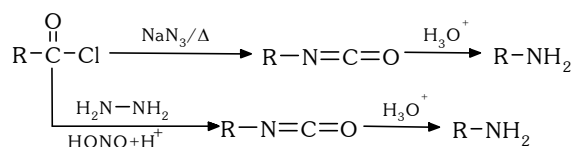
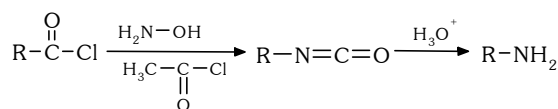
Hoffmann Boroamide Degradation :



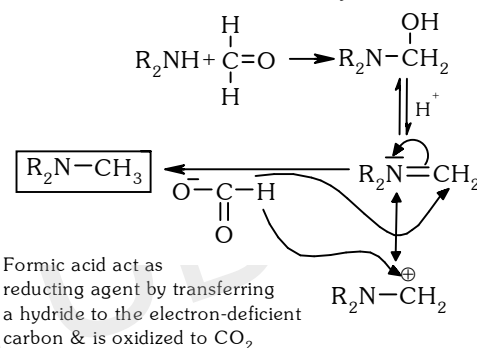
Schmidt Reaction :



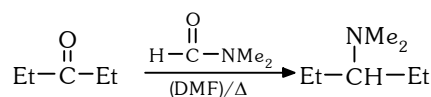
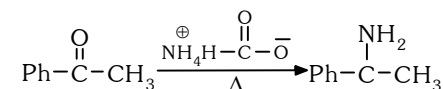
Lo en Reaction



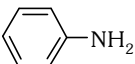
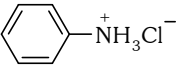
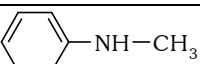
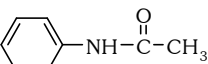
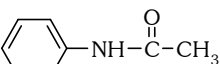
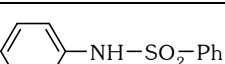
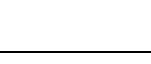
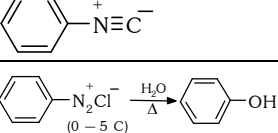
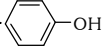
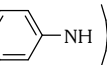
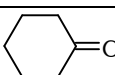
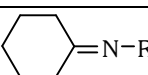
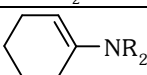
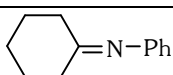
Eschevier Blarke synthesis



Reductive Amination Leuckart reaction



CHEMICAL PROPERTIES OF AMINES

Reagent	$R-\ddot{N}H_2$ (1)	R_2NH (2)	R_3N (3)	
1. HCl	$R-\overset{+}{N}H_3Cl^-$	$R_2NH_2Cl^-$	$R_3N^+-Cl^-$ H	
2. CH_3-Br	$R-NH-CH_3$	R_2NH-CH_3	$R_3N^+-CH_3Br^-$	
3. $H_3C-\overset{O}{\parallel}C-Cl$	$R-NH-\overset{O}{\parallel}C-CH_3$	$R_2N-\overset{O}{\parallel}C-CH_3$	No reaction	
4. $(CH_3-\overset{O}{\parallel}C)_2O$	$R-NH-\overset{O}{\parallel}C-CH_3$	$R_2N-\overset{O}{\parallel}C-CH_3$	No reaction	
5. $Ph-SO_2Cl$	$R-N-\overset{O}{\parallel}SO_2-Ph$ H ↓ NaOH [R-N-SO ₂ -Ph]Na ⁺	$R_2N-\overset{O}{\parallel}SO_2-Ph$ ↓ NaOH Insoluble	No reaction	
6. Carbylamine Test $CHCl_3/KOH$ ($:-CCl_2$)	$R-\overset{+}{N}\equiv C^-$	No reaction	No reaction	
7. $HNO=O / H^+$	$R-OH+N_2+HCl$	$R_2N-N=O$	$R_3N^+-HON=O$	 $\xrightarrow[\Delta]{H_2O}$ 
8. Hoffmann Mustard Oil Test				
1. $\begin{matrix} S \\ \\ C=S \end{matrix}$ $\Delta/HgCl_2$	$R-NH-\overset{S}{\parallel}C-SH$ $R-N=C=S + HgS$	$R_2N-\overset{S}{\parallel}C-SH$ No reaction	- No reaction	\xrightarrow{KOH}  \xrightarrow{HCl} $Ph-N=C=S + Ph-NH_2$
2. Hoffmann Test $\begin{matrix} COOEt \\ \\ COOEt \end{matrix}$	$\begin{matrix} CONH-R \\ \\ CONH-R \end{matrix}$ Oxamide (solid)	$\begin{matrix} O=C-NR_2 \\ \\ COOEt \end{matrix}$ Oxamic ester (liquid)	No reaction	$\begin{matrix} O=C-NH-Ph \\ \\ O=C-NH-Ph \end{matrix}$
$R'MgX$	$R'-H+R-NH-MgBr$	$R''H+R_2NMgBr$	No reaction	$R'H+PhNH-MgBr$
			No reaction	
$O=C\begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$	$(RNH)_2C=O$	$(R_2N)_2C=O$	No reaction	$Ph-N=C=O$
$Ph-N=C=O$	$Ph-NH-\overset{O}{\parallel}C-NH-R$	$Ph-NH-\overset{O}{\parallel}C-N\begin{matrix} R \\ R \end{matrix}$	No reaction	$Ph-NH-\overset{O}{\parallel}C-NH-Ph$
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	$R-CH_2-NH-OH$ $R-C=N-OH$ OH	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		$R_3C-NH_2 \xrightarrow{KMnO_4} R_3C-NH_2$		

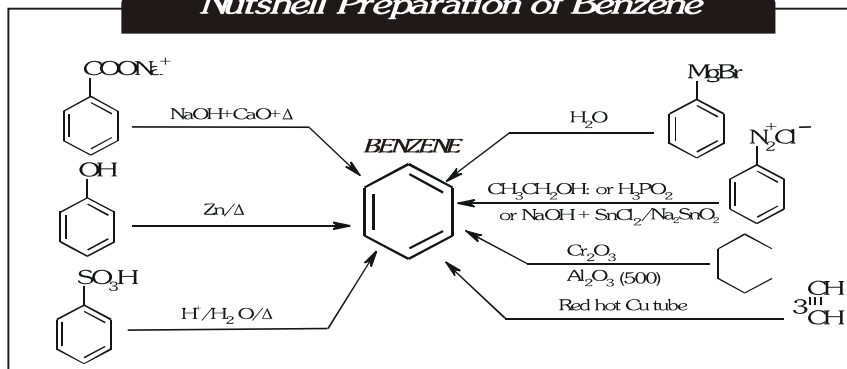
$\text{H}_3\text{C-I} \xrightarrow{\text{AgNO}_2, \text{C}_2\text{H}_5\text{OH}} \text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$
 $\text{H}_3\text{C-I} \xrightarrow{\text{NaNO}_2, \text{DMF or DMSO}} \text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$
 $\text{CH}_3\text{COCl} \xrightarrow{\text{H}_2\text{SO}_4 + \text{HNO}_3, 675\text{K}} \text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$
 $\text{CH}_3\text{COCl} \xrightarrow{\text{AgNO}_2, \text{NaOH/boil}} \text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{HNO}_3 + \text{H}_2\text{SO}_4, 675\text{K}}$
 $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_3$
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$
 $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{NO}_2 + \text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$

$\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{LiAlH}_4, \text{Et}_2\text{O}} \text{H}_3\text{C-NH}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{H}_2/\text{Pt}, \text{H}_2/\text{Raney Ni}} \text{H}_3\text{C-NH}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{NaOH}, \text{Br}_2} \text{H}_3\text{C-NH-CH}_2\text{Br}$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{NaOH}, \text{H}_3\text{C-CO-OEt}} \text{H}_3\text{C-NH-CH}_2\text{NO}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{NaOH}, \Delta} \text{H}_3\text{C-NH-CH=CH-NO}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\Delta} \text{CH}_2=\text{CH}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{Zn/HCl}, \text{Fe/HCl}, \text{Sn/HCl}} \text{H}_3\text{C-NH}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{Zn-NH}_4\text{Cl}, \text{H}_2\text{O}} \text{H}_3\text{C-NH-OH}$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{NaOH}, \Delta} \text{H}_3\text{C-NH-CH=CH-NO}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{NaOH}, \text{H}_3\text{C-CO-H}} \text{H}_3\text{C-NH-CH=CH-NO}_2$
 $\text{H}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{NaOH}} \text{H}_2\text{C=N-OH} \xrightarrow{\text{H}_2\text{SO}_4, 50\%} \text{H-C(=O)-H} + \text{H}_2\text{O}$

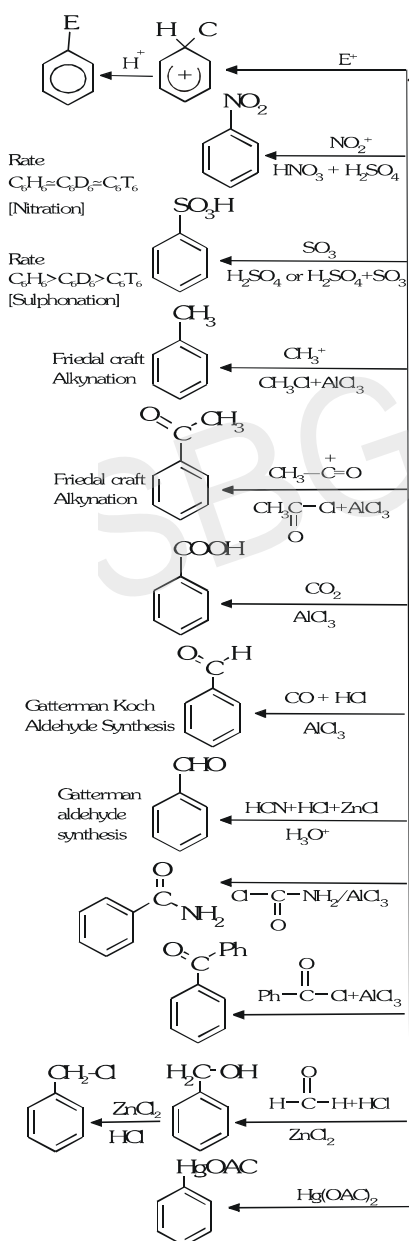
$\text{R-CH}_2\text{-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{HNO}_2} \text{R-C(=O)-NO}_2$
 $\text{R-C(=O)-NO}_2 \xrightarrow{\text{NaOH}} \text{red}$
 $\text{R}_2\text{CH-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{HNO}_2} \text{R}_2\text{CH-N=O}$
 $\text{R}_2\text{CH-N=O} \xrightarrow{\text{NaOH}} \text{Blue}$
 $\text{R}_3\text{C-N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix} \xrightarrow{\text{HNO}_2} \text{No Reaction}$
 $\text{No Reaction} \rightarrow \text{Victor-mayers Test}$

Nutshell Preparation of Benzene

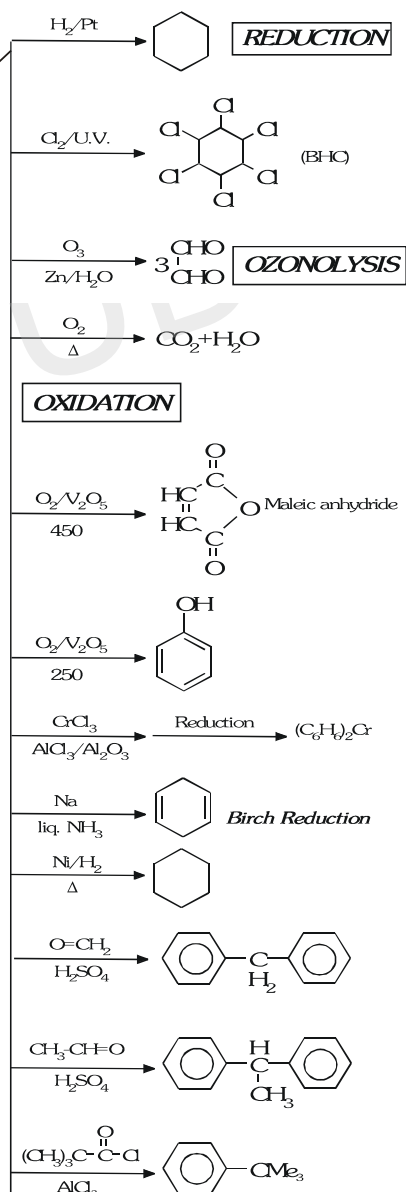
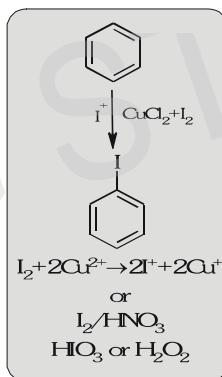


Nutshell Review and Preview of Benzene Reactions

Electrophilic Substitution Reactions



BENZENE



Electrophilic Substitution Reactions

OXIDATION

ETARD REACTION

OXIDATION

Oxidation

If α is absent

Nut Shell preparation 'Aromatic Halogen Compound'

The diagram illustrates the various chemical reactions of benzene to produce aromatic halogen compounds and other derivatives. The central benzene ring is the starting material for all these reactions.

Top Left Reactions:

- Iodination:** Benzene reacts with I_2 and HgO or HNO_3 to form iodobenzene.
- Chlorination (Rashig Process):** Benzene reacts with $HCl + \frac{1}{2} O_2$ and $CuCl + 300^\circ C$ to form chlorobenzene.

Top Right Reactions:

- Chlorination:** Benzene reacts with $Cl_2/FeCl_3$ to form chlorobenzene.
- Bromination:** Benzene reacts with $Br_2/FeBr_3$ to form bromobenzene.

Middle Right Reactions:

- Friedel-Crafts Alkylation:** Benzene reacts with CH_3Cl and $AlCl_3$ to form toluene.
- Oxidation:** Toluene is oxidized with $KMnO_4$ and OH^- to form benzoic acid.
- Silver Salt Formation:** Benzoic acid reacts with Ag_2O to form silver benzoate.
- Hanschler Reaction:** Silver benzoate reacts with Br_2 in CCl_4 under reflux to form bromobenzene.

Bottom Right Reactions:

- Sandmeyer Reaction:** Benzene reacts with $CuCl/HCl$ or Cu/HCl to form chlorobenzene.
- Gatterman Reaction:** Benzene reacts with $CuBr + HBr$ or Cu/HBr to form bromobenzene.

Bottom Left Reactions:

- Balz-Schiemann Reaction:** Benzene reacts with HFb_4/Δ to form fluorobenzene.
- Iodination:** Benzene reacts with AgI to form iodobenzene.

Bottom Center Reactions:

- Nitration:** Benzene reacts with HNO_3 and H_2SO_4 to form nitrobenzene.
- Reduction:** Nitrobenzene is reduced using (i) Sn/HCl or (ii) $NaNO_2/HCl/0-5^\circ$ to form aniline.

Chlorobenzene Synthesis and Reactions:

Wurtz-Fittig Reaction: Chlorobenzene reacts with CH_3Br in the presence of $\text{Na/Et}_2\text{O}$ to form toluene.

Fittig Reaction: Chlorobenzene reacts with Ph-Br in the presence of $\text{Na/Et}_2\text{O}$ to form biphenyl.

Reduction: Chlorobenzene is reduced by Na/NH_3 in liq. NH_3 to form benzylamine.

Grignard Reaction: Chlorobenzene reacts with MgCl in THF to form phenylmagnesium chloride, which then reacts with CO_2 and H_3O^+ to form benzoic acid.

Ullmann Reaction: Chlorobenzene reacts with Cu to form biphenyl.

Other Reactions: Chlorobenzene reacts with Aq. NaOH at 300°C and pressure to form phenol, with NaCN+CuCN at 200°C and atm to form benzonitrile, and with $\text{Aq. NH}_3/\text{Cu}_2\text{O}$ at 200°C and atm to form benzylamine.

DDT Synthesis: Chlorobenzene reacts with $\text{CH}_2=\text{C}(\text{Cl})\text{CH}_3$ in the presence of AlCl_3 to form DDT (2,2-bis(p-chlorophenyl) 1,1,1-trichloroethane).

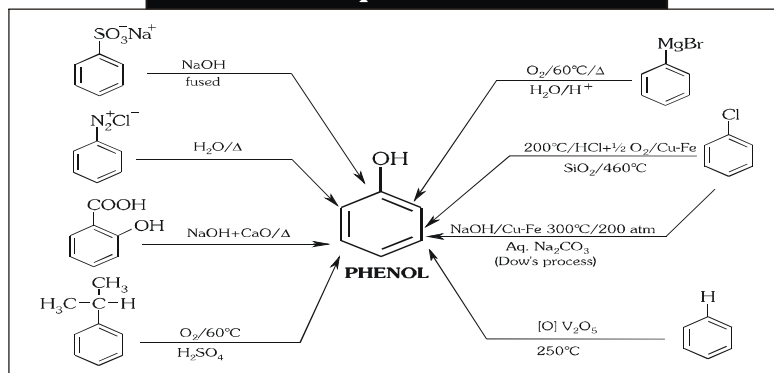
Reactivity Trends:

Physical Properties (b.p.s & Density): $\text{F} < \text{Cl} < \text{Br} < \text{I}$

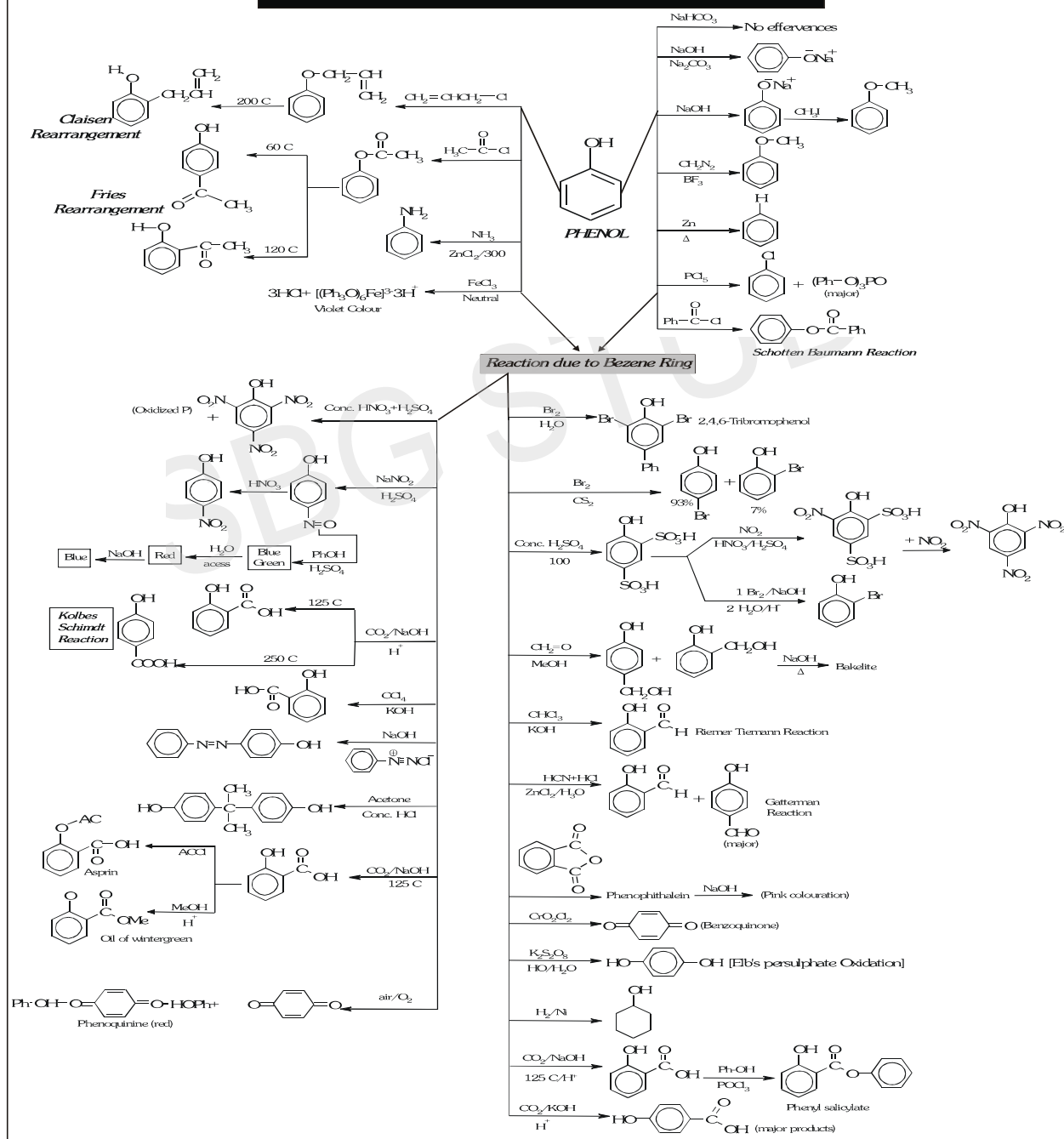
Melting Point (m.p.): $\text{Cl} > \text{O} & \text{m}:$

Chemical Reactivity (toward Nucleophile): $\text{F} > \text{Cl} > \text{Br} > \text{I}$

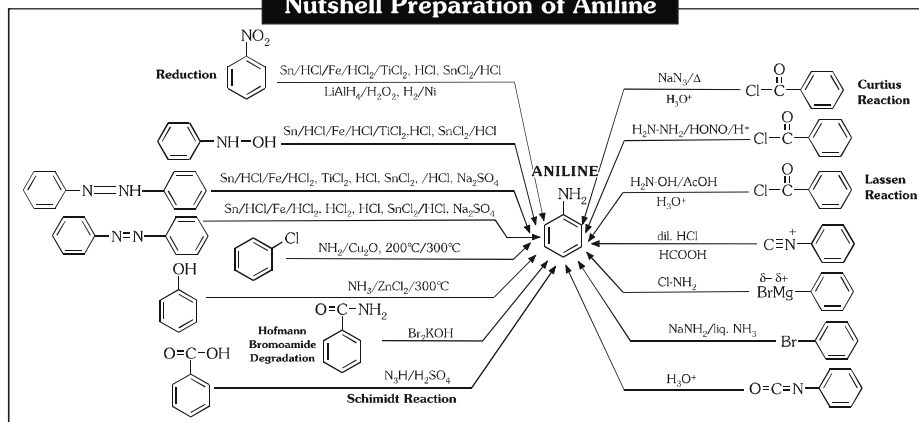
Nutshell Preparation of Phenol



Nutshell Review and Preview Phenol Reactions

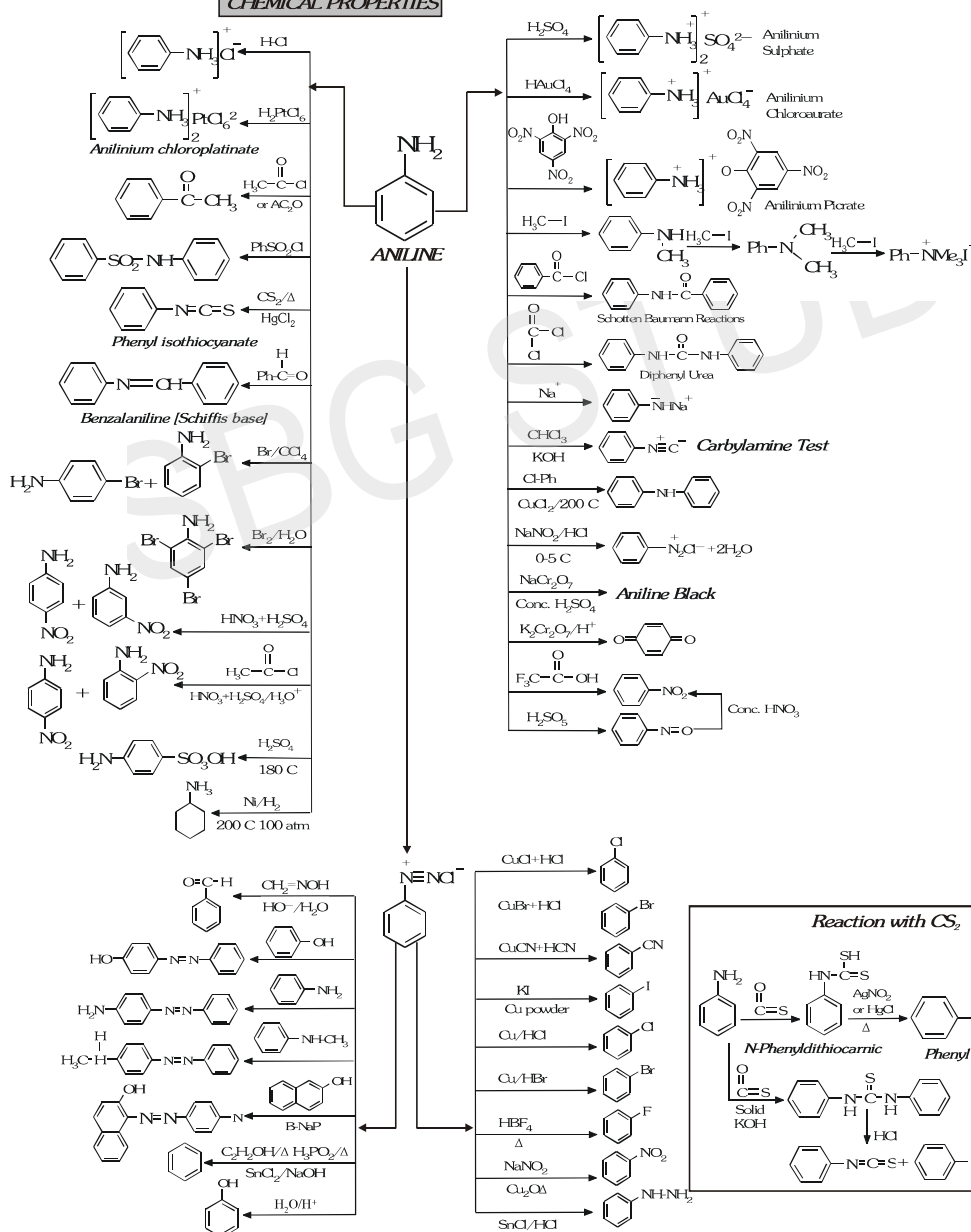


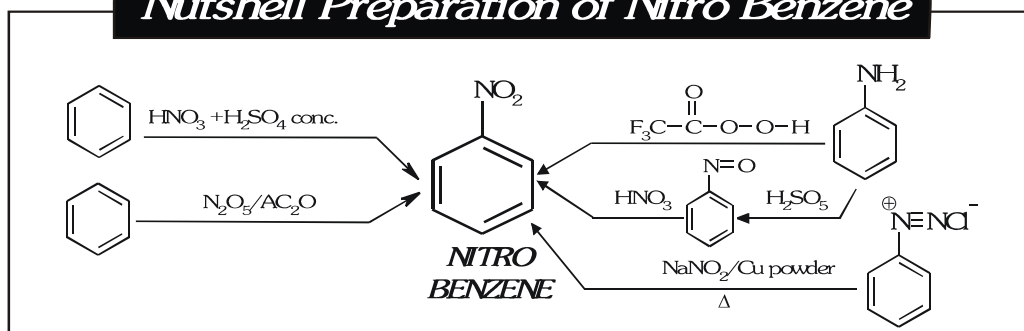
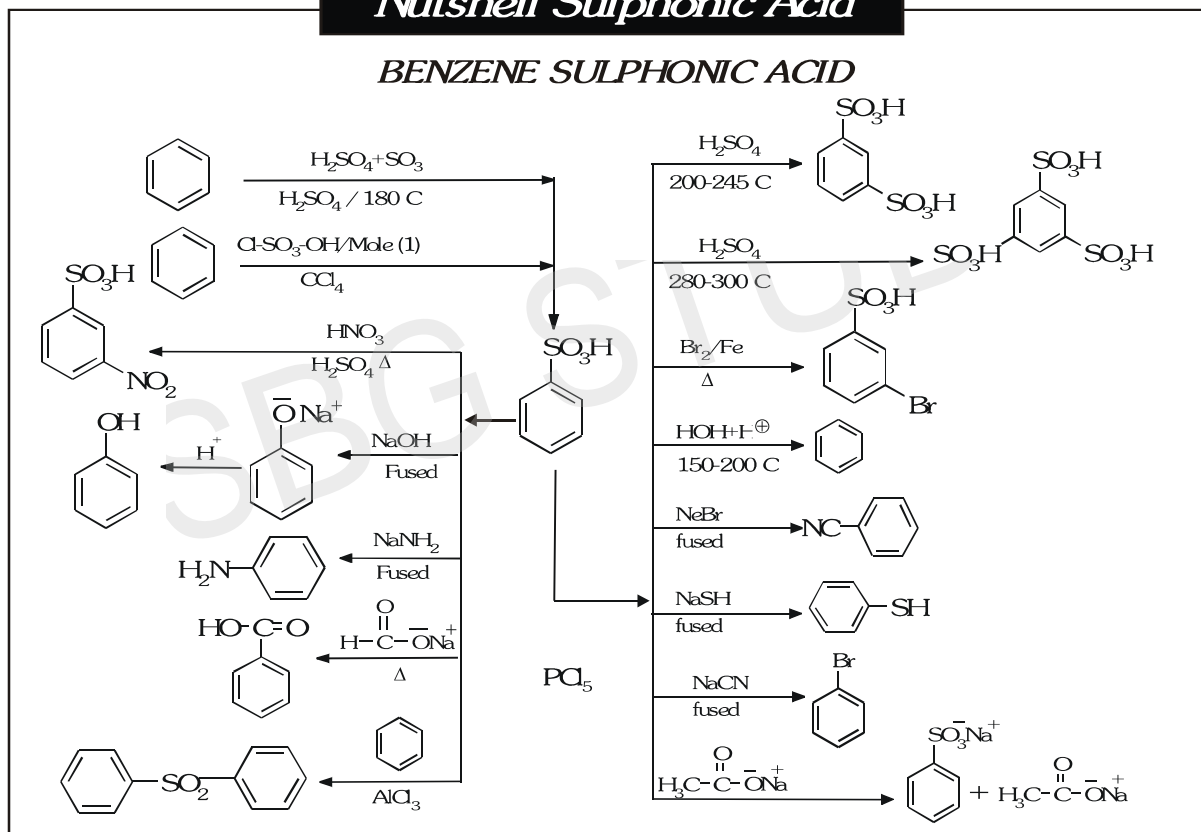
Nutshell Preparation of Aniline



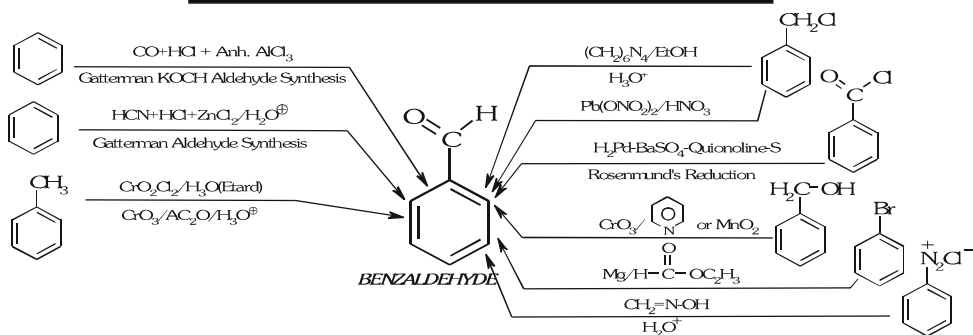
Nutshell Review and Preview of Aniline

CHEMICAL PROPERTIES

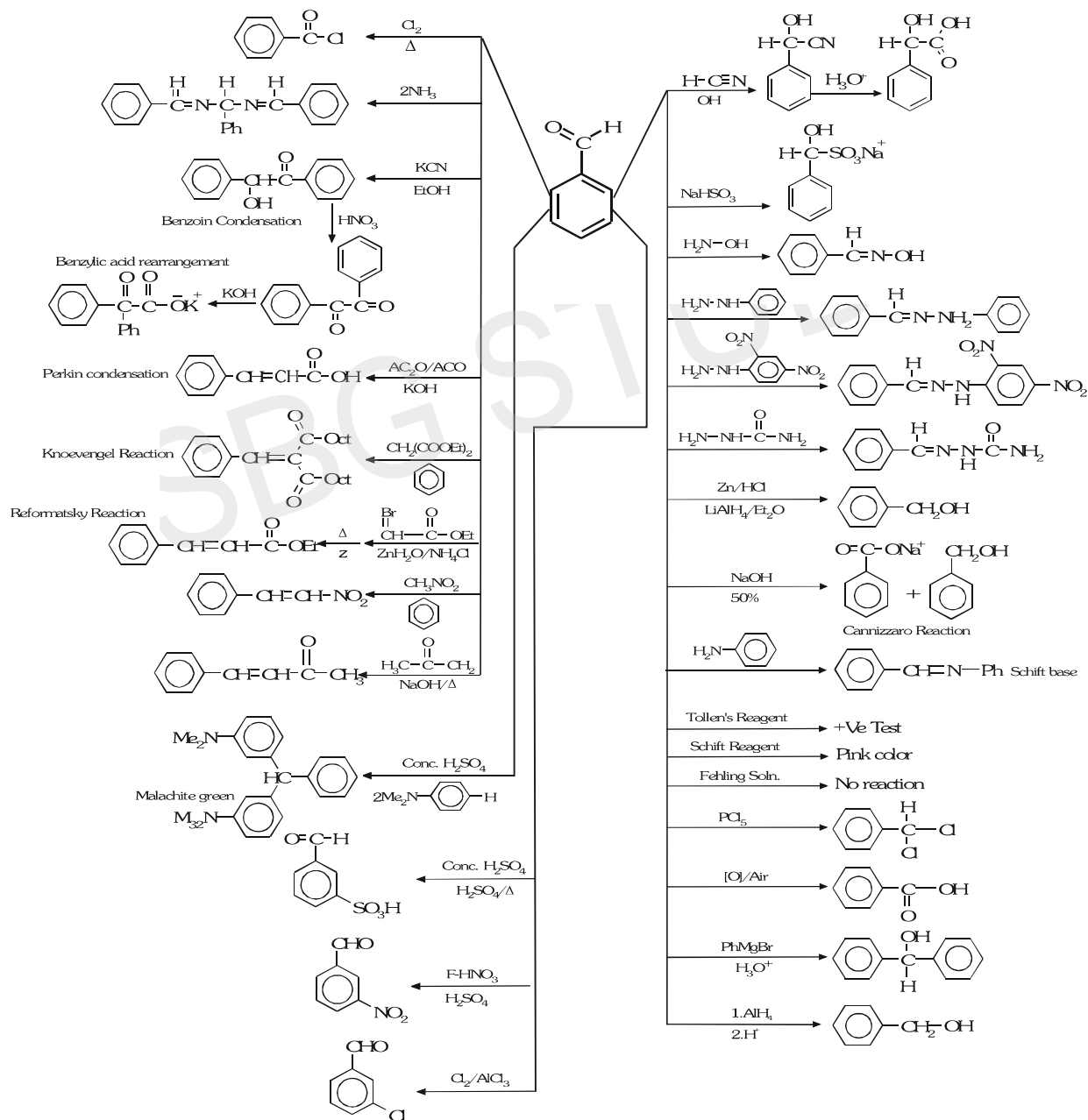


Nutshell Preparation of Nitro Benzene**Nutshell Sulphonic Acid****BENZENE SULPHONIC ACID**

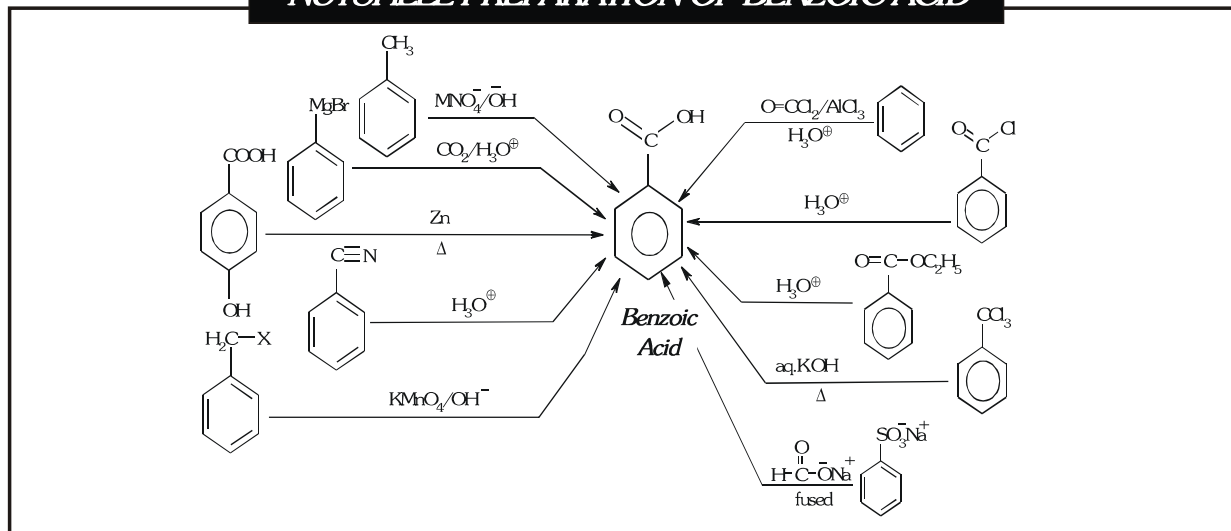
Nutshell Preparation of Benzaldehyde



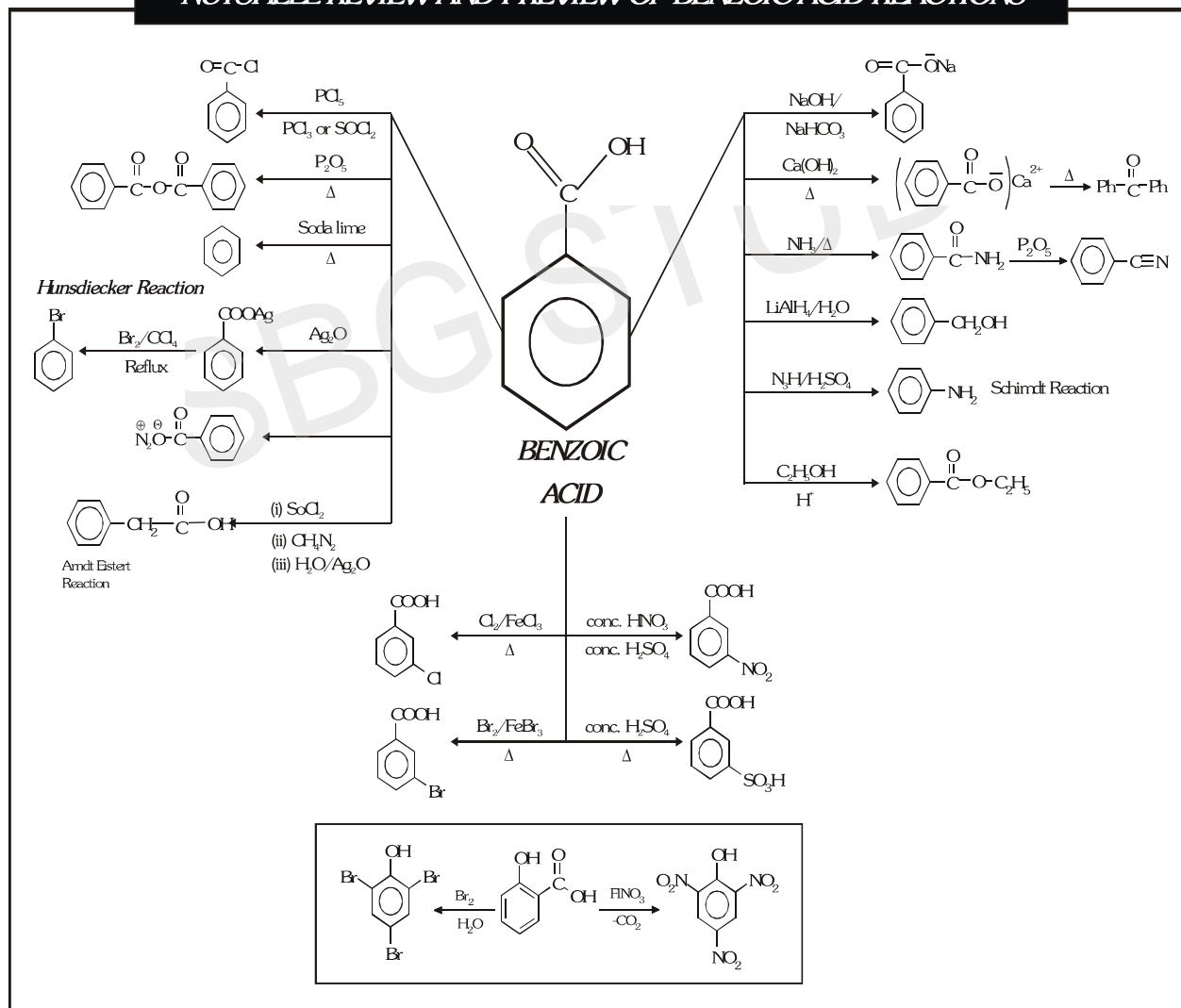
Nutshell Review and Review of Benzaldehyde Reactions



NUTSHELL PREPARATION OF BENZOIC ACID



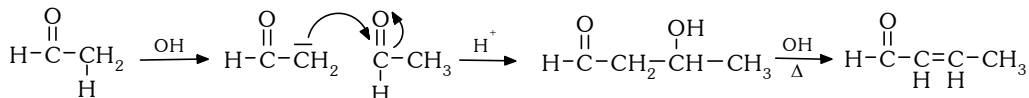
NUTSHELL REVIEW AND PREVIEW OF BENZOIC ACID REACTIONS



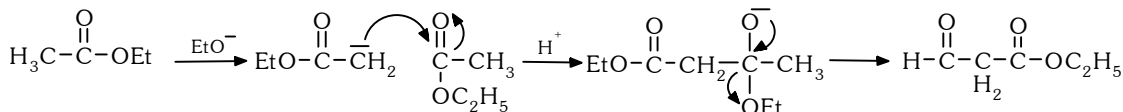
NUTSHELL REVIEW & aREVIEW OF

ORGANIC NAME REACTIONS

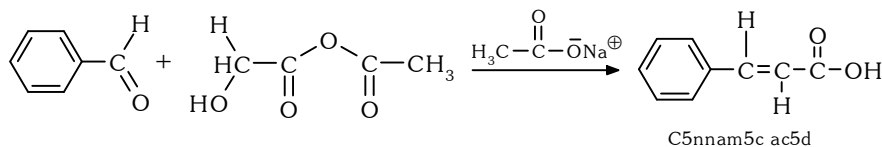
• **Aldol Condensation**



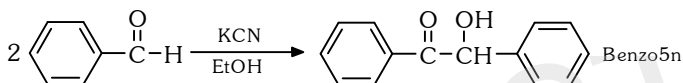
• **Claisen Condensation**



• **Perkin Condensation**



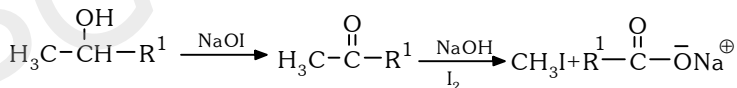
• **Benzoin Condensation**



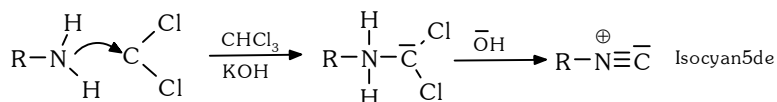
• **Wittig Reaction**



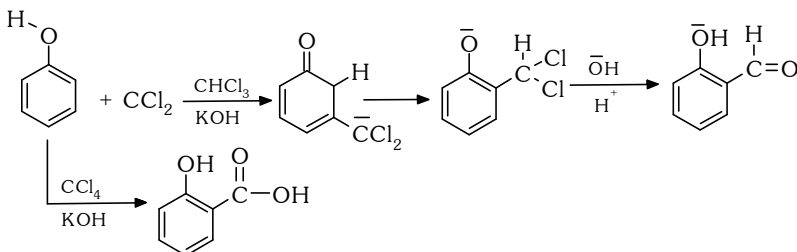
• **Haloform Reaction**



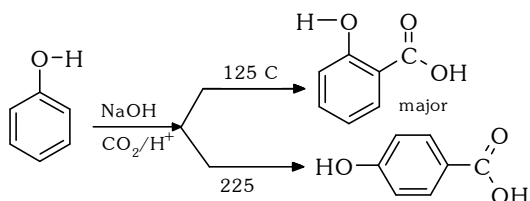
• **Carbylamine Test**



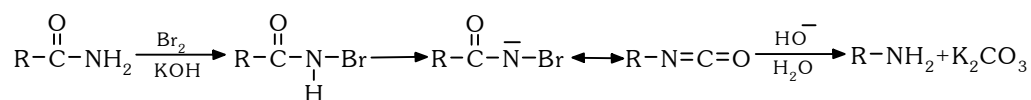
• **Reimer Tiemann Reaction**



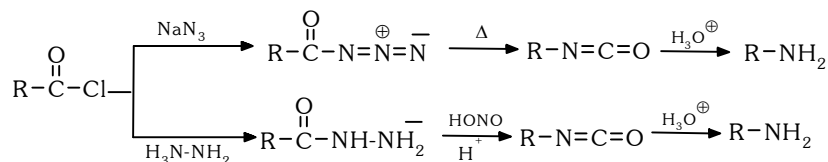
• **Kobayashi-Schmidt Reaction**



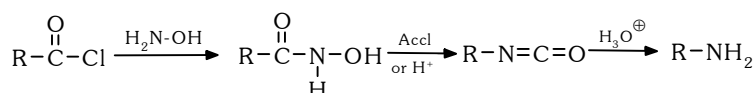
• **Hofmann Bromoamide Degradation**



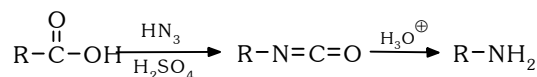
• **Curtius Reaction**



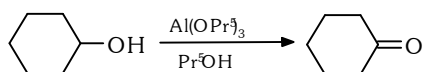
• **Lossen Reaction**



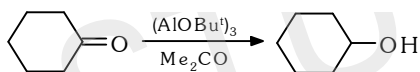
• **Schmidt Reaction**



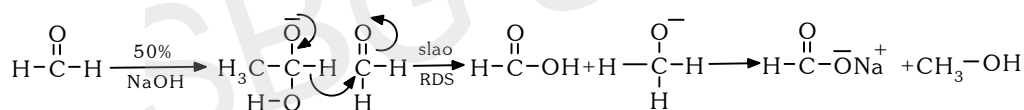
• **Meerwein aonndorfverly reduction**



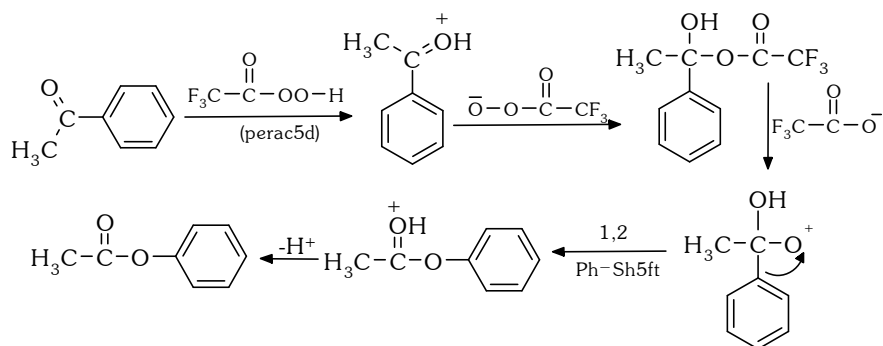
• **Oppeneuer Oxidation**



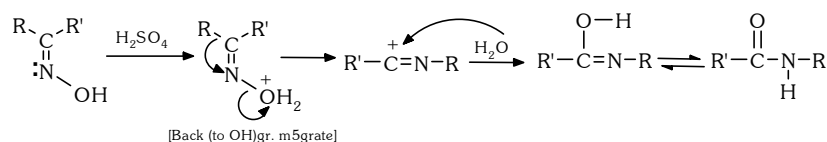
• **Cannizzaro reaction**



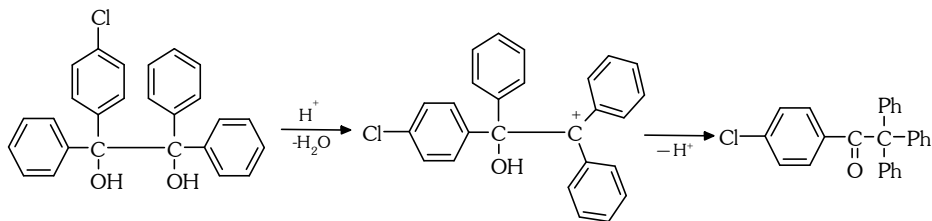
• **Bayer villiger oxidation**



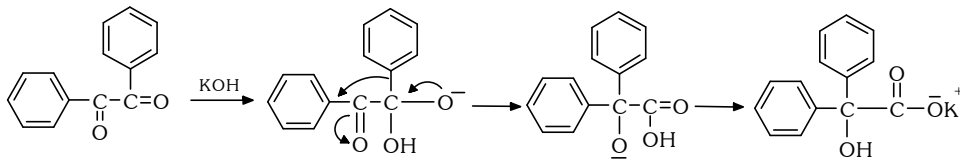
• **Beckmann Rearrangement**



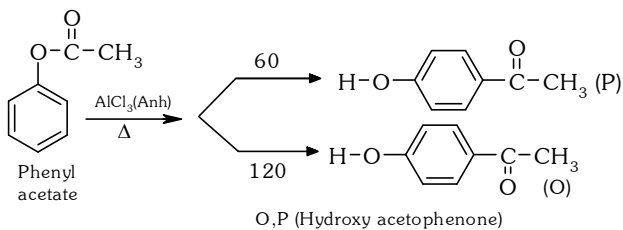
• **ainacol aincolone rearrangement**



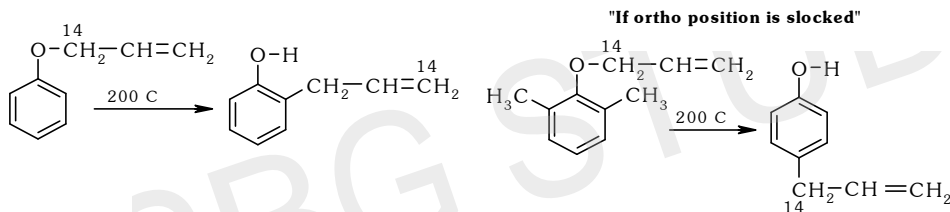
• **Benzylic acid rearrangement**



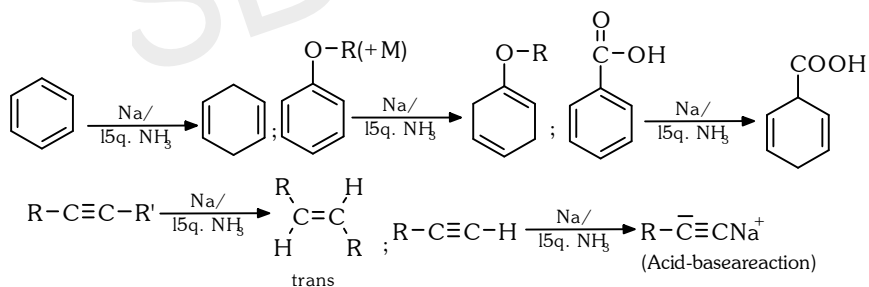
• **Fries Rearrangement**



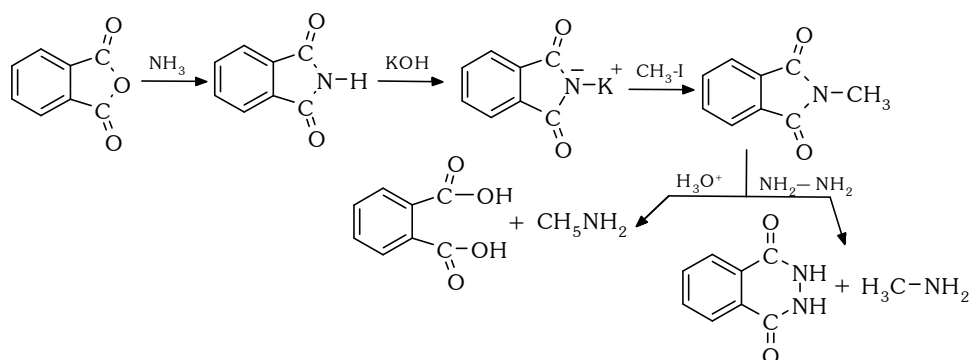
• **Claisen Rearrangement**



• **Birch Reduction**



• **Gabriel Synthesis**

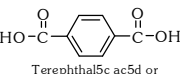

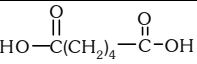
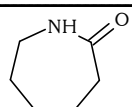


Name	Reactant	Reagent	Product
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl	Alkane
Coupling Reaction	$\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{C}_6\text{H}_5\text{OH} \text{ or } \text{C}_6\text{H}_5\text{NH}_2$	NaOH (phenol) HCl (Aniline)	Azo Dyne (Detection of OH or NH ₂ gr)
Diazotization		$\text{NaNO}_2 + \text{HCl}$ 0 - 5 °C	
Diels Alder Reaction		 Dienophile	 cycloaddition product
Etard reaction		$\text{CrO}_2\text{Cl}_2/\text{CS}_2$	 (Benzaldehyde)
Fittig Reaction	Halo benzene	Na/Dry ether	Biphenyl
Friedel Craft alkylation	+ R-X	Anhydrous AlCl_3	Alkyl Benzene
Friedel Craft acylation	+ $\text{R}-\text{C}(=\text{O})-\text{Cl}$ or $(\text{RCO})_2\text{O}$	Anhydrous AlCl_3	Acyl Benzene
Gattermann aldehyde synthesis	C_6H_6	$\text{HCN} + \text{HCl} + \text{ZnCl}_2/\text{H}_3\text{O}^+$	Benzaldehyde
Gattermann-Koch reaction	C_6H_6 (CO + HCl)	anhy AlCl_3	Benzaldehyde
Hell-Volhard-Zelinsky reaction	carboxylic acid having α-hydrogen atom	$\text{Br}_2/\text{red P}$	α-halogenated carboxylic acid
Hoffmann mustard oil reaction	primary amine + CS_2	HgCl_2/Δ	$\text{CH}_3\text{CH}_2-\text{N}=\text{C}=\text{S} + \text{HgS}$ (black)
Hunsdiecker reaction	Ag salt of carboxylic acid	$\text{Br}_2/\text{CCl}_4, 80^\circ\text{C}$	alkyl or aryl bromide
Kolbe electrolytic reaction	alkali metal salt of carboxylic acid	electrolysis	alkane, alkene and alkyne
Meerwein - Ponndorf	Ketone	$[(\text{CH}_3)_2\text{CHO}]_3\text{Al} + (\text{CH}_3)_2\text{CHOH}$	Secondary alcohol
Mendius reaction	alkyl or aryl cyanide	$\text{Na}/\text{C}_2\text{H}_5\text{OH}$	primary amine
Rosenmund reduction	acid chloride	$\text{H}_2, \text{Pd}/\text{BaSO}_4, \text{S, boiling xylene}$	aldehyde
Sabatier-Senderens reaction	Unsaturated hydrocarbon	Raney Ni/ H_2 , 200— 300 °C	Alkane
Sandmeyer reaction	$\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$	CuCl/HCl or CuBr/HBr or CuCN/KCN , heat	halo or cyanobenzene
Gattermann Reaction	$\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$	$\text{Cu}/\text{Hx}(\text{HBr}/\text{HBr}/\text{HBr})$	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	$\text{NaOH} + \text{C}_6\text{H}_5\text{COCl}$	benzoylated product
Stephen reaction	alkyl cyanide	SnCl_2/HCl	Aldehyde
Ullmann reaction	Iodobenzene	Cu (heat)	Biphenyl
Williamson synthesis	alkyl halide	sodium alkoxide or sodium phenoxide	ether
Wurtz-Fittig reaction	alkyl halide + aryl halide	Na/ether	alkyl benzene

ADDITION POLYMERS

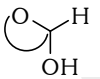
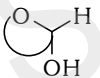
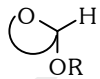
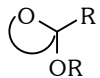
S. No	Name of polymer	Abbreviation	Starting Materials	Nature of polymer	Properties	Applications
I. alyolefins						
1.	Polyethylene or Polyethene		$\text{CH}_2=\text{CH}_2$	Low density homopolymer (branched chain growth)	Transparent, moderate tensile strength, high toughness	Packaging material bags, insulation for electrical wires and cables. Buckets, tubes, house ware pipes, bottles and toys
2.	Polypropylene or Polypropene or Herculon		$\text{CH}_3\text{CH}=\text{CH}_2$	Homopolymer, linear, chain growth	Harder and stronger than polyethene	Packaging 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. alydienes						
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 superresistant to aeroxidation, 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 superresistant to aeroxidation, and oils, gasoline etc.	Manufacturer of tyres, rubber soles, water proof shoes.
III. alyacrylates						
1.	Polymethylmethacrylate (Flexiglass Lucite, Acrylite 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, aircraft 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.	Orlon, acrilon used for making clothes, carpets, blankets and preparation of other polymers.
IV. alyhalofins						
1.	Polyvinyl chloride	PVC	$\text{CH}_2=\text{CH}-\text{Cl}$	Homopolymer, chain growth	Pliable (easily moulded)	(5) Plasticised with polyester polymers used in rain coats, hand bags, shower curtains, fabrics, shoe soles, vinyl flooring (55) Good electrical insulator, (55) Hose pipes.
2.	Polytetrafluoroethylene, or Teflon	PTFE	$\text{F}_2\text{C}=\text{CF}_2$	Homopolymer	Flexible and inert to solvents, boiling even in aquaregia, stable upto 598 K	(55) For nonstick utensils coat (55) Making gaskets, pump packings, valves, seals, non lubricated bearings.
3.	Polymonochlorotrifluoroethylene	PCTFE	$\text{ClFC}=\text{CF}_2$		Less resistant to heat and chemicals due to presence of chlorine atoms.	Similar to those of Teflon.

CONDENSATION POLYMERS

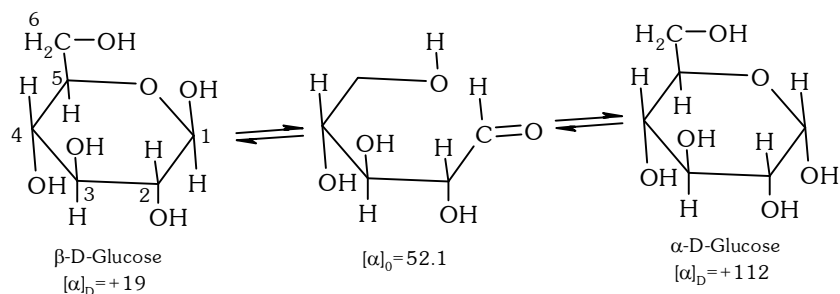
S. No	Name of polymer	Abbreviation	Starting Materials	Nature of polymer	Properties	Applications
I. Polyesters						
1.	Terylene or Dacron or Mylar		$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ Ethylene glycol or Ethane-1,2-diol And  Terephthalic acid or Benzene-1,4-dicarboxylic acid	Copolymer, step growth, linear	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		$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ 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 $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ Hexamethylenediamine	Copolymer, linear, step growth		
2.	Nylon-6,10		$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ Hexamethylenediamine and $\text{HOOC}(\text{CH}_2)_8\text{COOH}$ Sebacic acid	Copolymer, linear, step growth	High tensile strength, abrasions resistant, somewhat elastic	(5) Textile fabrics, carpets, brushes for (55) Substitution of metals in bearings (55) Gears elastic hosery. Mountaineering ropes, tyre cords, fabrics.
3.	Nylon-6 or Perlon L		 Caprolactam	Homopolymer, linear		Mountaineering ropes, tyre cords, fabrics.
Formaldehyde resins						
1.	Phenolformaldehyde resin or Bakelite		Phenol and formaldehyde	Copolymer, step growth		(5) with low degree polymerisation for bonding glue, wood, varnishes, lacquers. (55) With high degree polymerisation for combs, for mechanical 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

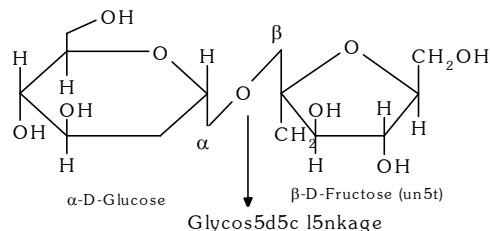
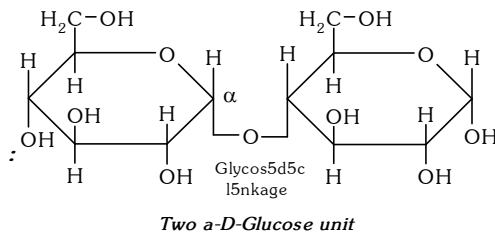
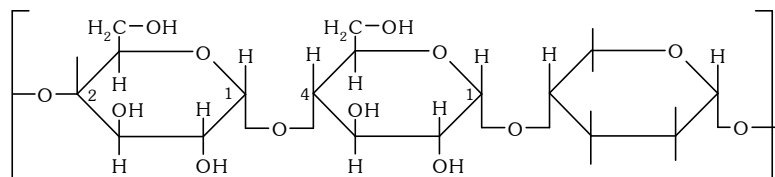
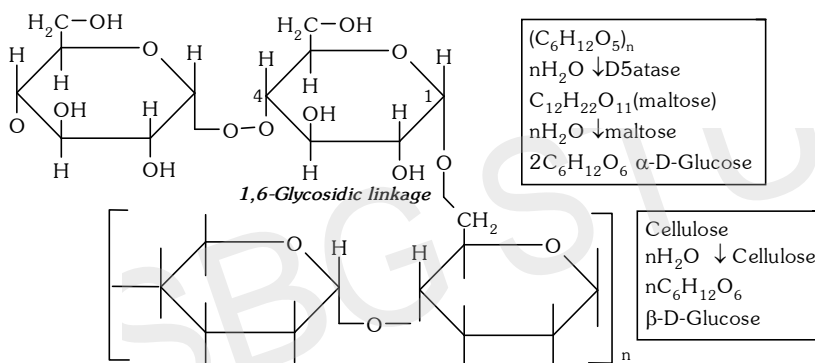
- Polyhydroxy aldehyde or Ketone (cycl5c hem5acetal/ or hem5acetal or acetal or ketal
- Monosaccharide ($C_nH_{2n}O_n$) : single unit, can't be hydrolysed : Glucose; fructose (by glycosyd5c l5nkage)
- Sucrose $\xrightarrow{H_3O^+}$ Glucose + Fructose; maltose $\xrightarrow{H_3O^+}$ 2 Glucose unit
- Lactose $\xrightarrow{H_3O^+}$ Glucose + Galactose
- Polysaccharide : Contain more than monosaccharides
- ($C_6H_{10}O_5$)_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	$\begin{array}{c} \alpha \\ \\ -C-C=O \\ \\ OH \end{array} / \begin{array}{c} O \\ \\ -C-C-C- \\ \\ OH \end{array}$  Hemiacetal  Hemiketal	 Acetal  Ketal
6. Example	All monosaccharide Glucose; fructose, mannose, galactose, Disaccharide : maltose; lactose	Disaccharide : Sucrose Polysaccharide : starch cellulose

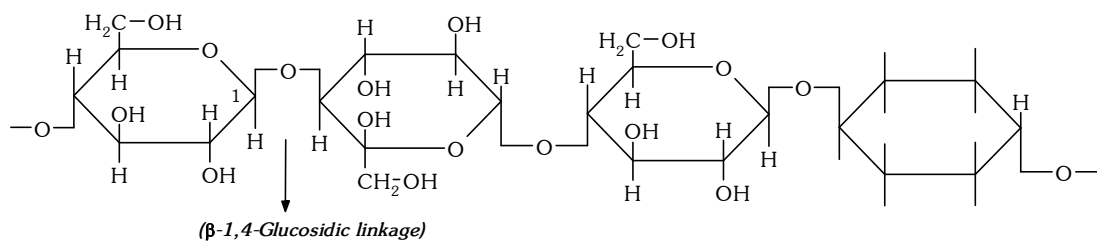
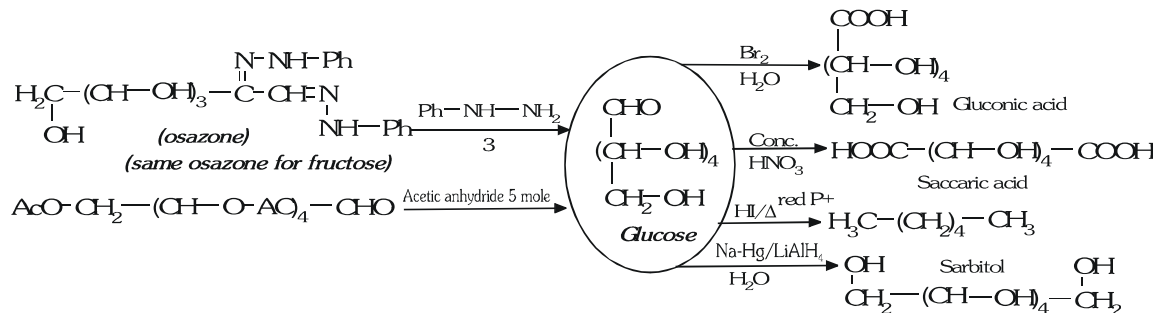
- Mutarotation:** When either form is placed in solution it slowly interconverts with the other via open chain aldehyde form & gradual change in specific rotation until equilibrium value is reached.



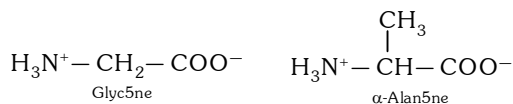
- Anomer's :** Differ in configuration at 1st carbon due to hemiacetal or ketal ring formation. The new asymmetric carbon is referred to as Anomeric carbon.
- Epimer's :** Diastereomer's which differ in conformation at one or more carbon [maltose & glucose (epimers carbon 5s C₂)]

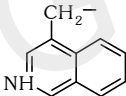
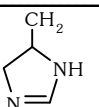
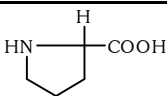
• **Sucrose :**• **Maltose**• **Starch :** (Amylose & Amylopectin)• **Amylose : (Straight Chain) :**(α -1,4 Glycosidic linkage)(5) Soluble in H_2O & gives blue colour with I_2 (55) 10 to 20%• **Amylopectin (Branch chain) : ($C_6H_{12}O_5$)_n**

1,4-Glycosidic linkage

• **Cellulose :** (Straight chain β -D-Glucose units)(β -1,4-Glycosidic linkage)

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	$\begin{array}{c} -\text{CH}-\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Ile
6.	Arginine	$\begin{array}{c} -(\text{CH}_2)_3\text{NH}-\text{C}-\text{NH}_2 \\ \\ \text{NH} \end{array}$	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

ISOELECTRIC 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 form 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 are called peptides.

- Peptide Linkage** : Linkage which unites the α-amino acid molecules together is called peptide linkage. It is -CO-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 chains coil 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 bending 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 acid 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 '-CO-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 propptips** : 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	Golden	Pale	Reddish	Blue
	red	yellow	violet	violet	

Basic nature increase down to the group

Reducing property :

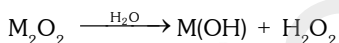
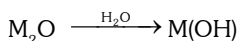
$\begin{cases} \text{Molten} \\ \text{aqueous} \end{cases}$	$Li < Na < K < Rb < Cs$
	$Li > K \approx Rb > Cs > Na$

➤ Chemical properties :

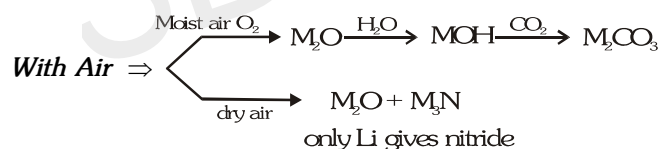
With O_2 \Rightarrow Lithium forms normal oxide $[Li_2O]$

Sodium forms peroxide (Na_2O_2)

K, Rb, Cs forms superoxide KO_2, RbO_2, CsO_2



With Watpr $\Rightarrow M + H_2O \longrightarrow MOH + H_2$



With NH_3 $\Rightarrow : M + (X + Y) NH_3 \longrightarrow [Na(NH_3)_X]^+ + [e(NH_3)_Y]^-$
ammoniated e^-

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

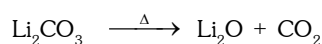
on standing $Li + NH_3 \longrightarrow Li_2NH$ (Lithmide)

$M(Na/K/Rb/Cs) + NH_3 \longrightarrow MNH_2$ (amide)

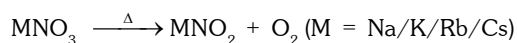
With Halidps $\Rightarrow M + X_2 \longrightarrow MX$

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

Carbonatps : Only Li_2CO_3 decomposes

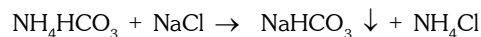
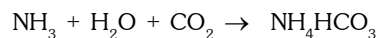


Nitratps : $LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$

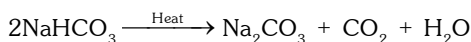


- Na_2CO_3 does not impart any colour to the flame but NaCl does because the thermal ionization of Na_2CO_3 does not take place at the temperature of flame of the burner.

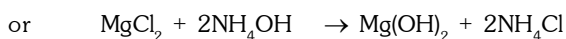
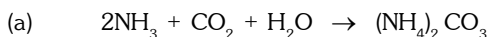
- In **Solvay's process**, CO_2 gas is passed through saturated brine (NaCl) solution when sparingly soluble NaHCO_3 separates out.



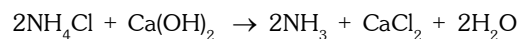
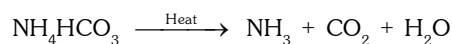
The NaHCO_3 formed above is calcined to form Na_2CO_3



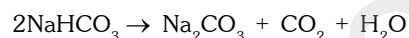
- The reactions taking place at different stages during the manufacture of Na_2CO_3 by Solvay process are given as under :



- (b) Ammonia recovery tower



- (c) Calcination of NaHCO_3



- (i) **Efflorescence** :

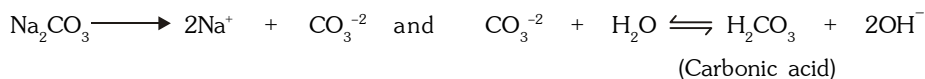
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ when exposed to air it gives out nine out of ten H_2O molecules.



(Monohydrate)

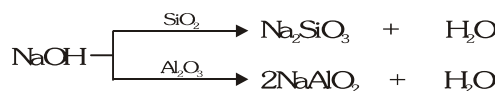
This process is called efflorescence. Hence washing soda loses weight on exposure to air.

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

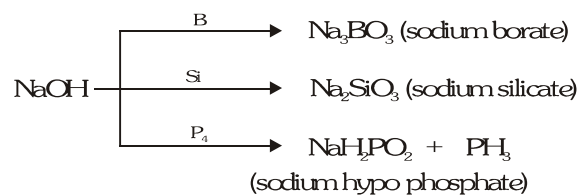


- (e) **Uses**

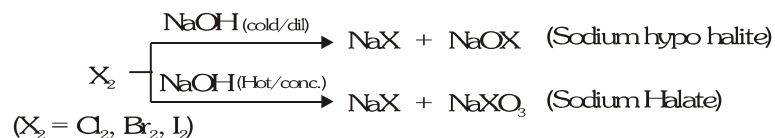
- (i) For making fusion mixture ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$)
- (ii) In the manufacture of glass, caustic soda, soap powders etc.
- (iii) In laundries and softening of water.
- (iii) NaOH is **strong base**



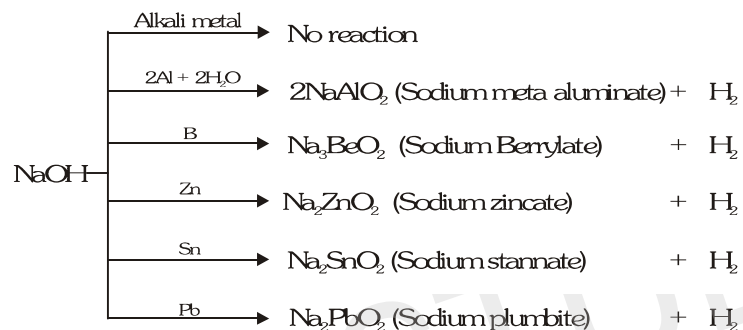
(iv) **Reaction with non metals** : no reaction with H_2 , N_2 and C



(v) **Reaction with halogens**



(vi) **Reaction with Metal** :



ALKALINE EARTH METALS

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

General oxidation state +2.

Atomic/Ionic size $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$

Ionisation energy $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$

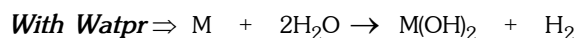
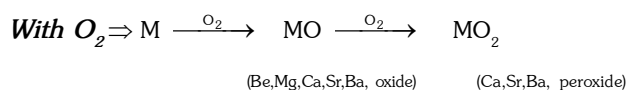
Flame colour **Ca - Brick rpd** **Sr - Crimson rpd**
Ba - Applp grppn

Basic nature increase down to the group

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

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

- Chemical properties :



With Air \Rightarrow 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 NH_3 \Rightarrow : Only Ca, Sr and Ba gives blue solution of ammoniated electron.

Carbonatps :

- (i) Except BeCO_3 , all the carbonates are stable towards heat



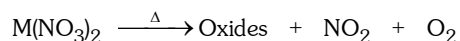
- (ii) Order of decreasing stability -



Nitratps :

- (i) Alkaline earth metals forms $\text{M(NO}_3)_2$ type nitrates. (M -Alkaline earth metal).

- (ii) All alkaline metals nitrates on heating gives oxides and $\text{NO}_2 + \text{O}_2$



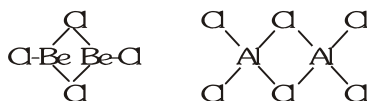
- **SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM**

- (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, Li_3N and Mg_3N_2 .
- (c) The oxides, Li_2O 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 CO_2 . Solid bicarbonates are not formed by lithium and magnesium.

- (e) Both LiCl and MgCl_2 are soluble in ethanol.
- (t) Both LiCl and MgCl_2 are deliquescent and crystallise from aqueous solution as hydrates, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$.

➤ **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 $[\text{Be}(\text{OH})_4]^{2-}$ and aluminates, $[\text{Al}(\text{OH})_4]^-$.
- (c) The chlorides of both beryllium and aluminium



have bridged chloride structures in vapour phase.

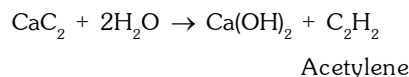
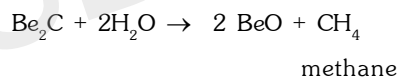
- (d) Salts of these metals form hydrated ions, Ex. $[\text{Be}(\text{OH}_2)_4]^{2+}$ and $[\text{Al}(\text{OH}_2)_6]^{3+}$ in aqueous solutions. Due to similar charge/ radius ratios of beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as BeF_4^{2-} and $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ and aluminium forms octahedral complexes like AlF_6^{3-} and $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$.

➤ 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.

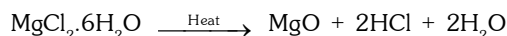


➤ Be_2C on treatment with H_2O forms CH_4 while CaC_2 forms C_2H_2 .



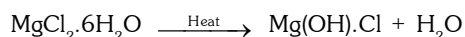
➤ BeCl_2 in the vapour phase above 900°C is monomeric ; below 900°C in the vapour exists as a mixture of monomer BeCl_2 and dimer Be_2Cl_4 , in the solid state, has a polymeric structure and when dissolved in a coordinating solvent it exists as a monomer.

➤ Anhydrous MgCl_2 cannot be prepared by the simple heating of hydrated magnesium chloride $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, as it gets hydrolysed to magnesium oxide.

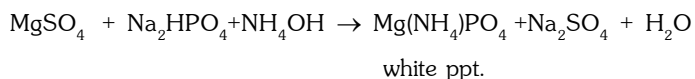


➤ Out of the oxides of group 2 elements only BeO is extremely hard, non volatile, has high melting point and it is amphoteric.

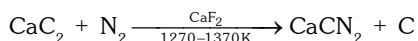
➤ **Anhydrous magnesium chloride** (MgCl_2) cannot be prepared by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. since on heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ undergoes hydrolysis with the evolution of HCl gas.



- 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.

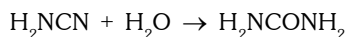
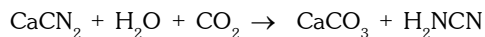


- Hydrolith (CaH_2) is calcium hydride.
- Calcium cyanamide (CaCN_2) is prepared by heating a mixture of CaC_2 in an atmosphere of N_2 at 1270–1370K with CaF_2 .

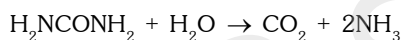


Its trade name is Nitrolim.

- 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.



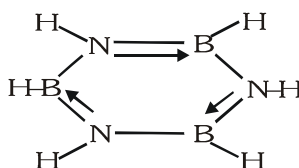
Urea



BORON FAMILY

- B_2O_3 and $B(OH)_3$ are acidic, Al_2O_3 and $Al(OH)_3$; Ga_2O_3 and $Ga(OH)_3$ are amphoteric while In_2O_3 and $In(OH)_3$ 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.

$$BF_3 < BCl_3 < BBr_3 < BI_3$$
- Borazine or Borazole or inorganic benzene is $B_3N_3H_6$.

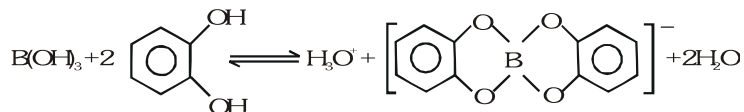


- Action of heat on orthoboric acid
 - (i) $H_3BO_3 \xrightarrow{100^\circ C} HBO_2 + H_2O$
 Orthoboric acid Metaboric acid
 - (ii) $4HBO_2 \xrightarrow{160^\circ C} H_2B_4O_7 + H_2O$
 Metaboric acid Tetraboric acid
- Above 160 C, it swells up giving frothy mass and finally forms boron trioxide, B_2O_3 .
- Some important ores of Boron are given as under.
 - (i) Boric acid, H_3BO_3
 - (ii) Borax, $Na_2B_4O_7 \cdot 10H_2O$
 - (iii) Colemanite, $Ca_2B_4O_{11} \cdot 5H_2O$
- Some important minerals of aluminium are given as under.
 - (i) Corundum, Al_2O_3
 - (ii) Bauxite, $Al_2O_3 \cdot 2H_2O$
 - (iii) Cryolite, Na_3AlF_6
 - (iv) Felspar, $KAlSi_3O_8$
- Melting and boiling points of halides of boron decrease in the order

$$BI_3 > BBr_3 > BCl_3 > BF_3$$
- Boric acid is a weak monobasic acid

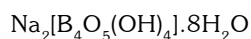
$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^{-1}$$

$$pK_a = 9.25$$
- 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, mannitol, catechol or sugar). The presence of these compounds greatly increases 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.

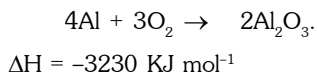
- **Borax**, which is normally written as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, contains tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ comprising BO_4 and BO_3 units. Thus, borax should have been formulated as



- **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 .

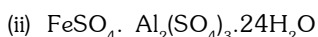
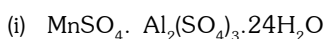


- **Aluminium chloride**, is a polymeric solid which exists as a dimer Al_2Cl_6 between 200–400 °C and then monomer up to 800 °C.
- **Thermite welding** Aluminium has got a very high affinity for oxygen.



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.

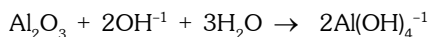
- **Pseudo alums** are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.



They are not isomorphous with true alums.

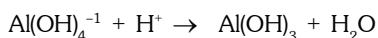
- **Extraction of Aluminium.** Al is usually extracted from Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. First, bauxite is purified from the impurities (Red bauxite contains Fe_2O_3 as impurity while white bauxite contains silica as impurity). Red bauxite can be purified by Baeyer's process or Hall's process while white bauxite is purified by Serpeck's process.

- **Bayer'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

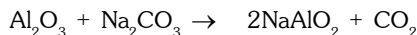
Fe_2O_3 left undissolved is filtered off. The treatment of $[\text{Al}(\text{OH})_4]^{-1}$ solution with a weak acid precipitates pure $\text{Al}(\text{OH})_3$.



(White ppt.)

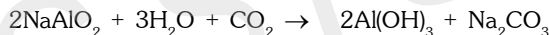
The $\text{Al}(\text{OH})_3$ precipitate is removed by filtration and ignited to get alumina, Al_2O_3 .

- **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.

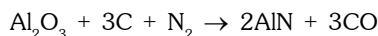
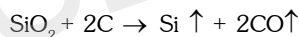


Sodium meta aluminate

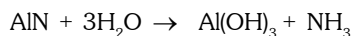
The water extract is heated up to 333K and CO_2 is passed through it. $\text{Al}(\text{OH})_3$ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_3 .



- **Serppeck'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.

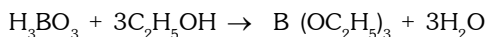


Aluminium nitride



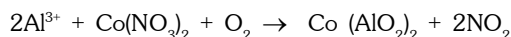
Electrolysis of Al_2O_3 to form aluminium. Pure alumina is dissolved in fused cryolite, Na_3AlF_6 at 1225 K by current of 100 amperes and 6 – 7 volts to get Al. The Al obtained is purified by Hoopes' process.

- **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 edged flame due to the formation of ethyl borate.



Ethyl borate

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



Blue residue

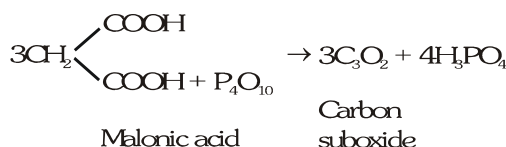
CARBON FAMILY

- **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 $\text{R} = -\text{CH}_3, -\text{C}_2\text{H}_5, -\text{C}_6\text{H}_5$
- **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 :

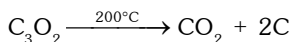
	C-C	Si-Si	Ge-Ge	Sn-Sn	Pb-Pb
Bond energy (KJ mol⁻¹)	348	222	167	155	-

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 a foul smelling gas which can be prepared by the dehydration of malonic acid with P_4O_{10} .



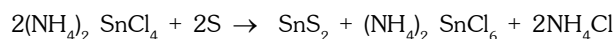
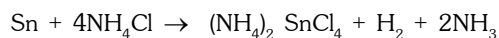
On heating upto 200°C, it decomposes into CO_2 and carbon.



The molecule is thought to have a linear structure.



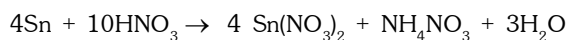
- Silicon polymers or silicones are polymeric organosilicon compounds containing Si - O - Si linkages. Their general formula is $(\text{R}_2\text{SiO})_x$. They may be linear, cyclic or cross linked polymers.
- **Mosaic gold** (SnS_2). Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under 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



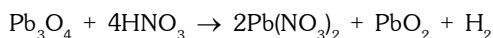
(b) Hot conc. HNO_3



Metastannic acid

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

- **Lpad dioxidp (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 tinds use in match industry as an oxidizing agent.

- **Thp main orps of lpad arp**

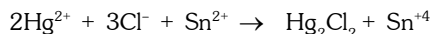
(i) Glena, PbS

(ii) Cerrusite, PbCO_3

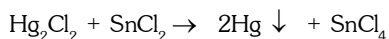
(iii) Anglesite, PbSO_4

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 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).



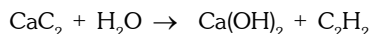
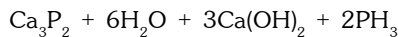
Mercurous chloride



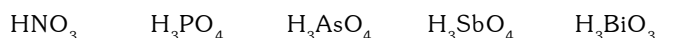
Black

NITROGEN FAMILY

- **Holmp'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.



- **Thp strpngth and solubilitips of oxyacids of 15 group plmpnts arp givpn as undpr.**



Strong Weak Weaker Amphoteric Basic

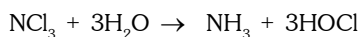
(Soluble) (Soluble) (Soluble) (Insoluble) (Insoluble)

- 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.

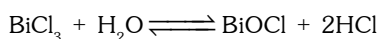
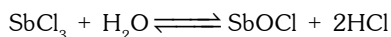
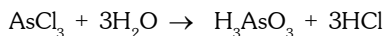
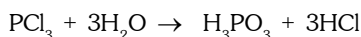
- The oxoacids of phosphorus are given as under :

Formula	Namp of acid No.	Oxidation of phosphorus	Commprnts about acidic naturp
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

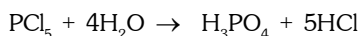
- NCl_3 is hydrolysed with H_2O to NH_3 and HOCl .



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



- PCl_5 on hydrolysis forms phosphoric acid, H_3PO_4 .

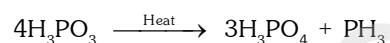


- With Nessler's reagent K_2HgI_4 , ammonium salts give a reddish brown ppt. of Million's base $\text{HgO} \cdot \text{Hg}(\text{NH}_2)\text{I}$

- 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.

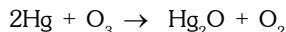
<i>Propprty</i>	<i>Whitp phosphorus</i>	<i>Rpd phosphorus</i>
(i) Physical state	Pale yellow sott solid, Can be cut with knite. White when treshly cut.	Red Phosphorus Dark and brittle powder
(ii) Odour	Garlic	Odourless
(iii) Density	1.8 g/cm ³	2.1 g/cm ³
(iv) Solubility	Soluble in CS ₂	Insoluble
(v) 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

- **Smokp scrppns**, involve the use of calcium phosphide, Ca₃P₂. The PH₃ gas obtained from Ca₃P₂ catches tire 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).



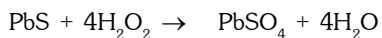
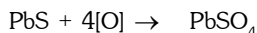
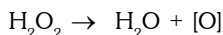
OXYGEN FAMILY

- 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.
- 10V H_2O_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.

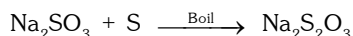


- SO_2 gas is dried by bubbling the mixture through conc. H_2SO_4 . It is not dried over quick lime (CaO) as it reacts with it to form calcium sulphite.



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

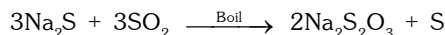
- (a) By boiling sodium sulphite with sulphur.



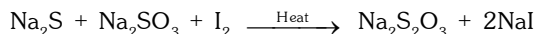
- (b) By boiling sulphur with NaOH



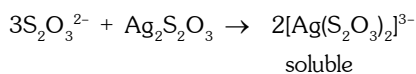
- (c) By passing SO_2 into Na_2S solution.



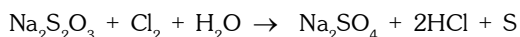
- (d) By spring's reaction



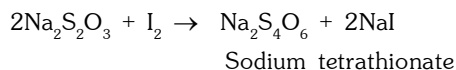
- **Conc. $\text{Na}_2\text{S}_2\text{O}_3$** does not give a white ppt. with AgNO_3 . This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.



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

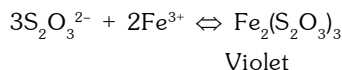


- **Sodium thiosulphate** is oxidized to sodium tetrathionate $\text{Na}_2\text{S}_4\text{O}_6$ by I_2

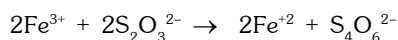


This reaction forms the basis of iodometric estimation of $\text{Cr}_2\text{O}_7^{2-}$ and Cu^{2+} salts.

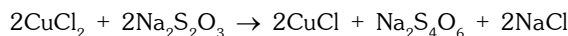
- **Sodium thiosulphate** reacts with FeCl_3 solution to form a violet coloured solution of ferric thiosulphate.



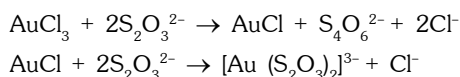
The violet colour disappears quickly due to the reduction of ferric chloride by $\text{S}_2\text{O}_3^{2-}$ ions,



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



- Sodium thiosulphate reduces auric salts to aurous salt.



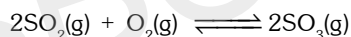
- **Neutral oxides** are those which are neutral towards litmus e.g., carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O) and nitric oxide (NO).

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

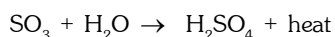
- H_2S gas is dried by passing over CaCl_2 or P_2O_5 .

- **Sulphur trioxide** (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 finely divided Pt or V_2O_5 at a pressure of 2atm. and temperature 700K.

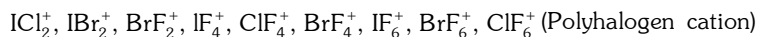
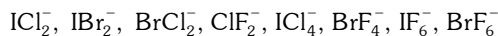


- SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.



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^-), Selenocyanate (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 :

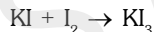
F_2	Cl_2	Br_2	I_2
158.8	242.6	192.8	151.1

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

- ***Test for chlorine :***

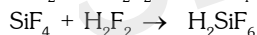
- It is a greenish yellow gas with irritating smell.
- It turns starch iodide paper blue.
- It bleaches litmus paper and indigo solution.

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



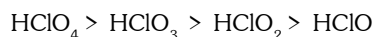
The solution behaves as a simple mixture of KI and I_2 .

- ***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 atom has highest oxidation number will have maximum number of oxygen atoms for participation in the extension of the \oplus 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 increase in atomic numbers of the halogen



SOME REAGENTS OR MIXTURES

- ***Lithophaon*** : A mixture of $\text{ZnS} + \text{BaSO}_4$ used as white paint.

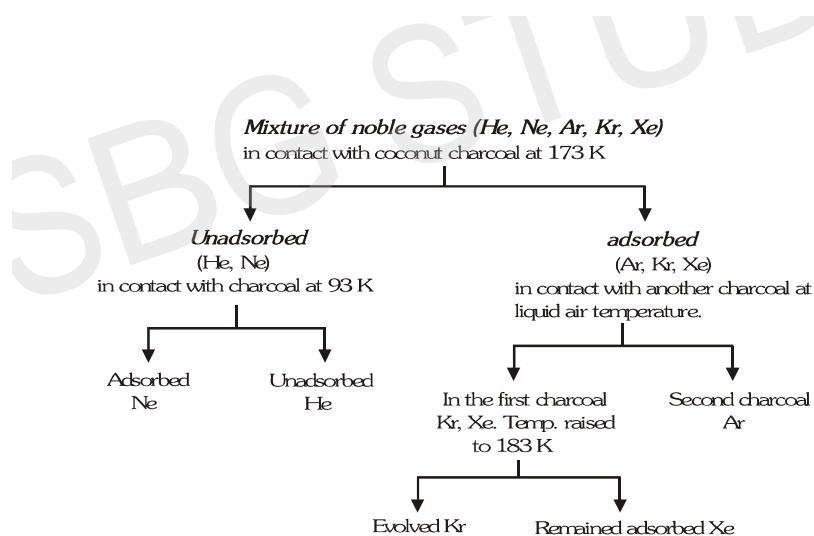
- ***Nitrolim*** : Calcium cyanamide + graphite used as fertilizer.

NOBEL GAS

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

<i>Elmpnt</i>	<i>Pprcpntagp by volump</i>	<i>Pprcpntagp 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.* cleveite, 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

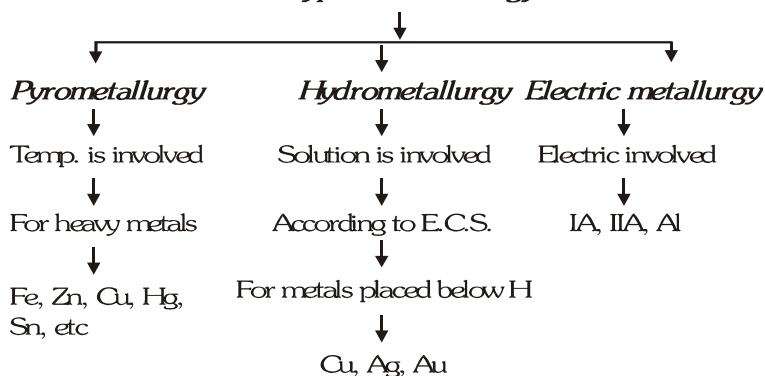


- The viscosity of He is extremely low, about $1/100^{\text{th}}$ of hydrogen gas.

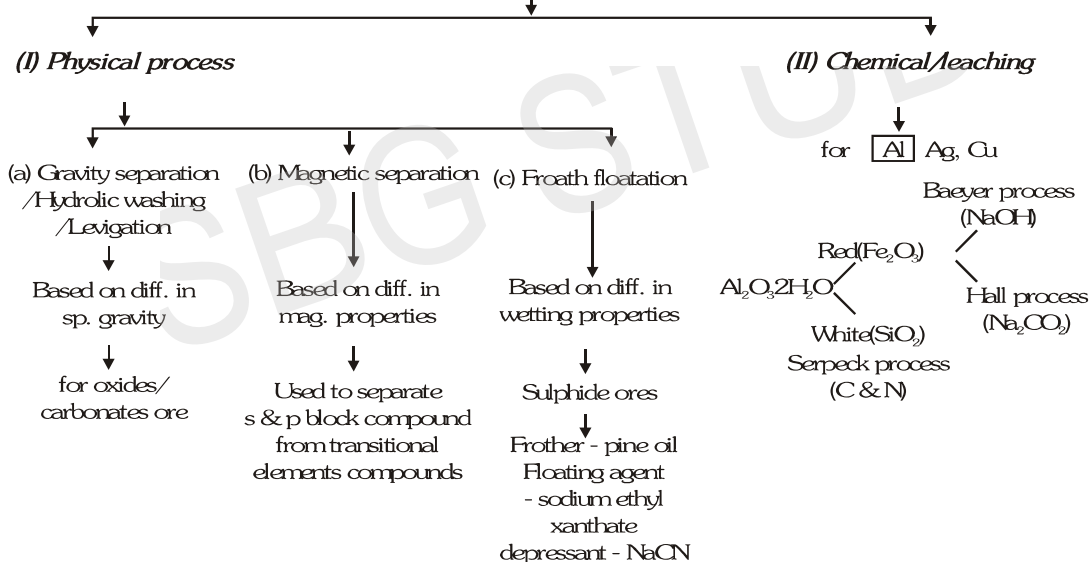
METALLURGY

➤ Bunch of process to extract metal from their respective ore

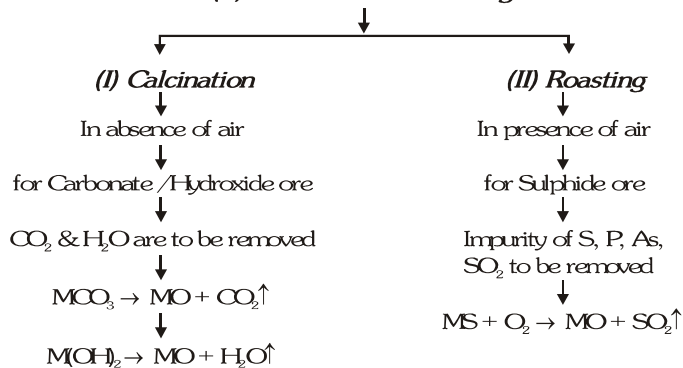
Orp : Minerals from which metal can be extracted economically :

Types of metallurgy**Metallurgical process :**

- Mining** : Ore obtain in big lumps (less reactive)
- Crushing/grinding/pulverization** : big lumps convert into powder (more reactive)
- Concentration** : To remove matrix/gangue from ore
To increase the concentration of ore particle in ore sample.

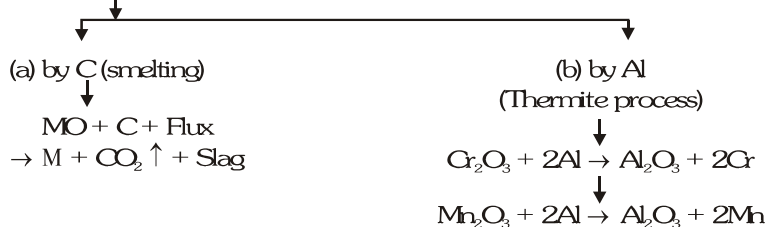
Concentration

Ag, Au, are concentrated by cyanide process.

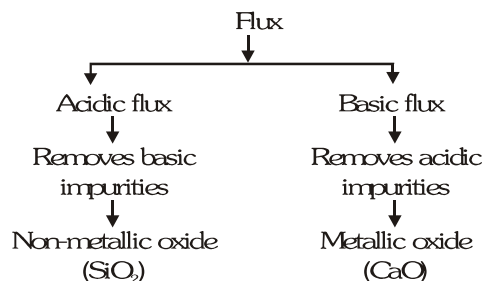
(4) Calcination & Roasting

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

(I) Chemical reduction



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



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-Heroult)

- Al can be extracted from Al₂O₃

- To decrease fusion temp. of Al₂O₃, Na₃AlF₆ & CaF₂ is to added

- Na₃AlF₆ & CaF₂ (Neutral flux) increase the conductivity & reduce the fusion temp.

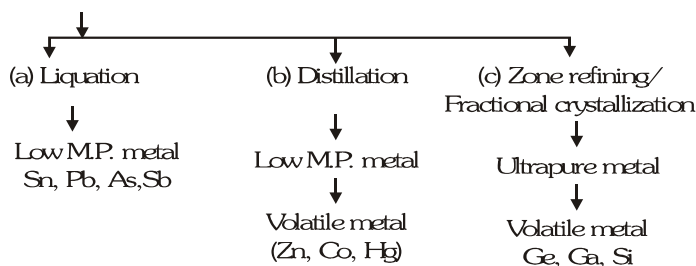
(ii) Extraction of Na (Down cell process)

- 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.

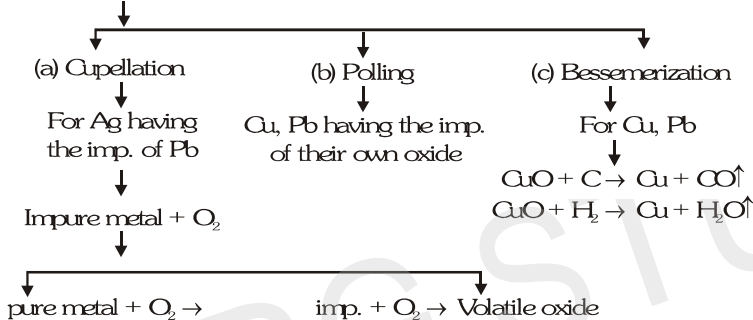
Refining : To obtain metal (99.98%)



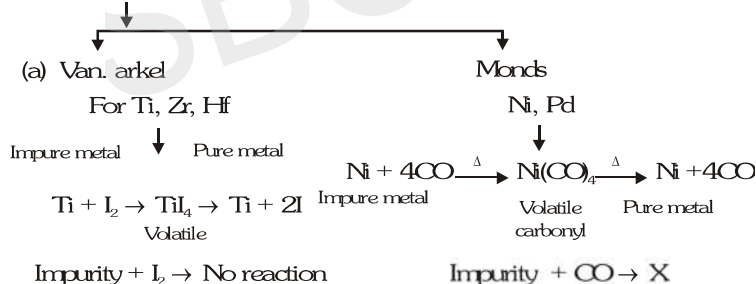
(I) Physical Process



(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.

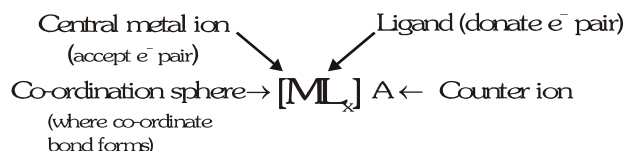
A summary of the occurrence and Extraction of some Metals is presented in the following table :

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 (impurities have more affinity for O_2 as compared 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) Poling (ii) Electrolytic method.	It is self reduction in a specially designed converter. 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 obtained in vapour 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. $\text{SnO}_2 + 2\text{C} \rightarrow \text{Sn} + 2\text{CO}$	Poling and Liquidation	Ore contains 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 $\text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{NaAg}(\text{CN})_2 + \text{N}_2\text{S}$ $2\text{NaAg}(\text{CN})_2 + \text{Zn} \rightarrow \text{Na}_2\text{Zn}(\text{CN})_4 + 2\text{Ag}$	Cupellation & electrolytic method	In hydrometallurgy Ag is obtained in the form of dark amorphous ppt.
Au E = 1.40	Native ore	1. Amalgamation. 2. Cyanide process	Cupellation & electrolysis method.	In hydrometallurgy Au is obtained in the form of dark amorphous ppt.

COORDINATION CHEMISTRY

- Addition compound $\begin{cases} \text{Double salt} \rightarrow \text{completely furnish into their constituents ions} \\ \text{Complex compound} \rightarrow \text{Do not furnish completely} \end{cases}$

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.
 $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{SO}_4 \leftrightarrow [\text{Co}(\text{H}_2\text{O})_5\text{SO}_4]\text{Cl}$
- (ii) **Hydrate isomerism :** Number of water molecule inside & outside the co-ordination sphere are different.
 $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl} \leftrightarrow [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O} \leftrightarrow [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
- (iv) **Linkage isomerism :** when ambidentate ligand is present in co-ordination sphere.
 $[\text{NC} \rightarrow \text{Ag} \leftarrow \text{CN}]^- \leftrightarrow [\text{NC} \rightarrow \text{Ag} \leftarrow \text{NC}]^- \leftrightarrow [\text{CN} \rightarrow \text{Ag} \leftarrow \text{NC}]^-$
- (iv) **Co-ordination isomerism :** In cationic anionic complex when ligand/metal ion interchange
 $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4] \leftrightarrow [\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$

- **Stero 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_{abcdet} have 15 geometrical isomerism.

➤ Ma_3b_3 have 2 geometrical isomerism [tac-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_{abcdet} optically active.

(ii) $M_{(AA)_2b_2}$ cis is optically active but trans does not.

(iii) $M_{(AA)_3}$ optically active.

Theorips of co-ordination compound :

(i) **Wprnpr thpory -**

(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 Rulp :**

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

(iii) **Valpnep bond thpory :**

(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 **Innpr orbital complpxps** and **Outpr orbital complpxps** 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.

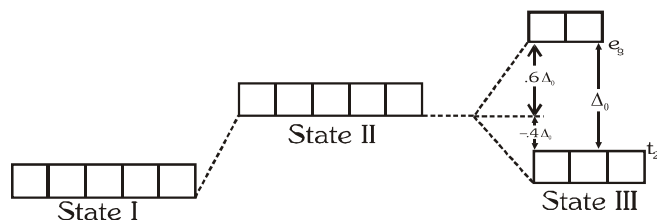
(iv) Then such type of complexes will be **diamagnptic** or **lpss paramagnptic** and will be called as **Low spin complpxps**

(v) All outer orbital complexes have **paramagnptic** nature and they are called as **High spin complpxps**

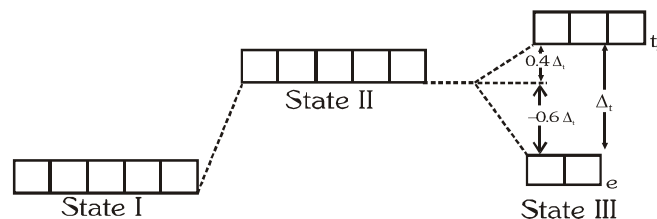
(iv) **Crystal Fipld Thpory :**

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 octahpdral



In tptrahpdral



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

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

(i) For octahedral CFSE = $\left[-0.4(n_{t_{2g}}) + 0.6(n_{e_g})\right]\Delta_0$ + Pairing 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 = $\left[-0.6(n_e) + 0.4(n_{t_2})\right]\Delta_t$ + Pairing energy (P.E.)

where n_{t_2} = number of electron in t_2 orbitals

n_e = number of electron in e orbitals

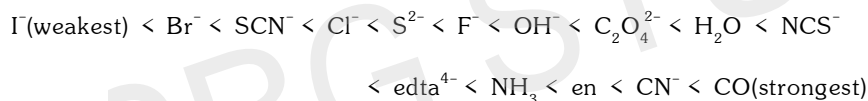
➤ **Factor affecting splitting**

- (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 :**

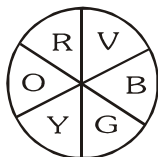
- (i) good σ donor
- (ii) good \oplus acceptor
- (iii) high negative charge
- (iv) Small in size

➤ **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.

d-BLOCK

- The t-blocks elements differ from those of d-blocks elements in that they have unstable electronic configuration in the outer shells in comparison to that of d-blocks element.

d-block elements electronic configuration

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

Most common oxidation state +2

- The colour in d-block elements is due to d-d excitation while in t-block element, it is due to t-t 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

Haber process = $Fe_2O_3 + Al_2O_3 + K_2O$

Ziegler Natta = $TiCl_4 + (C_2H_5)_3Al$

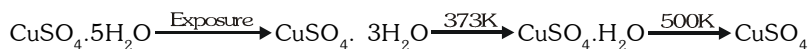
Phenol reagent = $FeSO_4 + H_2O_2$

Hydrogenation of Alkene = Ni/Pd

Decomposition of $KClO_3 = MnO_2$

Wilkinson catalyst = $RhCl + PPh_3$

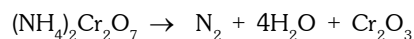
- Action of heat on copper sulphate



Bluish green

White

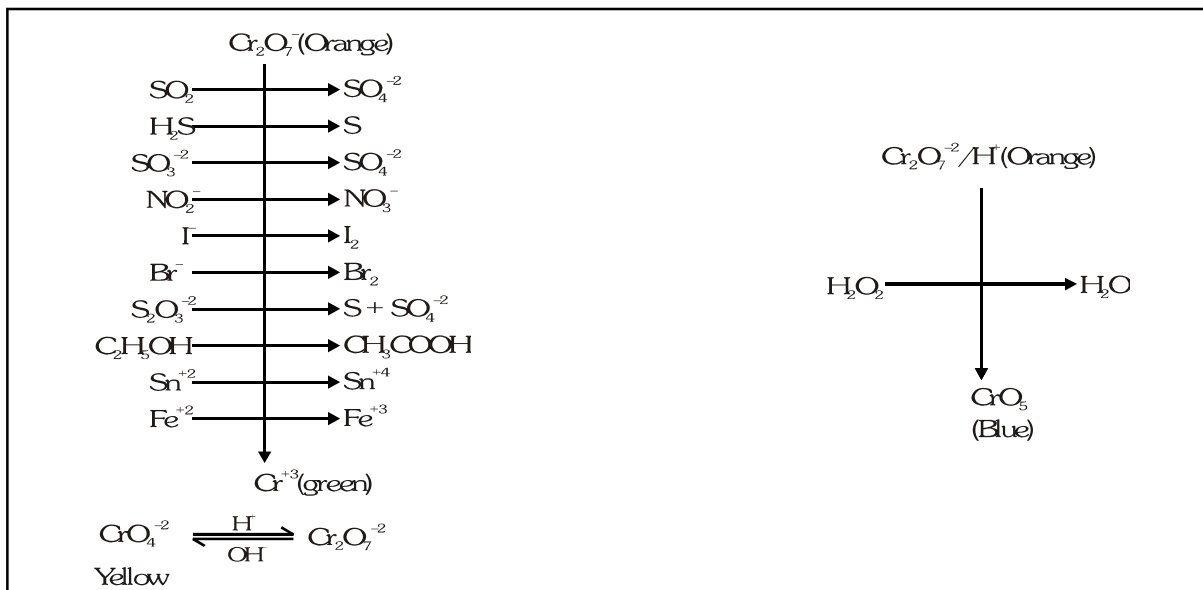
- **Chemical volcano.** When crystals of red coloured ammonium dichromate are heated, a violent action takes place accompanied by flashes of light and nitrogen is liberated leaving behind a dark green residue of chromium sesquioxide (Cr_2O_3)



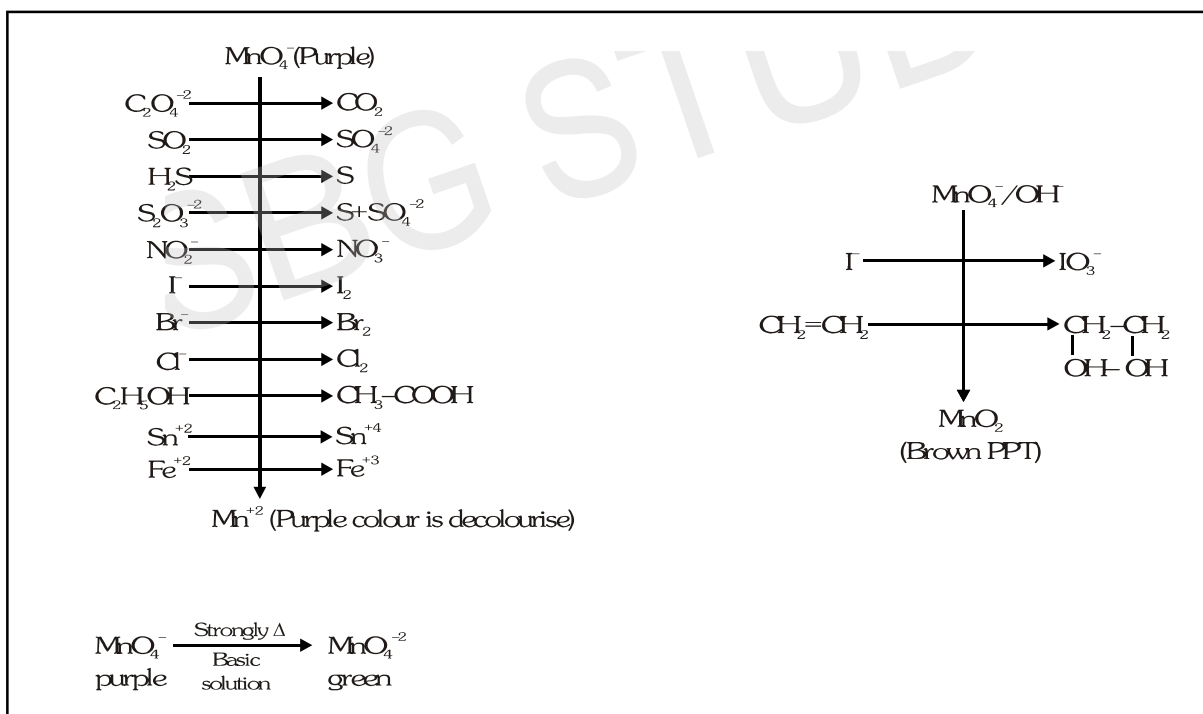
Ammonium dichromate

Chromium sesquioxide

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



➤ **Reaction of MnO_4^-**

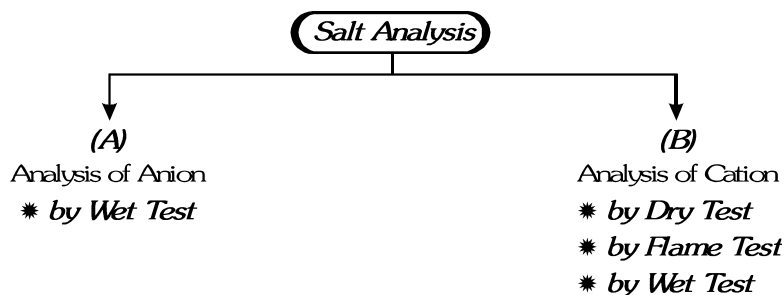


SALT ANALYSIS

Definition :

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

The identification of a substance usually involves its conversion into a new substance possessing characteristic properties with the help of one or more substances 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⁻)**

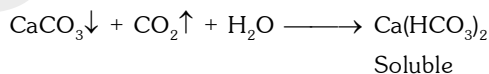
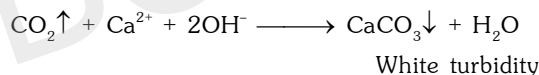
All carbonates except those of alkali metals and ammonium are insoluble in H₂O.

(i) Dilute HCl

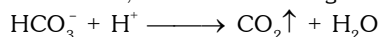
With dilute HCl, it decomposes with effervescence due to the evolution of carbon dioxide.



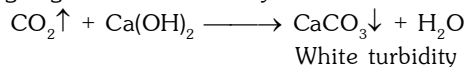
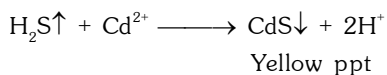
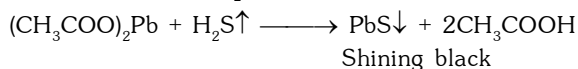
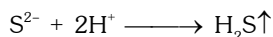
The gas produces white turbidity with lime water, Ca(OH)₂ or baryta water, Ba(OH)₂.

**(II) BICARBONATE (HCO₃⁻)****Dilute HCl**

With dilute HCl, all bicarbonates give effervescence due to the evolution of CO₂.

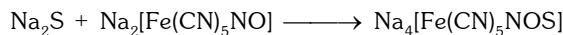


The gas gives white turbidity with lime water or baryta water.

**(III) SULPHIDE (S²⁻)****(i) Dilute HCl or Dilute H₂SO₄**

(ii) Sodium Nitroprusside Solution

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



Purple colour

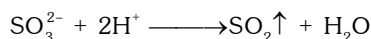
No reaction occurs with solutions of hydrogen sulphide or free gas. It however, filter paper moistened with a solution of the reagent is made alkaline with sodium hydroxide or ammonia solution, a purple colouration is produced with free hydrogen sulphide also.

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

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

Dilute HCl or Dilute H_2SO_4

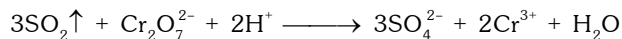
Dilute HCl or H_2SO_4 decomposes sulphites with the evolution of sulphur dioxide.



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.

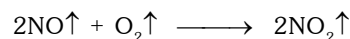
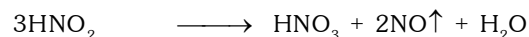


Green colour

(V) NITRITE (NO_2^-)

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

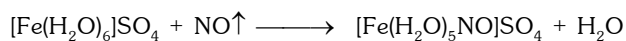
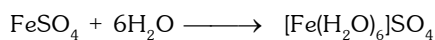
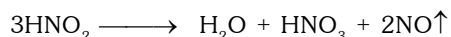
(i) Dilute HCl



Raddish-brown

(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

(2) RADICALS DETECTED WITH CONCENTRATED H_2SO_4 **(I) CHLORIDE (Cl^-)****(i) Concentrated H_2SO_4**

With concentrated H_2SO_4 , chlorides give 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

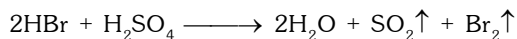


Yellow ppt

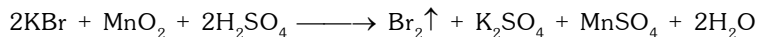
This test is given by ionic chlorides only. Chlorides of Hg^{2+} , Hg_2^{2+} , Pb^{2+} , Ag^+ , Sn^{4+} and Sb^{3+} do not respond to chromyl chloride test due to their covalent character, which allows them to ionise only slightly.

(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.



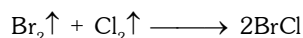
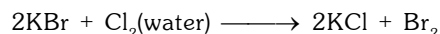
Reddish-brown

(ii) Manganous dioxide and Concentrated Sulphuric Acid

Reddish-brown

(iii) Chlorine Water

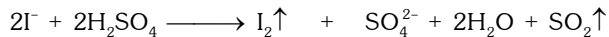
When chlorine water is added to a solution of bromide, free bromine is liberated which colours the solution orange-red. If CS_2 , $CHCl_3$ or CCl_4 is added to the solution and the liquid shaken, the bromine dissolves in the organic solvent and after allowing to stand forms a reddish-brown solution below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



Pale yellow solution

(III) IODIDE (I⁻)

(i) Concndratpd H₂SO₄



Violet vapours

(ii) Chlorinp Watpr



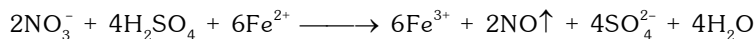
(IV) NITRATE (NO₃⁻)

(i) Concndratpd H₂SO₄



Reddish-brown vapours

(ii) Brown Ring Tpst



Brown ring

(V) ACETATE (CH₃CO₂⁻)

Dilutp Sulphuric Acid

On adding a small quantity of dilute H₂SO₄ to the acetate salt, acetic acid is produced, which can be easily recognized by its vinegar-like odour

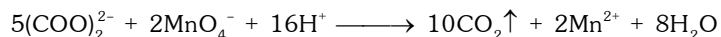


Vinegar like odour

(VI) OXALATE (C₂O₄²⁻)

Potassium Pprmanatp Solution

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



GROUP 'B' RADICALS

SULPHATE (SO₄²⁻)

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

Barium Chloridp Solution

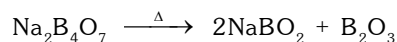
On adding BaCl₂ solution to a sulphate salt solution, a white precipitate ot barium sulphate (BaSO₄) insoluble in warm dilute hydrochloric acid and in dilute nitric acid but moderately soluble in boiling concentrated hydrochloric acid is torme.



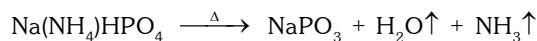
White ppt

ANALYSIS OF CATIONS

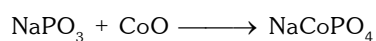
(1) Dry Tpsts

Borax Bpad Tpst :

Copper (II) metaborate

Microcosmic Salt Bpad Tpst

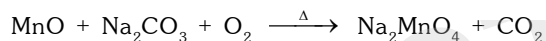
transparent bead



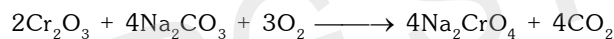
(blue bead)

Sodium Carbonatp Bpad Tpst

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



A yellow bead is obtained with chromium salt due to tormation ot sodium chromate (Na_2CrO_4)



(2) Flamp Tpsts

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

Colour	Cation
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_2Cl_2 White PbCl_2
II	IIA dil. HCl/ H_2S	Pb^{2+} , Cu^{2+} , Bi^{3+} , Hg^{2+} , Cd^{2+}	PbS CuS , Bi_2S_3 , HgS , CdS ↓ ↓ ↓ ↓ ↓ Black Black Brown Black Yellow
	IIB dil. HCl/ H_2S	As^{3+} , As^{5+} , Sb^{3+} , Sb^{5+} , Sn^{2+} , Sn^{4+}	As_2S_3 As_2S_5 Sb_2S_3 Sb_2S_5 SnS SnS_2 ↓ ↓ ↓ ↓ ↓ ↓ Yellow Yellow Orange Orange Brown Yellow
III	$\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$	Al^{3+} , Cr^{3+} , Fe^{3+}	$\text{Al}(\text{OH})_3$ $\text{Cr}(\text{OH})_3$ $\text{Fe}(\text{OH})_3$ ↓ ↓ ↓ White Green Brown
IV	$\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}/\text{H}_2\text{S}$	Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+}	NiS CoS MnS ZnS ↓ ↓ ↓ ↓ Black Black Pink/Butt/Skin Dirty white
V	$\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}/(\text{NH}_4)_2\text{CO}_3$	Ba^{2+} , Sr^{2+} , Ca^{2+}	BaCO_3 SrCO_3 CaCO_3 ↓ ↓ ↓ White White White
VI	No common group reagent	Na^+ , Mg^{2+} , K^+	No common ppt
Zpro	No common group reagent	NH_4^+	No common ppt (Generally identity 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:

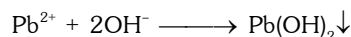
- | | |
|------------------|----------------|
| (i) Cold Water | (ii) Hot water |
| (iii) Dilute HCl | (iv) Conc. HCl |

(A) Group I (Pb^{2+} , Ag^+ , Hg_2^{2+}) RADICALS :

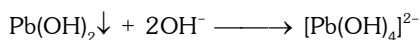
On adding dilute HCl to the salt solution a white precipitate is obtained, it indicates the presence of Pb^{2+} , Ag^+ or Hg_2^{2+} ion in the solution.

1 LEAD (II)

(i) Sodium Hydroxide Solution

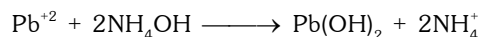


White ppt



Soluble

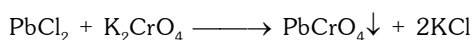
(ii) Ammonia Solution



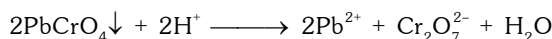
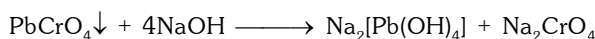
White ppt

(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.



Yellow ppt (chrome yellow)



2. SILVER (I)

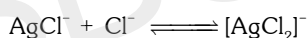
(i) Dilute Hydrochloric Acid

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



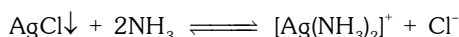
White ppt

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 complex is formed.



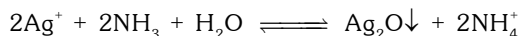
Soluble

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

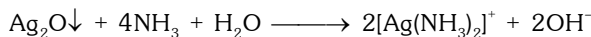


Soluble

(ii) Ammonia solution



Brown ppt

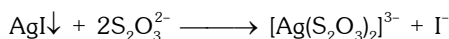
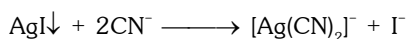


Soluble

(iii) Potassium Iodide Solution

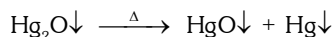
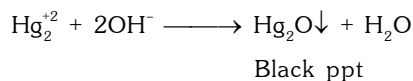


Yellow ppt

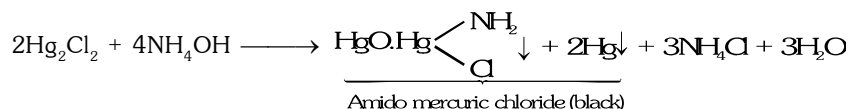


3. MERCURY (I)

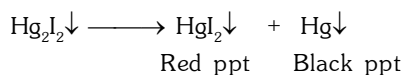
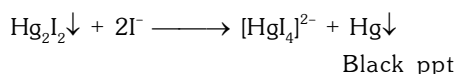
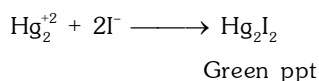
(i) Sodium Hydroxidp Solution



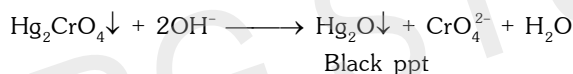
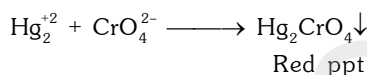
(ii) Ammonia Solution



(iii) Potassium Iodidp Solution



(iv) Potassium Chromatp Solution

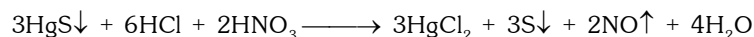


(B) Group II A (Pb^{2+} , Hg^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+}) RADICALS :

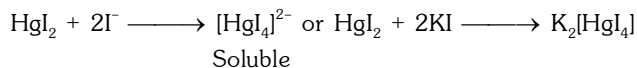
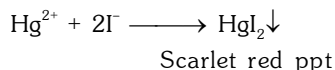
The precipitates of group IIA are insoluble in yellow ammonium sulphide.

1. MERCURY (II)

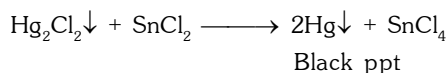
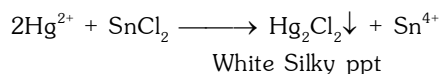
HgS precipitated dissolves in aqua regia forming undissociated HgCl_2 .



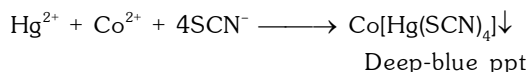
(i) Potassium Iodidp Solution



(ii) Tin(II) Chloridp Solution

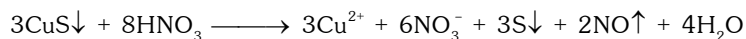


(iii) Cobalt(II) Thiocyanatp Tpst



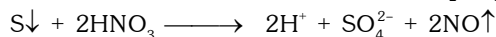
2. COPPER (II)

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



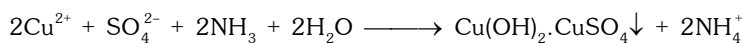
White ppt

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

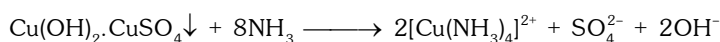


(i) Ammonia Solution

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.



Blue ppt

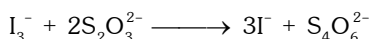


Deep-blue colouration

(ii) Potassium Iodide

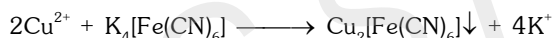


White ppt



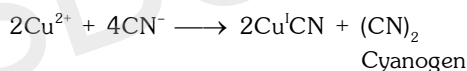
(iii) Potassium Hexacyanoferrate(II) solution

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

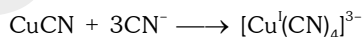


Chocolate-brown ppt

(iv) Test by NaCN & KCN



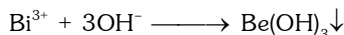
Cyanogen



3. BISMUTH (III)

(i) Sodium Hydroxide

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

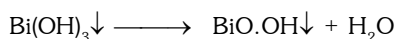


White ppt

The precipitate is soluble in acids.

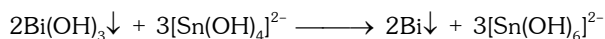


When boiled, the precipitate loses water and turns yellowish-white.

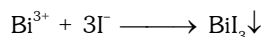


Yellowish-white ppt

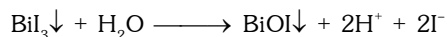
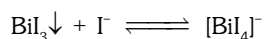
$\text{Bi}(\text{OH})_3$ when reduced by tetrahydroxostannate(II) ions give black precipitate of bismuth metal.



(ii) **Potassium Iodide**



Black ppt

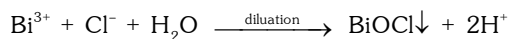


Orange ppt

(iii) **Water**



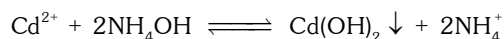
White ppt



White ppt

4. CADMIUM (II)

(i) **Ammonium Hydroxide**



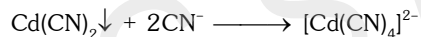
White ppt



(ii) **Potassium Cyanide**



White ppt



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.

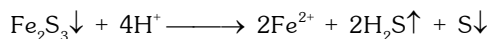
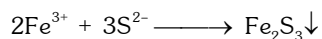
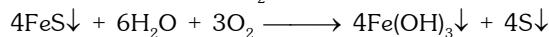
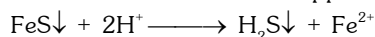
(C) Group III (Fe^{3+} , Al^{3+} , Cr^{3+})

1. IRON (III)

(i) **Ammonium Sulphide Solution**



Black ppt

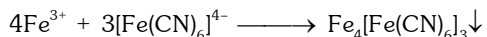


(ii) **Sodium Hydroxide Solution**

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.



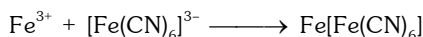
Reddish-brown ppt

(iii) *Potassium Hexacyanoferrate(II)*

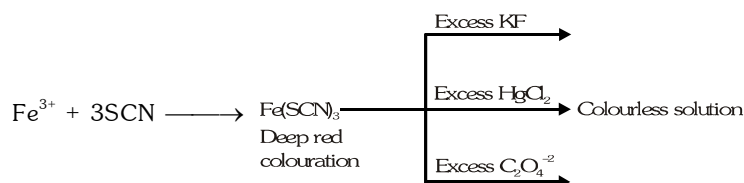
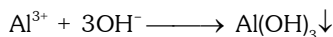
Prussian blue



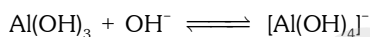
Raddish-brown ppt

(iv) *Potassium Hexacyanoferrate(III)*

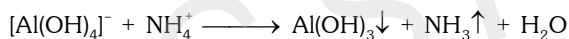
Brown colouration

(v) *Ammonium Thiocyanate Solution*2. *ALUMINIUM (III)**Sodium Hydroxide Solution*

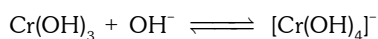
White ppt



Soluble

3. *CHROMIUM (III)*(i) *Sodium Hydroxide Solution*

Green ppt

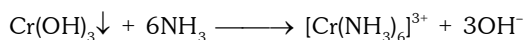


excess

Soluble

(ii) *Ammonia Solution*

Bluish-green ppt

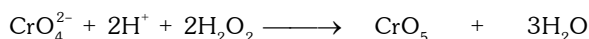


Excess

Pink colouration

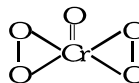
(iii) *Chromium Peroxide (Chromium Peroxide, Perochromic Acid) Test*

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.

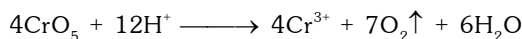


Blue colouration
in ether layer

Chromium pentoxide has the following structure :



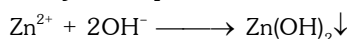
Because of the two peroxide groups, the compound is often called chromium peroxide. The name peroxochromic acid is less appropriate, because the compound does not contain hydrogen at all. In aqueous solution, the blue colour fades rapidly, because chromium pentoxide decomposes to chromium(III) and oxygen.



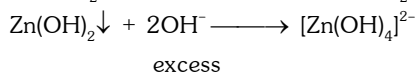
(D) Group IV (Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+})

1. ZINC (II)

(i) Sodium Hydroxide Solution



White gelatinous ppt



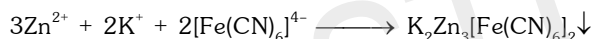
(ii) Ammonia Solution



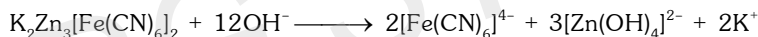
White ppt



(iii) Potassium Hexacyanoferrate(II)



White ppt



(iv) Ammonium tetrathiocyanatoperrate(II)

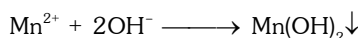


White ppt

2. MANGANESE (II)

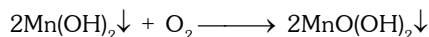
(i) Sodium Hydroxide Solution

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



White ppt

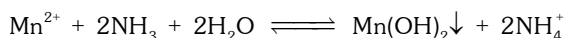
The precipitate is insoluble in excess reagent. It rapidly oxidizes on exposure to air, becoming brown, when hydrated manganese dioxide, MnO(OH)_2 , is formed.



Brown ppt

(ii) Ammonia Solution

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



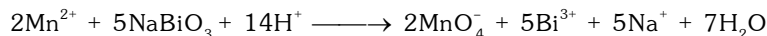
White ppt

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

(iii) Lead dioxide and Concentrated Nitric Acid



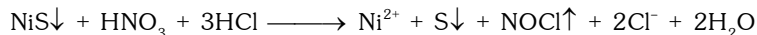
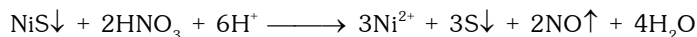
Purple colour

(iv) *Sodium Bismuthatep (NaBiO₃) Solution*

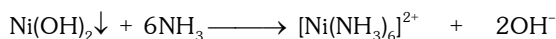
Purple colour

3. *NICKEL (II)*

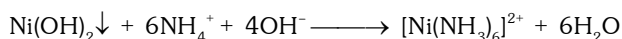
The black precipitate of NiS(II) is insoluble in cold dilute HCl and in acetic acid but dissolves in hot concentrated nitric acid and in aqua regia with the separation of sulphur.

(i) *Sodium Hydroxidp Solution*

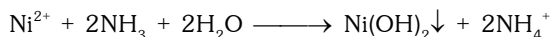
Green ppt



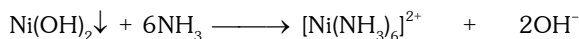
Deep-blue colouration



Deep-blue colouration

(ii) *Ammonia Solution*

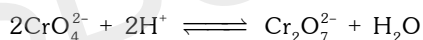
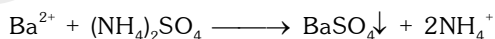
Green ppt



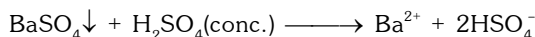
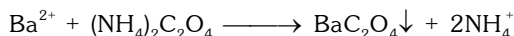
Deep-blue colouration

(E) *Group V (Ba²⁺, Sr²⁺, Ca²⁺)*1. *BARIUM (II)*(i) *Potassium Chromatp Solution*

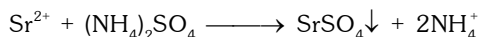
Yellow ppt

(ii) *Ammonium Sulphatp Solution*

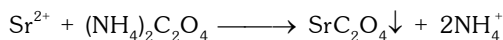
White ppt

(iii) *Ammonium Oxalatp Solution*

White ppt

2. *STRONTIUM (II)*(i) *Ammonium Sulphatp Solution*

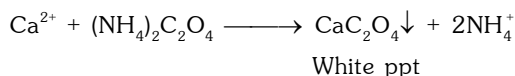
White ppt

(ii) *Ammonium Oxalatp Solution*

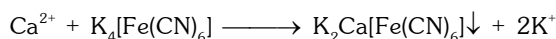
White ppt

3. CALCIUM (II)

(i) Ammonium Oxalate Solution



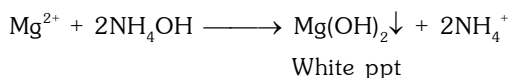
(ii) Potassium Hexacyanoferrate(II) Solution



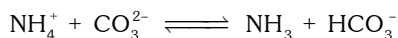
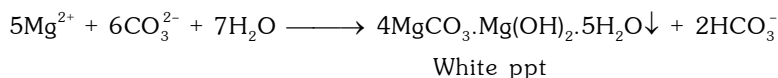
(F) Group VI (Na^+ , K^+ , Mg^{2+})

1. MAGNESIUM (II)

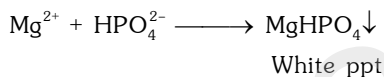
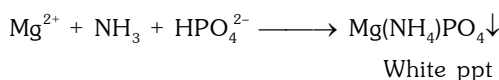
(i) Ammonia Solution



(ii) Ammonium Carbonate Solution



(iii) Disodium hydrogen phosphate Solution

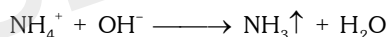


(G) Group V (NH_4^+)

1. AMMONIUM (NH_4^+)

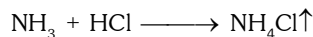
(i) Sodium Hydroxide Solution

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.



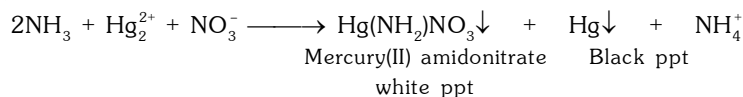
White fumes

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



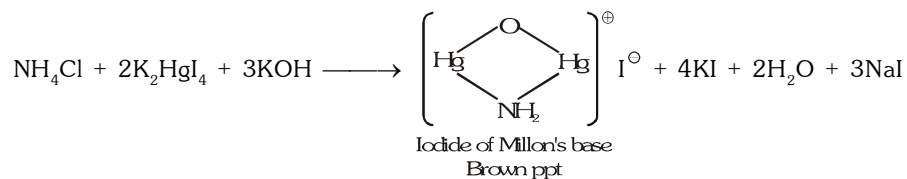
Deep-blue colouration

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



(ii) Nessler's Reagent

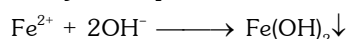
With Nessler's reagent (an alkaline solution of potassium tetraiodomercurate(II)), ammonium salts form a brown precipitate or brown or yellow colouration is produced depending on the amount of NH_4^+ ions present in the solution. The precipitate is a basic mercury(II) amido-iodine.



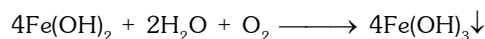
This test can detect even traces of NH_3 present in a sample.

IRON (II)

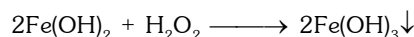
(i) **Sodium Hydroxide Solution**



White ppt

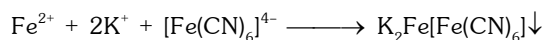


Reddish-brown ppt



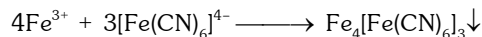
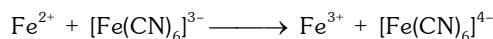
Reddish-brown ppt

(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

SBG STUDY

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