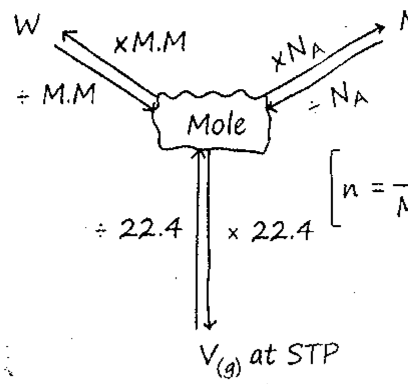
Contents

Physical Chemistry

1 Mole Concept

1. Mole calculation (Y MAP)



$$\left[n = \frac{W}{M.M} = \frac{N}{N_A}\right]$$

2. % Composition

$$\text{\% comp of element} = \frac{\text{A.W} \times \text{no. of atoms of given element in one molecule of compound}}{MW_{comp}} \times 100$$

Q. Find % of Ca, C & O in $CaCO_3$?

$$\% \ Ca = \frac{40 \times 1}{100} \times 100 = 40\%$$

$$\% \ C = \frac{12 \times 1}{100} \times 100 = 12 \ \%$$

$$\% \ O = \frac{16 \times 3}{100} \times 100 = 48 \ \%$$

3. Density

Density → Absolute density
Density → Relative density

Case 1: For solids and liquid.

1. $A.D(d) = \frac{\text{Mass}}{\text{Volume}} \left(\frac{g}{mL}\right)$

2. $R.D = \frac{d_{sub}}{d_{H_2O \text{ at } 4°C}}$ [R.D is unitless]
(sp. gravity)

Case 2: For gases

1. $A.D(d) = \frac{PM}{RT} \left(\frac{g}{L}\right)$

P = pressure (atm)
M = MW
R = gas const
$= .082 \ l \ atm \ mol^{-1} K^{-1}$
$= \left(\frac{1}{12}\right)$ approx.
T = Temp (K)

2. $R.D = \frac{M_1}{M_2}$ (at const P & T)

3. $V.D = \frac{M}{2}$

Q. Find V.D. of SO_2?

$V.D = M/2 = 64/2 = 32$

4. Avg atomic wt (for element having isotopes)

$$\text{Avg at wt} = \frac{\text{\% abundance of isotope}_1 \times AW_1 + \text{\% abundance of isotope}_2 \times AW_2 + \dots}{100}$$

Q. Find avg. atomic wt?

Isotopes	%abun	Avg at wt $= \frac{75 \times 35 + 25 \times 37}{100}$
Cl^{35}	75%	$= \frac{3550}{100}$
Cl^{37}	25%	$= 35.5$

5. Mean molar mass (for gaseous mix)

$$\text{Mean molar mass} = \frac{n_1 M_1 + n_2 M_2 + \dots}{n_1 + n_2 + \dots}$$

Q. Find mean molar mass

Gas	Mole%
O_2	16
N_2	80
CO_2	3
SO_2	1

mean molar mass $= \frac{16 \times 32 + 80 \times 28 + 3 \times 44 + 1 \times 64}{100}$

$= \frac{2948}{100} = 29.48$

6. Limiting reagent

n_i 4 6

$2SO_2 + O_2 \longrightarrow 2SO_3$

moles reacted $\frac{4}{2}$ $\frac{6}{1}$ SO_2 is L.R

$\boxed{2}$ 6

final moles 2×0 $(6-2) \times 1$ 2×2

$\boxed{0}$ $\boxed{4}$ $\boxed{4}$

Q. 4 moles of N_2 is reacted with 9 moles of H_2 to form NH_3 find

$$\begin{array}{lccc} n_i & 4 & 9 & \\ & N_2 & + \ 3H_2 \rightarrow & 2NH_3 \\ \text{moles reacted:} & \frac{4}{1} & \frac{9}{3} & H_2 \text{ is L.R} \\ & 4 & 3 & \\ \text{final moles:} & 1\times(4-3) & 0\times3 & 3\times2 \\ & \boxed{1} & \boxed{0} & \boxed{6} \end{array}$$

1. Moles of NH_3 formed = 6
2. Wt of NH_3 formed = 6 × 17 g
3. Molecules of NH_3 formed = 6 × N_A
4. Volume of $NH_3 g$ formed = 6 × 22.4L at STP
5. Moles of excess reactant left = 1
6. Wt of excess reactant left = 1 × 28g
7. Molecules of excess reactant left = 1 × N_A
8. Volume of excess reactant left = 1 × 22.4L at STP

7. Stoichiometric calculation: Here (1) C Balance (2) H (3) O

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$

	CH_4	O_2	CO_2	H_2O
Mole	1	2	1	2
Wt (g)	1×16	2×32	1×44	2×18
N	1×N_A	2×N_A	1×N_A	2×N_A
VatSTP	1×22.4	1×22.4	1×22.4	—

Q. Calculate wt of residue obtained when 1 mol of $CaCO_3$ is strongly heated?

$$CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}\uparrow$$

1 mol   1 mol

1 mol   1 × 56 = 56 gm

Q. How many litre of O_2 (g) at STP is required for complete combustion of 2 moles of C_5H_{10}?

$$C_5H_{10} + \frac{15}{2}O_2 \longrightarrow 5CO_2 + 5H_2O$$

1 mol $\frac{15}{2}$ mol

2 mol   15 mol

2 mol $\boxed{15 \times 22.4 \text{ L}}$ at STP

Q. How many moles of O_2 are needed to produce 5 mol of Fe_2O_3?

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$

3 mol   2 mol

$\frac{3}{2}$ mol   1 mol

$\frac{3}{2}$ × 5 mol   5 mol

$\boxed{= 7.5 \text{ mol}}$

8. Empirical and molecular formula

Element	%comp.	A.W	$\frac{\%}{\text{A.W}}$	Simplest ratio	Simplest whole no. ratio
C	40.6	12	$\frac{40.6}{12} = 3.3$	$\frac{3.3}{3.3} = 1$	1 × 2 = 2
H	5	1	$\frac{5}{1} = 5$	$\frac{5}{3.3} = 1.5$	1.5 × 2 = 3
O	54.4	16	$\frac{54.4}{16} = 3.3$	$\frac{3.3}{3.3} = 1$	1 × 2 = 2

E.F = $C_2H_3O_2$

EFW = 12×2+1×3+16×2=59

MF = $(E.F)_n$

$\left(n = \frac{M.F.W}{E.F.W}\right)$

$n = \frac{\cancel{118}}{\cancel{59}} = 2$

MF = $(C_2H_3O_2)_n$

= $(C_2H_3O_2)_2$

[M.F = $C_4H_6O_4$]

Q If M.W of comp = 118 then, find molecular formula.

9. Concentration terms

$\begin{pmatrix} \text{Soln} \longrightarrow \text{Solute} + \text{Solvent} \\ (A+B) \qquad\quad B \qquad\qquad A \end{pmatrix}$

(1) $\% \frac{W}{W}$ (mass %)

$x \% \frac{W}{W} \Rightarrow$ x gm solute is present in 100 gm sol^n

$$\left[\% \frac{W}{W} = \frac{W_{Solute}}{W_{Sol^n}} \times 100\right]$$

(2) $\% \frac{W}{V}$

$x \% \frac{W}{V} \Rightarrow$ x gm solute in 100 mL sol^n

$$\% \frac{W}{V} = \frac{W_{Solute}(g)}{V_{Sol^n}(mL)} \times 100$$

(3) $\% \frac{V}{V}$

$x \% \frac{V}{V} \Rightarrow$ x mL solute in 100 mL sol^n

$$\% \frac{V}{V} = \frac{V_{Solute(mL)}}{V_{Sol^n(mL)}} \times 100$$

(4) Molarity (M)

$$\left[M = \frac{n_B}{V_{Sol^n(L)}}\right]$$

(5) Molality (m)

$$\left[m = \frac{n_B}{W_A(kg)}\right]$$

(6) Normality (N) $\qquad [N = M \times n.f]$

$$N = \frac{\text{No. of gm eq}}{V_{Sol^n(L)}}$$

(7) Strength (S)

$$S = \frac{W_B}{V_{Sol^n(L)}}$$

(8) PPm (Parts per million)

$$PPm = \frac{W_B}{W_{Sol^n}} \times 10^6$$

(9) PPb (Parts per billion)

$$PPb = \frac{W_B}{W_{Sol^n}} \times 10^9$$

$$\left.\begin{matrix} \% \frac{W}{W} \\ \text{molality} \\ PPm \\ PPb \end{matrix}\right\} \text{Temp independent}$$

$$\left.\begin{matrix} \% \frac{W}{V} \\ \% \frac{V}{V} \\ M \\ N \\ S \end{matrix}\right\} \text{Temp dependent}$$

Relation b/w conc^n terms

(1) $\% \frac{W}{W}$ & M(molarity)

$$\left[M = \frac{10 x d}{MW_B}\right] \quad x \Rightarrow \% \frac{W}{W}$$

$d \Rightarrow$ density in $\frac{g}{mL}$

MW_B = molar mass of solute

(2) Relation b/w m and x

$$\left[m = \frac{x_B}{x_A} \times \frac{1000}{MW_A}\right]$$

x_B = mole fraction of solute

x_A = mole fraction of solvent

$[x_A + x_B = 1] \qquad x_A = \frac{n_A}{n_A+n_B}$; $x_B = \frac{n_B}{n_A+n_B}$

MW_A = molar mass of solvent

(3) Relation b/w m and M

$$\left[M = \frac{md}{1 + \frac{mMW_B}{1000}}\right]$$

(4) Relation b/w S(g/L) and M

$[S(g/L) = M \times MW_B]$

Q. Density of 2M aq. CH_3COOH is 1.2 g/mL

find (1) $\% \frac{W}{W}$ (2) m (3) x_{solute}

(1) $M = \frac{10 \times d}{MW_B}$ $\left(x = \% \frac{W}{W}\right)$

$2 = \frac{\cancel{10} \times x \times \cancel{1.2}}{\cancel{60}_5}$

$x = 10$

$\left(10\% \frac{W}{W}\ CH_3COOH\right)$

(2) $M = \frac{md}{1 + \frac{mMW_B}{1000}}$

$2 = \frac{m \times 1.2}{1 + \frac{m \times 60}{1000}}$

$m = ?$

(3) $M = \frac{x_B}{1 - x_B} \times \frac{1000}{18}$

Q. 6.022×10^{22} molecules of a compound 'x' has mass 10 gm. What is the molarity of sol^n containing 5 gm of 'x' in 2 L?

$\frac{\cancel{6.022 \times 10^{22}}}{\cancel{6.022 \times 10^{23}}_{10}} = \frac{10}{MW_x}$

$MW_x = 100$

$n_x = \frac{5}{100}$

$M_x = \frac{5}{100 \times 2} = 2.5 \times 10^{-2}$

10. Molarity in diff cases

Case 1: On dilution

$[M_1V_1 = M_2V_2]$

M_1 = Molarity before dilution

V_1 = Volume before dilution

M_2 = Molarity after dilution

V_2 = Volume after dilution

Case 2: On mixing

$$\left[M_{mix} = \frac{|M_1V_1 \pm M_2V_2|}{V_1 + V_2}\right]$$

Case 3: Molarity of ion

$$\left[M_{ion} = \frac{n_{ion}}{V_{sol^n}\ (L)}\right]$$

Q. Find molarity on mixing

200 mL of 1M HCl + 100 mL of 0.5M HCl

$M_{mix} = \frac{200 \times 1 + 100 \times 0.5}{300}$

$= \frac{200 + 50}{300} = \frac{25\cancel{0}}{30\cancel{0}} = \frac{5}{6}$

11. Volume strength of H_2O_2

x 'V' H_2O_2

$2H_2O_2 \longrightarrow 2H_2O + O_2$

1L $H_2O_2(aq)$ gives xL O_2 at S.T.P.

(1) $[V.S = 11.2 \times M]$

$(N = M \times nf)$

(2) $[V.S = 5.6 \times N]$

(3) $[S(g/L) = M \times MW_B]$

(4) $\left[\% \frac{W}{V} = \frac{S}{10}\right]$

12. % of free SO_3 (labelling of oleum)

% free SO_3 = y % strength oleum

% free $SO_3 = \frac{80}{18} \times (y - 100)$

13. % of available Cl_2

% avail. $Cl_2 = \frac{3.5 \times M \times V}{W_{gm}}$

14. Hardness of water in ppm

$\text{Hardness} = \frac{W_{CaCO_3}}{\text{total mass of } H_2O} \times 10^6$

(in terms of ppm of $CaCO_3$)

[d = 1 g/mL]

Practice

Q. Find % $\frac{W}{W}$ of 5.6 V H_2O_2

$(d = 1\ g/mL, MW_{H_2O_2} = 34)$

$V.S. = 11.2 \times M \qquad \left[M = \frac{1}{2}\right]$

$5.6 = 11.2 \times M$

$M = \frac{10\ xd}{MW_B} \qquad x = 1.7$

$\frac{1}{2} = \frac{10 \times x \times 1}{34} \qquad \left[1.7\ \%\ \frac{W}{W}\ H_2O_2\right]$

Q. 20 g $MgCO_3$ sample decomposes on heating to give CO_2 and 8 gm MgO. Find % purity of $MgCO_3$ in sample?

$MgCO_3 \longrightarrow MgO + CO_2$

$84\ gm \longleftrightarrow 40\ gm \qquad \frac{84}{\cancel{40}_{5}} \times 8\ gm \longrightarrow 8\ gm$

$\left[\%\ purity = \frac{W_{comp}}{W_{sample}} \times 100\right] = \frac{84}{\cancel{5 \times 20}} \times \cancel{100}$

$= 84\ \%$

Q. Find x_B of 1 molal aq sol^n?

$m = \frac{x_B}{x_A} \times \frac{1000}{MW_A}$

$1 = \frac{x_B}{(1 - x_B)} \times \frac{\overset{55.5}{\cancel{1000}}}{\cancel{18}} \qquad \left[\frac{1}{55.5} = \frac{x_B}{1 - x_B}\right]$

Q. $Conc^n$ aq sol^n of H_2SO_4 is 98% H_2SO_4 by mass & has density 1.8 gm/mL. Volume of acid required to make 1 Ltr of 0.1 M H_2SO_4 sol^n is?

$x = 98,\ d = 1.8 \qquad M = \frac{10\ xd}{MW_B}$

$M = \frac{10 \times \cancel{98} \times 1.8}{\cancel{98}} = 18\ M$

$18 \times V_1 = 1 \times 0.1 \Rightarrow V_1 = \frac{1}{180} L$

Q. How many moles of $PbCl_2$ will be formed from a rxn b/w 6.5 gm PbO and 3.2 gm HCl?

$n_i \qquad 0.029 \qquad 0.087$

$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$

$\frac{0.029}{1} \qquad \frac{0.087}{2} \qquad n_{PbO} = \frac{6.5}{224}$

moles reacted $\boxed{0.029} \qquad 0.0435 \qquad \boxed{0.029}$

$= 0.029$

$n_{HCl} = \frac{3.2}{36.5} = 0.087$

PbO is limiting reagent

n_{PbCl_2} formed $= 0.029$

2 Atomic Structure

1. Electromagnetic radiation

(1) $C = \nu \lambda$

$C \rightarrow 3\times10^{8}$ m/s, $\nu \rightarrow$ frequency, $\lambda \rightarrow$ wave length

(2) $\bar{\nu} = \frac{1}{\lambda}$

$1Fm = 10^{-15}m$
$1Pm = 10^{-12}m$
$1Å = 10^{-10}m$
$1nm = 10^{-9}m$
$1\mu m = 10^{-6}m$

Q. Which has highest frequency?

(A) γ-rays (B) Yellow
(C) Infrared (D) Radio wave

Electromagnetic Spectrum				Wave length ↑,	freq ↓		
Cosmic rays	Gamma rays	X-Ray	U.V radiation	Visible	Infrared	Microwaves	Radio waves
ν_{max}				VIBGYOR			ν_{min}
λ_{min}				$\lambda\uparrow, \nu\downarrow$			λ_{max}
Classical	gaadi	X	U	V	In	my	range

2. Planck's quantum theory

(1) $E = \frac{hc}{\lambda} = h\nu$ (for 1 quantum)

(2) $E = \frac{hc}{\lambda} n$ (for n quantum)

$E = n\frac{12400}{\lambda(Å)}$ ev [$1ev = 1.6\times10^{-19}J$]

Q. Find energy of a photon whose wave length is 310 nm.

$\lambda = 310$ nm $= 3100$ Å

$E = 1\times\frac{12400}{3100} = 4$ ev

$E = 4\times1.6\times10^{-19}$ J

$= 6.4\times10^{-19}$ J

Q. No. of photons emitted by a bulb of 40 watt in 1 min with 50% efficiency will be?

(Given: $\lambda = 620$ nm)

$\lambda = 6200$ Å $\quad E = P\times t$

$= 40\times60\times\frac{1}{2}$

$= 1200$ J

$$\frac{\cancel{1200}^{\,600}}{1.6\times10^{-19}} = n\times\frac{\cancel{12400}^{\,2}}{\cancel{6200}}$$

$$n = \frac{600}{1.6\times10^{-19}}$$

$= 375\times10^{19}$

$n = 3.75\times10^{21}$

3. Bohr's theory (for $1e^{\ominus}$ system)

$H, He^{+}, Li^{2+}, Be^{3+}\ldots\ldots Na^{10+}$ etc.

(1) Orbit angular momentum

$$mvr = \frac{nh}{2\pi} = n\hbar \qquad \left(\hbar = \frac{h}{2\pi}\right)$$

(2) Radius, $r = r_o\times\frac{n^2}{Z} = a_o\times\frac{n^2}{Z} = 0.53\times\frac{n^2}{Z}$ Å

r_o or a_o = Bohr radius = 0.53 Å

(3) Velocity $V = 2.18\times10^{6}\times\frac{Z}{n}$ m/s

(4) Total energy T.E $= -13.6 \times \frac{Z^2}{n^2} \frac{ev}{atom}$

(5) $T.E = -K.E = \frac{P.E}{2}$

(6) Time period $T \propto \frac{n^3}{Z^2}$

(7) Frequency $f = \frac{1}{T}$ $\quad f \propto \frac{Z^2}{n^3}$

(8) Ionization energy I.E $= +13.6 \times Z^2 \frac{ev}{atom}$

(9) Excitation energy E.E $= 13.6 \times Z^2$

$\left[1 - \frac{1}{n^2}\right] \frac{ev}{atom}$

(10) Binding energy B.E $= +13.6 \times \frac{Z^2}{n^2} \frac{ev}{atom}$

$= \frac{I.E}{n^2}$

$\begin{bmatrix} 3^{rd} \text{ E.S } n = 4 \\ 4^{th} \text{ E.S } n = 5 \end{bmatrix}$

Q. Find r, V, T.E, K.E, P.E of He^+ in 1^{st} excited state?

$n = 2 \quad ; \quad Z = 2$.

$r = r_o \times \frac{2^2}{2} = 2r_o$ or, $2a_o = 2 \times (0.53)Å$

$V = 2.18 \times 10^6 \times \frac{\cancel{Z}}{\cancel{Z}}$ m/s $= 2.18 \times 10^6$ m/s

$TE = -13.6 \times \frac{2^2}{2^2}$ ev/atom $= -13.6$ ev/atom

$KE = +13.6$ ev/atom

$PE = -13.6 \times 2 = -27.2$ ev/atom

Q. Find orbit A.M of 5^{th} orbit?

$mvr = \frac{5h}{2\pi} = 2.5 \frac{h}{\pi}$

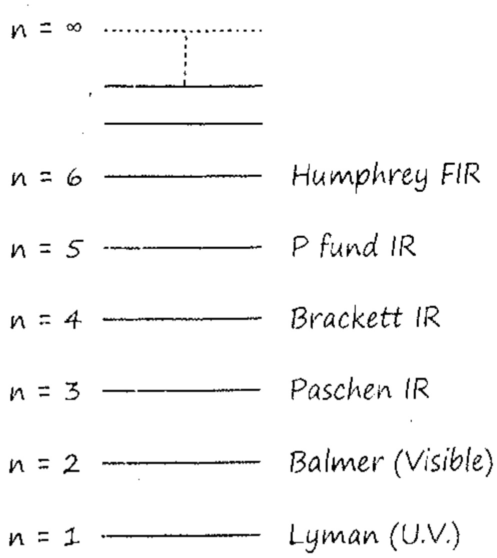
Q. Find I.E of Li^{2+} ion?

$I.E = +13.6 \times 3^2$

$= +13.6 \times 9$ ev/atom

$\left[\frac{mv^2}{r} = \frac{KZe^2}{r^2}\right]$

4. Hydrogen spectrum



Rydberg's formula

$R_H =$ Rydberg's const $\quad \frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$= 1.1 \times 10^7 m^{-1} \qquad (C = \nu \lambda) \left(\bar{\nu} = \frac{1}{\lambda}\right)$

Total no. of spectral lines during de. excitation from n_2 to n_1 orbit $= \frac{\Delta n(\Delta n + 1)}{2}$

$\Delta n = n_2 - n_1$

Total no. of spectral lines in particular series

$= n_2 - n_i$

series no.

$\begin{pmatrix} n_1 = \text{Lower energy level} \\ n_2 = \text{Higher energy level} \end{pmatrix}$

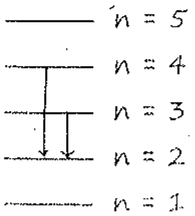
Q. Calculate λ of photon emitted when $e^\ominus$ makes transition from n = 2 to n = 1 in H atom?

$\frac{1}{\lambda} = R_H (1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$

$\frac{1}{\lambda} = R_H \times \frac{3}{4}$

$\left[\lambda = \frac{4}{3R_H}\right]$

Q. Calculate λ for 2^{nd} line of Balmer series for He^{+} ion?



$n_1 = 2 \quad n_2 = 4$

$$\frac{1}{\lambda} = R_H (2)^2 \left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

$$\frac{1}{\lambda} = R_H \times \cancel{4} \times \frac{1}{\cancel{4}}\left[1 - \frac{1}{4}\right]$$

$$\lambda = \frac{4}{3R_H}$$

Q. Find $\boxed{\text{series limit}}$ of Lyman series for Li^{2+}.

Last line

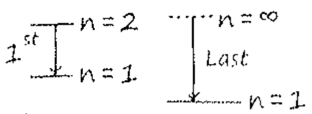
$Z = 3 \quad n_1 = 1 \quad n_2 = \infty$

$$\frac{1}{\lambda} = R_H (3)^2 \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$$

$$\left[\lambda = \frac{1}{9R_H}\right]$$

Q. Find λ_{max} and λ_{min} for Lyman series for H atom?

1^{st} line
Last line



$$\frac{1}{\lambda} = R_H (1)^2 \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$$

$$\frac{1}{\lambda} = R_H (1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$\left[\lambda_{min} = \frac{1}{R_H}\right]$$

$$\left(\lambda_{max} = \frac{4}{3R_H}\right)$$

Q. Find $\bar{v}$ (wave no.) when $e^{\ominus}$ makes transition from 3^{rd} E.S to ground state in Be^{3+} ion?

$$\frac{1}{\lambda} = \bar{v} = R_H (4)^2 \left[\frac{1}{1^2} - \frac{1}{4^2}\right]$$

$Z = 4, n_1 = 1, n_2 = 4 \quad \bar{v} = \cancel{16}R_H \times \frac{15}{\cancel{16}}$

$$[\bar{v} = 15 R_H]$$

Q. Find λ for H_{α} line for Lyman series for He^{+} ion?

1^{st} line

$n_1 = 1, \; n_2 = 2, \; Z = 2$

$\alpha \rightarrow 1^{st}$ line

$\beta \rightarrow 2^{nd}$ line

$\gamma \rightarrow 3^{rd}$ line

$\delta \rightarrow 4^{th}$ line

$$\frac{1}{\lambda} = R_H (2)^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$\frac{1}{\lambda} = \cancel{4}R_H \times \frac{3}{\cancel{4}} \left[\lambda = \frac{1}{3R_H}\right]$$

Q. Find total no. of spectral lines when $e^{\ominus}$ makes transition from 9^{th} E.S to 1^{st} E.S

$\Delta n = n_2 - n_1 = 8 \qquad n_2 = 10 \;;\; n_1 = 2$

$$S.L = \frac{8 \times (8+1)}{2}$$

$= 4 \times 9$

$= 36$

Q. Find spectral lines in Balmer series when $e^{\ominus}$ makes transition from 14^{th} E.S to G.S.?

$n_2 = 15 \qquad n_1 = 2$

S.L in Balmer series = 15 − 2 = 13

5. Debroglie hypothesis

(1) $\lambda = \dfrac{h}{P}$

(2) $\lambda = \dfrac{h}{mv}$ $\qquad$ m = mass (kg), v = m/s

(3) $\lambda = \dfrac{h}{\sqrt{2m\,KE}}$ $\qquad$ V = Volt potential, KE = J

(4) $\lambda = \dfrac{h}{\sqrt{2m\,qV}}$

(5) for $e^{\ominus}$ $\lambda = \dfrac{12.24}{\sqrt{V}}$ Å = $\sqrt{\dfrac{150}{V}}$ Å

(6) $2\pi r = n\lambda$ $\quad$ n = no. of waves made in one revolution

$$\left(r = r_o \times \frac{n^2}{Z} \text{Å} = 0.53 \times \frac{n^2}{Z} \text{Å}\right)$$

Q. Find λ when an $e^{\ominus}$ is moving with velocity of 10^{6} m/s

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^{6}} \text{ m}$$

$[\lambda \approx 7 \text{ Å}]$

Q. Find ratio of λ of α and proton $\left(\frac{\lambda_\alpha}{\lambda_p}\right)$ accelrated through same potential diff.

$$\lambda = \frac{h}{\sqrt{2mqV}}$$

$\alpha \quad P$

$m_\alpha = 4m_p$

$q_\alpha = 2q_p$

$$\lambda \propto \frac{1}{\sqrt{mq}}$$

$$\frac{\lambda_\alpha}{\lambda_p} = \sqrt{\frac{m_p q_p}{m_\alpha q_\alpha}}$$

$$= \sqrt{\frac{1}{4} \times \frac{1}{2}}$$

$$= \frac{1}{\sqrt{8}} = \frac{1}{2\sqrt{2}}$$

Q. Find λ when an $e^\ominus$ is accelerated by a potential diff of 15 V from rest?

$$\lambda = \sqrt{\frac{150}{V}}\ \text{Å}$$

$$\lambda = \sqrt{\frac{150}{15}}$$

$$[\lambda = \sqrt{10}\ \text{Å}]$$

6. Heisenberg's uncertainty principle

(1) $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ $\qquad \frac{h}{4\pi} = 0.52 \times 10^{-34}$

(2) $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$

(3) $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$

(4) $\Delta x \cdot |\Delta\lambda| \geq \frac{\lambda^2}{4\pi}$ $\qquad \lambda$ = wave length (m)

Q. If $\Delta x = 2\Delta p$ then find Δv?

$$\Delta x = 2\,m\Delta v$$

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m}$$

$$2m\,\Delta v \times \Delta v = \frac{h}{4\pi m}$$

$$(\Delta v)^2 = \frac{h}{8\pi m^2}$$

$$\Delta v = \sqrt{\frac{h}{8\pi m^2}}$$

$$= \frac{1}{2m}\sqrt{\frac{h}{2\pi}}$$

Q. Δx is 10^{-5} m of a particle of mass 0.25 gm then find Δv?

$$\Delta x \cdot \Delta v = \frac{0.52 \times 10^{-34}}{m}$$

$$10^{-5} \times \Delta v = \frac{0.52 \times 10^{-34}}{0.25 \times 10^{-3}}$$

$$[\Delta V = 2.1 \times 10^{-26}\ \text{m/s}]$$

Q. A golf ball has mass $\overset{0.1\ \text{kg}}{100\ \text{gm}}$ and speed of 100 m/s. If the speed can be measured within accuracy of 2% find Δx?

$$\Delta v = v \times \text{accuracy}$$

$$= \cancel{100} \times \frac{2}{\cancel{100}}$$

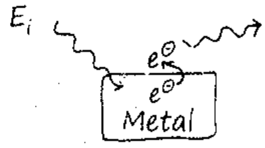
$$= 2\ \text{m/s}$$

$$\Delta x \cdot \Delta v = \frac{0.52 \times 10^{-34}}{m}$$

$$\Delta x \times 2 = \frac{0.52 \times 10^{-34}}{0.1}$$

$$[\Delta x = 0.26 \times 10^{-33}\ \text{m}]$$

7. Photo electric effect (P.E.E)



$Li < Na < K < Rb < Cs$ (W_{order})

$$[E_i = \Phi_{min} + K.E_{max}]$$

W_{min}

$$[h\nu = h\nu_0 + KE_{max}] \quad \left[KE_{max} = \frac{1}{2} mV^2_{max}\right]$$

$$\left[\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + KE_{max}\right]$$

ν = freq. of incident light (λ = W.L of incident light)

ν_0 = Threshold freq (min) $\qquad$ (λ_0 = Threshold W.L) (max)

Q. Calculate KE(J) of an $e^{\ominus}$ emitted when radiation of frequency $\nu = 1.1 \times 10^{15}\ s^{-1}$ hits the metal ($\nu_0 = 6 \times 10^{14}\ s^{-1}$)

$h\nu = h\nu_0 + KE$

$h \times 11 \times 10^{14} = h \times 6 \times 10^{14} + KE$

$KE = 5 \times h \times 10^{14}$

$= 5 \times 6.6 \times 10^{-34} \times 10^{14}$

$= 5 \times 6.6 \times 10^{-20}\ J$

Q. Light of $\lambda = 310$ nm is used in an exp of P.E.E with Li (w = 2.5 ev)

Find (a) max KE (b) Stopping potential

$E_i = \Phi + KE_{max}$

$\frac{12400}{\lambda(\text{Å})} = \Phi + KE_{max}$

$\frac{\cancel{12400}^{4}}{\cancel{3100}} = 2.5 + KE_{max}$

$4 - 2.5 = KE_{max}$

(a) $KE_{max} = 1.5\ eV = 1.5 \times 1.6 \times 10^{-19}\ J$

(b) $[\ V_0 = 1.5\ \text{Volt}\ ]$

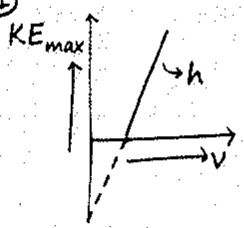
Imp. Points

1. Intensity ↑, no. of ejected $e^{\ominus}$s ↑
2. Frequency ν ↑, $K.E_{max}$ ↑
3. P.E.E is obs only when $[\ \nu > \nu_0\ ]$
   $E_i > \Phi$

Graphs $h\nu = h\nu_0 + KE_{max}$

$[\ KE_{max} = h\nu - h\nu_0\ ]$

①



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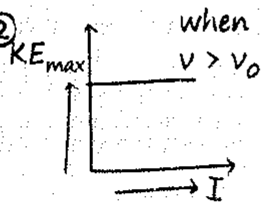

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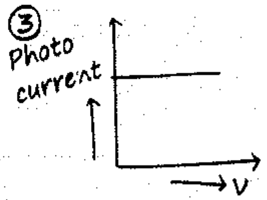

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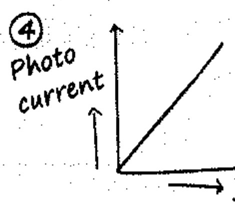


Q. The no of metals which will show P.E.E when light of 310 nm (3100 Å) wavelength falls on following metals

metal	~~Li~~	~~Na~~	~~K~~	~~Mg~~	Cu	Ag	Fe	pt
Φ(ev)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6

$Ei = \frac{12400}{3100} = 4\ ev$

8. Quantum no.

(1) Principal Q.N (n)

(a) It describes the shell or orbit or energy level

(b) n = 1, 2, 3, 4, 5 ....

K, L, M, N, O ....

(c) Orbit angular momentum

$mvr = \frac{nh}{2\pi}$

(d) $\left.\begin{array}{l}\text{Total orbitals} = n^2 \\ \text{total } e^{\ominus}\text{s} = 2n^2\end{array}\right]$ in n^{th} orbit

(2) Azimuthal Q.N (ℓ)

(a) It describes shape of subshell or sub orbit (sub energy level)

(b) ℓ = 0 to n − 1

$\begin{bmatrix} \ell = 0 & 1 & 2 & 3 & 4 \\ s & p & d & f & g \end{bmatrix}$

(c) Orbital angular momentum

$= \sqrt{\ell(\ell+1)}\,\frac{h}{2\pi}$

$= \sqrt{\ell(\ell+1)}\,\hbar$

(d) $\left.\begin{array}{l}\text{Total orbitals} = (2\ell + 1) \\ \text{total } e^{\ominus}\text{s} = 2\,(2\ell + 1)\end{array}\right]$ in subshell ℓ.

(3) Magnetic Q.N (m or m_l)

(a) Orientation of subshell.

(b) m = − ℓ to + ℓ

$\ell = 0$ □ m = 0

$\ell = 1$ □□□ m = ±1, 0

$\ell = 2$ □□□□□ m = ±2, ±1, 0

(4) **Spin Q.N (S or m_s)**

(a) Spin either C.W or A.C.W

(b) $S = \pm \frac{1}{2}$

(c) Spin angular momentum

$= \sqrt{S(S+1)} \frac{h}{2\pi}$

$= \sqrt{S(S+1)} \hbar$

$S = \frac{n}{2}$ (n = no. of unpaired $e^{\ominus}$s)

(d) Total spin $= \pm \frac{n}{2}$

(e) Spin multiplicity $= (2S + 1)$

$S = \frac{n}{2}$

Q. Total no. of orbitals in

(a) $n = 3$ (b) $\ell = 2$

Orbitals $= n^2$ Orbitals $= (2\ell + 1)$

$= 3^2$ $= (2 \times 2 + 1)$

$= 9$ $= 5$

Q. Describe the subshell

n	ℓ	Subshell
3	0	3 s
4	1	4 p
5	2	5 d
2	2	~~2d~~ (not possible)

Q. Find orbital A.M

(a) 2 s $\sqrt{0(0+1)}\ \hbar = 0$

(b) 3 p $\sqrt{1(1+1)}\ \hbar = \sqrt{2}\,\hbar$

(c) 4 d $\sqrt{2(2+1)}\ \hbar = \sqrt{6}\,\hbar$

(d) 5 f $\sqrt{3(3+1)}\ \hbar = \sqrt{12}\,\hbar$

Q. Find orbit A.M

(a) 4 p $4\hbar$

(b) 5 d $5\hbar$

(c) 1 s $1\hbar$

(d) 6 f $6\hbar$

$\left[\hbar = \frac{h}{2\pi}\right]$

Q. Incorrect set of Quantum no.

	n	ℓ (0 to $n-1$)	m ($-\ell$ to $+\ell$)	s
(A)	4	0	0	$+\frac{1}{2}$
(B)	3	1	1	$-\frac{1}{2}$
(C)	2	0	0	$-\frac{1}{2}$
~~(D)~~	3	1	-2	$+\frac{1}{2}$

Q. Find spin A.M when no. of U.P $e^{\ominus}$s is 2

$n = 2$ $S = \frac{n}{2} = \frac{2}{2} = 1$

S.A.M $= \sqrt{1(1+1)}\,\hbar = \sqrt{2}\,\hbar$

Q. Find spin multiplicity and total spin if no. of U.P $e^{\ominus}$s is 2

$n = 2$ T.S $= \pm\frac{n}{2} = \pm\frac{2}{2} = \pm 1$

S.M $= 2s + 1 = 2 \times 1 + 1 = 3$

$S = \frac{n}{2} = \frac{2}{2} = 1$

(**) Q. No. of $e^{\ominus}$s present in d-orbital?

~~(A)~~ 2 (B) 6

(C) 10 (D) 14

Imp. Points

1. (a) Total nodes $= n - 1$
   (b) Radial or spherical nodes $= n - \ell - 1$
   (c) Nodal plane $= \ell$ or Angular node $= \ell$

   for given subshell

2. Energy of subshell [Bohr burry rule or ($n + \ell$) rule]

   $E \propto (n + \ell)$ [if $(n + \ell)$ is same, $E \propto n$]

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

   n = no. of UP$e^{\ominus}$s

Q. Find magnetic moment

(A) Fe^{2+} (B) Cu^{2+}

$_{26}Fe^{2+} \rightarrow [Ar]4s^0\, 3d^6$

$\boxed{\uparrow\downarrow}\underbrace{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}_{n\,=\,4}$

$M.M = \sqrt{4(4+2)} = \sqrt{24}$

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

$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\underbrace{\boxed{\uparrow}}_{n\,=\,1}$

$M.M = \sqrt{1(1+2)} = \sqrt{3}$

Q. Find no. of total nodes, Nodal planes, angular nodes and Radial nodes

Subshell	T.N	R.N	N.P	A.N
$n = 3, \ell = 0$ 3s	2	2	0	0
$n = 4, \ell = 1$ 4p	3	2	1	1
$n = 5, \ell = 2$ 5d	4	2	2	2

Q. Compare the energy of subshell

(A) 3p	(B) 3s	(C) 5d	(D) 4p
$n = 3$	$n = 3$	$n = 5$	$n = 4$
$\ell = 1$	$\ell = 0$	$\ell = 2$	$\ell = 1$
$n+\ell=4$	$n+\ell=3$	$n+\ell=7$	$n+\ell=5$

[C > D > A > B]

3 Gaseous State

Gas Laws

1. Boyle's Law

$P \propto \frac{1}{V}$ [at const n, T]

$[P_1V_1 = P_2V_2]$

2. Charle's Law

$V \propto T$ [at const n and P]

$\left[\frac{V_1}{T_1} = \frac{V_2}{T_2}\right]$

$T = K$

3. Gay Lussac's Law

$P \propto T$ [at const n and V]

$\left[\frac{P_1}{T_1} = \frac{P_2}{T_2}\right]$

4. Avogadro's Law

$V \propto n$ [at const P and T]

$\left[\frac{V_1}{n_1} = \frac{V_2}{n_2}\right]$

Combined Gas Law

$\left[\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\right]$

Ideal Gas Eq^n

$PV = nRT$

$P \Rightarrow$ atm

$V \Rightarrow$ L

$n \Rightarrow$ moles

$R \Rightarrow 0.0821$ or $\frac{1}{12}\ \frac{\text{L atm}}{\text{mol-K}}$

$T \Rightarrow K$

Dalton's Law of partial pressure for non reacting gaseous. mix. The total pressure is the sum of partial pressure of each gas.

$\boxed{1 + 2 + 3 \ldots\ldots}$ $[P_T = P_1 + P_2 + P_3 + \ldots\ldots]$

$P_{gas} = \chi_{gas} \times P_T$

Kinetic Theory of Gases

Postulates

1. There is no force of attrc^n b/w gas molecules
2. Mass of gas molecule is negligible (Point mass)
3. The collisions b/w gas molecules are perfectly elastic
4. The motion of gas molecules is chaotic (Random)
5. The avg. K.E. of gas molecules is directly proportional to absolute temp (Temp in K)

Avg KE $\propto$ T $\qquad \frac{R}{N_A} = K$

[Avg KE per mole $= \frac{3}{2}$ RT] $K = 1.38 \times 10^{-23}$

$R = \frac{25}{3}$ J/mol/k

For n moles Avg KE $= \frac{3}{2}$ nRT

Avg KE per molecule $= \frac{3}{2}$ KT

Kinetic gas eq^n

$PV = \frac{1}{3} mN V^2_{rms}$

P = Pa $\qquad$ N = No. of molecules

$V = m^3$

m = Kg

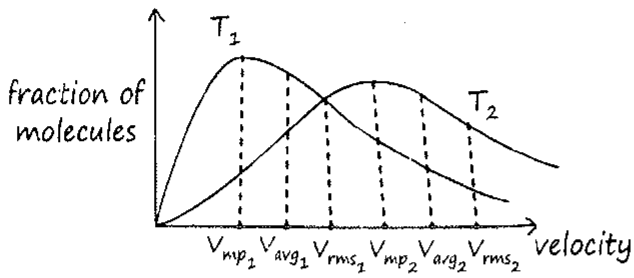
V_{rms} = m/s

Molecular Speeds

V_{rms} (root mean square)	V_{avg} (average)	V_{mp} (most probable)
$V_{rms} = \sqrt{\dfrac{3RT}{M}} = \sqrt{\dfrac{3P}{d}}$ V_{rms} = m/s $R = \dfrac{25}{3}$ J/mol/k T = K M = molar mass (kg)	$V_{avg} = \sqrt{\dfrac{8RT}{\pi M}} = \sqrt{\dfrac{8P}{\pi d}}$ $\dfrac{RT}{M} = \dfrac{KT}{m}$ $d = \dfrac{PM}{RT}$ $\dfrac{RT}{M} = \dfrac{P}{d}$	The velocity possessed by max fraction of molecules $V_{mp} = \sqrt{\dfrac{2RT}{M}} = \sqrt{\dfrac{2P}{d}}$ $\sqrt{3} > \sqrt{\dfrac{8}{\pi}} > \sqrt{2}$ $V_{rms} > V_{avg} > V_{mp}$ $\boxed{R > A > M}$

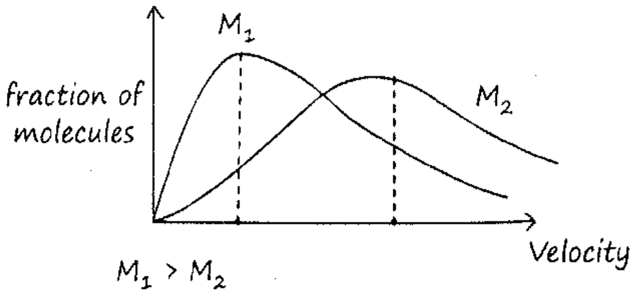
Maxwell Distribution Curve

Case 1: For same gas at diff temp.



$T_2 > T_1$

Case 2: For diff gas at same temp.



$M_1 > M_2$

Graham's Law of diffusion/Effusion

Diffusion # The spontaneous flow of gas molecules from higher conc^n to Lower conc^n.

Effusion # Diffusion from pin hole or small hole or orifice.

Law # The rate of diffusion/Effusion is inversely proportional to the square root of the density at constt T and P.

$$r \propto \frac{1}{\sqrt{d}} \propto \frac{1}{\sqrt{V.D}} \propto \frac{1}{\sqrt{M.W}}$$

$$\left[\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}\right]$$

Q. Compare rate of diffusion?

	CH_4,	CO_2,	SO_2
MW	16	44	64
rate	r_1	r_2	r_3

$$\boxed{r_1 > r_2 > r_3}$$

Q. The r.O.D of methane at a given temp is twice that of a gas x.

Find MW^x?

$$\frac{r_{CH_4}}{r_X} = 2 \qquad \frac{MW_X}{16} = 4$$

$$\sqrt{\frac{MW_X}{16}} = 2 \qquad [\, MW_X = 64 \,]$$

Rate

1. Volume

$$r = \frac{V}{t} \text{ (diffused)}$$

2. Length

$$r = \frac{\ell}{t} \text{ (travelled)}$$

3. Moles

$$r = \frac{n}{t} \text{ (diffused)}$$

	Gas 1	Gas 2
V	V_1	V_2
t	t_1	t_2
ℓ	ℓ_1	ℓ_2
n	n_1	n_2
MW	M_1	M_2

1. $\frac{V_1}{V_2} \times \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

2. $\frac{\ell_1}{\ell_2} \times \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

3. $\frac{n_1}{n_2} \times \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

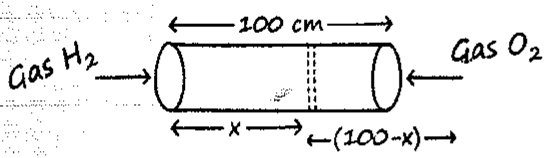
Q. Two gases A and B having same volume diffuse through a porous portion in 20 and 10 sec respectively. The M.W of A is 49 u. Find MW_B?

$$\frac{\cancel{V_A}}{\cancel{V_B}} \times \frac{t_B}{t_A} = \sqrt{\frac{MW_B}{MW_A}}$$

$$\frac{10}{20} = \sqrt{\frac{MW_B}{49}}$$

$$\frac{1}{4} = \frac{MW_B}{49} \qquad \text{i.e, } MW_B = \frac{49}{4}$$

Q.



Find the distance from H_2 end where they will meet first?

$$\frac{x}{100-x} \times \frac{1}{1} = \sqrt{\frac{32}{2}}$$

$$\frac{x}{100-x} = 4$$

$$x = 400 - 4x$$

$$5x = 400$$

$$\boxed{x = 80 \text{ cm}}$$

If Pressure is Variable at Const temp

$$r \propto \frac{P}{\sqrt{d}} \propto \frac{P}{\sqrt{MW}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

$$\left(\frac{n_1}{n_2}\right)_{\substack{\text{effused}\\ \text{out}}} = \left(\frac{n_1}{n_2}\right)_{\text{initially}} \sqrt{\frac{M_2}{M_1}}$$

Q. A football bladder contains equimolar proportions of H_2 and O_2. The composition by mass of the mixture effusing out of punctured football is in the ratio.

$$\left(\frac{n_{H_2}}{n_{O_2}}\right)_{\substack{\text{effused}\\ \text{out}}} = \left(\frac{n_{H_2}}{n_{O_2}}\right)_{\text{initial}} \sqrt{\frac{M_{O_2}}{M_{H_2}}}$$

$$\frac{n_{H_2}}{n_{O_2}} = 1 \times \sqrt{\frac{32}{2}} = 4$$

$$\frac{W_{H_2}}{W_{O_2}} \times \frac{MW_{O_2}}{MW_{H_2}} = 4 \qquad \left[\frac{W_{H_2}}{W_{O_2}} = \frac{4 \times 2}{32} = \frac{1}{4}\right]$$

Real Gas

1. **Compressibility factor (Z)**

$$Z = \frac{V_{real}}{V_{ideal}} = \frac{V_{obs}\, P}{n\, RT}$$

$$= \frac{P(V_m)_{obs}}{RT}$$

Z

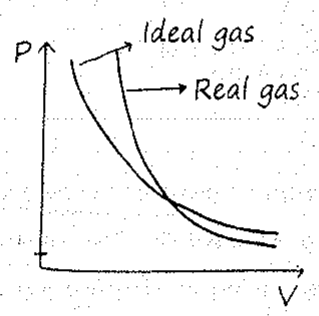
-ve deviation

+ve deviation

Z = 1 (No deviation)	Z < 1	Z > 1
⇨ Real gas = Ideal gas	⇨ Real gas	⇨ Real gas
⇨ No force of attraction and repulsion	⇨ Attraction force > repulsive force	⇨ Attraction force < repulsive force
⇨ Can not be liquefied	⇨ Easy to liquefy or compress	⇨ Diff to liquefy or compress

2. Graphical analysis

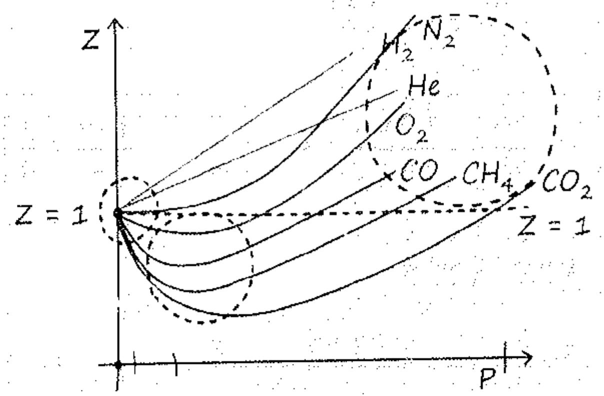
(1) P vs V



At very Low pressure real gas behaves like ideal gas.

At Low pressure and High temp Real gas behaves like ideal gas.

(2) Z vs P



Case 1: At very Low pressure

$\boxed{Z = 1}$

Case 2: At Low pressure or moderate

$\boxed{Z < 1}$

Case 3: At High pressure

$\boxed{Z > 1}$

Case 4: H_2 and He

(a) At very Low pressure

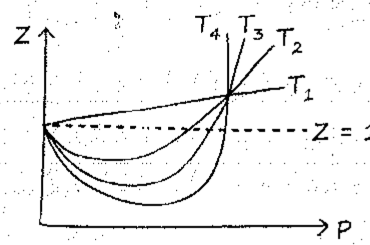
[Z = 1]
(moderate)

(b) At Low and High pressure

[Z > 1]

H_2 or He behave like a typical real gas at very low temp

(3) Z vs P for a gas at diff temp



$[T_1 > T_2 > T_3 > T_4]$

3. Vander Waal's Eq^n

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

P.C.T = Pressure correction term = $\frac{+n^2a}{V^2}$

V.C.T = Volume correction term = $-nb$

a = V.W const ∝ Intermolecular attraction forces

b = excluded volume = $4V_m$
or co volume

$= 4 \times \frac{4}{3}\pi r^3 \times N_A$

Unit of 'a' atm L^2 mol^{-2}

Unit of 'b' L mol^{-1}

Case 1: At very Low pressure

a = neglected

b = neglected

$$\left(P + \frac{\cancel{n^2a}}{V^2}\right)^0 (V - \cancel{nb})^0 = nRT$$

$$PV = nRT$$

$$PV_m = RT$$

$$\frac{PV_m}{RT} = 1$$

$$\boxed{Z = 1}$$

Case 2: At Low or moderate pressure

b = neglected

$$\left(P + \frac{n^2a}{V^2}\right)(V - \cancel{nb})^0 = nRT$$

$$\left(P + \frac{a}{V_m^2}\right)(V_m) = RT$$

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{RTV_m} = 1$$

$$\boxed{Z = 1 - \frac{a}{RTV_m}}$$

$$\boxed{Z < 1}$$

Case 3: At high pressure

a = neglected

$$\left(P + \frac{\cancel{n^2a}}{V^2}\right)^0 (V - nb) = nRT$$

$$P(V_m - b) = RT$$

$$PV_m - Pb = RT$$

$$\frac{PV_m}{RT} - \frac{Pb}{RT} = 1$$

$$\boxed{Z = 1 + \frac{Pb}{RT}}$$

$$\boxed{Z > 1}$$

Liquefaction of the Gases

Critical Parameters #

1. Critical temp (T_C) # The temp above which gas can not be liquified even at very high P.

   $$\left[T_C = \frac{8a}{27Rb}\right]$$

2. Critical pressure (P_C)

   $$\left[P_C = \frac{a}{27b^2}\right]$$

3. Critical volume (V_C)

   $$[V_C = 3b]$$

4. Compressibility factor at critical point

   $$Z_C = \frac{P_CV_C}{RT_C} = \frac{3}{8} < 1$$

ease of liquefaction $\propto a \propto \frac{1}{b} \propto T_C$

Order of liquefaction

$H_2 < N_2 < O_2 < CO < CH_4 < CO_2 < HCl < NH_3 < SO_2$

⇨ Boyle's Temp (T_B). The temp at which real gas mostly behaves like ideal gas

$$\left[T_B = \frac{a}{Rb}\right]$$

⇨ Inversion Temp (T_i)

$$\left[T_i = \frac{2a}{Rb}\right]$$

$$\boxed{T_i > T_B > T_C}$$

Practice

Q. The Z is Less than unity at STP therefore:

(A) $V_m = 22.4$ L (B) $V_m < 22.4$ L ✓
(C) $V_m > 22.4$ L (D) $V_m = 44.8$ L

$$Z = \frac{PV_m}{RT} < 1 \quad ; \quad V_m < \frac{RT}{P}$$

$$\boxed{V_m < 22.4L}$$

Q. A real gas most closely approaches the ideal behaviour at?

(A) 15 atm & 200 K

(B) 1 atm and 273 K

(C) 0.5 atm & 500 K ✓

(D) 15 atm and 500 K

Q.

Gases	$a(L^2 atm\ mol^{-2})$
O_2	1.36
N_2	1.39
NH_3	4.17
CH_4	2.25

Write order of liquefaction?

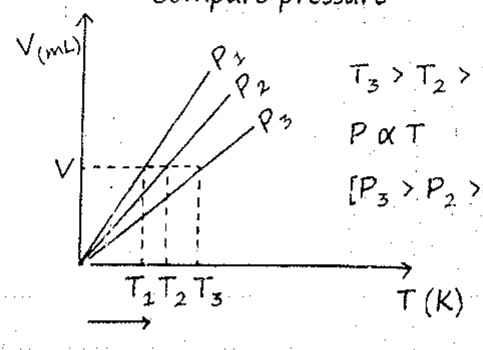
liquefaction $NH_3 > CH_4 > N_2 > O_2$

Q. At High pressure, Vanderwaals equ^n reduces to

(A) $PV = RT$ (B) $PV = RT + \frac{a}{V}$
(C) $PV = RT + Pb$ ✓ (D) $PV = RT - \frac{a}{V^2}$

$$\left[Z = 1 + \frac{Pb}{RT}\right]$$

Q. Compare pressure



$T_3 > T_2 > T_1$

$P \propto T$

$[P_3 > P_2 > P_1]$

Q. The pressure of 1: 4 mixture (mole ratio) of H_2 and O_2 enclosed in a vessel is 1 atm. Find partial pressure of O_2 (N/m^2)?

$$P_{O_2} = x_{O_2} \times P_T$$

$$= \frac{n_{O_2}}{n_{H_2} + n_{O_2}} \times P_T = \left(\frac{1}{\frac{n_{H_2}}{n_{O_2}} + 1}\right) \times P_T$$

$$= \frac{1}{\left(\frac{1}{4}+1\right)} \times 1 = \frac{4}{5} \text{ atm}$$

$$P_{O_2}(N/m^2) = \frac{4}{5} \times 10^5$$

Q. A balloon is filled with H_2 at R.T. it will burst if pressure exceeds 0.2 bar.

If at 1 bar the gas occupies 2L volume, up to what volume can the balloon be expanded?

T = const $\quad P_1V_1 = P_2V_2$

$$1 \times 2 = 0.2 \times V_2$$

$$[V_2 = 10 \text{ L}]$$

Q. Calculate volume occupied by 8.8 gm CO_2 at 27°C and 1 atm pressure?

$$PV = nRT$$

$$1 \times V = \frac{8.8}{44} \times \frac{1}{12} \times 300 \quad [V_{(L)} = 5L]$$

$$V(L) = \frac{\cancel{2}}{\cancel{10}} \times \frac{1}{\cancel{12}_{\,6}} \times 30\cancel{0} = 5$$

Practice

Q. Consider three 1L flask A, B and C filled with gases NO, NO_2 and N_2O respectively each at 1atm and 273 K. In which flask do the molecules have the highest avg KE?

All have same avg KE $\quad$ [avg KE $\propto$ T]

Q. V_{rms} of gas is $30\sqrt{R}$ m/s at 27°C. Find molar mass of gas?

$$30\sqrt{R} = \sqrt{\frac{3R \times 300}{M}}$$

$$900\,R = \frac{900\,R}{M} \quad ; \quad M = 1\ \text{Kg mol}^{-1}$$

Q. 6×10^{22} gas molecules each of mass 10^{-24} kg are taken in the vessel of 10 L. Find pressure (Pa)? (Given $V_{rms} = 100$ m/s)

$$P \times 10 \times 10^{-3}$$

$$= \frac{1}{\cancel{3}} \times 10^{-24} \times 6 \times 10^{22} \times \overset{2}{\cancel{1}}0000$$

$[P = 2 \times 10^4\ \text{Pa}]$

Q. Incorrect regarding KTG?

(A) Gas particles are considered as point mass

(B) The molecules are in random motion

(C) When molecules collide, they lose energy

(D) When gas is heated, the molecules move faster

4 Thermodynamics

(1) System # The part of universe which is under observation is called system.

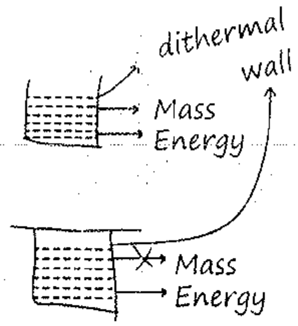
(2) Surroundings # The rest part of the universe (other than system)

System + Surrounding = 'The Universe'

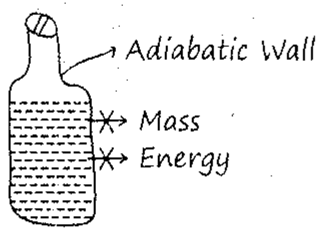
Types of System

(1) Open

(2) Closed



(3) Isolated



Properties of System

(1) Intensive # Mass or size independent

P (Pressure), T (Temp), d (density), molar heat capacity, specific heat capacity, vapour pressure, refractive index

$\left[\frac{E}{E} = I\right]$

Intensive prop are non additive

(2) Extensive # Mass or size dependent

H (Enthalpy), E (Internal energy), C (Total Heat Capacity), G (Gibb's free energy), S (Entropy), M (Mass), V (Volume), M (Mole)

Extensive prop are additive in nature

State and Path Function

State Func^n # Depends on initial (P_1, V_1, T_1) and final state. ((P_2, V_2, T_2) e.g. ΔU, ΔG, ΔS or ΔE)

Path Func^n # Depends on path of the process. eg

q and w

↓ ↓

Heat Work

Internal Energy (ΔU)

(1) The sum of all energy like KE, PE, BE etc

(2) State Func^n

$\Delta U = U_2 - U_1$

(3) Depends on Temp

Heat ⟹ Energy transfer due to temp diff
Work ⟹ The energy against external pressure

1st Law of Thermodynamics

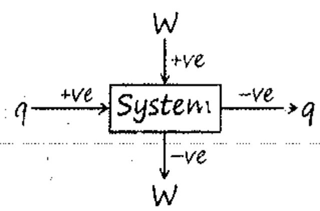
[$\Delta U = q + w$]

(1) Heat absorbed by the system = +ve

(2) Heat released by the system = −ve

(3) Work done by the system = −ve

(4) Work done on the system = +ve



[1 Cal = 4.2 ≃ 4 J]

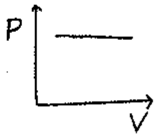
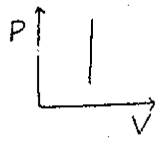
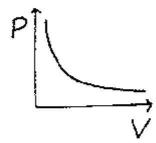
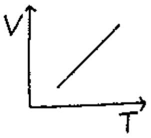
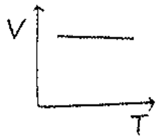
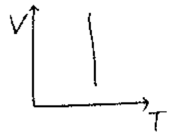
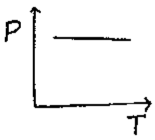
Q. Find ΔU, if a system absorbs 15kJ of heat and does 5kJ of work?

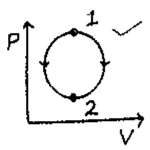
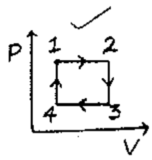
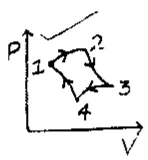
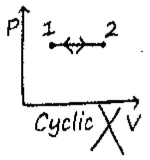
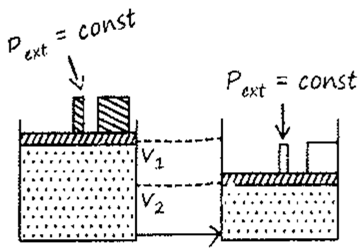
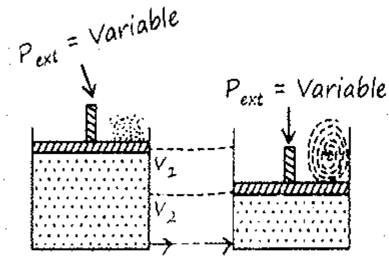
$q = +15kJ \quad W = -5kJ$

$\Delta U = q + w$

$\therefore 15 - 5 = 10kJ$

Processes

Isobaric $\Delta P = 0$	Isochoric ($\Delta V = 0$)	($\Delta T = 0$) Isothermal
		 $PV = nRT$ $PV = \text{const}$ $P \propto \frac{1}{V}$
 $PV = nRT$ $[V \propto T]$		
	 $PV = nRT$ $P \propto T$	

Cyclic	Irreversible	Reversible
 In cyclic process, initial and final states are same with the formation of loop.    $1 \to 2 \to$ Isobaric Exp (Heating) $2 \to 3 \to$ Isochoric Cooling $3 \to 4 \to$ Isobaric Cooling $4 \to 1 \to$ Isochoric Heating	 # at const. ext pressure # one step process # fast process	 # at variable ext pressure # multi step # slow

Heat Capacity

(1) C or C_T # The amount of Heat absorbed by a system to increase its temp by 1°C.

$$C = \frac{+q}{\Delta T}; \left(\frac{J}{K}\right)$$

(2) C_m : $C_m = \frac{+q}{n\Delta T}; \left(\frac{J}{mol\text{-}K}\right)$

(3) Specific heat capacity C_S or $SC_S = \frac{+q}{m\Delta T}\left(\frac{J}{gm\text{-}K}\right)$

(4) C_P ; $C_P = \frac{+q_p}{\Delta T}$

Heat change at const. pressure = ΔH

(5)* $C_{P,m}$; $C_{P,m} = \frac{+q_p}{n\Delta T}$

$[\Delta H = nC_{P,m}\Delta T]$

(6) $C_{P,S}$; $C_{P,S} = \frac{+q_p}{m\Delta T}$

(7) C_V ; $C_V = \frac{+q_V}{\Delta T}$

(8)* $C_{V,M}$; $C_{V,M} = \frac{+q_V}{n\Delta T}$

isochoric process $w = 0$ $[\Delta U = q_v]$

$[\Delta U = nC_{V,m}\Delta T]$

(9) $C_{V,S}$: $\left[C_{V,S} = \frac{+q_V}{m\Delta T}\right]$

Imp. points related to heat capacity

(1) Mayer's relation $[C_{P,M} - C_{V,M} = R]$

(2) Heat Capacity C or $C_T \longrightarrow$ path func^n

C_P & $C_V \longrightarrow$ are not path func^n

(3) Heat capacity may vary from $-\infty$ to ∞ depending upon the process.

(4) $C_T = nC_m = mC_S$

$[C_m = MW \times C_S]$

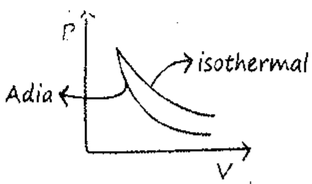
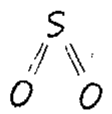
(5) Isothermal $C = \infty$

Isobaric $C = C_P$

Isochoric $C = C_V$

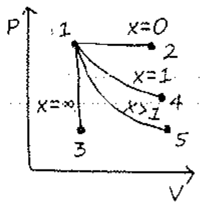
Adiabatic $(q = 0)$ $C = 0$

Adiabatic Process

	Gas	f	$C_V = \frac{fR}{2}$ C_V	C_P	$\left(\chi = 1 + \frac{2}{f}\right)$ χ
$[q = 0]$ $\Delta U = q + w$ $\Delta U = 0 + W_{ad}$	Mono atomic He, Ne, Ar etc	3T	$\frac{3R}{2}$	$\frac{5R}{2}$	5/3
$[\Delta U = W_{ad}]$ for Rev. adiabatic process $\left.\begin{cases} PV^{\gamma} = Const \\ TV^{\gamma-1} = Const \\ P^{1-\gamma}T^{\gamma} = Const \end{cases}\right\} \gamma = \frac{C_P}{C_V}$ Poisson's ratio	H_2, N_2, O_2, F_2 etc Diatomic or Triatomic linear CO_2: O = C = O	3(T) + 2(R) = 5	$\frac{5R}{2}$	$\frac{7R}{2}$	7/5
Isothermal vs Adiabatic 	Triatomic non linear SO_2 	3(T) + 2(R) = 6	$\frac{6R}{2} = 3R$	4R	4/3

$W, q, \Delta U$ and ΔH Calculation

Process	Work done by the system	q	$\Delta U = q + w$ i.e, $\Delta U\ (q_r)$	$\Delta H\ (q_p)$
(1) Reversible Isothermal $(P_1V_1 = P_2V_2)$ $R = \frac{1}{12}$; W = L atm $= \frac{25}{3}$; W = J = 2 ; W = Cal	$W = -nRT \ln\left(\frac{V_2}{V_1}\right)$ $W = -2.3\ nRT \log_{10}\left(\frac{V_2}{V_1}\right)$ $W = -2.3\ nRT \log_{10}\left(\frac{P_1}{P_2}\right)$	$q = -W$	0	0
(2) Irreversible isothermal	$W = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$ $P_{ext} \approx P_2$	$q = -W$	0	0
(3) Isobaric	$W = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$ $= -nR\Delta T$	$q_p = \Delta H = nC_p\Delta T$	$q_V = \Delta U = nC_V\Delta T$	$q_p = \Delta H = nC_p\ \Delta T$
(4) Isochoric	$w = 0$	$q_v = \Delta U = nC_V\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_p\Delta T$
(5) Rev. Adiabatic $(T_2 < T_1)$	$W_{rev} = \frac{nR(T_2 - T_1)}{\gamma - 1}$ $= nC_V\Delta T$	$q = 0$ $PV^{\gamma} = $ Const. $TV^{\gamma-1} = $ Const. $P^{1-\gamma}T^{\gamma} = $ Const.	$\Delta U = nC_V\Delta T$	$\Delta H = nC_p\Delta T$
(6) Irr. Adiabatic	$W_{irr} = \frac{nR(T_2 - T_1)}{\gamma - 1}$ $= nC_V\Delta T$	$q = 0$ $nC_V(T_2 - T_1) = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_p\Delta T$
(7) Cyclic Process All State Func^n = 0	Area enclosed in PV diagram If C.W $\Rightarrow$ W = −Ve If ACW $\Rightarrow$ W = +ve	$q = -W$	0	0

(8) Polytropic Process $[PV^{\gamma} = Const]$ 	$W = \dfrac{P_2V_2 - P_1V_1}{X - 1}$ $W = \dfrac{nR\Delta T}{X - 1}$	$\Delta U = nC_V\Delta T$ $q = nC\Delta T$ $\left[C = C_V + \dfrac{R}{1 - X}\right]$	$\Delta H = nC_P\Delta T$

Relation b/w ΔH and ΔU

$[\Delta H = \Delta U + \Delta n_g RT]$

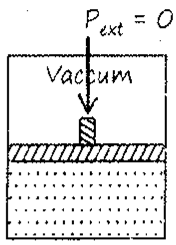
$[q_p = q_v + \Delta n_g RT]$

Case 1: If $\Delta n_g = 0$; $\Delta H = \Delta U$

Case 2: If $\Delta n_g < 0$; $\Delta H < \Delta U$

Case 3: If $\Delta n_g > 0$; $\Delta H > \Delta U$

Free Expansion



$\Delta U = 0$; $q = 0$, $W = 0$

Q. The workdone during the expansion of gas from a volume of $14dm^3$ to $16dm^3$ against a constant external pressure of 2atm at const temp is?

$W_{irr} = -P_{ext}(V_2 - V_1)$

$= -2 * (16 - 14) = -2 \times 2$

$= -4$ L-atm

1 L atm = 100 J = 24 cal = 100×10^7 erg

[1 L-atm > 1 cal > 1 J > 1 arg]

Q. If ΔH for Reaction

$N_2 + 3H_2 \rightarrow 2NH_3$ is -92kJ/mol at 300K, find ΔU (in kJ/mol) at 300K?

$\Delta H = \Delta U + \Delta n_g RT$

$-92000 = \Delta U + (-2) \times \dfrac{25}{\cancel{3}} \times \overset{100}{\cancel{300}}$

$\Delta U = -92000 + 5000 = -87000$

$\Delta U = -87$kJ/mol

Q. 3 moles of an ideal gas expanded spontaneously into Vaccum. The work done will be?

$[W = 0]$

Q. Which is intensive prop?

(A) ΔH (B) ΔU

(C) Volume ✓(D) Specific heat

Q. Which is not state func^n?

(A) q_P — ΔH (B) q_V — ΔU

(C) W_{ad} ✓(D) $W_{isother}$

$\Delta U = \overset{0}{\cancel{q}} + W_{ad}$

$[\Delta U = W_{ad}]$

Q. 1 mole of an ideal gas at 300K is expanded isothermally from initial volume of 1L to 10L find w, q and ΔU (in cal)?

$W_{rev} = -2.3\, nRT \log_{10}\left(\dfrac{V_2}{V_1}\right)$

$= -2.3 \times 1 \times 2 \times 300 \log_{10}\left(\dfrac{10}{1}\right)$

$= -2.3 \times 600$ cal

$= -23 \times 60$ cal

$\underline{\underline{-1380}}$ cal

$W_{rev} = -1.3$ Kcal

$\Delta U = 0$

$q = -W = -(-1.3 \text{ Kcal})$

$= +1.3$ Kcal

Q. 5 mol of O_2 gas is heated at const volume from 10°C to 20°C. Find ΔU

Given: $C_P = \frac{Cal}{mol\text{-}K}$; $R = 2\frac{Cal}{mol\text{-}K}$

$\Delta U = nC_V\Delta T$ $\quad C_P - C_V = R$

$= 5 \times 5 \times 10$ $\quad 7 - C_V = 2$

$= 250$ Cal $\quad C_V = 5$

Q. Find Δn_g if we consider the combustion of 1 mol liquid ethanol if reactants and products are at 298K?

$$\underset{(l)}{C_2H_5OH} + \underset{(g)}{3O_2} \longrightarrow \underset{(g)}{2CO_2} + \underset{(l)}{3H_2O}$$

$\Delta n_g = 2 - 3 = -1$

Q. If a gas absorbs 100J of Heat and expands by $500 cm^3$ against a const pressure of 2×10^5 N/m^2 find ΔV?

$q = +100$ $\quad W = -P\Delta V$

$= -2 \times 10^5 \times 500 \times 10^{-6} \frac{N}{M^2} \times m^3$

$= -100$ J

$\Delta U = q + W = 100 - 100 = 0$

Q. A gas expands adiabatically at const pressure such that $T \propto V^{-1/2}$ find γ?

$TV^{\gamma-1} = const$ $\quad T = KV^{-1/2}$

$\gamma - 1 = \frac{1}{2}$ $\quad TV^{1/2} = K$

$\gamma = \frac{1}{2} + 1 = \frac{3}{2}$

Q. 1 mol of an ideal gas $\left(C_{V,M} = \frac{5R}{2}\right)$ at 300K and 5 atm is expanded adiabatically to a final pressure of 2 atm against a constant pressure of 2 atm find final temp of gas?

$$nC_V(T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

$$1 \times \frac{5R}{2}(T_2 - 300) = -2\left(\frac{1 \times R \times T_2}{2} - \frac{1 \times R \times 300}{5}\right)$$

$$\frac{5RT_2}{2} - 750R = -RT_2 + 120R$$

$$\frac{7\cancel{R}T_2}{2} = 870\cancel{R}$$

$$T_2 = \frac{870 \times 2}{7} = 298.5 \text{ K}$$

Q. Calculate the final temp of a monoatomic ideal gas that is expanded Rev. and adia. from 2L to 16L at 300 K?

$TV^{\gamma-1} = const$ $\quad \gamma - 1 = \frac{5}{3} - 1 = \frac{2}{3}$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{2/3}$$

$$\frac{T_2}{300} = \left(\frac{2}{16}\right)^{2/3} = \left(\frac{1}{2}\right)^{\cancel{3}\times 2/\cancel{3}} = \frac{1}{4}$$

$$T_2 = \frac{300}{4} = 75 \text{ K}$$

Entropy

(1) The degree of Randomness or disorderness is called Entropy.

(2) Entropy is a state function and Extensive prop.

(3) $\Delta S = S_2 - S_1 = S_f - S_i$

(4) Unit J/K or Cal/K

(5) Mathematically entropy can be defined as the heat absorbed at a particular temp in rev process

$$\left[\Delta S = \frac{q_{rev}}{T}\right]$$

Factors Affecting Entropy

(1) Physical state : (S < L < G) (order of S)

(2) For chemical Rxn : $\Delta n_g > 0$; $\Delta S > 0$

$\Delta n_g < 0$; $\Delta S < 0$

(3) Temp : $\Delta S \propto T$

(4) Pressure : $\Delta S \propto \frac{1}{P}$

(5) Mixing : S + S

L + L $\quad [\Delta S > 0]$

G + G

Calculation of Entropy in diff process

General Formulae

(1) $\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$

(2) $\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right)$

Case 1: In Isobaric process

$$\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right)$$

Case 2: In Isochoric process

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$$

Case 3: In Isothermal process

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right)$$

Case 4: In reversible adiabatic process ($q_{rev} = 0$)

$\Delta S = 0$; Rev adiabatic processes are also known as Isoentropic processes

Case 5: In irreversible adiabatic process, use

General formulae

Entropy Change During Phase Transition

(1) Entropy of fusion $S \rightleftharpoons L$

$$\left[\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}\right]$$

(2) Entropy of vap. $L \rightleftharpoons G$

$$\left[\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}\right]$$

(3) Entropy of sublimation $S \rightleftharpoons G$

$$\left[\Delta S_{Sub} = \frac{\Delta H_{Sub}}{T_S}\right]$$

Some famous points related to Entropy

1. Entropy Graphite > Diamond
2. On rusting of Fe, Entropy increases
3. On dissolution, Entropy increases

   $NH_4Cl + aq. \longrightarrow NH^+_{4(aq)} + Cl^-_{(aq)}$
4. Ag^+ on reaction with HCl, Entropy decreases

   $Ag^+ + HCl \longrightarrow AgCl_{ppt} + H^+$
5. On boiling of egg, Entropy increases due to denaturation of protein.
6. On stretching of rubber band, Entropy decreases.

Practice questions on Entropy

Q. The enthalpy change for transition of liquid to steam is 40 kJ/mol at 400K find ΔS for the process?

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{\cancel{40} \times 10^3}{\cancel{400}} \text{ J/K} = 100 \text{ J/K}$$

Q. $\Delta S < 0$ for

(A) $Br_{2(l)} \longrightarrow Br_{2(g)}$

(B) $N_2(10 \text{ atm}) \longrightarrow N_2(1 \text{ atm})$

(C) $C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$

$\Delta n_g = 2 - 1 = 1 > 0$

(D) Fe (400 K) $\longrightarrow$ Fe (300 K)

Q. 3 mol of an ideal gas expand rev from a volume of 8 dm^3 to 80 dm^3 at 300 K. Find ΔS (J/K)?

$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$

$= 3 \times \frac{25}{3} \times 2.3 \log_{10}\left(\frac{80}{8}\right)$

$= 25 \times 2.3$

$= 57.5$ J/K

Q. $\Delta S < 0$ for

(A) Dissolution of I_2 in a solvent ($I_{2(s)} \rightarrow I_{2(aq)}$)

(B) HCl is added to $AgNO_3$ and Agcl ppt is formed

(C) A partition is removed to allow gases to mix

(D) On boiling of egg

2^{nd} Law of Thermodynamics (SLOT)

(1) The entropy of universe is always increasing.

(2) All Natural process are irreversible and spontaneous process.

(3) $[\Delta S_{Univ} \geq 0]$

$\Delta S_{Univ} > 0$ Irr (Natural) $\quad \Delta S_{Univ} = 0$ Rev

ΔS_{Univ} in Irr.

System T_1, q amount of heat is released by the system

Surr. T_2, q amount of heat is absorbed by the surr.

$$\Delta S_{Univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$= \left(\frac{-q}{T_1}\right) + \left(\frac{+q}{T_2}\right) > 0$$

ΔS_{Univ} in Rev ($T_1 = T_2$)

$$\Delta S_{Univ} = \frac{-q}{T} + \frac{q}{T} = 0$$

Gibb's Free Energy

(1) It is the part of total energy of the system which can be converted to do useful work (non expansion work)

Energy = Useful work + Randomness energy

$H = G + TS$

$(G = H - TS)$

(2) It is an extensive prop and state func^n

$\Delta G = G_2 - G_1 = G_f - G_i$

(3) Gibb's helmholtz eqn

$[\Delta G = \Delta H - T\Delta S]$

it is used to predict the spon.

(4) The decrease in Gibb's free energy is equal to max useful work or non experiment

$[W_{useful} = -\Delta G]$

(5) Relation b/w ΔG_{sys} and ΔS_{univ}

$[\Delta G_{sys} = -T\Delta S_{univ}]$

Case 1: $\Delta S_{univ} > 0$; $\Delta G_{sys} < 0$ spon

Case 2: $\Delta S_{univ} < 0$; $\Delta G_{sys} > 0$ non spon

Case 3: $\Delta S_{univ} = 0$; $\Delta G_{sys} = 0$ Eq^m

Criteria for spon		$[\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}]$
ΔH	ΔS	Criteria for spontaneity
+ve	+ve	$\lvert T\Delta S\rvert > \lvert \Delta H\rvert$
+ve	−ve	Always non spontaneous
−ve	+ve	Always spontaneous
−ve	−ve	$\lvert \Delta H\rvert > \lvert T\Delta S\rvert$

Relation b/w $\Delta G°$ and k_{eqb}(eqm const)

$$\alpha A_{(g)} + \beta B_{(g)} \longrightarrow \gamma C_{(g)} + \delta D_{(g)}$$

$\Delta G = \Delta G° + RT \ln Q$

ΔG = Gibb's free energy at Temp T_K

$\Delta G°$= Standard Gibb's free energy

R = gas const,

T = Temp (K)

Q = Rxn quotient

At eq^m $\Delta G = 0$

$Q = K_{eq}$

$0 = \Delta G° + RT \ln K_{eq}$

$$\boxed{\Delta G° = -RT \ln K_{eq}}$$

Relation b/w $\Delta G°$ and $E°_{cell}$ (standard Emf of Cell)

$[\Delta G° = -nF E°_{cell}]$

n = no. of $e^{\ominus}$s involve in the balanced Rxn

F = Faradays constant = 96500 C

$E°_{cell}$ = standard emf of cell

$= (E°_R)_C - (E°_R)_A$

$-RT \ln K_{eq} = -nF E°_{cell}$

$$\left[E°_{cell} = \frac{RT}{nF} \ln K_{eq}\right]$$

Q. For a rxn ΔH = 40.63 kJ/mol and ΔS = 100 J/K find ΔG at 27°C?

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

$= 40.63 \times 1000 - 300 \times 100$

$= 40630 - 30000$

$\Delta G = 10630$

$\Delta G = 10.63$ kJ/mol

Q. For a rxn $N_2 + 3H_2 \longrightarrow 2NH_3$ $\Delta H = -100$ kJ/mol and $\Delta S = -200$ J/K. Calculate temp. at which rxn will proceed in forward dir^n?

at eq^m $\quad \Delta G = 0$

$$\Delta H = T\Delta S$$

$$T = \frac{-100 \times \overset{5}{\cancel{1000}}}{-\cancel{200}} = 500\text{ K}$$

[T < 500]

Q. The $\Delta G°$ for a rxn at 27°C is X Kcal/mol. If eq^m const is 100 then X is

$$\Delta G° = -2.3\ RT \log_{10} K$$

$$X \times 1000 = -2.3 \times 2 \times 300 \log 10^2$$

$$X = \frac{-2.3 \times 12\cancel{00}}{10\cancel{00}} = \frac{-27.6}{10} = -2.76$$

Q. Favoured conditon for spontaneous reaction when ΔH and ΔS both are +ve?

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

at $|\Delta H| < |T\Delta S|$ ie at $T > \Delta H/\Delta S$

$\Delta G < 0$ spontaneous.

Gibb's Free Energy

Third Law of thermodynamics

At 0K, the entropy of pure perfect crystalline solid is taken as zero

Exceptions
(1) NO, N_2O
(2) CO, CO_2
(3) Mixture of isotopes
(4) Ice

5 Thermochemistry

It is the heat involved in a chemical Rxn.

Endothermic $R + Heat \longrightarrow P$ $\quad \Delta_r H = +ve$

Exothermic $R \longrightarrow P + Heat$ $\quad \Delta_r H = -ve$

Different types of Heat of Reaction

1. Heat of formation ($\Delta_f H^o$)

The heat absorbed or released when 1 mol of a comp. is formed by most stable form of elements in standard state.

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(\ell)}$$

$$\underset{(Graphite)}{C_{(s)}} + 2H_{2(g)} \longrightarrow CH_{4(g)}$$

$\Delta_f H^o = 0$ for $H_{2(g)}, O_{2(g)}, N_{2(g)}, F_{2(g)}, Cl_{2(g)}$

$Br_{2(\ell)}, I_{2(s)}, C_{(graphite)}$

$P_{4(white)}, S_{8(Rhombic)}$

2. Heat of combustion ($\Delta^o_{comb} H$)

The heat released when 1 mol of a substance is combined with excess of O_2 to form products

eg. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

3. Heat of transition ($\Delta^o_{trans} H$)

The heat absorbed or released during conversion of one allotropic form to another form

$C_{(graphite)} \longrightarrow C_{(diamond)}$

4. Heat of neutralization ($\Delta^o_{neu} H$)

It is the heat released when 1 gram equivalent of an acid is neutralized by 1 gram equivalent of base

$\underset{SA}{H^+} + \underset{SB}{O^-H} \longrightarrow H_2O$; $\Delta^o_{neu} H = -13.7$ kcal/mol

$= -57.1$ kJ/mol

order of magnitude of $\Delta^o_{neu} H$ of (SA + SB) > (WA + SB) > (WA + WB)

5. Heat of ionisation (or dissociation) (ΔH^o_{diss} or ΔH^o_{ion})

The heat required for the complete dissociation of 1 mol of acid (or Base)

$HA \longrightarrow H^+ + A^-$; $\Delta^o H_{diss}$

$\Delta^o H_{diss} \uparrow$, weaker is the acid

6. Enthalpy of Hydration (ΔH^o_{hyd})

Case 1: For salt

(anhy.) $CuSO_{4(s)} + 3H_2O \rightarrow CuSO_4 \cdot 3H_2O_{(s)}$

(partially hydrated) $CuSO_4 \cdot 3H_2O_{(s)} + 2H_2O \rightarrow CuSO_4 \cdot 5H_2O_{(s)}$

Case 2: For ion

$$Cl^{\ominus}_{(g)} + aq \longrightarrow Cl^-_{(aq)}$$

$[\Delta H^o_{hyd}(H^+, aq) = 0]$

$[\Delta H^o_f(H^+, aq) = 0]$

7. Enthalpy of solution (ΔH^o_{sol})

$KCl_{(s)} + aq \longrightarrow KCl_{(aq)}$

$MgSO_{4(s)} + aq \longrightarrow MgSO_{4(s)}$

8. Enthalpy of dilution (ΔH^o_{dil})

$$\underset{C_1}{HCl \cdot 40H_2O} + aq \longrightarrow \underset{C_2}{HCl_{(aq)}}$$

9. Heat of atomisation ($\Delta_a H^o$)

It is the enthalpy change when 1 mol of given molecule is dissociated into free atoms in gas phase

$H_{2(g)} \longrightarrow 2H_{(g)}$

$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)}$

10. Bond energy (B.E or E or $\Delta H^o_{B.E.}$)

It is the avg of enthalpies when 1 mol of a particular bond between two atoms is broken in gaseous phase

$H_{2(g)} \longrightarrow 2H_{(g)} \quad \Delta H^o_{B.E} \text{ or } \Delta H^o_{B.D.E}$

$CH_{4(g)} \longrightarrow CH_{3(g)} + H_{(g)}$; $B.D.E_1$

$CH_{3(g)} \longrightarrow CH_{2(g)} + H_{(g)}$; $B.D.E_2$

$CH_{2(g)} \longrightarrow CH_{(g)} + H_{(g)}$; $B.D.E_3$

$CH_{(g)} \longrightarrow C_{(g)} + H_{(g)}$; $B.D.E_4$

$$B.E = \frac{B.D.E_1 + B.D.E_2 + B.D.E_3 + B.D.E_4}{4}$$

Calculation of $\Delta_r H^o$ when $\Delta_f H^o$ is given

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$

$$\Delta_r H^o = [\gamma \times \Delta H^o_{f(C)} + \delta \times \Delta H^o_{f(D)}] - [\alpha \times \Delta H^o_{f(A)} + \beta \times \Delta H^o_{f(B)}]$$

Q. Find $\Delta_r H^o$ for the reaction

$ZnO_{(s)} + CO_{(g)} \longrightarrow Zn_{(s)} + CO_{2(g)}$

Given:

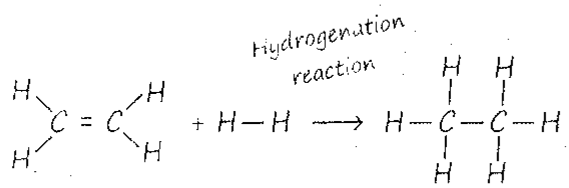
Comp.	$\Delta_f H^o$(kJ/mol)
$ZnO_{(s)}$	-350
$CO_{2(g)}$	-390
$CO_{(g)}$	-110

$\Delta_r H^o = \Delta_f H^o_{(CO_2)} - (\Delta_f H^o_{(ZnO)} + \Delta_f H^o_{(CO)})$

$= -390 - (-350 - 110)$

$= +70$ kJ/mol (Here $\Delta H^o_f(Zn)(s) = 0$)

Calculation of $\Delta_r H^o$ when B.E is given



$\Delta_r H^o = (B.E)_R - (B.E)_P$

$= [B.E_{C=C} + 4B.E_{C-H} + B.E_{H-H}]$

$- [6B.E_{C-H} + B.E_{C-C}]$

Q. Find $\Delta_r H^o$ for the Rxn

$C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}$

Given:

Bonds	BE (kJ/mol)
C - H	414
C - C	347
C = C	615
H - H	435

$\Delta_r H^o = [615 + 4 \times 414 + 435]$

$- [6 \times 414 + 347]$

$= -125$ kJ/mol

Hess's Law

The total change of heat content of a reaction is same whether the reaction is carried out by direct path or indirect path

$$\begin{tikzcd} A \arrow[r, "\Delta_r H_1^o"] \arrow[d, "\Delta_r H_2^o"'] & B \\ C \arrow[r, "\Delta_r H_3^o"'] & D \arrow[u, "\Delta_r H_4^o"'] \end{tikzcd}$$

$[\Delta_r H_1^o = \Delta_r H_2^o + \Delta_r H_3^o + \Delta_r H_4^o]$

1. $A \longrightarrow B \qquad \Delta_r H_1^o$

   $B \longrightarrow A \qquad \Delta_r H_2^o = -\Delta_r H_1^o$

2. $A \longrightarrow B \qquad \Delta_r H_1^o$

   $aA \longrightarrow aB \qquad \Delta_r H_2^o = a \times \Delta_r H_1^o$

3. $A \longrightarrow B \qquad \Delta_r H_1^o$

   $C \longrightarrow D \qquad \Delta_r H_2^o$

   $A + C \longrightarrow B + D \qquad \Delta_r H_3^o = \Delta_r H_1^o + \Delta_r H_2^o$

Q.

	Reaction	$\Delta_r H$ (kJ/mol)
①	$\frac{1}{2} A \longrightarrow B$	+ 150
②	$3B \longrightarrow 3C + D$	- 125
③	$E + A \longrightarrow 2D$	+ 350

Find ΔH for ④ $B + D \longrightarrow E + 3C$

$2 \times ① - ③ + ② = ④$

$2 \times 150 + (-350) + (-125) = \Delta H$

$300 - 350 - 125 = \Delta H$

$\Delta H = -175$ kJ/mol

Q. ① $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

$\Delta H = -27$ kJ/mol

② $FeO + CO \longrightarrow Fe + CO_2$

$\Delta H = -16.5$ kJ/mol

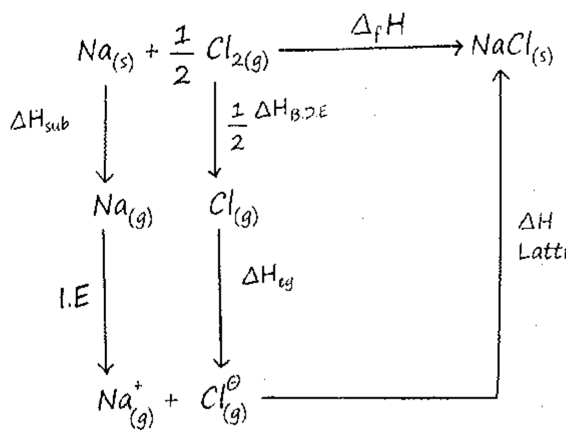
Find ΔH for ③ $Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

$① - 2 \times ② = ③$

$-27 + (+16.5 \times 2) = \Delta H$

[$\Delta H = +6$ kJ/mol]

Born Habers Cycle



$$\Delta_f H = \underbrace{\Delta H_{sub} + I.E + \frac{1}{2} \Delta H_{B.D.E}}_{} + \Delta H_{eg} + \Delta H_{Lattice}$$

Kirchoff's Equation

At const. pressure

$$(\Delta H)_{T_2} - (\Delta H)_{T_1} = \Delta C_P (T_2 - T_1)$$

$$\Delta C_P = (C_P)_P - (C_P)_R$$

At const. volume

$$(\Delta U)_{T_2} - (\Delta U)_{T_1} = \Delta C_V (T_2 - T_1)$$

$$\Delta C_V = (C_V)_P - (C_V)_R$$

Q. Find ΔH at 400 K for

$\frac{1}{2} N_2 + O_2 \longrightarrow NO_2$; $\Delta H_{300k} = -35$ kJ/mol

Given:

Gas	C_P ($JK^{-1}mol^{-1}$)
NO_2	35
N_2	30
O_2	30

$\Delta C_P = 35 - \frac{1}{2} \times 30 - 30$

$= 5 - 15 = -10$ JK^{-1} mol^{-1}

$(\Delta H)_{400} - (-35) = \frac{-10 \times 100}{1000} = -1$

[$(\Delta H)_{400} = -36$ kJ/mol]

Entropy of chemical Reaction

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$

$\Delta_r S^o = (S_m^o)_P - (S_m^o)_R$

$= [\gamma \times S^o_{m(C)} + \delta \times S^o_{m(D)}]$

$- [\alpha \times S^o_{m(A)} + \beta \times S^o_{m(B)}]$

Gibb's free energy of a Reaction

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$

$\Delta_r G^o = [\gamma \times \Delta_f G^o_{(C)} + \delta \times \Delta_f G^o_{(D)}]$

$- [\alpha \times \Delta_f G^o_{(A)} + \beta \times \Delta_f G^o_{(B)}]$

Q. Find $\Delta_r S^o$ $\quad \frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightleftharpoons XY_3$

Comp.	S_m^o ($JK^{-1}mol^{-1}$)
X_2	60
Y_2	40
XY_3	50

$\Delta_r S^o = S^o_{m(XY_3)} - \frac{1}{2} \times S^o_{m(X_2)} - \frac{3}{2} \times S^o_{m(Y_2)}$

$= 50 - \frac{1}{\cancel{2}} \times \overset{30}{\cancel{60}} - \frac{3}{\cancel{2}} \times \overset{20}{\cancel{40}}$

$= 20 - 60$

$= -40$ $JK^{-1}mol^{-1}$

Practice

Q. Which is correct for free expansion?

(A) $q = 0, \quad \Delta T \neq 0, \quad w = 0$

(B) $q \neq 0, \quad \Delta T = 0, \quad w = 0$

(C) $q = 0, \quad \Delta T = 0, \quad w = 0$

(D) $q = 0, \quad \Delta T < 0, \quad w \neq 0$

Q. Which is intensive property?

(A) ΔH (B) ΔS

(C) Specific heat (D) Volume

Q. For $A_{2(g)} \longrightarrow 2A_{(g)}$ correct option is

	ΔH	ΔS
(A)	+	–
(B) →	+	+
(C)	–	–
(D)	–	+

Q. For formation of $CH_{4(g)}$; ΔU^o is $-x \frac{kJ}{mol}$

Find ΔH^o

$$\underset{(Graphite)}{C_{(S)}} + 2H_{2(g)} \xrightarrow{\Delta n_g = 1-2=-1} CH_{4(g)} \; ; \; \Delta U^o = -x$$

$$\Delta H^o = \Delta U^o + \Delta n_g RT = -x \times 10^3 + (-1RT)$$

$$= -x \times 10^3 - RT$$

Q. For $H_2O_{(\ell)}$ (1 bar, 373K) $\longrightarrow$ $H_2O_{(g)}$ (1 bar, 373 K)

Correct option is

	ΔG	ΔS
(A)	0	+
(B)	0	–
(C)	+	0
(D)	–	+

$H_2O(\ell) \rightleftharpoons H_2O_{(g)}$

$\Delta G = 0$

$\Delta S = +ve$

Q.
$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] \arrow[r] & B \end{tikzcd}$$

Given: $\Delta S_{A \to C} = 50$ e.u

$\Delta S_{C \to D} = 30$ e.u

$\Delta S_{B \to D} = 20$ e.u

Find $\Delta S_{A \to B}$

$$\Delta S_{A \to B} = \Delta S_{A \to C} + \Delta S_{C \to D} + \Delta S_{D \to B}$$

$$= 50 + 30 - 20 = 60 \text{ e.u}$$

Q. Find $\Delta_f H^o$ (HCl)

Given: (kJ/mol)

Bond	B.E
H–H	434
Cl–Cl	242
H–Cl	430

$$\frac{1}{2} H_{2(g)} + \frac{1}{2} Cl_{2(g)} \longrightarrow H\text{–}Cl_{(g)}$$

$$\Delta_r H^o = \Delta_f H^o = \frac{1}{2} B.E_{H\text{-}H} + \frac{1}{2} B.E_{Cl\text{-}Cl} - B.E_{H\text{-}Cl}$$

$$= \frac{1}{2} \times 434 + \frac{1}{2} \times 242 - 430$$

$$= -92 \text{ kJ/mol}$$

Q. $X_2O_{4(\ell)} \longrightarrow 2\,XO_{2(g)}$; $\Delta U = 2$ kCal/mol

$\Delta S = 20$ Cal/K/mol at 300k. find ΔG

$$\Delta G = \Delta H - T\Delta S = \Delta U + \Delta n_g RT - T\Delta S$$

$$= 2000 + 2 \times 2 \times 300 - 300 \times 20$$

$$= 2000 + 1200 - 6000$$

$$= 3200 - 6000$$

$$= -2800 = -2.8 \text{ kCalmol}^{-1}$$

Q. 200 mL of 0.1 M H_2SO_4 is mixed with 150 mL of 0.2 M KOH. Find the value of heat evolved (in kJ)

$\Delta_{neu} H = -57.1 \text{ kJ mol}^{-1}$

Eq. of $H_2SO_4 = 0.1 \times 2 \times 200 \times 10^{-3} = 0.04$

Eq. of KOH $= 0.2 \times 1 \times 150 \times 10^{-3} = \boxed{0.03}$

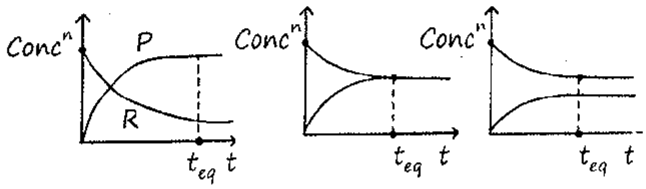
1 eq $\Rightarrow$ 57.1 kJ

0.03 eq $\Rightarrow 0.03 \times 57.1$ kJ $= 1.7$ kJ

6 Chemical Equilibrium

$$R \rightleftharpoons P$$

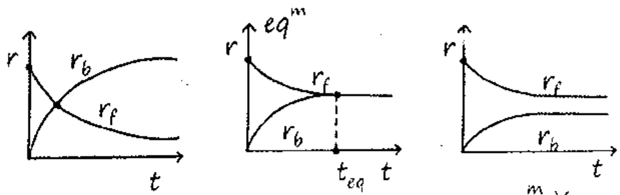
1. Conc^n vs time



at eqn Conc^n = Const   Conc^n = Const & equal   Conc^n = Const

2. Rate vs time

at eq^m $[r_f = r_b]$



eq^m X $[r_f = r_b]$ eq^m X

r_f = rate of forward Rxn

r_b = rate of Backward Rxn

Law of Mass Action

The rate of rxn is directly proportional to the product of active masses of reactants to raised the power of respective stoichiometric co-efficient.

For solids active masses = 1 $\left[C = \frac{d}{M}\right]$

$$\alpha A_{(g)} + \beta B_{(g)} \underset{K_b}{\overset{K_f}{\rightleftharpoons}} \gamma C_{(g)} + \delta D_{(g)}$$

$r_f \propto [A]^\alpha [B]^\beta$; $r_b \propto [C]^\gamma [D]^\delta$

$r_f = K_f [A]^\alpha [B]^\beta$; $r_b = K_b [C]^\gamma [D]^\delta$

at equilibrium $r_f = r_b$; $K_P = \dfrac{P_C^\gamma P_D^\delta}{P_A^\alpha P_B^\beta}$

eq^m const $K_C = \dfrac{K_f}{K_b} = \dfrac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$

eq^m const

$$\alpha A_{(g)} + \beta B_{(g)} \rightleftharpoons \gamma C_{(g)} + \delta D_{(g)}$$

$$K_{eqb} = \frac{K_f}{K_b}$$

$K_C = \dfrac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$ $K_P = \dfrac{P_C^\gamma P_D^\delta}{P_A^\alpha P_B^\beta}$

Unit ; $K_C = \left(\dfrac{mol}{L}\right)^{\Delta n_g}$ $K_P = (atm)^{\Delta n_g}$

$\Delta n_g = (\gamma + \delta) - (\alpha + \beta)$

Q. 2 moles of PCl_5, 4 moles of PCl_3 and 1 mole of Cl_2 are present in 10 L container at eq^m find K_C of

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$; $\Delta n_g = 2 - 1 = 1$

$$K_C = \frac{\cancel{\frac{4}{10}}^{2} \times \frac{1}{10}}{\cancel{\frac{2}{10}}} = 0.2(M)^1$$

Relation b/w K_P and K_C

$$[K_P = K_C (RT)^{\Delta n_g}]$$

Case 1: $\Delta n_g > 0$; $K_P > K_C$

Case 2: $\Delta n_g < 0$; $K_P < K_C$

Case 3: $\Delta n_g = 0$; $K_P = K_C$

Case 4: If $T = \dfrac{1}{R} = 12$ K

$K_P = K_C$ for any value of Δn_g

$R = 0.0821 \dfrac{L\ atm}{mol\text{-}k} = \dfrac{1}{12}$

Q. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta n_g = 2 - 4 = -2$

$K_P < K_C$

$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$; $\Delta n_g = 3 - 2 = 1$

$K_P > K_C$

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ $\quad \Delta n_g = 2 - 2 = 0$

$K_P = K_C$

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ $\quad \Delta n_g = 1 - 0 = 1$

$K_P > K_C$

Q. Find K_P of following rxn at 480 K if $K_C = 10$ M

$A_{(s)} \rightleftharpoons B_{(s)} + C_{(g)}$

$K_P = K_C (RT)^{\Delta n_g}$

$= 10 \left(\frac{1}{\cancel{12}} \times \overset{40}{\cancel{480}}\right)^1$

$= 10 \times 40 = 400$ atm

Q. Find temp at which $\frac{K_P}{K_C} = 3$ for

$SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$

$K_P = K_C (RT)^{\Delta n_g}$

$\frac{K_P}{K_C} = (RT)^1$

$RT = 3$

$T = \frac{3}{R}$

$T = \frac{3}{1/12} = 36$ K

Apps of K

K ↑ Product stable

K ↓ Reactant stable

$K = \frac{[P]}{[R]}$ $\quad$ K ↑ (P) more stable at eqb.
K ↓ (R) more stable at eqb.

Q. Product is more stable in case of

(A) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\quad K_1 = 2.3 \times 10^{-2}$

(B) $N_2 + O_2 \rightleftharpoons 2NO$ $\quad K_2 = 200$

(C) $H_2 + I_2 \rightleftharpoons 2HI$ $\quad K_3 = 294$

(D) $XeO + \frac{1}{2}O_2 + F_2 \rightleftharpoons XeO_2F_2$ $\quad K_4 = 1.4 \times 10^{-3}$

Factors Affecting K

Van't Hoff eq^n

1. Temp

$$\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

ΔH = Heat of Rxn

R = gas const

= 8.314

$= \frac{25}{3} \frac{J}{mol\text{-}K}$

$= 2 \frac{Cal}{mol\text{-}K}$

Endo (ΔH = +ve)	Exo (ΔH = −ve)
$T_1 < T_2$	$T_1 < T_2$
$K_1 < K_2$	$K_2 < K_1$
T↑ K↑	T↑ K↓

2. Stoichiometry of Rxn

Case 1: $R \rightleftharpoons P$ $\quad K_1$

$P \rightleftharpoons R$ $\quad K_2 = \frac{1}{K_1}$

Case 2: $R \rightleftharpoons P$ $\quad K_1$

$aR \rightleftharpoons aP$ $\quad K_2 = K_1^a$

Case 3: $R \rightleftharpoons P$ $\quad K_1$

$S \rightleftharpoons T$ $\quad K_2$

$R + S \rightleftharpoons P + T$ $\quad K_3 = K_1 \times K_2$

Q. $2HCl_{(g)} \rightleftharpoons H_{2(g)} + Cl_{2(g)}$ $K_C = 4 \times 10^{-34}$ at 25°C

find K_C for $\frac{1}{2} H_{2(g)} + \frac{1}{2} Cl_{2(g)} \rightleftharpoons HCl_{(g)}$

$$K_2 = \left(\frac{1}{K_1}\right)^{\frac{1}{2}} = \left(\frac{1}{4 \times 10^{-34}}\right)^{\frac{1}{2}}$$

$$= \frac{1}{2 \times 10^{-17}} = \frac{10}{2} \times 10^{16}$$

$$= 5 \times 10^{16}$$

> Eq^m const depends only on the temp. and the stoichiometry of reaction

Q. Find K_{eqb} at 127°C if eq^m const is 4 at 27°C for the Rxn

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H = -46$ kJ/mol

$$\log_{10}\left(\frac{K_2}{4}\right) = \frac{-46 \times 10^3}{2.3 \times 8.3}\left[\frac{1}{300} - \frac{1}{400}\right]$$

$$= -2400 \times \frac{1}{100}\left[\frac{1}{3} - \frac{1}{4}\right]$$

$$= -24 \times \frac{1}{12}$$

$$\log_{10}\left(\frac{K_2}{4}\right) = -2$$

$$\frac{K_2}{4} = 10^{-2}$$

$$K_2 = 4 \times 10^{-2}$$

Degree of Dissociation

$$D.O.D = \frac{\text{No. of moles dissociated}}{\text{Initial moles taken}}$$

Case 1: n_i 2 0

$A \rightleftharpoons B$

n_{eq} $2-x$ x

D.O.D of A $= \frac{x}{2}$

Case 2: n_i 2 0

$2A \rightleftharpoons B$

n_{eq} $2-2x$ x

D.O.D of A $= \frac{2x}{2} = x$

Case 3: n_i 2 3 0

$A + 2B \rightleftharpoons C$

n_{eq} $2-x$ $3-2x$ x

D.O.D of A $= \frac{x}{2}$

D.O.D of B $= \frac{2x}{3}$

Case 4: n_i 2 3 0

$2A + 2B \rightleftharpoons 3C$

n_{eq} $2-2x$ $3-2x$ $3x$

D.O.D of A $= \frac{2x}{2} = x$

D.O.D of B $= \frac{2x}{3}$

Case 5: n_i 5 8 0

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

n_{eq} $5-x$ $8-3x$ $2x$

D.O.D of $N_2 = \frac{x}{5}$

D.O.D of $H_2 = \frac{3x}{8}$

Case 6: n_i 4 0 0

$2SO_3 \rightleftharpoons 2SO_2 + O_2$

n_{eq} $4-2x$ $2x$ x

D.O.D of $SO_3 = \frac{2x}{4} = \frac{x}{2}$

Case 7: n_i 6 7 0 0

$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$

n_{eq} $6-4x$ $7-5x$ $4x$ $6x$

D.O.D of $NH_3 = \frac{4x}{6} = \frac{2x}{3}$

D.O.D of $O_2 = \frac{5x}{7}$

Apps of D.O.D

To Find Eq^m constants

Case 1: Calculation of K_C

n_i a b 0

$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$

n_{eq} $a-x$ $b-x$ x

C_{eq} $\left(\frac{a-x}{V}\right)$ $\left(\frac{b-x}{V}\right)$ $\left(\frac{x}{V}\right)$

$$K_C = \frac{\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

Case 2: Calculation of K_P

n_i	a	b	0
	$A_{(g)}$ +	$B_{(g)}$ $\rightleftharpoons$	$C_{(g)}$
n_{eq}	$a-x$	$b-x$	x
X_{eq}	$\frac{a-x}{a+b-x}$	$\frac{b-x}{a+b-x}$	$\frac{x}{a+b-x}$
P_{eq}	$\frac{(a-x)P}{(a+b-x)}$	$\frac{(b-x)P}{(a+b-x)}$	$\frac{xP}{(a+b-x)}$

$$K_P = \frac{\left(\frac{xP}{a+b-x}\right)}{\frac{(a-x)P}{(a+b-x)} \times \frac{(b-x)P}{(a+b-x)}}$$

Q. $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ at certain temp only 50% HI is dissociated find K_C

n_i	2	0	0
	$2HI_{(g)} \rightleftharpoons$	$H_{2(g)}$ +	$I_{2(g)}$
n_{eq}	$2-2x$	x	x

D.O.D of HI $= \frac{2x}{2} = x = \frac{1}{2}$

n_{eq}	1	$\frac{1}{2}$	$\frac{1}{2}$
C_{eq}	$\frac{1}{V}$	$\frac{1}{2V}$	$\frac{1}{2V}$

$$K_C = \frac{\frac{1}{2V} \times \frac{1}{2V}}{\left(\frac{1}{V}\right)^2} = \frac{1}{4}$$

Q. $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$ if initially A & B both are taken in equal amount but at eq_m $[D]_{eq}$ $2[A]_{eq}$ find K_C?

n_i	a	a	0	0
	$A_{(g)}$ +	$B_{(g)}$ $\rightleftharpoons$	$C_{(g)}$ +	$D_{(g)}$
n_{eq}	$a-x$	$a-x$	x	x
C_{eq}	$\frac{a-x}{V}$	$\frac{a-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$
C_{eq}	$\frac{a-2a/3}{V}$	$\frac{a-2a/3}{V}$	$\frac{2a/3}{V}$	$\frac{2a/3}{V}$

$$K_C = \frac{\frac{2\cancel{a}}{\cancel{3}} \times \frac{2\cancel{a}}{\cancel{3}}}{\frac{\cancel{a}}{\cancel{3}} \times \frac{\cancel{a}}{\cancel{3}}} = 4$$

$\frac{x}{\cancel{V}} = 2\left(\frac{a-x}{\cancel{V}}\right)$

$x = 2a - 2x$

$3x = 2a$

$x = \frac{2a}{3}$

Q. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ for rxn initially the mole ratio was 1 : 3 of $N_2 : H_2$. At eq^m 50% of each has reacted, if the eq^m pressure is P. Find K_P?

n_i	1	3	0
	N_2 +	$3H_2$ $\rightleftharpoons$	$2NH_3$
n_{eq}	$1-x$	$3-3x$	$2x$
n_{eq}	$\frac{1}{2}$	$\frac{3}{2}$	1
X_{eq}	$\frac{1/2}{3}$	$\frac{3/2}{3}$	$\frac{1}{3}$
X_{eq}	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{1}{3}$
P_{eq}	$\frac{P}{6}$	$\frac{P}{2}$	$\frac{P}{3}$

$\Delta n_g = 2 - 4 = 2$

D.O.D of $N_2 = \frac{x}{1} = \frac{1}{2}$

$$K_P = \frac{(P/3)^2}{(P/6)\,(P/2)^3}$$

$$= \frac{\frac{1}{\cancel{9}\,3}}{\frac{1}{\cancel{6}\,2} \times \frac{1}{8}} P^{-2} = \frac{\frac{1}{3}}{\frac{1}{16}} P^{-2} = \frac{16}{3P^2} (atm)^{-2}$$

Q. Write expression of K_P for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Given D.O.D = x. eq^m total pressure is P

n_i	1	0	0
	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
n_{eq}	$1-x$	x	x
X_{eq}	$\frac{1-x}{1+x}$	$\frac{x}{1+x}$	$\frac{x}{1+x}$
P_{eq}	$\frac{(1-x)P}{(1+x)}$	$\frac{xP}{1+x}$	$\frac{xP}{1+x}$

$$K_P = \frac{\frac{x^2 P^{\cancel{2}}}{(1+x)^{\cancel{2}}}}{\frac{(1-x)\cancel{P}}{\cancel{(1+x)}}} = \frac{x^2 P}{1-x^2}$$

$1 >>> x$

$K_P = x^2 P$

$x = \sqrt{\frac{K_P}{P}}$ $\boxed{x \propto \frac{1}{\sqrt{P}}}$

Calculation of K_P if pressure is given.

Q. In the Rxn the eq^m pressure is 12 atm. If 50% CO_2 reacts find K_P

$$\begin{array}{llll} P_i & P_O & & 0 \\ C_{(s)} + & CO_{2(g)} & \rightleftharpoons & 2CO_{(g)} \\ P_{eq} & P_O - P_x & & 2P_x \\ P_{eq} & P_O - \frac{P_O}{2} & & 2 \times \frac{P_O}{2} \\ P_{eq} & \frac{P_O}{2} & & P_O \end{array}$$

$$\text{D.O.D of } CO_2 = \frac{P_x}{P_O} = \frac{1}{2}$$

$$P_x = \frac{P_O}{2}$$

$$\frac{P_O}{2} + P_O = 12 ; \frac{3P_O}{2} = 12 ; P_O = 8$$

$$K_P = \frac{(P_O)^2}{(P_O/2)} = 2P_O = 2 \times 8 = 16 \text{ (atm)}$$

Q. For the rxn, the observed pressure is 1.12 atm find K_P?

$$\begin{array}{lccc} & & 0 & 0 \\ NH_4HS_{(s)} & \rightleftharpoons & NH_{3(g)} + & H_2S_{(g)} \\ & & P_x & P_x \end{array}$$

$2P_x = 1.12$

$P_x = 0.56$

$K_P = P_x \times P_x$

$= 0.56 \times 0.56 = 0.3136 \text{ (atm)}^2$

Relation b/w D.O.D and Vapour density

$$\left[\alpha = \frac{D-d}{d(n-1)}\right] \quad (n \neq 1)$$

α = D.O.D

D = V.D of Reactant

$$\text{V.D} = D = \frac{M.W_{Reactant.}}{2}$$

d = V.D of Rxn mix

Significance of n

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

n = moles of products = 2

$$2NH_3 \rightleftharpoons N_2 + 3H_2 \Rightarrow NH_3 \rightleftharpoons \frac{1}{2} N_2 + \frac{3}{2} H_2$$

$$n = \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$$

Q. The V.D of gaseous mix is 58 at 250°C for the Rxn

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ Find D.O.D?

$$d = 58 \qquad D = \frac{208.5}{2} = 104.25$$

$$\alpha = \frac{D-d}{d(n-1)} = \frac{104.25 - 58}{58(2-1)} ; \alpha = 0.8$$

[% D.O.D = 80%]

Le-chatelier's principle

1. **Effect of $conc^n$**

   $R \rightleftharpoons P$

   $[R]\uparrow \longrightarrow ; [P]\uparrow \longleftarrow$

   $[R]\downarrow \longleftarrow ; [P]\downarrow \longrightarrow$

2. **Effect of Pressure**

   (1) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\quad (4 \rightleftharpoons 2)$

   $\boxed{P\uparrow n\uparrow \longrightarrow}$ $\boxed{P\downarrow n\downarrow}$

   (2) $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ $\quad (2 \rightleftharpoons 3)$

   $\boxed{P\uparrow n\uparrow \longleftarrow}$ $\boxed{P\downarrow n\downarrow \longrightarrow}$

   (3) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

   $\Delta n_g = 0$ No. effect of pressure change

3. **Effect of temp**

   a) Endothermic Rxn $\quad \Delta H = +ve$

   $R + Heat \rightleftharpoons P$

   $T\uparrow \longrightarrow T\downarrow \longleftarrow$

   b) Exothermic Rxn $\quad \Delta H = -ve$

   $R \rightleftharpoons P + Heat$

   $T\uparrow \longleftarrow T\downarrow \longrightarrow$

4. **Effect of Catalyst**

   Does not affect the eq^m

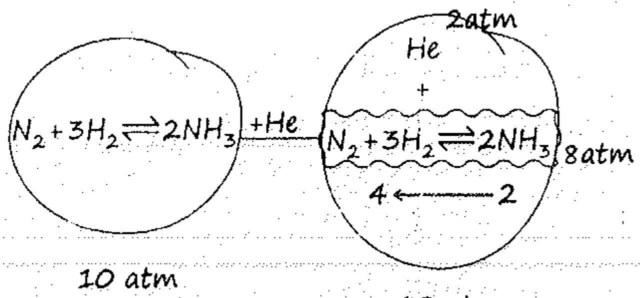
5. **Effect of addition of inert gas**

   Case 1: at const volume

   Does not affect the eq^m

   Case 2: at const pressure

   Rxn will shift in that $direc^n$ where no. of moles increases.



10 atm

10 atm

$\boxed{P \downarrow n \downarrow}$

the rxn will proceed in the dir^n where no. of moles increases

Q. Predict the direction of eq^m?

$$N_{2(g)} + 3H_{2(g)} \underset{4 \longleftarrow\!\!\longrightarrow 2}{\rightleftharpoons} 2NH_{3(g)} + \text{Heat}$$

(1) $[N_2] \uparrow \longrightarrow$

(2) $[NH_3] \uparrow \longleftarrow$

(3) $P \uparrow n \uparrow \longrightarrow$

(4) $T \uparrow \longleftarrow$

(5) By adding catalyst

(6) Addition of Ne at const pressure $\longleftarrow$

Reaction Quotient

$$\alpha A_{(g)} + \beta B_{(g)} \rightleftharpoons \gamma C_{(g)} + \delta D_{(g)}$$

$$Q_C = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

[A], [B]

[C], [D]

not at eq^m

Case 1: $Q_C = K_C$; eq^m

Case 2: $Q_C > K_C$; B.W.R

Case 3: $Q_C < K_C$; F.W.R

7 Ionic Equilibrium

- Substance
  - Electrolytes (dissociate into ions)
    - $\alpha = 1$ Complete dissociation strong electrolytes
    - $0 < \alpha < 1$ partial dissociation weak electrolytes
  - Non Electrolytes (do not dissociate into ions) $\alpha = 0$ Ex: Urea, glucose, Fructose, etc

- Conductivity
  - Conductor (conduct electricity)
    - Metallic flow (electricity due to free $e^{\ominus}$s) T ↑ conductivity ↓
    - Electrolytic flow (electricity due to free ions) T ↑ conductivity ↑
  - Non Conductor (do not conduct electricity)

Strong Electrolytes		Weak Electrolytes	
SA	SB	WA	WB
H_2SO_4, $HClO_4$, $HClO_3$, HNO_3, HCl, HBr, HI ** All types of salts	All alkali metal hydroxides & $Ba(OH)_2$	H_2SO_3, $HClO_2$, HClO HNO_2, All oxyacids of P, All organic carboxylic acids, HCN, H_3BO_3, H_2CO_3, HF	All alkaline earth metal hydroxides except $Ba(OH)_2$, $Al(OH)_3$, All Organic Bases, NH_3, d-block metal hydroxides

Acid Base theory

Arrhenius theory		Bronsted theory	
AA	AB	BA	BB
Donate H^+ ion in aq. solution; HX, H_2SO_4, H_3PO_4, $HClO_4$, HCN etc.	OH donor in aq. solution. Ex: MOH, $M(OH)_2$, $M(OH)_3$	H^+ donor	H^+ acceptor
$HX \xrightarrow{H_2O} H^+ + X^-$ $H^+ \xrightarrow{H_2O} H_3O^+ \xrightarrow{H_2O} H_5O_2^+ \xrightarrow{H_2O} H_7O_3^+$ etc ** H_3BO_3 is not AA.	$MOH \xrightarrow{H_2O} M^+ + \bar{O}H$ $\bar{O}H \xrightarrow{H_2O} H_3O_2^- \xrightarrow{H_2O} H_5O_3^-$ etc	$HX \longrightarrow H^+ + X^-$ * All AA are BA	$X^{\ominus} \xrightarrow{H^+} HX$ $HCO_3^{\ominus} \xrightarrow{H^+} H_2CO_3$ $H_2PO_4^{\ominus} \xrightarrow{H^+} H_3PO_4$ $HCO_3^- \xrightarrow{H^+} H_2CO_3$ $HO^{\ominus} \xrightarrow{H^+} H_2O$

Lewis Theory

L.A	L.B
Lone pair acceptor H^+, CO_2, SF_4, PF_5, BCl_3, $AlCl_3$, $FeCl_3$ etc L.B: $O = C = O$	Lone pair donor $X^\ominus$, $\overset{\ominus}{O}H$, $\ddot{N}H_3$, $H_2\ddot{O}$ etc

Acid Base Theory

Base + $H^+ \longrightarrow$ Conjugate Acid

WB SCA

SB WCA

$NO_3^\ominus + H^+ \longrightarrow HNO_3$

WB SCA

$HCO_3^\ominus + H^+ \longrightarrow H_2CO_3$

SB WCA

Conjugate acid-base pair

Acid $\longrightarrow H^+$ + Conjugate Base

SA W.C.B

WA S.C.B

$HNO_3 \longrightarrow H^+ + NO_3^-$

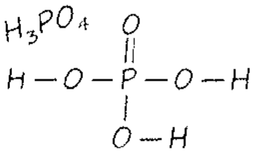
SA WCB

$HF \longrightarrow H^+ + F^-$

WA SCB

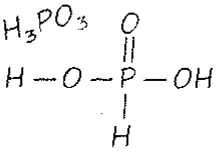
1. Acid base theory

H_3PO_4

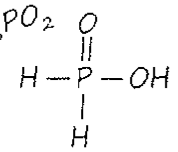


HPO_3^{2-} Amphiprotic ✗

H_3PO_3



H_3PO_2



2. Amphiprotic Species

H^+ donor as well as H^+ acceptor

$HCO_3^\ominus \xrightarrow{-H^+} CO_3^{2-}$

$HCO_3^\ominus \xrightarrow{+H^+} H_2CO_3$

$H_2PO_4^\ominus \xrightarrow{-H^+} HPO_4^{2-} \xrightarrow{-H^+} PO_4^{3-}$

$H_2PO_4^\ominus \xrightarrow{+H^+} H_3PO_4$

$H_2PO_2^\ominus \xrightarrow{-H^+} \times$

$H_2PO_2^\ominus \xrightarrow{+H^+} H_3PO_2$

$H_2PO_3^\ominus \xrightarrow{-H^+} HPO_3^{2-}$

$H_2PO_3^\ominus \xrightarrow{+H^+} H_3PO_3$

pH Calculation

$pH = -\log[H^+]$

$pOH = -\log_{10}[\bar{O}H]$

\# $pH + pOH = 14$ at 25°C

$[H^+] = 10^{-7} = [\bar{O}H]$

\# $pH + pOH = 12$ at 90°C

$[H^+] = 10^{-6} = [\bar{O}H]$

$T \uparrow k_w \uparrow$

Case 1: Strong acid/Base

(1) $[H^+] \geqslant 10^{-6}$ M

Q. Find pH of 10^{-3} M HCl

$[H^+] = 10^{-3}$ M

$pH = -\log 10^{-3} = 3$

$pH = 3$

$-\log(a \times 10^{b}) = b - \log a$

(2) $[H^+] < 10^{-6}$

Q. Find pH of 10^{-8} M HCl

$[H^+] = 10^{-8}$ M

$pH = -\log 10^{-8} = 8$ ✗

$[H^+]_{net} = [H^+]_{from\ acid} + [H^+]_{from\ H_2O}$

$= 10^{-8} + 10^{-7}$

$= 10^{-8}[1 + 10] = 11 \times 10^{-8}$

$pH = -\log(11 \times 10^{-8}) = 8 - \log 11$

$pH = 6.9$

Case 2: pH of mix of two SA & SB

$$[H^+]/[OH^-] = \frac{[N_1V_1 \pm N_2V_2]}{V_1 + V_2}$$

$$= \frac{[M_1V_1nf_1 \pm M_2V_2nf_2]}{V_1 + V_2}$$

Q. Find pH

50 mL of $\frac{M}{5}$ HCl + 50 mL of $\frac{M}{10}$ H_2SO_4

$$[H^+] = \frac{M_1V_1nf_1 + M_2V_2nf_2}{V_1 + V_2}$$

$$= \frac{\frac{1}{5} \times 50 \times 1 + \frac{1}{10} \times 50 \times 2}{50 + 50}$$

$$= \frac{10 + 10}{100} = \frac{20}{100} = 2 \times 10^{-1}$$

$p^H = -\log(2 \times 10^{-1}) = 1 - \log 2 = 1 - 0.3$

$p^H = 0.7$

Q. Find pH

75 mL of $\frac{M}{2}$ $Ba(OH)_2$ + 25 mL of $\frac{M}{1}$ HCl

$$[OH^-] = \frac{\left|\frac{1}{\cancel{2}} \times 75 \times \cancel{2} - 1 \times 25 \times 1\right|}{100}$$

$$[OH^-] = \frac{|75 - 25|}{100} = \frac{50}{100} = \frac{1}{2}$$

$p^{OH} = -\log \frac{1}{2} = \log 2 = 0.3$

$p^H = 14 - 0.3 = 13.7$

Case 3: pH of weak monobasic acid

or

Weak monoacidic base

$$\overset{C}{HA} \rightleftharpoons H^+ + A^- \quad K_a$$

$$\alpha = \sqrt{\frac{K_a}{C}} \; ; \; [H^+] = \sqrt{K_aC}$$

$$pH = \frac{1}{2}[pK_a - \log C]$$

✦ **Degree of dissociation of weak electrolyte is inversely proportional to square root of the conc^n or directly proportional to square root of dilution** $\left[\alpha = \frac{1}{\sqrt{C}} \text{ or } \alpha \propto \sqrt{V}\right]$

Q. Calculate pH of 0.1 M CH_3COOH ($K_a = 10^{-5}$)

$pH = \frac{1}{2}(Pk_a - \log C)$ $\qquad P^{Ka} = -\log K_a$

$= \frac{1}{2}(5 - \log 10^{-1})$ $\qquad = -\log 10^{-5}$

$\qquad = 5$

$= \frac{1}{2}(5 + 1)$

$= \frac{6}{2}$ $\qquad \alpha = \sqrt{\frac{10^{-5}}{10^{-1}}} = \sqrt{10^{-4}} = 10^{-2}$

pH = 3 $\qquad [H^+] = \sqrt{K_aC}$

$= \sqrt{10^{-5} \times 10^{-1}}$

$= \sqrt{10^{-6}} = 10^{-3}$

Case 4: pH of weak poly basic acid

or

Weak poly acidic base

H_3PO_4, H_2CO_3, H_2S etc

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $\qquad Ka_1$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ $\qquad Ka_2$

$HPO_4^{2-} \rightleftharpoons H^+ + HPO_4^{3-}$ $\qquad Ka_3$

$Ka_1 > Ka_2 > Ka_3$

$$\alpha = \sqrt{\frac{Ka_1}{C}} \; ; \; [H^+] = \sqrt{Ka_1C} = [H_2PO_4^-]$$

$pH = \frac{1}{2}[PKa_1 - \log C]$ $\qquad [HPO_4^{2-}] = Ka_2$

$$[PO_4^{3-}] = \frac{Ka_2Ka_3}{[H^+]}$$

Q. Find pH of 0.1 M H_3PO_4

$Ka_1 = 10^{-3}$, $Ka_2 = 10^{-8}$, $Ka_3 = 10^{-13}$

$pH = \frac{1}{2}[PKa_1 - \log C]$

$= \frac{1}{2}(3 - \log 10^{-1})$

$= \frac{4}{2}$ $\qquad \alpha = \sqrt{\frac{10^{-3}}{10^{-1}}} = \sqrt{10^{-2}} = 10^{-1}$

pH = 2 $\qquad [H^+] = [H_2PO_4^-] = \sqrt{10^{-3} \times 10^{-1}} = 10^{-2}$

$[HPO_4^{2-}] = 10^{-8}$

$$[PO_4^{3-}] = \frac{10^{-8} \times 10^{-13}}{10^{-2}} = 10^{-19}$$

Case 5: PH of mix of two weak acid

or

two weak bases

$$[H^+] = \sqrt{Ka_1C_1 + Ka_2C_2}$$

or

$$[OH^-] = \sqrt{Kb_1C_1 + Kb_2C_2}$$

C_1 & C_2 conc^n after mixing

Q. Find P^H of Soln obtained by mixing equal volumes of 0.02 M HOCl ($Ka_1 = 2 \times 10^{-4}$) and 0.2 M CH_3COOH ($Ka_2 = 2 \times 10^{-5}$)

$$C_1 = \frac{0.02}{2} = 0.01 \; ; \; C_2 = \frac{0.2}{2} = 0.1$$

$$[H^+] = \sqrt{2 \times 10^{-4} \times 10^{-2} + 2 \times 10^{-5} \times 10^{-1}}$$

$$= \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = \sqrt{4 \times 10^{-6}}$$

$$= 2 \times 10^{-3}$$

$$P^H = -\log(2 \times 10^{-3}) = 3 - \log 2 = 3 - 0.3$$

$P^H = 2.7$

Case 6: P^H of mix of WA and SA

or

WB and SB

WA C_1 Ka_1

SA C_2

$$[H^+] = \frac{-C_2 \pm \sqrt{C_2^2 + 4Ka_1C_1}}{2}$$

Q. Find P^H of mix of 10^{-4} M HCl & 10^{-2} M CH_3COOH ($K_a = 2 \times 10^{-5}$)

$$[H^+] = \frac{-10^{-4} \pm \sqrt{(10^{-4})^2 + 4 \times 2 \times 10^{-5} \times 10^{-2}}}{2}$$

$$= \frac{-10^{-4} + \sqrt{10^{-8} + 8 \times 10^{-7}}}{2}$$

$$= \frac{-10^{-4} + \sqrt{10^{-8} + 80 \times 10^{-8}}}{2}$$

$$= \frac{-10^{-4} + \sqrt{81 \times 10^{-8}}}{2} = \frac{-10^{-4} + 9 \times 10^{-4}}{2}$$

$$= \frac{8 \times 10^{-4}}{2} = 4 \times 10^{-4}$$

$$P^H = -\log(4 \times 10^{-4})$$

$$= 4 - \log 4 = 4 - 0.6 = 3.4$$

Case 7: P^H of Amphiprotic species

$$HCO_3^{\ominus} \xrightarrow{+H^+} H_2CO_3$$

$$HCO_3^{\ominus} \xrightarrow{-H^+} CO_3^{2-}$$

$$\left[P^H = \frac{P^{K_{a_1}} + P^{K_{a_2}}}{2}\right]$$

$H_2PO_4^{\ominus}$ $\qquad$ HPO_4^{2-}

$$\left[P^H = \frac{P^{K_{a_1}} + P^{K_{a_2}}}{2}\right] \qquad \left[P^H = \frac{P^{K_{a_2}} + P^{K_{a_3}}}{2}\right]$$

Q. Find P^H of a) 0.01 M NaH_2PO_4

b) 0.1 M Na_2HPO_4

for H_3PO_4 $K_{a_1} = 10^{-3}$

$K_{a_2} = 10^{-8}$

$K_{a_3} = 10^{-13}$

a) $P^H = \frac{3 + 8}{2} = \frac{11}{2} = 5.5$

b) $P^H = \frac{8 + 13}{2} = \frac{21}{2} = 10.5$

Salt hydrolysis

WA + SB (CH_3COONa)

$$CH_3COO^{\ominus} + H_2O \rightleftharpoons CH_3COOH + OH^- \; (K_H)$$

(1) Anionic hydrolysis

(2) $K_H = \frac{K_w}{K_a}$

(3) $h = \sqrt{\frac{K_H}{C}}$

(4) $P^H = 7 + \frac{1}{2}[PK_a + \log C]$

$P^H > 7$ Nature of sol^n after hydrolysis is basic

SA + WB (NH_4Cl)

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \quad (K_H)$

(1) Catonic

(2) $K_H = \frac{K_w}{K_b}$

(3) $h = \sqrt{\frac{K_H}{C}}$

(4) $P^H = 7 - \frac{1}{2}[PK_b + \log C]$

$P^H < 7$ Nature of sol^n after hydrolysis is Acidic

WA + SB (CH_3COONH_4)

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH \quad K_H$

(1) Cationic and anionic both

(2) $K_H = \frac{K_w}{K_a K_b}$

(3) $h = \sqrt{K_H}$ (D.O. hydrolysis is independent of $conc^n$ of salt)

(4) $P^H = 7 + \frac{1}{2}[PK_a - PK_b]$

$K_a > K_b$; $PK_a < PK_b$; $pH < 7$ Acidic

$K_a < K_b$; $PK_a > PK_b$; $pH > 7$ Basic

$K_a = K_b$; $PK_a = PK_b$; $pH = 7$ Neutral

✦ Salt of SA + SB does not hydrolyse ($P^H = 7$)

Q. Which salts will have highest P^H?

(A) KCl
SA + SB
$P^H = 7$

(B) Na_2CO_3
WA + SB
$P^H > 7$

(C) $CuSO_4$
SA + WB
$P^H < 7$

(D) N.O.T

Q. Pk_b for CN^- is 4.7. The P^H of 0.5M aq. NaCN sol^n is

($PK_a + PK_b = 14$; $PK_a = 14 - 4.7 = 9.3$)

WA + SB $\quad P^H = 7 + \frac{1}{2}[PK_a + \log C]$

$= 7 + \frac{1}{2}[9.3 + \log \frac{1}{2}]$

$= 7 + \frac{1}{2}[9.3 - 0.3]$

$= 7 + 4.5 = 11.5$

Q. K_b for NH_4OH is 2×10^{-5} find K_H of NH_4Cl

SA + WB $\quad K_H = \frac{K_w}{K_b} = \frac{10^{-14}}{2 \times 10^{-5}}$

$= 0.5 \times 10^{-9}$

$= 5 \times 10^{-10}$

Q. In correct match $\quad P^H < 7$ Acidic

(A) $FeCl_3$ In H_2O – Basic
SA + WB

(B) NH_4Cl " " – Acidic
SA + WB

(C) CH_3COONH_4 " " $\longrightarrow K_a = K_b$
WA + WB
$P^H = 7$ Neutral

(D) Na_2CO_3 " " – Basic
WA + SB $\quad P^H > 7$

Buffer Solutions

The solutions which resist the change in P^H by adding small amount of strong acid or strong base

$CH_3COOH + CH_3COONa$ (WA + Salt of WA with SB)

Acidic buffer

$CH_3COO^{\ominus} + H^+ \longrightarrow CH_3COOH$

$CH_3COOH + \bar{O}H \longrightarrow CH_3CO\bar{O} + H_2O$

$NH_4OH + NH_4Cl$ (WB + Salt of SA with WB)

Basic Buffer

$\downarrow H^+$ or $\bar{O}H$

$NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O$

$NH_4^+ + \bar{O}H \longrightarrow NH_4OH$

Acidic buffer can be prepared by three ways

1. $CH_3COOH + CH_3COONa$
WA (Salt of WA + SB)

2. WA is mixed with SB ($n_{WA} > n_{SB}$)

$$\overset{10}{CH_3COOH} + \overset{5}{NaOH} \rightleftharpoons \overset{0}{CH_3COONa} + \overset{0}{H_2O}$$

$\frac{10}{1} \qquad \frac{5}{1}$

moles after Rxn $(10-5)$ 0 5 5

$\boxed{\cancel{5}}$ 0 $\boxed{\cancel{5}}$ 5

3. Salt of (WA + SB) with SA ($n_{Salt} > n_{SA}$)

$$\begin{array}{lcccc} n_i & 10 & 5 & 0 & 0 \\ \text{moles} & CH_3COONa & + HCl \rightleftharpoons & CH_3COOH & + NaCl \\ \text{after Rxn} & \frac{10}{1} & \frac{5}{1} & & \\ & (10-5) & 0 & 5 & 5 \\ & \boxed{\cancel{5}} & 0 & \boxed{\cancel{5}} & 5 \end{array}$$

Examples of Buffer Solutions

→ Acidic

WA Salt of WA + SB

1. $HCN + NaCN$
2. $H_3BO_3 + Na_2B_4O_7$
3. $H_2CO_3 + NaHCO_3 \Rightarrow$ Used to maintain P^H of blood (7.26 – 7.42)
4. $H_3PO_4 + NaH_2PO_4$
5. $CH_3COOH + CH_3COONa$
6. $HNO_2 + NaNO_2$

→ Basic

WB Salt of WB + SA

1. $CH_3NH_2 + CH_3\overset{+}{N}H_3Cl^-$
2. $NH_4OH + NH_4Cl$
3. $PhNH_2 + PhN\overset{+}{H}_3Cl^-$
4. $C_5H_5N + C_5H_5N\overset{+}{H}Cl^-$

→ Salt of WA + WB

CH_3COONH_4, NH_4CN, $AgCN$ etc.

Calculation of P^H of Buffer Solutions

Henderson's Eq^n Acidic

$$P^H = P^{Ka} + \log_{10}\frac{[Salt]}{[Acid]}$$

$$= P^{Ka} + \log_{10}\frac{[Conjugate\ base]}{[Acid]}$$

Basic

$$P^{OH} = P^{Kb} + \log_{10}\frac{[Salt]}{[Base]}$$

$$= P^{Kb} + \log_{10}\frac{[Conjugate\ acid]}{[Base]}$$

Calculation of P^H of Buffer Solutions

Q. 50 mL of 2M CH_3COOH mixed with 10 mL of 1M CH_3COONa will have an approx P^H of ($K_a = 10^{-5}$)

$$P^H = 5 + \log\left(\frac{\frac{n_{Salt}}{\cancel{V_{Solution}}}}{\frac{n_{acid}}{\cancel{V_{Solution}}}}\right)$$

$$= 5 + \log\left(\frac{10 \times 1}{50 \times 2}\right)$$

$$= 5 + \log\frac{1}{10}$$

$$= 5 - \log 10$$

$$= 5 - 1$$

$$P^H = 4$$

Q. 0.05M NH_4OH solution is dissolved in 0.001M NH_4Cl solution find P^H($K_b = 10^{-5}$)

$$P^{OH} = 5 + \log\left(\frac{0.001}{0.05}\right)$$

$$= 5 + \log\left(\frac{1}{50}\right)$$

$$= 5 - \log 50$$

$$= 5 - 1.7$$

$$P^{OH} = 3.3$$

$$P^H = 14 - 3.3$$

$$\boxed{P^H = 10.7}$$

Q. $\frac{N}{10}$ CH_3COOH was titrated with $\frac{N}{10}$ NaOH. When 75% of titration is over then find P^H? ($K_a = 10^{-5}$)

$$\underset{[25\%]}{CH_3COOH} + NaOH \rightleftharpoons \underset{[75\%]}{CH_3COONa} + H_2O$$

$$P^H = P^{Ka} + \log\left(\frac{75}{25}\right)$$

$$= 5 + \log 3$$

$$= 5 + 0.48$$

$$\boxed{P^H = 5.48}$$

Q. $P^H - P^{Ka} = 1$ will be applicable for an acidic buffer when

(A) [Acid] = [Conju base]

(B) [Acid] × 10 = [Conju base]

(C) [Acid] = [Conju base] × 10

(D) N.O.T

$$P^H = P^{Ka} + \log\frac{[\text{Conju base}]}{[\text{Acid}]}$$

$$\frac{[\text{Conju base}]}{[\text{Acid}]} = 10$$

$$P^H - P^{Ka} = \log\frac{[\text{Conju base}]}{[\text{Acid}]}$$

$$1 = \log\frac{[\text{Conju base}]}{[\text{Acid}]}$$

Buffer Range

$$\frac{1}{10} \le \frac{[\text{Conju base}]}{[\text{Acid}]} \le 10$$

$[(P^{Ka} - 1 \le P^H \le P^{Ka} + 1)]$

Maximum buffer action $[P^H = P^{Ka}]$

Buffer Capacity

$$\text{Buffer capacity} = \frac{\text{No. of moles of strong acid or strong base added per L of Sol}^n}{\text{Change in } P^H \text{ of buffer}}$$

Q. When 2 moles of HCl is added to 1 L of an acidic buffer Sol^n its P^H changes from 3.9 to 3.4 find its buffer capacity

$$B.C = \frac{2}{0.5} = 4$$

Solubility and Solubility Product

Solubility

Max. no. of moles of solute dissolved in a solvent to obtain 1 L sol^n.

$$\text{Solubility} \rightleftharpoons \frac{mol}{L}$$

$$\left[\text{Solubility}\left(\frac{g}{L}\right) = \text{Solubility}\left(\frac{mol}{L}\right) \times MW\right]$$

Relation between k_{sp_o} & s_o

$$\begin{array}{cccc} s & & 0 & 0 \\ A_xB_{y(s)} & \rightleftharpoons & xA^{y+}_{(aq)} + & yB^{x-}_{(aq)}, \ k_{sp} \\ - & & xs & ys \end{array}$$

$$k_{sp} = (xs)^x (ys)^y$$

$$\boxed{k_{sp} = x^x\, y^y\, s^{x+y}}$$

NaCl, $x = 1$ $y = 1$

$k_{sp} = 1^1 \times 1^1 \times s^{1+1} = s^2$

Compound	x	y	Relation between s and k_{sp}
$Ba^{2+}SO_4^{2-}$	1	1	$k_{sp} = 1^1 \times 1^1 \times s^{1+1} = s^2$
$(NH_4^+)_2SO_4^{2-}$	2	1	$k_{sp} = 2^2 \times 1^1 \times s^{2+1} = 4s^3$
$Hg^{2+}Cl_2^-$	1	2	$k_{sp} = 1^1 \times 2^2 \times s^{1+2} = 4s^3$
$K_3^+PO_4^{3-}$	3	1	$k_{sp} = 3^3 \times 1^1 \times s^{3+1} = 27s^4$
$Ca_3^{2+}(PO_4^{3-})_2$	3	2	$k_{sp} = 3^3 \times 2^2 \times s^{3+2} = 108s^5$
$\overset{+}{Hg} - \overset{+}{Hg}$ $Hg_2^{2+}Cl_2$ **	1	2	$k_{sp} = 1^1 \times 2^2 \times s^{1+2} = 4s^3$
$Ag_2^+CrO_4^{2-}$	2	1	$k_{sp} = 2^2 \times 1^1 \times s^{2+1} = 4s^3$
			# $Na^+K^+Rb^+PO_4^{3-}$ $k_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times s^{1+1+1+1} = s^4$

Q. If solubility of Ag_2SO_4 is $10^{-2}\ \frac{mol}{L}$ then find its k_{sp}?

$Ag_2SO_4 \quad x = 2, \quad y = 1$

$k_{sp} = 2^2 \times 1^1 \times s^{2+1}$

$= 4s^3$

$= 4 \times (10^{-2})^3 = 4 \times 10^{-6} \left(\frac{mol}{L}\right)^3$

Q. If k_{sp} of AgCl is $10^{-10} \left(\frac{mol}{L}\right)^2$ then find its solubility in gm/L?

$AgCl \quad x = 1 \quad y = 1$

$k_{sp} = 1^1 \times 1^1 \times s^{1+1} = s^2$

$10^{-10} = s^2$

$s = 10^{-5}\ \frac{mol}{L}$

$s\left(\frac{gm}{L}\right) = s\left(\frac{mol}{L}\right) \times MW_{salt}$

$= 10^{-5} \times 143.5$

$s\left(\frac{gm}{L}\right) = 1.435 \times 10^{-3}$

Solubility in common ion effect

By adding common ion, solubility of Salt decreases. Solubility ↓

$AgCl_{(s)} \rightleftharpoons \underset{(aq)}{Ag^+} + \underset{(aq)}{Cl^-} \quad K_{sp}$

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

Q. Find solubility of AgCl $\left(K_{sp} = 10^{-10} \left(\frac{mol}{L}\right)^2\right)$

(a) In H_2O

(b) In 0.1 M $AgNo_3$

(c) In 0.1 M $CaCl_2$

(a) In H_2O

$\overset{s}{AgCl} \rightleftharpoons \overset{0}{Ag^+} + \overset{0}{Cl^-} \quad K_{sp}$

$\quad - \qquad\quad s \qquad s$

$K_{sp} = (s)^1 \times (s)^1 = S^2$

$10^{-10} = S^2$

$\boxed{S = 10^{-5}\ M}$

(b) In 0.1 M $AgNO_3$

$\overset{s}{AgCl} \rightleftharpoons \overset{0}{Ag^+} + \overset{0}{Cl^-} \quad K_{sp}$

$\quad - \qquad 0.1 + \cancel{s}^{0} \qquad s$

$AgNO_3 \longrightarrow Ag^+ + NO_3^-$

0.1 M $\qquad$ 0.1 M $\qquad$ 0.1 M

$K_{sp} = (0.1)^1 \times (S)^1$

$S = \frac{10^{-10}}{0.1} = 10^{-9}\ \frac{mol}{L}$

(c) In 0.1 M $CaCl_2$

$\overset{s}{AgCl} \rightleftharpoons \overset{0}{Ag^+} + \overset{0}{Cl^-} \quad K_{sp}$

$\quad - \qquad s \qquad \cancel{s}^{0} + 0.2$

$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$

0.1 M $\qquad$ 0.1 M $\qquad$ 2 × 0.1 M

0.2 M

$K_{sp} = (s)^1 \times (0.2)^1$

$S = \frac{10^{-10}}{0.2} = 5 \times 10^{-10} \left(\frac{mol}{L}\right)$

Ionic product of salt

$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

$K_{IP} = [A^{y+}]^x\ [B^{x-}]^y$

Case ① $K_{IP} = K_{sp}$ — Saturated solⁿ

Case ② $K_{IP} > K_{sp}$ — ppt occurs

Case ③ $K_{IP} < K_{sp}$ — Unsaturated solⁿ

Q. The ppt of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when following are mixed.

	$[Ca^{2+}]$	$[F^-]$
(A)	10^{-3} M	10^{-5} M
(B)	10^{-5} M	10^{-3} M
(C)	10^{-2} M	10^{-3} M
(D)	10^{-4} M	10^{-4} M

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$K_{IP} = [Ca^{2+}]\ [F^-]^2$

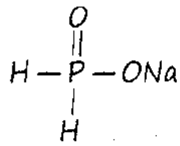
(A) $K_{IP} = 10^{-3} \times (10^{-5})^2 = 10^{-13}$; $K_{sp} > K_{IP}$

(B) $K_{IP} = 10^{-5} \times (10^{-3})^2 = 10^{-11}$; $K_{sp} > K_{IP}$

(C) $K_{IP} = 10^{-2} \times (10^{-3})^2 = 10^{-8}$; $K_{sp} > K_{IP}$

Some Imp points

① Types of Salts



(a) Normal salts

$NaCl$, Na_2SO_4, Na_3PO_4 etc.

(b) Acid salts

$NaHCO_3$, $NaHSO_4$

NaH_2PO_2

(c) Basic salts

$Zn(OH)Cl$, $Mg(OH)Cl$ etc.

(d) Double salts

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Potash alum

(e) Complex salts

$[Ag(NH_3)_2]Cl$, $[Cu(NH_3)_4]SO_4$ etc.

(f) Mixed salts

$NaKS$, $NaKRbPO_4$ etc.

② Isohydric Sol^n

Sol^n having same $[H^+]$ Conc^n

$[H^+]_1 = [H^+]_2$

$\sqrt{Ka_1c_1} = \sqrt{Ka_2c_2}$

$[Ka_1c_1 = Ka_2c_2]$

③ Relative strength of acids

$$R.S = \frac{[H^+]_1}{[H^+]_2} = \frac{\sqrt{Ka_1c_1}}{\sqrt{Ka_2c_2}}$$

WA + SB Mixing ($K_a(CH_3COOH) = 10^{-5}$)

Case 1: 75mL of 0.1 M CH_3COOH

+

25mL of 0.1 M NaOH

$n_{WA} = 75 \times 0.1 = 7.5$ mmol

$n_{SB} = 25 \times 0.1 = 2.5$ mmol

	A	+ B	$\longrightarrow$ S	+ H_2O
Moles	7.5	2.5	0	0
after Rxn	$\boxed{5}$	0	$\boxed{2.5}$	2.5

$$pH = 5 + \log\left(\frac{2.5}{5}\right)$$

$$pH = 5 + \log\frac{1}{2} = 5 - \log 2 = 5 - 0.3 = 4.7$$

Case 2: 50 mL of 0.1 M CH_3COOH

+

50 mL of 0.1 M NaOH

$n_{WA} = 5$ $\qquad C = \frac{5}{100} = \frac{1}{20}$

$n_{SB} = 5$

A	+ B	$\longrightarrow$ S	+ H_2O
5	5	0	0
0	0	5	5

$$pH = 7 + \frac{1}{2}\left[5 + \log\frac{1}{20}\right]$$

$$= 7 + \frac{1}{2}[5 - \log 20] = 7 + \frac{1}{2}[5 - 1.3]$$

$$= 7 + \frac{1}{2} \times 3.7 = 7 + 1.85 = 8.85$$

Case 3: 25mL of 0.1 M CH_3COOH

+

75 mL of 0.1 M NaOH

$n_{WA} = 2.5$; $n_{SB} = 7.5$

A	+ B	$\longrightarrow$ S	+ H_2O
2.5	7.5	0	0
0	$\boxed{5}$	2.5	2.5

$$[OH^-] = \frac{5}{100} = \frac{1}{20}$$

$$pOH = -\log\frac{1}{20} = \log 20 = 1.3$$

$[pH = 14 - 1.3 = 12.7]$

8 Redox Reactions

Concept of Oxidation Number

Real or imaginary charge present on an atom.

H^- O.N = +1 O^{2-} O.N = −2

$\overset{+1}{H}\,\overset{-1}{Cl}$ $\overset{+1}{H}-\overset{-1\,-1}{O}-\overset{+1}{H}$

Rules#

1. O.N of H is generally +1 but in Metal hydrides it is −1

$\overset{+1}{M}\,\overset{-1}{H}$ $\overset{+2}{M}\,\overset{-1}{H_2}$

2. O.N of 'O' is usually −2 but

− 1 in peroxides O_2^{2-} $\left(\overset{-1}{O}-\overset{-1}{O}\right)$

$-\frac{1}{2}$ in superoxides O_2^{-1}

$-\frac{1}{3}$ in ozonide $KO_3\left(1+3x=0 \Rightarrow x=-\frac{1}{3}\right)$

+ 1 in O_2F_2

+ 2 in OF_2

$+\frac{1}{2}$ in $O_2^+\,[AsF_6]^-$

3. O.N of Halogens (Except F) is usually −1 to +7

$F \Rightarrow -1$ in all compounds

4. Alkali metals ⇒ + 1 always
Alkaline earth metals ⇒ + 2 always } in their compounds
5. O.N of N is usually −3 to +5
6. O.N of element in elemental state is always zero

O_2, P_4, S_8, N_2, X_2 etc.

7. The sum of O.N of all the elements in a compound is always zero.
8. The sum of O.N of all the elements in an ion is always equal to charge on that ion
9. O.N in covalent bond

E.N A<B

$\overset{\circ}{A}-\overset{\circ}{A}$ $\underset{+1}{A}-\underset{-1}{B}$ $\underset{+2}{A}=\underset{-2}{B}$ $\underset{+3}{A}\equiv\underset{-3}{B}$

10. O.N in coordinate bond

$A \leftarrow B$ EN A<B

$\underset{+1}{H}-\underset{-1-2}{N}\equiv\underset{+2}{C}$ $\underset{+1}{H}-\overset{+}{\underset{-1\,-3}{N}}\equiv\overset{-}{\underset{+3}{C}}$

+1 −3 +2 +1 −3 +2

Find average O.N. of underlined atom

1. $K\underline{Cl}O_3$

$1 + x + 3 \times (-2) = 0$

$x = +5$

2. $\underline{Fe}_{0.94}O$

$0.94\,x - 2 = 0$

$x = \frac{2}{0.94} = \frac{200}{94}$

3. $\underline{S}_4O_6^{2-}$

$4x - 12 = -2$

$4x = 10$

$x = 2.5$

4. $Na_2\underline{S}_2O_3$

$2 + 2x - 6 = 0$

$x = 2$

5. $H_5\underline{I}O_6$

$5 + x - 12 = 0$

$x = 7$

6. $H\underline{N}_3$

$1 + 3x = 0$

$x = -\frac{1}{3}$

7. $[\,\underline{Ni}\,(CO)_4\,]$

$x + 4 \times 0 = 0$

$x = 0$

8. $[\underline{Co}(NH_3)_4(H_2O)Cl]SO_4$

$x + 4 \times 0 + 0 - 1 - 2 = 0$

$x = +3$

9. $YBa_2\underline{Cu}_3O_7$

$3 + 4 + 3x - 14 = 0$

$3x = 7$

$x = \frac{7}{3}$

10. $(N_2H_5^+)_2\underline{S}O_4$

$2 + x - 8 = 0$

$x = +6$

11. $\underline{N}H_4^+ \,\}\, \underline{N}O_3^-$

$x + 4 = 1 \qquad x - 6 = -1$

$x = -3 \qquad x = +5$

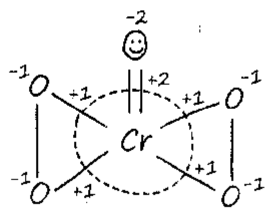
12. $[\underline{Fe}(CN)_6]^{4-}$

$x + 6 \times (-1) = -4$

$x = +2$

Calculation of O.S. (Individual O.N)

1. CrO_5 $\qquad \overset{-1}{O} - \overset{-1}{O}$

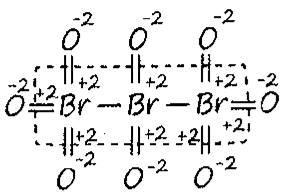


O.N of 'Cr' = +6

O.N of 'O' = −1

O.N. of O in Peroxy bond (P.L)= 2

2. Br_3O_8



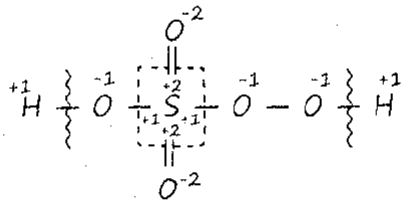
O.N of 'Br' = +4 & +6

O.N of 'O' = −2

P.L = 0

3. Caro's acid

H_2SO_5

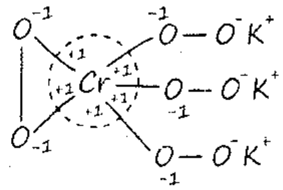


O.N of 'S' = +6

O.N of 'O' = −1 & −2

P.L = 1

4. K_3CrO_8



O.N of 'Cr' = +5

O.N of 'O' = −1

O.N of 'K' = +1

P.L = 4

5. C_3O_2

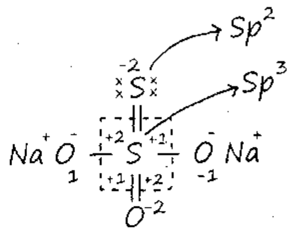
$\overset{-2}{O} = \overset{+2}{C} = \overset{0}{C} = \overset{+2}{C} = \overset{-2}{O}$

O.N of 'C' = 0 & +2

O.N of 'O' = −2

P.L = 0

6. $Na_2S_2O_3$ $\quad$ E.N $Sp^2 > Sp^3$



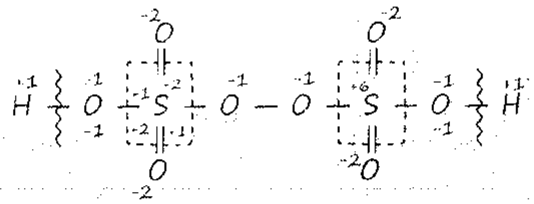
O.N of 'S' = −2 & +6

O.N of 'O' = −2

O.N of 'Na' = +1

P.L = 0

7. $H_2S_2O_8$



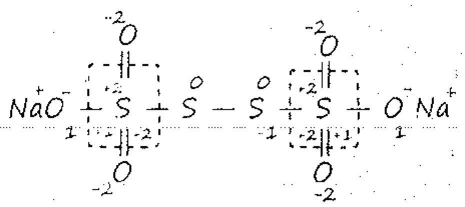
O.N of 'S' = +6

O.N of 'O' = -1 & -2

O.N of 'H' = +1

P.L = 1

8. $Na_2S_4O_6$



O.N of 'S' = +5 & 0

O.N of 'O' = -2

O.N of 'Na' = +1

P.L = 0

How to Find P.L without drawing the Structure

P.L is present when

Avg O.N > Max O.N $\rightarrow$ Group no.

$\underline{Cr}O_5$ $\quad x - 10 = 0$

Yes, P.L. is present

$H_2\underline{S}O_5$ $\quad 2 + x - 10 = 0$

$x = +8 > +6$

Yes P.L is present

How to find no. of P.L without drawing the structure

Case 1: When only one central atom is present

$$P.L = \frac{\text{Avg O.N} - \text{Max O.N}}{2}$$

CrO_5

$$P.L = \frac{10-6}{2} = \frac{4}{2} = 2$$

$K_3\underline{Cr}O_8$ $\quad 3 + x - 16 = 0$

$x = 13 > 6$

$$P.L = \frac{13-6}{2} = \frac{7}{2} = 3.5$$

P.L = 4

Case 2: When two C.A are present

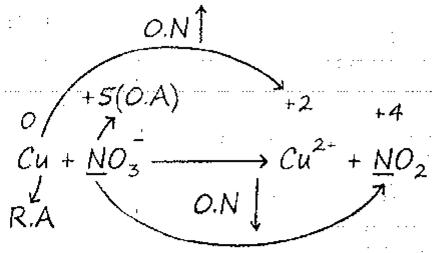
P.L = Avg O.N - Max O.N

$H_2S_2O_8$ $\quad 2 + 2x - 16 = 0$

$x = 7 > 6$

P.L = 7 - 6 = 1

Oxidising and Reducing agent



O.N ↑ , Oxidises itself, R.A

O.N ↓ , Reduces itself, O.A

Case 1 : If C.A is in its max O.N

Reduces itself , O.A

$\overset{+7}{KMnO_4}$, $\overset{+6}{K_2Cr_2O_7}$, $\overset{+5}{HNO_3}$ etc.

Case 2: If C.A is in its min O.N

Oxidises itself , R.A

$\overset{-2}{H_2S}$, $\overset{12\ -1}{SnCl_2}$, $\overset{+1}{HCl}$ etc.

Case 3: If C.A is in its intermediate O.N

Oxidises and Reduces itself , O.A & R.A both

$\overset{+3}{HNO_2}$, $\overset{+5}{HIO_3}$ etc.

Normality (N)

$$N = \frac{\text{No. of gm equivalent}}{V_{(L)}}$$

$$\text{No. of gm equivalent} = \frac{W}{E.W}$$

$$E.W = \frac{\text{Atomic or Molecular weight}}{\text{n. factor}}$$

$$N = M \times n_f$$

n.factor

Case (1) for acids

n_f = no. of H^+ ions furnished in the sol^n (or, no. of lone pairs accefted) per moleate

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$

$n_f = 1$

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

$n_f = 1$

$H_3PO_4 \quad n_f = 1, 2, 3$

$H_3PO_3 \quad n_f = 1, 2$

$H_3PO_2 \quad n_f = 1$

$H_3BO_3 \quad n_f = 1$

Case (2) for Bases

n_f = no. of $\bar{O}H$ ions furnished in the sol^n per molecule

$M\,OH \quad n_f = 1$

$M(OH)_2 \quad n_f = 1, 2$

$M(OH)_3 \quad n_f = 1, 2, 3$

Case (3) for Salts

n_f = Total +ve charge or total -ve charge per molecule

$\overset{+1}{Na}Cl \quad n_f = 1$

$\overset{+2}{Ca}Cl_2 \quad n_f = 2$

$\overset{2+}{Ca}_3(PO_4)_2 \quad n_f = 6$

$\overset{+3}{Al}PO_4 \quad n_f = 3$

Case (4) Redox Reaction

1. When only one atom can undergo either oxidation or reduction

nf = Total change in O.N. per molecule

1. Acidic medium (A.M) $K\overset{+7}{Mn}O_4 \xrightarrow{5 \times 1 = 5} Mn^{2+}$

2. Basic medium (B.M) $K\overset{+7}{Mn}O_4 \xrightarrow{1 \times 1 = 1} K_2\overset{+6}{Mn}O_4$

3. Neutral or Slightly alkaline $K\overset{+7}{Mn}O_4 \xrightarrow{3 \times 1 = 3} \overset{+4}{Mn}O_2$

$\frac{135}{BNA}$

$K_2\overset{+6}{Cr_2}O_7 \xrightarrow[H^+]{3 \times 2 = 6} \overset{+3}{Cr^{3+}}$

$nf = 6$

2. When two or more atoms can undergo either oxidation or reduction

n_f = total change in O.N. per molecule

$\overset{+2}{Fe}\overset{-1}{S_2} \longrightarrow \overset{+3}{Fe^{3+}} + \overset{+4}{S}O_2$ ($1 \times 1 = 1$; $5 \times 2 = 10$)

$n_f = n_{f1} + n_{f2} = 1 + 10 = 11$

$\overset{+2}{Fe}\overset{+3}{C_2}O_4^{2-} \longrightarrow \overset{+3}{Fe^{3+}} + \overset{+4}{C}O_2$ ($1 \times 1 = 1$; $1 \times 2 = 2$)

$n_f = 1 + 2 = 3$

3. Disproportionation Reaction

$$n_f = \frac{n_1 n_2}{n_1 + n_2}$$

(1) $\overset{0}{X_2} \longrightarrow \overset{-1}{X^\ominus} + \overset{+5}{X}O_3^\ominus$ ($1 \times 2 = 2$; $5 \times 2 = 10$)

$$n_f = \frac{2 \times 10}{2 + 10} = \frac{20}{12} = \frac{5}{3}$$

(2) $\overset{0}{P_4} \longrightarrow \overset{-3}{P}H_3 + H_2\overset{+1}{P}O_2^\ominus$ ($3 \times 4 = 12$; $1 \times 4 = 4$)

$$n_f = \frac{12 \times 4}{12 + 4} = \frac{48}{16} = 3$$

(3) $\overset{0}{S_8} \longrightarrow \overset{-2}{S^{2-}} + \overset{+2}{S_2}O_3^{2-}$ ($2 \times 8 = 16$; $2 \times 8 = 16$)

$$n_f = \frac{16 \times 16}{16 + 16} = 8$$

Titration

1. **Acid - Base titration**

No. of gram equivalent of Acid = no. of gram equivalent of Base

No. of gram equivalent $= n \times n_f$

$= N \times V_{(L)} = M \times N_f' \times V_{(L)}$

(1) $n_1 \times nf_1 = n_2 \times nf_2$

(2) $n_1 \times nf_1 = M_2 \times nf_2 \times V_{(L)}$

(3) $M_1 \times nf_1 \times V_1 = M_2 \times nf_2 \times V_2$

2. **Redox titration**

$O.A + R.A \longrightarrow O.P + R.P$

gram equivalent of O.A = gram eq. of R.A

(1) $n_1 \times n_{f_1} = n_2 \times n_{f_2}$

(2) $n_1 \times n_{f_1} = M_2 \times n_{f_2} \times V_{2(L)}$

(3) $M_1 \times n_{f_1} \times V_1 = M_2 \times nf_2 \times V_2$

Q. Find the no. of moles of $K_2Cr_2O_7$ needed to oxidise one mole of Cu_2S in A.M?

1 × 2 = 2

$\overset{+1}{Cu_2}\overset{-2}{S} \longrightarrow \overset{+2}{Cu^{2+}} + \overset{+4}{S}O_2$ $\quad n_f = 2 + 6 = 8$

6 × 1 = 6

$K_2Cr_2O_7 \longrightarrow Cr^{3+}$ $\quad n_f = 6$

$n_{eqv.}(Cu_2S) = n_{eqv.}(K_2Cr_2O_7)$

$n_1 \times nf_1 = n_2 \times nf_2$

$1 \times 8 = n_2 \times 6$

$n_2 = \frac{8}{6} = \frac{4}{3}$

Q. How many moles of $KMnO_4$ are needed to oxidised a mixture of 1 mol of each $FeSO_4$ and FeC_2O_4 in A.M?

1 × 1 = 1

$\overset{+2}{Fe}SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3$ $\quad n_f = 1$

1 × 1 = 1

$\overset{+2}{Fe}C_2O_4 \longrightarrow \overset{+3}{Fe^{3+}} + \overset{+4}{C}O_2$ $\quad n_f = 1 + 2 = 3$

1 × 2 = 2

$KMnO_4 \longrightarrow Mn^{2+}$ $\quad n_f = 5$

$n_{eqv.}(KMnO_4) = n_{eqv.}(FeSO_4) + n_{eqv.}(FeC_2O_4)$

$n_1 \times nf_1 = n_2 \times nf_2 + n_3 \times nf_3$

$n_1 \times 5 = 1 \times 1 + 1 \times 3$

$\left[n_1 = \frac{4}{5}\right]$

Q. Find volume of 6M HNO_3 needed to oxidize 5.6 gm of Fe^{2+} to Fe^{3+} where HNO_3 gets converted to NO?

1 × 1 = 1

$Fe^{2+} \longrightarrow Fe^{3+}$ $\quad n_f = 1$

3 × 1 = 3

$H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{N}O$ $\quad n_f = 3$

$n_{eqv.}(HNO_3) = n_{eqv.}(Fe^{2+})$

$M_1 \times V_1 \times nf_1 = n_2 \times nf_2$

$6 \times V_1 \times 3 = \frac{5.6}{56} \times 1$

$V_1 = \frac{0.1}{18} = \frac{1}{180}$ L

Q. How much amount of $CuSO_4 \cdot 5H_2O$ is required for liberation of 2.54 gm I_2 when titrated with KI?

1 × 1 = 1

$\overset{+2}{Cu}SO_4 \cdot 5H_2O + K\overset{-1}{I} \longrightarrow \overset{+1}{Cu_2}I_2 + \overset{0}{I_2}$

$n_f = 1$ $\quad n_f = 2$

1 × 2 = 2

$n_{eqv.}(CuSO_4.5H_2O) = n_{eqv.}(I_2)$

$n_1 \times nf_1 = n_2 \times nf_2$

$\frac{W_1}{249.5} \times 1 = \frac{2.\cancel{54}}{2\cancel{54}_{100}} \times 2$

$W_1 = \frac{499}{100} = 4.99$ gm

Q. Find $E.W_{N_2}$ in $\overset{0}{N_2} \xrightarrow{\textcircled{3}\times 2 = \textcircled{6}} \overset{-3}{NH_3}$

$$E.W_{N_2} = \frac{MW_{N_2}}{n_f} = \frac{28}{6} = \frac{14}{3}\ g$$

Q. Find O.A and R.A

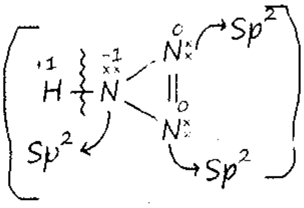
$$\underset{0}{C} + 4H\underset{+5}{N}O_3 \longrightarrow \underset{+4}{C}O_2 + 2H_2O + \underset{+4}{N}O_2$$

O.N ↑   O.N ↓

$C \longrightarrow R.A$

$HNO_3 \longrightarrow O.A$

Q. Find O.N of N in HN_3 $H-N = \overset{+}{N} = N$



$N \Rightarrow 0\ \&\ -1$

$H \Rightarrow +1$

Q. O.N of Fe in Haemoglobin? Fe^{2+}

Q. $2\,MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + 8H_2O$

the balance equation coeff. for MnO_4^-, $C_2O_4^{2-}$ and H^+ are respectively?

(A) 2, 5, 16 ✓   (B) 16, 5, 2

(C) 2, 16, 5   (D) 5, 2, 16

9 Solid State

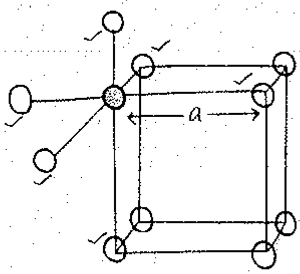
Unit Cell and Lattice

The simplest unit which can repeat itself over again and again to form Lattice

Types of cubic unit cell

1. Simple cubic (S.C) primitive
2. Body centered cubic (B.C.C) nonprimitive
3. Face centered cubic (F.C.C) nonprimitive

1. Simple cubic (primitive)



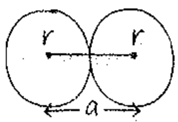
8 corners ⇒ atoms
Sharing of corners
$= \frac{1}{8}$ per unit cell

(1) Z_{eff} = Effective no. of atoms per unit cell

$$= 8 \times \frac{1}{8} = 1$$

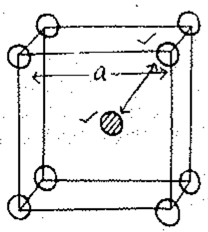
(2) Nearest neighbours or C.N = 6

(3) Relation b/w radius of atom & edge length



$\boxed{2r = a}$

2. B.C.C



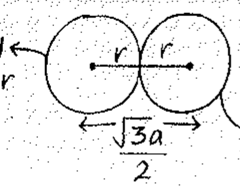
1 B.C ⇒ 1 atom
8 corners ⇒ 8 atoms
Sharing of corners
$= \frac{1}{8}$ per unit cell

(1) Z_{eff} = Effective no. of atoms per unit cell

$$= 8 \times \frac{1}{8} + 1 = 2$$

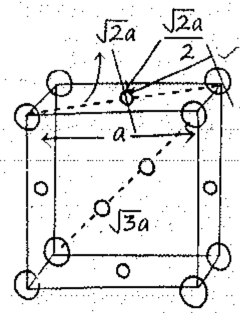
(2) Nearest neighbours or C.N = 8

(3) Relation b/w radius of atom & edge length



$\left[2r = \frac{\sqrt{3}a}{2}\right]$

3. F.C.C



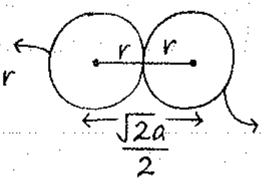
6 F.C ⇒ 6 atom
8 corners ⇒ 8 atoms
Sharing of corners $= \frac{1}{8}$
Sharing of F.C $= \frac{1}{2}$
} per unit cell

(1) Z_{eff} = Effective no. of atoms per unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$$

(2) Nearest neighbours or C.N = 12

(3) Relation b/w radius of atom & edge length



$\left[2r = \frac{\sqrt{2}a}{2}\right]$

Packing Fraction or Packing Efficiency

The space or fraction occupied by atoms in unit cell.

$$\left[\% \text{ P.F} = \frac{Z \times V_{atom}}{V_{unit\ cell}} \times 100\right]$$

Case 1: In S.C

$$\%PF = \frac{1 \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

$(a = 2r)$

$$PF = \frac{\pi}{6} \times 100$$

PF = 52.4%

% void = 100 − %PF
= 47.6%

Case 2: In B.C.C

$$\% PF = \frac{2 \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

$$\left(2r = \frac{\sqrt{3}a}{2}\right)$$

$$PF = \frac{\sqrt{3}\pi}{8} \times 100$$

PF = 68 %

% void = 32%

Case 3: In F.C.C

$$\% PF = \frac{4 \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

$$\left(2r = \frac{\sqrt{2}a}{2}\right)$$

$$PF = \frac{\pi}{3\sqrt{2}} \times 100$$

= 74%

% void = 26%

Points

1. Z_{eff}
2. C.N
3. Relation b/w a and r
4. % PF
5. % void

Case 1: In S.C

$Z_{eff} = 1$

C.N = 6

Relation between r & a = 2r = a

$\% P.F = 52.4\% = \left(\frac{\pi}{6}\right)$

% void = 47.6 %

Case 2: In B.C.C

$Z_{eff} = 2$

C.N = 8

Relation between r & a = $2r = \frac{\sqrt{3}a}{2}$; $r = \frac{\sqrt{3}}{4}a$

$\% pF = 68\% = \left(\frac{\sqrt{3}\pi}{8}\right)$

% Void = 32%

Case 3: In F.C.C

$Z_{eff} = 4$

C.N = 12

Relation between a & r = $2r = \frac{\sqrt{2}a}{2}$; $r = \frac{a}{2\sqrt{2}}$

$\% PF = 74\% = \left(\frac{\pi}{3\sqrt{2}}\right)$

% Void = 26%

Q. A $\longrightarrow$ Each corner

B $\longrightarrow$ Alternate Face center

Find simplest formula?

$A_{8 \times \frac{1}{8}}$ $B_{2 \times \frac{1}{2}}$

[AB]

Q. Na crystallizes in BCC unit cell of Edge length 4.3 Å find radius of Na

$$2r = \frac{\sqrt{3}a}{2}$$

$$r = \frac{\sqrt{3} \times 4.3}{4}$$

$$= \frac{1.73 \times 4.3}{4} \text{ Å}$$

Q. A $\longrightarrow$ each Corner $\left(\frac{1}{8}\right)$

B $\longrightarrow$ B.C (1)

C $\longrightarrow$ each F.C $\left(\frac{1}{2}\right)$

D $\longrightarrow$ each E.C $\left(\frac{1}{4}\right)$

Find simplest formula

$A_{8 \times \frac{1}{8}}$ B_1 $C_{6 \times \frac{1}{2}}$ $D_{12 \times \frac{1}{4}}$

$[A B C_3 D_3]$

Q. A $\longrightarrow$ each Corner B $\longrightarrow$ each F.C

When one of the B is missing then find new E.F?

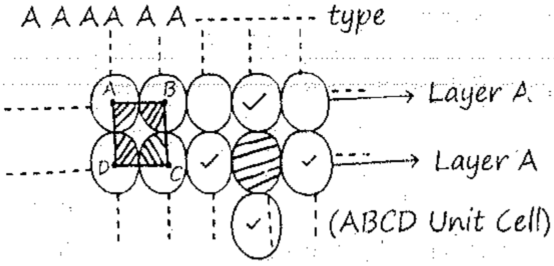
$A_{8 \times \frac{1}{8}}$ $B_{5 \times \frac{1}{2}}$

$A\ B_{\frac{5}{2}}$ $[A_2 B_5]$

Closed Packing Case 1: In 2D

1. Square closed packing

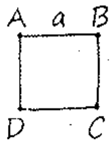
(a) Arrangement



(b) $Z_{e.f} = 4 \times \frac{1}{4} = 1$

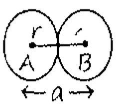
(c) C.N = 4

(d) Packing fraction



$$\% PF = \frac{Z_{eff} \times A_{disc}}{A \text{ unit cell}} \times 100$$

$$\% PF = \frac{1 \times \pi r^2}{a^2} \times 100$$



(2r = a)

$$\% PF = \frac{\pi}{4} \times 100 = 78.5\%$$

$$\% void = 100 - 78.5 = 21.5\%$$

2. Hexagonal closed packing

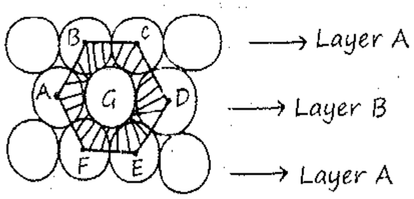
(a) Arrangement

ABABAB .... type

ABCDEFG

Hexagonal

Unit Cell(2D)

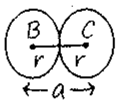


(b) $Z_{eff} = 1 + 6 \times \frac{1}{3} = 1 + 2 = 3$

(c) C.N = 6

(d) Packing fraction

$$\% PF = \frac{3 \times \pi r^2}{6 \times \frac{\sqrt{3}}{4} a^2} \times 100$$



2r = a

$$\% PF = \frac{\pi}{2\sqrt{3}} \times 100 = 91\%$$

% void = 9%

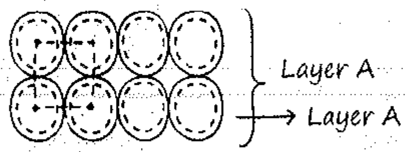
Stability ∝ PF

HCP(2D) > SCP(2D)

Closed Packing Case 2: In 3D

1. Simple cubic packing

(a) Arrangement



AAAAAA .... type

(b) $Z_{eff} = 1$

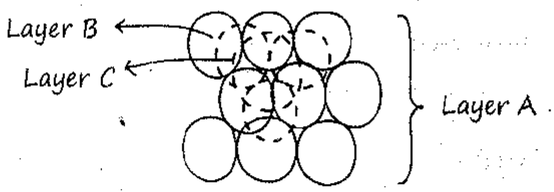
(c) C.N = 6

(d) % PF = 52.4%

% void = 47.6%

2. Cubic closed packing (CCP) or (FCC)

(a) Arrangement



ABC ABC ABC ABC .... type

(1) Layer A is HCP (2D)

(2) Layer B is placed over voids of Layer A

(3) Layer C is placed over unoccupied voids of Layer A & B.

(b) $Z_{eff} = 4$

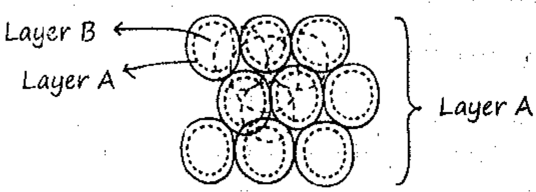
(c) C.N = 12

(d) % PF = 74%

% void = 26%

3. Hexagonal closed packing (HCP 3D)

(a) Arrangement

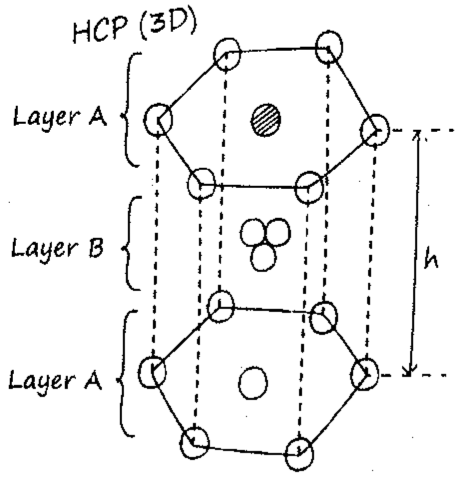


AB AB AB AB AB AB AB .... type

(1) Layer A is HCP (2D)

(2) Layer B is placed over voids of Layer A

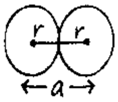
(3) 3^{rd} Layer A is same as that of first Layer A



(b) $Z_{eff} = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6}$
$= 6$

(c) C.N = 12

(d) $2r = a$



(e) Height of HCP (3D)

$= 4\sqrt{\frac{2}{3}}\, r$

(f) Base Area of HCP

$= 6 \times \frac{\sqrt{3}}{4} a^2$

(g) $\left(V_{\substack{HCP \\ 3D}}\right)_{unit\ cell} = 24\sqrt{2}\, r^3$

(h) $\%PF = \dfrac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}\, r^3} \times 100$

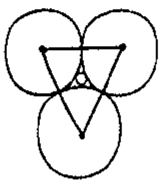
$= \dfrac{\pi}{3\sqrt{2}} \times 100$

$= 74\ \%$

(i) % void = 26%

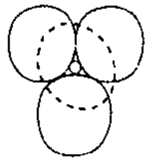
Types of Voids

1. Triangular void



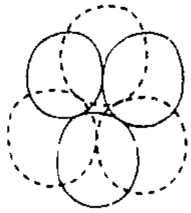
C.N = 3
of
void
H.C.P (2D)

2. Tetrahedral voids (T.V or T.H.V or Td void)



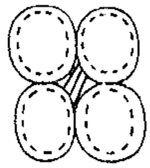
C.N = 4
CCP or FCC
H.C.P (3D)

3. Octahedral void (O.H.V or O.V or Od void)



C.N = 6
CCP or FCC
H.C.P (3D)

4. Cubical void



C.N = 8
Simple cubic

Size of void Triangular < T.H.V < O.H.V < cubical

$(***\#)^{\infty}$ Valid in HCP(3D) & (Closest packed store) CCP(fcc)

$\left\{ \begin{array}{l} \text{If No. of atoms } (Z_{eff}) = N \\ \text{T.H.V} = 2N; \quad \text{O.H.V} = N \end{array} \right.$

Q. A $\longrightarrow$ HCP (3D) 4

B $\longrightarrow$ 100 % OHV 4

A_4B_4 AB

Q. A $\longrightarrow$ CCP (fcc) 6

B $\longrightarrow$ 50 % OHV $6 \times \frac{1}{2}$

A_6B_3 A_2B

Q. A $\longrightarrow$ CCP (fcc) 4

B $\longrightarrow$ $\frac{2}{3}$ THV $\frac{2}{3} \times 8 = \frac{16}{3}$

$A_4B_{\frac{16}{3}}$ $A_{12}B_{16}$

A_3B_4

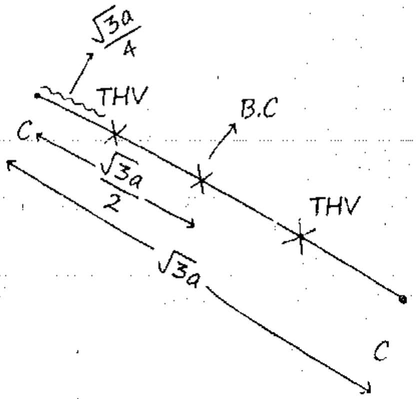
Q. A $\longrightarrow$ HCP (3D) 6

B $\longrightarrow \frac{1}{3}$ OHV $\quad 6 \times \frac{1}{3} = 2$

$A_6B_2 \qquad A_3B$

T.H.V and O.H.V in fcc unit cell

Case 1: T.H.V

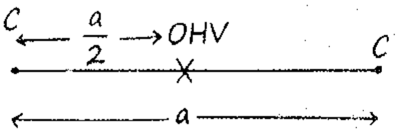


\# Two THV on each body diagonal per FCC unit cell

\# Total THV = 8

Case 2: O.H.V

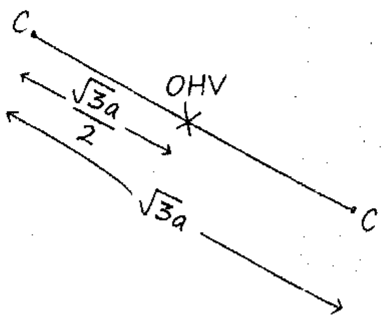
1. At Edge center



\# Total number of OHV at edge center FCC per unit cell

$= 12 \times \frac{1}{4} = 3$

2. At Body center



\# OHV at body centre = 1

Total OHV = 3 + 1 = 4

Density of Unit Cell

$$d = \frac{Z \times M}{N_A \times a^3} = \frac{Z \times W}{N \times a^3}$$

d = density (gm/cc)

Z = No. of atoms per unit cell

M = Molar mass

N_A = avogadro's No = 6×10^{23}

a = edge length (cm)

W = Weight (gm)

N = No. of atoms

Q. An element with density 2.8 gm/cc forms a fcc unit cell with edge length 400 pm. Calculate Molar mass of element

$$d = \frac{Z \times M}{N_A \times a^3} ; M = \frac{d N_A a^3}{Z}$$

$$= \frac{2.8 \times 6 \times 10^{23} \times (400 \times 10^{-10})^3}{4}$$

= 26.8 g/mol

Q. An element has BCC structure with a cell edge of 300 pm. the density of element is 8 gm/cc. How many atoms are present in 200 gm of element?

$$N = \frac{Z \times W}{d \times a^3}$$

$$= \frac{2 \times 200}{8 \times (300 \times 10^{-10})^3}$$

$$= \frac{50}{27 \times 10^{-24}}$$

$$= \frac{50}{27} \times 10^{24} \text{ atoms}$$

Radius Ratio	Radius Ratio	C.N	Examples
$R.R = \frac{r_{void}}{r_{atom}}$	$0.155 \le \frac{r_c}{r_a} < 0.225$	3	B_2O_3
$= \frac{r_c}{r_a}$	$0.225 \le \frac{r_c}{r_a} < 0.414$	4	ZnS
$= \frac{r^+}{r^-}$	$0.414 \le \frac{r_c}{r_a} < 0.732$	6	NaCl
	$0.732 \le \frac{r_c}{r_a} < 1$	8	CsCl

Q. If the radii of A^+ and B^- are 95 pm and 181 pm respectively, then find C.N. of 'A^+'?

$$R.R = \frac{r^+}{r^-} = \frac{95}{181} = 0.52$$

$$0.414 \le \frac{r_c}{r_a} < 0.732$$

C.N of A^+ = 6

Q. The ionic radii of Rb^+ and $I^{\ominus}$ are respectively 1.46 Å and 2.16 Å. The most probable type of structure exhibited by it is?

(A) CsCl (B) NaCl

(C) Zns (D) N.O.T

$$R.R = \frac{r^+}{r^-} = \frac{1.46}{2.16} = 0.67$$

$$0.414 \le \frac{r_c}{r_a} < 0.732$$

Some Imp Ionic Comp

Comp	Location of Ions	Formula Unit	C.N (C:A)	Relation b/w a and r
(1) NaCl (Rock salt structure)	$Cl^{\ominus} \rightarrow$ CCP (fcc) $Na^+ \rightarrow$ 100% OHV	4	6 : 6	$r_c + r_a = \frac{a}{2}$
(2) CsCl	$Cl^{\ominus} \rightarrow$ S.C $Cs^+ \rightarrow$ Body center	1	8 : 8	$r_c + r_a = \frac{\sqrt{3}a}{2}$
(3) ZnS (Zinc blende)	$S^{2-} \rightarrow$ CCP or fcc $Zn^{2+} \rightarrow$ 50% THV or Alternate T.H.V	4	4 : 4	$r_c + r_a = \frac{\sqrt{3}a}{4}$
(4) CaF_2 (Fluorite structure)	$Ca^{2+} \rightarrow$ CCP or fcc $F^{\ominus} \rightarrow$ 100% THV	4	8 : 4	$r_c + r_a = \frac{\sqrt{3}a}{4}$
(5) Na_2O (Anti fluorite structure)	$O^{2-} \rightarrow$ fcc or CCP $Na^+ \rightarrow$ 100% THV	4	4 : 8	$r_c + r_a = \frac{\sqrt{3}a}{4}$

(6) Spinel

$\overset{+2}{A}\overset{+3}{B_2}O_4$ Exp: $\overset{+2}{Mg}\overset{+3}{Al_2}O_4$

$O^{2-} \longrightarrow$ CCP or fcc

$A^{2+} \longrightarrow \frac{1}{8}$ T.H.V

$B^{3+} \longrightarrow \frac{1}{2}$ O.H.V

(7) Inverse Spinel

$\overset{3+}{B}(\overset{+2}{A}\overset{+3}{B})O_4$ e.g, Fe_3O_4: $\overset{+3}{Fe}(\overset{+2}{Fe}\ \overset{+3}{Fe})O_4$

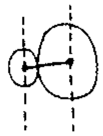
$O^{2-} \longrightarrow$ CCP or fcc

$B^{3+} \longrightarrow \frac{1}{8}$ T.H.V

$A^{2-} \longrightarrow \frac{1}{4}$ O.H.V

$B^{3+} \longrightarrow \frac{1}{4}$ O.H.V

Q. CsBr has cubic structure with edge length 4.2Å find the shortest inter ionic distance?



$r_c + r_a = \frac{\sqrt{3}a}{2} = \frac{1.73 \times 4.2}{2} = 3.6$Å

Q. Edge length of M^+X^- (fcc structure) (NaCl) is 7.2Å find radius of $X^\ominus$ (Given $r_{M+} = 1.6$ Å)

$$r_c + r_a = \frac{a}{2}$$

$$1.6 + r_a = \frac{7.2}{2} = 3.6$$

$$a = 2\text{Å}$$

Q. In a solid 'AB' having the 'NaCl' structure. 'A' atoms occupy the corners of cubic unit cell. If all the face centered atoms along one of the axes are removed then find E.F?

B $\longrightarrow$ Corner + f.C $\quad 8 \times \frac{1}{8} + 4 \times \frac{1}{2}$

A $\longrightarrow$ E.C + B.C $\quad 12 \times \frac{1}{4} + 1$

$A_{1+2}\,B_{3+1}$

A_3B_4

Defects

↓

Stoichiometric

Schottky

cations and anions are missing from the crystal in stoichiometric ratio

High Radius Ratio

High C.N

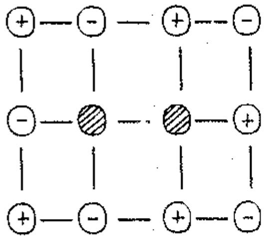
Density decreases

Exp

NaCl, KCl

CsCl, KBr

etc



Frenkel (Dislocation)

One of the ion (usually cation) is dislocated from its usual Lattice point to some other interstitial site

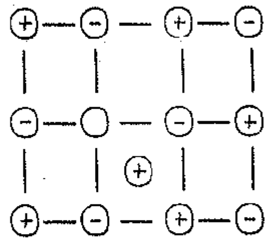
Density remains same

Low C.N

Exp

ZnS, AgCl

AgI etc



AgBr

Exhibit both schottky and Frenkel defect

Defects

↓

Non-Stoichiometric

Metal Excess | Metal deficiency

$3Fe^{2+} \rightarrow 2Fe^{3+}$

+6 +6

+2 +3

$Fe_{0.93}O - Fe_{0.96}O$

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

$Na \xrightarrow{\Delta} Na^{+} + e^{\ominus}$

NaCl

$LiCl \rightarrow$ Pink

$NaCl \rightarrow$ Yellow

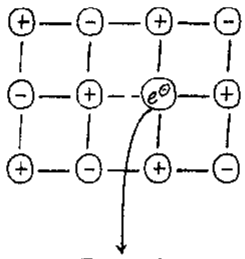
$KCl \rightarrow$ Violet

colored due to F-center

Intensity α

no. of f-centers

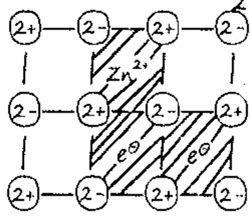
due to anion vacancy



F-center

due to Excess cation

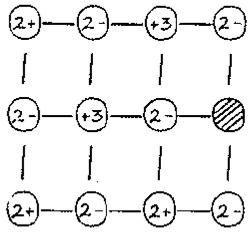
$ZnO \xrightarrow{\Delta} Zn^{2+} + 2e^{\ominus} + \frac{1}{2}O_2\uparrow$



$ZnO \rightarrow$ white when cold

yellow when hot

$[O^{-2} \underset{-\Delta}{\overset{+\Delta}{\rightleftharpoons}} \frac{1}{2}O_2 + 2e^{-}]$



Defects

↓

Impurity defect

When NaCl is doped with $SrCl_2$

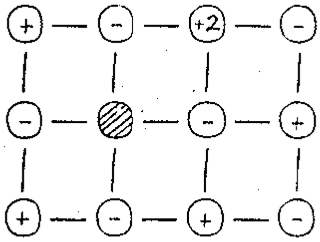
When AgCl is doped with $CdCl_2$

$NaCl \longrightarrow Na^{+} + Cl^{-}$

$SrCl_2 \longrightarrow Sr^{2+} + 2Cl^{-}$

$2Na^{+} \longrightarrow 1\ Sr^{2+}$

+2 +2



No. of cation vacancy

=

No. of Sr^{2+} ions

Some Imp. Points

1. Different b/w crystalline and Amorphous solid

Crystalline	Amorphous
(1) Regular arrangement	(1) Irregular arrangement
(2) Anisotropic	(2) Isotropic
(3) Sharp M.P	(3) Range of M.P
(4) Long range order	(4) Short range order
Exp: SiO_2(quartz), NaCl, KCl, CsCl etc	Exp: SiO_2(Silica), Rubber, plastic

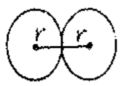
2. Types of crystalline solids

	Molecular	Ionic	Metallic	Covalent (Network)
Constituent particles	Molecules	ions	+ve charged kernel & delocalised $e^{\ominus}s$	Covalently bonded atoms
forces	Hydrogen bond & V.W forces	Electrostatic	Metallic bond	Covalent bond
Exp	Ar, I_2, CO_2, CCl_4, H_2O(ice)	NaCl, MgO, CSCl, CaF_2 etc	Cu, Ag, Au etc	SiC, SiO_2, Si, $C_{diamond}$ graphite, AlN etc
Electrical conductivity	Insulator	Insulator in solid but conductor in molten & aq sol^n	Conductor	Insulator & conductor
M.P	Low	High	Fairly high	Very high

3. P.F of Diamond cubic struc.

$C \longrightarrow$ CCp or fcc (4)

$C \longrightarrow 50\%\ THV\left(8 \times \frac{1}{2} = 4\right) \quad Z_{eff} = 8$



$$\%\ PF = \frac{8 \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

$$\left(2r = \frac{\sqrt{3}a}{4}\right) \qquad \%\ PF = \frac{\frac{32}{3}\pi r^3}{\left(\frac{8r}{\sqrt{3}}\right)^3} \times 100$$

$$= \frac{\sqrt{3}\pi}{16} \times 100 = 34\%$$

$$a = \frac{8r}{\sqrt{3}}$$

4. Effect of Temp and pressure on C.N of comp.

P ↑   C.N ↑

T ↑   C.N ↓

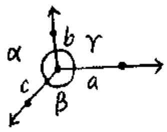
$$C.N \quad 6:6 \underset{T\uparrow}{\overset{P\uparrow}{\rightleftharpoons}} 8:8$$

NaCl Type   CsCl Type

5. Coordination No.

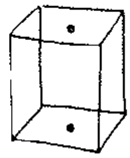
Type of Neighbour		Distance	Number
SC	Nearest Neighbour	a	6
	Next	$\sqrt{2}a$	12
BCC	Nearest	$\frac{\sqrt{3}a}{2}$	8
	Next	a	6
FCC	Nearest	$\frac{a}{\sqrt{2}}$	12
	Next	a	6

6. Types of crystals



	Crystal	Interaxial distance	Interaxial angles	Bravais Lattice (14)
Cu	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	3(SC, BCC, FCC)
Rh	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	1(SC)
Te	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	2(SC, BCC)
He	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$	1(SC)
aur	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	4(SC, BCC, FC, EC*)
mona	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$; $\beta \neq 90^\circ$	2(SC, EC)
Tere clinic par	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	1(SC)

E.C.
End Center



Practice

Q. Find % of Fe^{2+} ions in $Fe_{0.93}O$?

$(Fe_{93}O_{100})$ Let Fe^{2+} ions $= x$

Fe^{3+} ions $= 93 - x$

$$2x + 3(93 - x) = 200$$

$$2x + 279 - 3x = 200$$

$$x = 79$$

$$\% \text{ of } Fe^{2+} \text{ ions} = \frac{79}{93} \times 100$$

Q. Which of the following is Pseudo Solid or Super cooled liq?

(A) Si (B) CO_2

(C) Ag (D) Glass

Q. If NaCl is doped with 10^{-3} mol % $SrCl_2$, what is the conc^n of cation vacancies?

No. of cation vacancies = No. of Sr^{2+} ions

$= 10^{-3} \times 10^{-2} \times N_A$

$= 10^{-5} \times 6 \times 10^{23}$

$= 6 \times 10^{18}$ per mole

10 Solutions

1. Vapour Pressure

The pressure exerted by the vapour over the surface of liq. at eqb. in closed container is called V.P of liq.
[at eqb. Rate of evaporation = Rate of condensation]

Factors affecting V.P

1. Temp.

$[V.P \propto T]$

2. $V.P \propto \frac{1}{I.M.F}$

Q. Compare V.P and B.P of the given halides

Hydrogen Bonding HF HCl HBr HI

B.P HCl < HBr < HI < HF

$\left[V.P \propto \frac{1}{B.P}\right]$

V.P HCl > HBr > HI > HF

2. Raoult's Law

Case 1: For two volatile liq

A + B

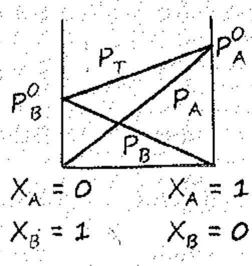
Solvent Solute

$P_S = P_T = P_A + P_B$

$[P_T = P^\circ_A x_A + P^\circ_B X_B]$

If A is more volatile than B

P_T or P_S = Total pressure



P_A = V.P of A in sol^n

P_B = V.P of B in sol^n

P°_A = V.P of pure A

P°_B = V.P of pure B

X_A = mole fraction of A
X_B = mole fraction of B
} in Solution phase

Case 2: When solute is non volatile

$P_T = P_A + P_B$

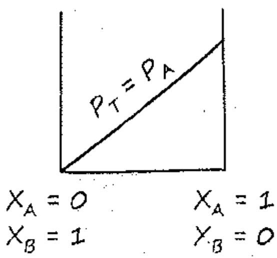
$F_T = P_A$

$[P_T = P^\circ_A X_A]$

$P_T = P^\circ_A(1 - X_B)$ $\quad P^\circ_A X_B = P^\circ_A - P_T$

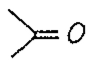
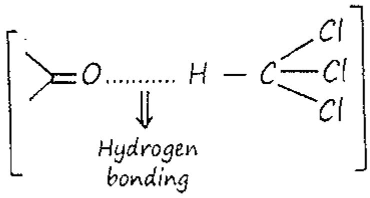
$P_T = P^\circ_A - P^\circ_A X_B$ $\quad \left[X_B = \frac{P^\circ_A - P_T}{P^\circ_A}\right]$

RLVP



B is solute

Types

Ideal	Non ideal: +ve deviation	Non ideal: -ve deviation
1. Obeys R.L	1. Does not Obeys R.L	1. Does not Obeys R.L
2. $(P_T)_{obs} = (P_T)_{cal}$	2. $(P_T)_{obs} > (P_T)_{cal}$	2. $(P_T)_{obs} < (P_T)_{cal}$
3. Inter molecular force b/w A-A and B-B are similar to Intermolecular force b/w A-B	3. IMF(A-B) < IMF(A-A) or IMF(B-B)	3. I.M.F(A-B) > IMF(A-A) & IMF(B-B)
4. $\Delta H_{mix} = 0$ $\Delta V_{mix} = 0$ $\Delta S_{mix} > 0$ $\Delta G_{mix} < 0$	4. $\Delta H_{mix} > 0$ $\Delta V_{mix} > 0$ $\Delta S_{mix} > 0$ $\Delta G_{mix} < 0$	4. $\Delta H_{mix} < 0$ $\Delta V_{mix} < 0$ $\Delta S_{mix} > 0$ $\Delta G_{mix} < 0$
<u>Examples</u> 1. Bromo ethane & chloro ethane 2. Benzene + Toluene 3.  & 	1. $CCl_4 + C_6H_6$ 2. $CCl_4 + CH_3OH$ 3. $CCl_4 + C_2H_5OH$ 4. $\boxed{C_2H_5OH + H_2O}$	1. $HNO_3 + H_2O$ * 2.  $+ CHCl_3$ 3. $CHCl_3 + CH_3COOH$ 4. $HCl + H_2O$
	1. CCl_4 + ... = +ve 2. $CHCl_3$ + ... = -ve 3. C_6H_6 + ... = +ve 4. acid + ... = -ve	

Q. Which is not equal to zero for an ideal solⁿ?

(A) ΔH_{mix} (B) ΔS_{mix} ✓

(C) ΔV_{mix} (D) None of these

Q. Which is Temp. dependent?

(A) Molality

(B) Molarity ✓

(C) Mole fraction

(D) Weight percentage

Q. If 3 moles of A is mixed with 2 moles of B find P_A, P_B and P_T?

(Given: $P_B^\circ = 100$ mm of Hg

$n_A = 3$; $P_A^\circ = 200$ mm of Hg)

$n_B = 2$; $P_A = P_A^\circ X_A = \cancel{200}^{40} \times \frac{3}{\cancel{5}}$

$= 120$ mm of Hg

$X_A = \frac{3}{5}$; $X_B = 1 - \frac{3}{5} = \frac{2}{5}$

$P_B = P_B^0 X_B = \cancel{100}^{20} \times \frac{2}{\cancel{5}} = 40$ mm of Hg

$P_T = P_A P_B = 120 + 40 = 160$ mm of Hg

Q. Which exhibit negative deviation?

(A) $CCl_4 + C_6H_6$

(B) $C_2H_5OH + H_2O$

(C) acetone + $CHCl_3$ ✓

(D) $CCl_4 + CH_3OH$

3. Colligative properties

M.I*

The property which depends on no. of solute particles irrespective of its nature

Van't Hoff factor (i)

$$= \frac{\text{Normal molar mass}}{\text{abnormal molar mass}}$$

$$= \frac{\text{Observed C.P}}{\text{Normal C.P}}$$

$$= \frac{\text{No. of moles after association/dissociation}}{\text{No. of moles before association/dissociation}}$$

Calculation of (i)

Case 1: For dissociation $KCl \rightarrow K^+ + Cl^-$

$i > 1$ $[\, i = 1 + (n - 1)x \,]$ $n = 2$

n = no. of ions produced per molecule x = D.O.D

Case 2: For association

$i < 1$ $i = 1 + \left(\frac{1}{n} - 1\right)x$

n = no. of associated to form one molecule x = D.O.A

e.g.2 $CH_3COOH \rightleftharpoons (CH_3COOH)_2$

$\boxed{n = 2}$

Case 3: $i = 1$ for neither association nor dissociation

Q. Calculate D.O.D for $Ba(NO_3)_2$ if $i = 2.74$

$Ba(NO_3)_2 \rightarrow Ba^{2+} + 2NO_3^-$

$i = 1 + (n - 1)x$

$2.74 = 1 + (3 - 1)x$ $n = 3$

$\frac{1.74}{2} = x$ $x = 0.87$

% D.O.D = 87%

Q. Find i for $Ca_3(PO_4)_2$ if D.O.D is 100 %

$[\, i = 1 + (n - 1)x \,]$ $x = 1$

$i = 1 + n - 1$

$\boxed{i = n}$ $\boxed{i = 5}$

Note: Glucose Urea $i = 1$

Colligative prop formulae :

1. R.L.V.P (Relative lowering in V.P) $\Rightarrow$ $\frac{P_A^\circ - P_S}{P_A^\circ} = i x_B$

$i\left(\frac{n_B}{n_B + n_A}\right)$

$$\left[\frac{P_A^\circ - P_S}{P_A^\circ} = i\,\frac{n_B}{n_A}\right]$$

2. E.B.P (Elevation in Boiling point) $[\Delta T_b = iK_b m]$

$T_b - T_b^\circ$ T_b = B.P of sol^n

T_b° = B.P of solvent

$K_b = 0.52$ K kg mol^{-1} for H_2O

m = molality

3. D.F.P (Depression in freezing point)

$\Delta T_f = i\, K_f\, m$

$T_f^\circ - T_f$ T_f = F.P of sol^n

T_f° = F.P of solvent

$K_f = 1.86$ K kg mol^{-1}. for H_2O

m = molality

4. Osmotic pressure :

$\Pi = i\,CRT$

C = conc^n i.e. $\left(\frac{mol}{L}\right)$

R = gas const

T = K

Π = pressure (atm)

1 2

Π_1 Π_2

1. $\Pi_1 = \Pi_2$ (isotonic)
2. $\Pi_1 > \Pi_2$ (1 is hypertonic or 2 is hypotonic)
3. $\Pi_1 < \Pi_2$ (1 is hypo or 2 is hypertoric)

Practice

Q. Compare freezing point of given compounds.

(A) $\overset{i=3}{K_2SO_4}$ (B) $\overset{i=2}{NaCl}$

(C) $\underset{i=1}{\text{Urea}}$ (D) $AlCl_3$ $i = 4$

$i\uparrow$ $\Delta T_f \uparrow$ $T_f \downarrow$

C > B > A > D

Q. Compare B.P of given compounds.

(A) 0.1 M $\overset{i=2}{KCl}$ (B) 0.1 M $\overset{i=3}{BaCl_2}$

(C) 0.1 M $\underset{i=4}{FeCl_3}$ (D) 0.1 M $\underset{i=5}{Fe_2(SO_4)_3}$

$i\uparrow$ $\Delta T_b \uparrow$ $T_b \uparrow$

D > C > B > A

Q. The van't Hoff factor k3[Fe(CN)6] is 4. Which of the following has same van't hoff factor?

(A) $\overset{i=2}{NaCl}$ (B) $\overset{i=3}{Na_2SO_4}$

(C) $\underset{i=5}{Al_2(SO_4)_3}$ (D) $\underset{i=4}{Al(NO_3)_3}$ ✓

Q. 0.5 M sol^n of $\overset{i=1}{\text{Urea}}$ is isotonic with

(A) 0.5 M NaCl (B) 0.5 M Sugar ✓

(C) 0.5 M $BaCl_2$ (D) 0.5 M Benzoic acid in benzene

$\Pi = icRT$

i same

Π same

Q. 0.2 molal acid $\overset{i=2}{HA}$ is 20% ionized in aq. sol^n (K_f = 1.86 K/molality^{-1})

Find F.P of sol^n? $i = 1 + (n - 1)x$

$\Delta T_f = i K_f m$ $i = 1 + (2 - 1) \times 0.2$

$i = 1.2$

$0 - T_f = 1.2 \times 1.86 \times 0.2$

$[T_f = -0.45\ °C]$

Q. 2×10^{-3} m aq. sol^n of an ionic comp $[Co(NH_3)_5NO_2]Cl$ freezes at $-0.00732°C$

Find i? (K_f = 1.86°C/m) $[Co(NH_3)_5NO_2]Cl$

$\Delta T_f = i K_f m$

$0 - (-0.00732) = i \times 1.86 \times 2 \times 10^{-3}$

$[i = 2]$

Q. The V.P of pure $CH_3OH(A)$ is 0.15 bar at 25°C. The V.P of this liq. in sol^n is 0.09 bar calculate mole fraction of B?

$P_A^\circ = 0.15$ bar ; $P_A = 0.09$ bar

$P_A = P_A^\circ X_A \Rightarrow \frac{0.09}{0.15} = X_A$

$X_A = \frac{3}{5}$; $X_B = 1 - \frac{3}{5} \Rightarrow \frac{2}{5}$

Q. At 40°C the vap. pressure of CH_3OH (A) and EtOH(B) sol^n is represented by $P = 120X_A + 138]^{torr}$ where X_A is mole fraction of MeOH. Find values of $\left(\frac{P_B^\circ}{X_B}\right)_{X_A \to 0}$ and $\left(\frac{P_A^\circ}{X_A}\right)_{X_A \to 1}$

$X_B = 1$; $X_A = 0$ $P_B^\circ = 138$ torr

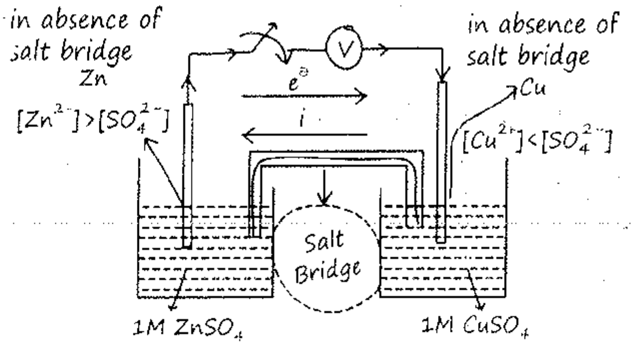
$X_B = 0$; $X_A = 1$ $P_A^\circ = 258$ torr

$\left(\frac{P_B^\circ}{X_B}\right)_{X_A \to 0} = 138$ torr

$\left(\frac{P_A^\circ}{X_A}\right)_{X_A \to 1} = 258$ torr

1. Electrochemical Cell (Galvanic or Voltaic cell)

Daniel Cell



Anode Oxi: $Zn \rightarrow Zn^{2+} + Ze^{\ominus}$

Red Cathode: $Cu^{2-} + 2e^{\ominus} \rightarrow Cu$

Anode [L O A N] (RRCP)
Left, Oxidation, Anode, Neg

Cell representation

$$\begin{matrix} L \downarrow R & & L \downarrow R \\ Zn_{(s)} \mid Zn^{2+}_{(aq)} & \| & Cu^{2+}_{(aq)} \mid Cu_{(s)} \end{matrix}$$

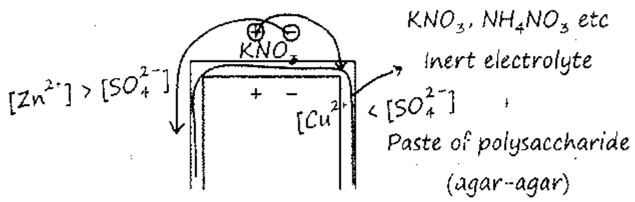
Cell Rxn

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Standard Cell potential (E°_{cell})

$$E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A$$

Salt Bridge & its func^n



+ KCl is not used as electrolyte in case of:
  Ag, Tl, Pb, Hg
  Aji Thailand Pyar Hogya Main
+ Mobility of Cation ≈ Mobility of anion

Main Function of salt bridge.

(1) To maintain electrical neutrality

(2) To complete inner circuit without mixing of two sol^n

(3) To reduce liq–liq junc. potential

Q. For following Galvanic cell find E°_{cell}

$$\overset{0 \xrightarrow{oxi} +2}{Fe_{(s)} \mid Fe^{2+}_{(aq)}} \;\|\; \overset{+2 \xrightarrow{Red} 0}{Cu^{2+}_{(aq)} \mid Cu_{(s)}} \rightarrow C$$

(1M) (1M)

$E^\circ_{Fe^{2+} \mid Fe} = -0.44$ V

Given $E^\circ_{Fe \mid Fe^{2+}} = +0.44$ V

$E^\circ_{Cu^{2+} \mid Cu} = +0.34$ V

$E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A$
$= (+0.34) - (-0.44)$
$= 0.78$ V

ΔG° and K_{eq} for Galvanic Cell

(1) $\Delta G^\circ = -nFE^\circ_{cell}$

n = No. of electrons involved in balanced cell reaction

F = 96500 C

(2) $\Delta G^\circ = -RT \ln K_{eq}$

$R = 2\ cal \left(= \frac{25}{3}\right) J/mol/k$

Q. Find ΔG° & K_{eq} for Daniel cell

$E^\circ_{cell} = 1.1$ V

$\Delta G^\circ = -2 \times 96500 \times 1.1 \quad = -212.3 \times 10^3$

$\Delta G^\circ = -RT \ln K_{eq} \quad = \frac{-25}{3} \times 298 \ln k_{eq}$

$[\Delta G^\circ = -212.3\ kJ] \quad [K_{eq} = 10^{37}]$

ΔG° is Extensive (additive)

E°_{cell} is Intensive (non additive)

Q. Given $E^\circ_{Cu^{2+} \mid Cu^+} = +0.15$ V

$E^\circ_{Cu^+ \mid Cu} = +0.5$ V

Find $E^\circ_{Cu^{2+}|Cu}$?

(1) $Cu^{2+} + e^{\ominus} \longrightarrow Cu^{+}$ $\quad E_1^\circ = 0.15\ V$

(2) $Cu^{+} + e^{\ominus} \longrightarrow Cu$ $\quad E_2^\circ = 0.5\ V$

(3) $Cu^{2+} + 2e^{\ominus} \longrightarrow Cu$ $\quad E_3^\circ = ?$

$3 = 1 + 2$

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

$-n_3FE_3^\circ = -n_1FE_1^\circ - n_2FE_2^\circ$

$n_3FE_3^\circ = n_1FE_1^\circ + n_2FE_2^\circ$

$2E_3^\circ = 1 \times (0.15) + 1 \times (0.5)$

$E_3^\circ = \dfrac{0.65}{2} = 0.325\ V$

Nernst Eq^n

$\alpha A_{(aq)} + \beta B_{(g)} \longrightarrow \gamma C_{(aq)} + \delta D_{(s)}$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{n} \log \frac{[C]^\gamma}{[A]^\alpha P_B^\beta}$$

At Eq^m $E_{cell} = 0$ $\qquad Q = K_{eq} \Rightarrow E^\circ_{cell} - \dfrac{RT}{nf} \ln k_{eqb}$

$$\left[E^\circ_{cell} = \frac{0.06}{n} \log \text{ at } 25^\circ c\ K_{eq}\right]$$

Q. Find EMF of cell

$$\overset{L}{Mg_{(s)}} \,\Big|\, \overset{R}{\underset{(0.1\ M)}{Mg^{2+}_{(aq)}}} \,\Big\|\, \overset{L}{\underset{(0.001\ M)}{Ag^{+}_{(aq)}}} \,\Big|\, \overset{R}{Ag_{(s)}} \qquad E^\circ_{cell} = 3.17\ V$$

$Mg_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2Ag$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{n} \log \frac{[Mg^{2+}]}{[Aq^{+}]^2}$$

$$= 3.17 - \frac{0.06}{2} \log \frac{10^{-1}}{(10^{-3})^2}$$

$= 3.17 - 0.03 \times \log 10^5$

$= 3.17 - 0.03 \times 5$

$= 3.17 - 0.15$

$= 3.02\ V$

Concentration Cell

Same half electrode is present with diff conc^n or pressure

$E^\circ_{cell} = 0$

(1) $Zn_{(s)} \,|\, \underset{C_1M}{Zn^{2+}_{(aq)}} \,\|\, \underset{C_2M}{Zn^{2+}_{(aq)}} \,|\, Zn_{(s)}$

$$\left[E_{cell} = \frac{0.06}{n} \log \left(\frac{C_2}{C_1}\right)\right]$$

Cond^n for spontaneous $\Delta G < 0 \Rightarrow E_{cell} > 0 \Rightarrow C_2 > C_1$

(2) $Pt, \underset{P_1}{H_{2(g)}} \,|\, \underset{1M}{H^{+}_{(aq)}} \,\|\, \underset{1M}{H^{+}_{(aq)}} \,|\, \underset{P_2}{H_{2(g)}}, Pt$

$Pt, H_2 \,|\, HCl \,|\, H_2, Pt$

$$E_{cell} = \frac{0.06}{n} \log \left(\frac{P_1}{P_2}\right)$$

Cond^n for spontaneous

$\Delta G < 0$; $E_{cell} > 0$; $P_1 > P_2$

(3) $Pt, \overset{P_1}{Cl_2} \,|\, \underset{1M}{Cl^-} \,\|\, \underset{1M}{Cl^-} \,|\, \overset{P_2}{Cl_2}, Pt$

$PtCl_2 \,|\, HCl \,|\, Cl_2, Pt$

$$E_{cell} = \frac{0.06}{n} \log \left(\frac{P_2}{P_1}\right)$$

Cond^n for spontaneous

$\Delta G < 0$; $E_{cell} > 0$; $P_2 > P_1$

2. Electrochemical Series

Le	Li	Ni	Neeche	kahe
kar	K	Sn	Suno	$E_R^\circ = -ve$
Barah	Ba	Pb	Pyar	↑
Sardar	Sr	H	hai	$E_R^\circ = 0$
Ka	Ca	Cu	Kyun	↓
Naam	Na	I	aai	$E_R^\circ = +ve$
Maonge	Mg	Ag	Aaj	
ali	Al	Hg	Hongkong main	
mahan	Mn	Br	Britney	
zan	Zn	Pt	patai	
kar	Cr	O	aur	
Fenke	Fe	Cl	kilobar	
C.D.	Cd	Au	Sona Laai	
loi	Co	F	free main	

Apps

(1) Reactivity of metals and Reducing power decreases top to bottom.

(2) Metal displacement

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

$Cu + ZnSO_4 \longrightarrow CuSO_4 + Zn$ ✗

(3) Non metal displacement

I $\quad F_2 + KI \longrightarrow KF + I_2$

Br $\quad Cl_2 + KF \longrightarrow \times$

Cl

F

Electrochemical Series

Q. Metal $\quad E^\circ_{R.} (M^{2+}/1M)$

Li	−3.05 V
Ba	−2.9 V
Na	−2.71 V
Mg	−2.37 V

Compare reducing power

Li > Ba > Na > Mg

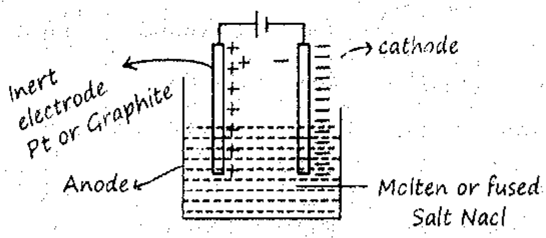
Q. Compare reactivity

Ba, Zn, K, Cu

[K > Ba > Zn > Cu]

Reactivity

3. Electrolytic Cell



Products of electrolysis

1. Molten NaCl $\longrightarrow Na^+ + Cl^-$

At cathode $\quad Na^+ + e^\ominus \longrightarrow Na_{(s)}$

At anode $\quad Cl^\ominus \longrightarrow \frac{1}{2} Cl_{2(g)} + e^\ominus$

Na(s) deposited at cathode

$Cl_{2(g)}$ evolved at anode $\quad NaCl \longrightarrow Na^+ + Cl^-$

2. $\boxed{\text{Aq. Nacl}}$ $\quad H_2O \longrightarrow H^+ + OH^-$

P.D.T. (Preferential discharge theory)

Case 1: For cation

$E^\circ_R \uparrow$ top to bottom

that ion will migrate first

At cathode $\quad H^+ + e^\ominus \longrightarrow \frac{1}{2} H_2(g)$

Case 2: Ease of Migration

$$SO_4^{2-} < NO_3^- < OH^- < Cl^- < Br^- < I^-$$

At anode $\quad Cl^\ominus + \longrightarrow \frac{1}{2} Cl_{2(g)} + e^\ominus$

$\left.\begin{array}{l}\text{(1) } H_{2(g)} \text{ evolved at Cathode} \\ \text{(2) } Cl_{2(g)} \text{ evolved at Anode}\end{array}\right\}$ Nature after Electrolysis is Basic medium

Electrolyte	Electrode	Product at cathode	Product at anode
Aq $CuSO_4$	Pt or graphite	Cu	O_2
Aq $AgNO_3$	Pt or graphite	Ag	O_2
Aq NaOH	Pt or graphite	H_2	O_2
Aq $AgNO_3$	Ag electrode	$Ag^+ + e^\ominus \rightarrow Ag$	$Ag \rightarrow Ag^+ + e^\ominus$
Conc H_2SO_4	Pt or graphite	$2H^+ + 2e^\ominus \rightarrow H_2$	$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^\ominus$
Aq NaCl	Hg electrode	$Na^+ + e^\ominus \rightarrow Na \xrightarrow{Hg} Na_{(Hg)}$	Cl_2

Faradays Law

1st Law $\quad W \propto Q$

$W = ZQ$ (Z = electrochemical equivalent)

$$W = \frac{E.\,It}{F}$$

$$\frac{W}{E} = \frac{It}{F}$$

2nd Law $\quad [n_1 \times n_{f_1} = n_2 \times n_{f_2}]$

$$\left[n \times n_f = \frac{It}{F}\right]$$

Q. How long should a current of 0.25 Amp be passed through a molten metal salt to deposite that much weight of metal which is equal to its Electrochemical equivalent.

$W = Z$; $W = ZQ$

$Q = 1$; $it = 1$

$0.25 \times t = 1$

$[t = 4 \text{ amp}]$

3^{rd} Law

$Na^+ + e^{\ominus} \longrightarrow Na$

$1F \longrightarrow 1$ mol Na

Q. How much charge is req for following Rxns

(1) 1 mol $Al^{3+} \longrightarrow Al$

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

$3F \longrightarrow 1$ mol Al

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

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

$2F \longrightarrow 1$ mol Cu

(3) 1 mol $MnO_4^- \longrightarrow Mn^{2+}$

$\overset{+7}{Mn}O_4^- + 5e^{\ominus} \longrightarrow \overset{+2}{Mn}{}^{2+}$

$5F \longrightarrow 1$ mol Mn^{2+}

4. Resistance, Conductance, resistivity conductivity of a cell

(1) Resistance (R) (ohm)

$\left[R_{unit} = \dfrac{\rho \ell}{A}\right] \Omega$ (ohm)

ρ = Resistivity or sp. resistance

l = Sep. b/w electrodes (cm)

A = Area of cros-section (cm^2)

(2) Resistivity (unit)

$\left[\rho_{unit} = \dfrac{RA}{\ell}\right]$ ohm-cm (Ω-cm)

(3) Conductance (G)

$(ohm)^{-1}$ or mho

$((\Omega)^{-1}$ or $\mho)$

$\left[G = \dfrac{1}{R}\right]$

(4) Conductivity or sp. conductance (K) (unit)

$\kappa_{unit} = \dfrac{1}{\rho}$

$\left[\kappa = \dfrac{\ell}{RA}\right]$ $ohm^{-1}\ cm^{-1}$

Mho cm^{-1}

(5) Cell const (σ or G^*) $(\Omega)^{-1}\ cm^{-1}$

$\left[\sigma = \dfrac{\ell}{A}\right] cm^{-1}$ $\mho\ cm^{-1}$

$S\ cm^{-1}$

Q. If K of 0.1 N KCl is $1.2 \times 10^{-2}\ S\ cm^{-1}$ and $R = 60\ \Omega$ find G^*

$K = 1.2 \times 10^{-2}\ s\ cm^{-1}$

$R = 60$

$R = \dfrac{\rho l}{A}$

$R = \dfrac{1}{K} \times G^*$

$G^* = RK = 60 \times 1.2 \times 10^{-2}$

$= 72 \times 10^{-2}$

$= 0.72\ cm^{-1}$

Molar Conductivity

$\left[\Lambda_m = \dfrac{\kappa \times 1000}{M}\right]$ $(N = M \times nf)$

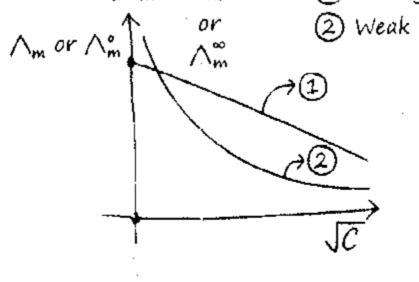
Equivalent Conductivity

$\left[\Lambda_{eq} = \dfrac{\kappa \times 1000}{N}\right]$ $\left[\Lambda_{eq} = \dfrac{\Lambda_m}{n.f}\right]$

Variation of Λ_m & Λ_{eq} with Conc^n

$[\Lambda_m = \Lambda_m^{\circ} - A\sqrt{C}]$ ① Strong Electro $\alpha = 1$

② Weak Electro $\alpha < 1$



5. KOHLRAUSCH LAW

$A_xB_y \rightarrow xA^{y+} + yB^{x-}$

$\Lambda^{o}_{m}(A_xB_y) = x \times \lambda^{\circ}_m A^{y+} + y \times \lambda^{\circ}_m B^{x-}$

$\lambda^{\circ}_{eq}(A_xB_y) = \lambda^{\circ}_{eq} A^{y+} + \lambda^{\circ}_{eq} B^{x-}$

$CaCl_2$

$\Lambda^\circ_m = \lambda^\circ_{m(Ca^{2+})} + 2 \times \lambda^\circ_{m(Cl^-)}$

$\Lambda^\circ_{eq} = \lambda^\circ_{eq(Ca^{2+})} + \lambda^\circ_{eq(Cl^-)}$

App of K.L

(1) $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m}$

(2) $K_a = \dfrac{C\alpha^2}{1-\alpha}$

(3) $\Lambda_m = \dfrac{K \times 1000}{S}$ $\quad K_{sp} = x^x y^y s^{x+y}$

(4) CH_3COONa, $\boxed{CH_3COOH}$, HCl, NaCl

$\Lambda^\circ_{mCH_3COOH} = \Lambda^\circ_{m(CH_3COONa)} + \Lambda^\circ_{m(HCl)} - \Lambda^\circ_{m(NaCl)}$

Q. The conductivity of 10^{-2} M CH_3COOH is 3.9×10^{-5} S cm^{-1} find K_a & α (Given $\Lambda^\circ_{m(CH_3COONa)}$ = 390 S cm^2 mol^{-1}

$C = 10^{-2}$, $K = 3.9 \times 10^{-5}$

$\Lambda^C_m = \dfrac{3.9 \times 10^{-5} \times 1000}{10^{-2}}$

$= 3.9$

$\alpha = \dfrac{3.9}{390} = 10^{-2}$

$K_a = \dfrac{10^{-2} \times (10^{-2})^2}{1 - \cancel{10^{-2}}\,0}$

$= 10^{-6}$

Q. The conductivity of saturated soln of $Ba_3(PO_4)_2$ is 1.2×10^{-5} S cm^{-1} & Λ°_m of $Ba_3(PO_4)_2$ is 1200 S cm^2 mol^{-1} find K_{sp}

$\Lambda^\circ_m = \dfrac{K \times 1000}{S}$

$12\cancel{00} = \dfrac{1.\cancel{2} \times 10^{-5} \times 1\cancel{000}}{S \times 1\cancel{0}}$

$S = 10^{-5}$

$K_{sp} = 3^3 \times 2^2 \times S^{3+2} = 27 \times 4 \times S^5$

$= 108 \times (10^{-5})^5 = 108 \times 10^{-25}$

Q. Calculate $\Lambda^\circ_{m(CH_3COOH)}$

Given

Electrolyte	S cm^2 mol^{-1}
CH_3COONa	91
HCl	426
NaCl	126

$\Lambda^\circ_{m(CH_3COOH)} = \Lambda^\circ_{m(CH_3COONa)} + \Lambda^\circ_{m(HCl)} - \Lambda^\circ_{m(NaCl)}$

$= 91 + 426 - 126$

$= 391$ S cm^2 mol^{-1}

Effect of dilution on K & Λ_m

dilution $\uparrow$ K $\downarrow$ $\Lambda_m \uparrow$

12 Chemical Kinetics

Rate of Reaction

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$

Unit of R.O.R $\left(\begin{array}{l} mol\ \ell^{-1}\ time^{-1} \\ atm\ time^{-1} \end{array}\right)$

Avg

$$R.O.R = -\frac{\Delta[A]}{\alpha \Delta t} = -\frac{\Delta[B]}{\beta \Delta t} = +\frac{\Delta[C]}{\gamma \Delta t} = +\frac{\Delta[D]}{\delta \Delta t}$$

R.O. dissappearance of A $= -\frac{\Delta[A]}{\Delta t}$ R.O.D of B $= -\frac{\Delta[B]}{\Delta t}$

R.O. Appearance. of C $= +\frac{\Delta[C]}{\Delta t}$ R.O.A of D $= +\frac{\Delta[D]}{\Delta t}$

$$\text{Instantaneous R.O.R} = -\frac{d[A]}{\alpha dt} = -\frac{d[B]}{\beta dt} = +\frac{d[C]}{\gamma dt} = +\frac{d[D]}{\delta \Delta t}$$

At $\Delta t \longrightarrow 0$; Avg rate = Instantaneous rate

Q. Write Expression of Rate of Rxn

$N_2 + 3H_2 \longrightarrow 2NH_3$

$$\text{Avg R.O.R} = \frac{-\Delta[N_2]}{1\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \frac{+\Delta[NH_3]}{2\Delta t}$$

$$\text{Instantaneous R.O.R} = \frac{-d[N_2]}{1\ dt} = \frac{-d[H_2]}{3\ dt} = \frac{+d[NH_3]}{2\ dt}$$

R.O.D of $N_2 = \frac{-\Delta[N_2]}{\Delta t}$

R.O.D of $H_2 = \frac{-\Delta[H_2]}{\Delta t}$

R.O.A of $NH_3 = \frac{+\Delta[NH_3]}{\Delta t}$

Q. If R.O.D of SO_2 is 2×10^{-3} M sec^{-1} then find R.O.A of SO_3

$2SO_2 + O_2 \rightarrow 2SO_3$

$$R.O.R = \frac{-\Delta[SO_2]}{2\Delta t} = \frac{-\Delta[O_2]}{1\ \Delta t} = \frac{+\Delta[SO_3]}{2\Delta t}$$

$$\frac{\text{R.O.D of } SO_2}{\cancel{2}} = \frac{\text{R.O.A of } SO_3}{\cancel{2}}$$

R.O.A of $SO_3 = 2 \times 10^{-3}$ M sec^{-1}

Rate Law

$\alpha A + \beta B \rightarrow \gamma C + \delta D$

$\gamma \propto [A]^x [B]^y \Rightarrow \left[\begin{array}{l} \gamma = K[A]^x [B]^y \\ \gamma = R.O.R \\ K = \text{rate const. or velocity const} \end{array}\right.$

$\alpha = x$, $\beta = y$ — for elementary reaction

or

x & $y \Rightarrow$ orders — 1^{st} step reaction

or

x = order w.r.t A — Single step reaction

y = order w.r.t B — R.D.S

$x + y = P$ or n — overall order of reaction [Unit of K = $(M)^{1-P}\ time^{-1}$]

Q. Find order of the Reaction

$A \xrightarrow{k = 10^{-3} sec^{-1}} B$

Unit of k = $(M)^{1-P}\ sec^{-1}$

$\boxed{P = 1}$ 1^{st} order

Q. For $r = k\,[A]^n\,[B]^m$ on doubling the conc^n of A and halving the conc^n of B, the ratio of new rate to the earlier rate will be?

$$r^1 = k\, 2^n [A]^n \frac{1}{2^m} [B]^m = k\, 2^{n-m} [A]^n [B]^m$$

$$\left[\frac{r^1}{r} = 2^{n-m}\right]$$

Q. Find the unit of rate const for zero and 2^{nd} order reaction?

Unit of k $\Rightarrow (M)^{1-P}\ time^{-1}$

$P = 0$ — M $time^{-1}$

$P = 2$ — $M^{-1}\ time^{-1}$

Q. Write R.O.R for

$H_2 + I_2 \longrightarrow 2HI$

Instantaneous R.O.R

$$= \frac{-d[H_2]}{1\ dt} = \frac{-d[I_2]}{1\ dt} = \frac{+d[HI]}{2\ dt}$$

	Order		Molecularity
(1)	Exprimental quantity	(1)	Theoretical quantity
(2)	Order can be zero, -ve, +ve fractional	(2)	Molecularity can be 1, 2 and 3
(3)	Order = Stoichiometric cofficient for 1 step or Elementary Rxn	(3)	Molecularity = Stoichiometric Coefficient
(4)	For complex Rxn order can be calculated by mech.	(4)	There is no meaning of molecularity for complex reaction. $\boxed{\text{R.D.S}} \rightarrow$ Molecularity can be defined

Calculation of order of Reaction

Case 1: Find order of given reaction: $2A + 3B \rightarrow 4C$

Exp	[A]	[B]	Initial rate
1	0.1 M	0.1 M	2×10^{-4} M sec^{-1}
2	0.1 M	0.2 M	4×10^{-4} M sec^{-1}
3	0.2 M	0.2 M	16×10^{-4} M sec^{-1}

$r = k[A]^x [B]^y$ $[r = k[A]^2 [B]^1]$

Find (k)

$2 \times 10^{-4} = k(0.1)^x (0.1)^y$ —(1) $2 \times 10^{-4} = k(0.1)^x (0.1)$

$4 \times 10^{-4} = k(0.1)^x (0.2)^y$ —(2) $k = 0.2\,(M)^{-2}\,sec^{-1}$

$16 \times 10^{-4} = k(0.2)^x (0.2)^y$ —(3)

$\frac{1}{2}$: $\frac{1}{2} = \left(\frac{1}{2}\right)^y$ $\frac{2}{3}$: $\frac{1}{4} = \left(\frac{1}{2}\right)^x$ Overall order

$\boxed{y = 1}$ $\boxed{x = 2}$ = 3

Case 2: Find order of given reaction $A_2 + B_2 \xrightarrow{K} 2AB$; follows the mech below $r = k[A_2]^x [B_2]^y$

1. $A_2 \rightleftharpoons A + A$ (fast) $K_C = \dfrac{[A]^2}{[A_2]}$
2. $A + B_2 \xrightarrow{k_1} AB + B$ (slow) (RDS)
3. $A + B \longrightarrow AB$ (fast)

$r = k_1[A]^1 [B_2]^1$

$= k_1 (k_C[A_2])^{\frac{1}{2}} [B_2]$

$r = k [A_2]^{\frac{1}{2}} [B_2]$

Order w.r.t $A_2 = \dfrac{1}{2}$

Order w.r.t $B_2 = 1$

Overall order $= \dfrac{1}{2} + 1 = \dfrac{3}{2}$

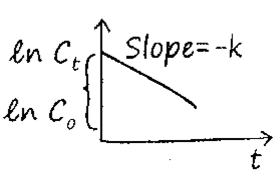
(M.I*)

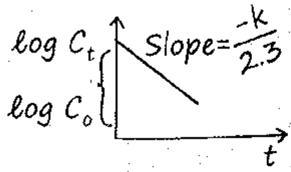
1^{st} order rxn $\overset{C_o}{\underset{C_t}{A}} \longrightarrow$ Product

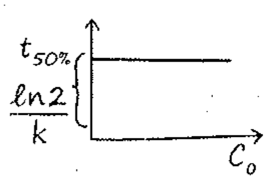
1. $\dfrac{-d[A]}{dt} = K[A]$
2. $Kt = \ln\left(\dfrac{C_o}{C_t}\right) = \ln\left(\dfrac{a}{a-x}\right)$
3. $t_{50\%} = \dfrac{\ln 2}{K} = \dfrac{0.693}{K}$ (Independent of C_o)
4. $t_{75\%}$ $t_{90\%}$ $t_{99\%}$ $t_{99.9\%}$ $t_{99.99\%}$

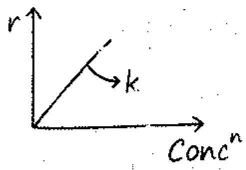
   $2t_{50\%}$ $3.33t_{1/2}$ $6.66t_{1/2}$ $10t_{1/2}$ $13.34t_{1/2}$

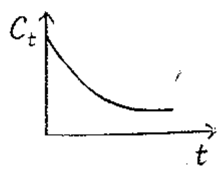
   $\left[Kt_{X\%} = \ln\left(\dfrac{100}{100-x}\right)\right]$
5. D.O.D $\alpha = 1 - e^{-Kt}$
6. $C_t = C_o e^{-Kt}$
7. Graphs











Q. For 1^{st} order rxn the $conc^n$ of reactant decreases from 0.8 M to 0.4 M in 15 min. The time taken for the $conc^n$ to change from 0.1 M to 0.025 M is

$$C_o \xrightarrow[t_{1/2}]{} \frac{C_o}{2} \xrightarrow{t_{1/2}} \frac{C_o}{4} \xrightarrow{t_{1/2}} \frac{C_o}{8} \ldots\ldots\ldots$$

$$0.8\,M \xrightarrow[t_{1/2}=15]{} 0.4\,M \quad \left\{ \begin{array}{l} 0.1 \xrightarrow[t_{1/2}]{} 0.05 \xrightarrow[t_{1/2}]{} 0.025 \\ t = 2t_{1/2} = 2\times 15 = 30\,min \end{array} \right.$$

Q. In the given eq^n $kt = \ln C_o - \ln C_t$; the curve b/w $\ln C_t$ V_s t is

$[\ln C_t = -kt + \ln C_o]$ Straight line

$[y = -mx + C]$

Q. $t = 0 \quad \overset{P_i}{A_{(g)}} \rightarrow 2B_{(g)} + C_{(g)}$

Initial pressure $= P_i$
Pressure at time $t = P_t$
Write expression of k?

$t = t;\ P_i - P_x \quad 2P_x \quad P_x$

$\left(kt = \ln \frac{a}{a-x}\right)$

$\left(kt = \ln\left(\frac{P_i}{P_i - P_x}\right)\right)$

$P_t = P_i - P_x + 2P_x + P_x$

$P_t = P_i + 2P_x$

$P_x = \left(\frac{P_t - P_i}{2}\right)$

$$k.t = \ln\left(\frac{P_i}{P_i - \left(\frac{P_t - P_i}{2}\right)}\right)$$

$$= \ln\left(\frac{2P_i}{2P_i - P_t + P_i}\right)$$

$$\left[kt = \ln\left(\frac{2P_i}{3P_i - P_t}\right)\right]$$

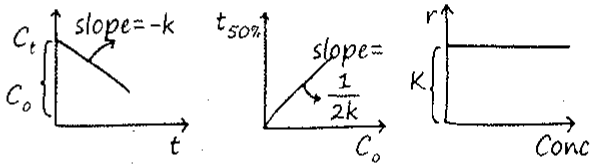
n^{th} order rxn

$$\left[Kt = \frac{C_o^{1-n} - C_t^{1-n}}{1-n}\right] \quad n \neq 1$$

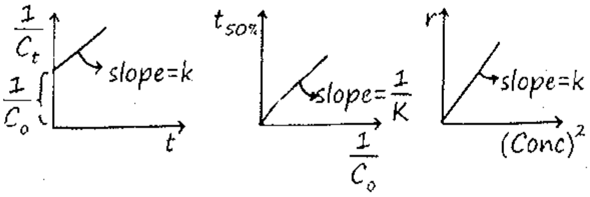
$$\boxed{t_{1/2} \propto C_o^{1-n}}$$

Zero order n = 0	2^{nd} order n = 2
$C_t = -kt + C_o$	$\frac{1}{C_t} = kt + \frac{1}{C_o}$
$t_{50\%} = \frac{C_o}{2k}$ $[t_{1/2} \propto C_o]$	$t_{50\%} = \frac{1}{kC_o}$ $t_{50\%} \propto \frac{1}{C_o}$
$[T_{75\%} = 1.5t_{50\%}]$	$[t_{75\%} = 3t_{50\%}]$

1. Zero order rxn $\qquad r = k[A]^o = k$



2. 2^{nd} order rxn $\qquad r = K[A]^2$



Q. For a zero order rxn, $k = 0.01\ M\ sec^{-1}$. Find $conc^n$ of reactant after 10 sec if initial $conc^n$ is 1 M.

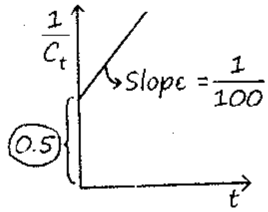
$C_t = -kt + C_o$

$C_t = -10^{-2} \times 10 + 1$

$= 1 - 0.1$

$[C_t = 0.9\ M]$

Q. For 2^{nd} order rxn find C_o & k



$\frac{1}{C_t} = kt + \frac{1}{C_o}$

$\frac{1}{C_o} = 0.5 \Rightarrow [C_o = 2M]$

$k = \frac{1}{100}$

$= 10^{-2}\ M^{-1}\ sec^{-1}$

Temp. dependence on rate & rate const

$$\frac{r_{T+10}}{r_T} = (\mu)^{\frac{\Delta T}{10}} \quad (\mu = \text{Temp. coeff. (2 to 3)})$$

$$= (2)^{\frac{\Delta T}{10}} \quad ((\mu = 2)\ \text{generally})$$

Q. If Temp. Coeff. is 2 then calculate rate of rxn at 60°C if at 20°C it is r?

$$\frac{r_{60°C}}{r_{20°C}} = (2)^{\frac{40}{10}} = 2^4$$

$[r_{60°C} = 16r_{20°C}]$

Arrhenius Eq^n

$[k = Ae^{-Ea/RT}]$

k = rate const

A = Arrhenius const or frequency factor

E_a = Activation energy

R = Universal gas const

$= 2\ Cal k^{-1}\ mol^{-1} = \frac{25}{3} (= 8.3)\ Jk^{-1}\ mol^{-1}$

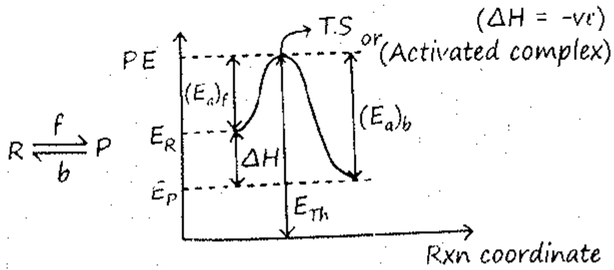
T = Temp (k)

$$\ell n\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.3R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Energy profile diagrams

Case 1: For Exothermic Rxn

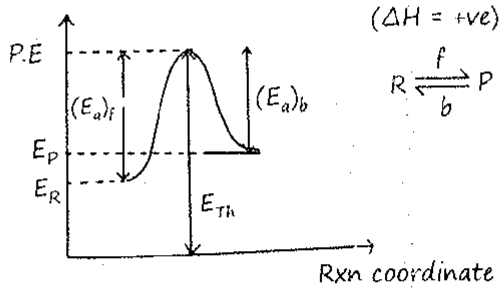


$\Delta H = E_P - E_R = (E_a)_f - (E_a)_b$

E_{Th} = Threshold energy

E_a = Activation energy

Case 2: For Endothermic Rxn



$\Delta H = E_P - E_R = (E_a)_f - (E_a)_b$

Practice

Q. If conc^n of reactants is increased by 'X' the rate const K becomes

(A) $e^{K/X}$ (B) K/X

(C) K (D) X/K

Q. For rxn XA $\longrightarrow$ YB (log 2 = 0.3)

$$\log\left(\frac{-d[A]}{dt}\right) = \log\left(\frac{-d[B]}{dt}\right) + 0.3$$

Find $\frac{X}{Y}$

$$\log\left(\frac{-d[A]}{dt}\right) = \log\left(\frac{-d[B]}{dt}\right) + \log 2$$

$$\frac{-d[A]}{dt} = 2\left(\frac{-d[B]}{dt}\right)$$

X = 2

$y = 1 \Rightarrow \frac{X}{Y} = \frac{2}{1}$

Q. For the rxn $A \xrightarrow{k}$ products, the rate of rxn is doubled when the conc^n of A is increased by 4 times find order of reaction

$r = k[A]^x$ $2 = 2^{2x}$

$2r = k(4[A])^x$ $2x = 1$

$2 = 4^x$ $x = \frac{1}{2}$

Q. Find $(E_a)_b$ if ΔH = +54 kJ/mol for Rxn $N_2O_4 \longrightarrow 2NO_2$ and $E_a(f)$ = + 57 kJ/mol

$\Delta H = (E_a)_f - (E_a)_b$

$54 = 57 - (E_a)_b$

$[\ (E_a)_b = +3\ kJ/mol\ ]$

Inorganic Chemistry

1 Periodic Table

Atomic size

+ In period (L to R) ÷ $z_{eff}\uparrow$ Attrc$^n\uparrow$ size$\downarrow$
+ In group (T to B) ÷ shell no$\uparrow$ size$\uparrow$

Exceptions

1. Inert gas has highest radii in respective period

   H < He

   Ne > Li > Be > B > C > N > O > F

   Ar > Na > Mg > Al > Si > P > S > Cl

2. 3d series

   Sc > Ti > V > Cr < Mn > Fe ≈ Co ≃ Ni < Cu < Zn

3. $r_{Al} \approx r_{Ga}$ (due to poor screening of 3d $e^{\ominus}$s)

Q. Compare size

1. Li, K, Na

   Li < Na < K

2. V, Fe, Mn

   Mn > V > Fe

3. Ne, B, Be

   Ne > Be > B

4. Sc Y La

   Sc < Y < La

5. Ti, Zr, H_f

   Ti < Zr ≈ H_f

6. Al, B, Ga, In

   B < Al ≈ Ga < In

3d Sc Ti V -----
4d Y Zr Nb -----
5d La H_f T_a -----

(Zr ≈ H_f, Nb ≈ T_a)

1. Ionic Radius

1. L to R

   Isoelectronic species

   $$\left[\text{Size} \propto \frac{1}{\text{Atomic no.}}\right]$$

(M.I*)

1. $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$
2. $P^{3-} > S^{2-} > Cl^- > K^+ > Ca^{2+}$
2. T to B

   Shell no$\uparrow$ Size$\uparrow$

(M.I*)

(a) $Li^+(g) < Na^+(g) < K^+(g) < Rb^+(g) < Cs^+(g)$

(b) $F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$

3. $A^{\ominus} > A > A^+$

   $N^- > N > N^+$

2. Hydrated radius

$Li^+(aq) > Na^+(aq) > K^+(aq) > Rb^+(aq) > Cs^+(aq)$

Imp.

Hydrated radius$\uparrow$ conductance or Ionic mobility$\downarrow$

3. Ionisation Energy

($\Delta_i H$ or IE or IP)

1. Inert gas has highest I.E. in respective period due to fully filled configuration.
2. 2^{nd} period

   Li Be B C N O F Ne

   Li < B < Be < C < O < N < F < Ne

3. 3^{rd} period

   Na Mg Al Si P S Cl Ar

   Na < Al < Mg < Si < S < P < Cl < Ar

   I.E: 1^{st} Be > B,
   $(1s^2 2s^2)$ $(1s^2 2s^2 2p^1)$

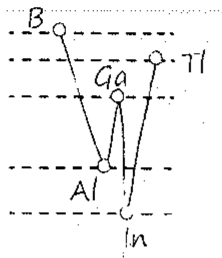
2^{nd} I.E. Be < B

I.E: 1^{st} N > O,

$(1s^2 2s^2 2p^3)$ $(1s^2 2s^2 2p^4)$

2^{nd} I.E. N < O

4. Boron family



B > Tl > Ga > Al > In

Tl > In (Lanthanoid Contraction)

Ga > Al (poor screening of $3de^{\ominus}s$)

5. [5d > 3d > 4d]

↓

(due to L.C)

Q. Compare I.E

1. Be C N

Be < C < N

2. O N Ne

Ne > N > O

3. P S Ar

Ar > P > S

4. Ti Zr H_f

H_f > Ti > Zr

5. Mg Ca Sr

Mg > Ca > Sr

6. Al Ga In

Ga > Al > In

4. **Electron gain enthalpy ($\Delta_{eg}H$)**

Exceptions

1. 2^{nd} period

Be < Ne < N < B < Li < C < O < F

Beta ne na Bolkar Ladki Ko Fasaya

(zero or +ve)

2. 3^{rd} period

Mg < Ar < Al < Na < P < Si < S < Cl

maine aur alka ne pyari si shadi karli

(zero or +ve)

3. 3 period > 2 period

(due to vacant 'd' orbitals)

4. Cl > F > Br > I

5. S > Se > Te > Po > O

↓

due to compact nature

6. Inert gases have zero or +ve electron gain enthalpy.

Q. Compare $\Delta_{eg}H$

1. Li Be O

Be < Li < O

2. Na Ar Si

Ar < Na < Si

3. Se O S

S > Se > O

4. F Cl Br

Cl > F > Br

5. Si C

Si > C

6. N B F

N < B < F

5. **Electronegativity**

The tendency of an atom to attract shared pair $e^{\ominus}s$ towards itself.

$A \xrightarrow{+} B$ (B > A) EN

$A \xleftarrow{+} B$ (B < A) EN

Trends

1. L to R EN↑
2. T to B EN↓

1	1.5	2	2.5	3	3.5	4
Li	Be	B	C	N	O	F

H, P (2.1)

C, I, S (2.5)

N, Cl

3 3.1

$A < A^+ < A^{2+}$

$A > A^- > A^{2-}$

6. Nature of oxides

1. Non metallic oxides → Acidic
2. Metallic oxides → Basic
3. Neutral oxides

   NO, N_2O, CO

4. Amphoteric oxides

   V_2O_5, Cr_2O_3, ZnO, Al_2O_3, SnO, PbO, BeO, SnO_2, PbO_2

   V, Cr, Zn, Al, Sn, Pb, Be

5. Amphoteric Metals

   Vema car zanabe aali sanak pade bey main

Acidic Strength

1. L to R

   N.M.C↑ A.S↑

2. T to B

   N.M.C↓ A.S↓

$\boxed{\overset{+1}{H_3PO_2} > \overset{+3}{H_3PO_3} > \overset{+5}{H_3PO_4}}$ due to Reso

3. Oxides of same element

   A.S ∝ O.N $(\overset{+6}{SO_3} > \overset{+4}{SO_2})$

4. A.S of oxyacids

   A.S ∝ O.N

   $\overset{+7}{HClO_4} > \overset{+5}{HClO_3} > \overset{+3}{HClO_2} > \overset{+1}{HClO}$

   $\overset{+6}{H_2SO_4} > \overset{+4}{H_2SO_3}$

Q. Which of the following order is incorrect according to the prop against it?

(A) $F_2 > Cl_2 > Br_2 > I_2$ Oxidising power

(B) $HI > HBr > HCl > HF$ Acidic strength

$Cl_2 > Br_2 > F_2 > I_2$

(C) $F_2 > Cl_2 > Br_2 > I_2$ B.D.E ✓

(D) $F > Cl > Br > I$ E.N

Q. Compare basic strength

Na_2O, CuO, MgO, Al_2O_3

$Na_2O > MgO > CuO > Al_2O_3$

Q. Compore I.P

C N O F

C < O < N < F

Q. Compare E.N

S P N O

P < S < N < O

Q. Compare ionic radii

Ca^{2+}, K^+, Cl^-, S^{2-}

$Ca^{2+} < K^+ < Cl^- < S^{2-}$

Q. Which is an amphoteric oxide

(A) CaO (B) SO_3

(C) SnO ✓ (D) SiO_2

2 Chemical Bonding

1. Fajan's rule

Small cation, polarising power↑ bigger anion Polarisabilty↑

& high charge on cation or anion causes polarisation↑ covalent character↑

C.C $\overset{+}{Na}\overset{-}{F} > \overset{+}{K}\overset{-}{F}$ [charge dominates over size]

C.C $\overset{+}{Na}\overset{-}{F} < \overset{2+}{Mg}\overset{-}{F_2}$

Q. Compare covalent character?

1. $\overset{2+}{Be}Cl_2 \xrightarrow{decreases} \overset{2+}{Ba}Cl_2$

2. $\overset{+}{Na}\overset{-}{Cl} < \overset{2+}{Mg}\overset{-}{Cl_2} < \overset{3+}{Al}\overset{-}{Cl_3}$

3. $\overset{+}{Li}\overset{-}{F} \xrightarrow{increases} \overset{+}{Li}\overset{-}{I}$

4. $\overset{+}{Cu}\overset{-}{Cl} > \overset{+}{Na}\overset{-}{Cl}$

Pseudo inert gas config. > Inert gas config.

Inert + $3d^{10}$

2. V.B.T (Valence bond theory)

$s + s \rightarrow \sigma$

$s + p \rightarrow \sigma$

$p + p$ (Head on or end to end) $\rightarrow \sigma$

$p + p$ (Lateral or sidewise) $\rightarrow \pi$

Imp. Points

1. s can not form π
2. Strength α overlapping area for same principal Q.N

   $p - p > s - p > s - s$

3. Strength of π bond

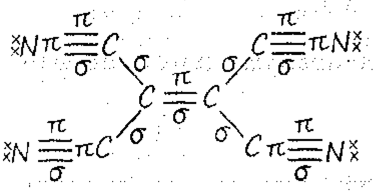
   $2p\pi - 2p\pi > 2p\pi - 3d\pi > 2p\pi - 3p\pi > 3p\pi - 3p\pi$

4. π bond is weaker than σ

5. $A \equiv A > A = A > A - A$ (Bond Strength)

6. $A \underset{\sigma}{\overset{\pi}{\equiv}} B$ $A \underset{\sigma}{\overset{\delta}{\equiv}} B$

Q. Find σ and π bonds in $C_2(CN)_4$



9π, 9σ, 4 L.P

3. Hybridisation

1	2	3	4	5	6	7	8
Li	Be	B	C	N	O	F	Ne

1. Find valence $e^{\ominus}$s of central atom

   He × → $2e^{\ominus}$, O → $6e^{\ominus}$, N → $5e^{\ominus}$

2. Find sharing $e^{\ominus}$s of side atom

3. σ + L.P + U.P $e^{\ominus}$ = 2 sp

   = 3 sp^2

   = 4 sp^3

   = 5 $sp^3d(dz^2)$

   = 6 $sp^3d^2(d_{x^2-y^2}, dz^2)$

   = 7 $sp^3d^3(d_{xy}, d_{yz}, d_{zx})$

$4 - 4 = 0e^{\ominus} = 0$ L.P

- CH_4 $4\sigma + 0$ L.P = 4 sp^3

$5 - 3 = 2e^{\ominus} = 1$ L.P

- NH_3 $3\sigma + 1$ L.P = 4sp^3

$8 - (4+2) = 2e^{\ominus} = 1$ L.P

- XeO_2F_2 $2\sigma + 2\sigma + 1$ L.P = 5sp^3d

$6 - 6 = 0e^{\ominus} = 0$ L.P

- $PCl_6^{\ominus}$ 6σ + 0LP = 6 sp^3d^2

$4 - 4 = 0e^{\ominus} = 0$ L.P

- PCl_4^{+} 4σ + 0LP = 4 sp^3

Q. Find hybridisation of underlined atom

$6 - (2+2) = 2e^{\ominus} = 1$ L.P

1. OSF_2 SO_1F_2 $1\sigma + 2\sigma$ + 1LP = 4 sp^3

$8 - 2 = 6e^{\ominus} = 3$ L.P

2. $I_3^{\ominus}$ $II_2^{\ominus}$ 2σ + 3LP = 5 sp^3d

$6-6 = 0e^{\ominus} = 0$ L.P

3. $\underline{N}_2^{\ominus}$ $\underline{N}H_2^{\ominus}$ $2\sigma+0LP=2$ sp

$8-6 = 2e^{\ominus} = 1$ L.P

4. $\underline{B}rO_{③}^{\ominus}$ $3\sigma+1LP=4$ sp^3

$8-(2+2) = 4e^{\ominus} = 2$ L.P

5. $\underline{Xe}\,O_{①}F_{②}$ $1\sigma+2\sigma+2LP=5$ sp^3d

$4-4 = 0e^{\ominus} = 0$ L.P

6. $\underline{N}O_{②}^{+}$ $2\sigma+0LP=2$ sp

$6-6 = 0e^{\ominus} = 0$ L.P

7. $\underline{N}O_{③}^{\ominus}$ $3\sigma+0LP=3$ sp^2

Species	Cationic part	Anionic part
PCl_5 (s)	PCl_4^+ (sp^3)	PCl_6^- (sp^3d^2)
PBr_5 (s)	PBr_4^+ (sp^3)	Br^-
N_2O_5 (s)	NO_2^+ (sp)	NO_3^- (sp^2)
XeF_6 (s)	XeF_5^+ (sp^3d^2)	F^-
Cl_2O_6 (s)	ClO_2^+ (sp^2)	ClO_4^- (sp^3)

Odd $e^{\ominus}$ molecules

$5-4=1e^{\ominus}=1upe^{\ominus}$

$\underline{N}O_{②}$

$2\sigma+1upe^{\ominus}=3sp^2$

$\dot{C}H_3$ sp^2

$\dot{C}F_3$ sp^3

4. V.S.E.P.R theory

L.p–L.p > L.p–B.p > B.p–B.p

Geometry or structure

BP (σ) + L.P = 2 Linear

= 3 Trigonal planar

= 4 Tetrahedral

= 5 T.B.P

= 6 Octahedral

= 7 P.B.P

B.P (σ)	L.P	Shape
2	0	Linear
2	1	Angular or v-shape or Bent
2	2	Angular or v-shape or Bent
2	3	Linear
3	0	Trigonal planar
3	1	Trigonal pyramidal
3	2	T-shape
4	0	Tetrahedral
4	1	see-saw
4	2	sq. planar
5	0	T.B.P (Trigonal bi pyramidal)
5	1	Sq. pyramidal
6	0	octahedral
6	1	distorted octahedral
7	0	P.B.P(pentagonal bi pyramidal)

Hybridisation	Molecules	B.P (σ)	L.P	Shape	(σ +LP) Geometry
sp^3d	$8-2=6e^{\ominus}=3LP$ $XeF_{②}$ 2σ	2	3	Linear	5 T.B.P
sp^3d	$8-(4+2)=2e^{\ominus}=1LP$ $XeO_{②}F_{②}$ 4σ	4	1	see-saw	5 T.B.P
sp^3	$8-6=2e^{\ominus}=1LP$ $ClO_{③}^{\ominus}$ 3σ	3	1	Trigonal pyramidal	4 Tetrahedral
sp^3	I_3^+ $6-2=4e^{\ominus}=2LP$ $II_{②}^{\oplus}$ 2σ	2	2	Bent	4 Tetrahedral

5. Dipole moment (μ)

$\mu = 0$ non polar

$\mu \neq 0$ polar

1. (B.P)	σ	L.P	$\mu = 0$
	2	0	$BeCl_2$
	3	0	BF_3
	4	0	CH_4
	5	0	PCl_5
	6	0	SF_6
	7	0	IF_7

2. (B.P)	σ	L.P	$\mu = 0$
	2	3	XeF_2
	4	2	XeF_4

Q. Polar or non polar?

$8-2=6e^{\ominus}=3L.P$

1. $I_3^{\ominus}$ $II_{②}^{\ominus}$

$2\sigma + 3L.p$ $\mu=0$ non polar

$4-4=0e^{\ominus}=0L.p$

2. $PCl_{④}^{\oplus}$

$4\sigma + 0L.p$ $\mu=0$ non polar

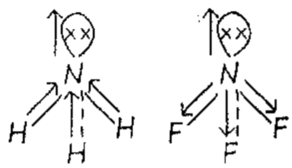
$6-4=2e^{\ominus}=1L.p$

3. $SF_{④}$

$4\sigma + 1L.p$ $\mu \neq 0$ non polar

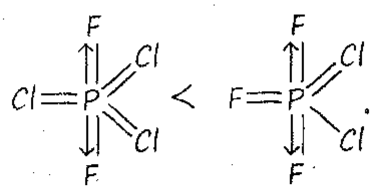
Some Imp. Points

1. $NH_3 > NF_3$

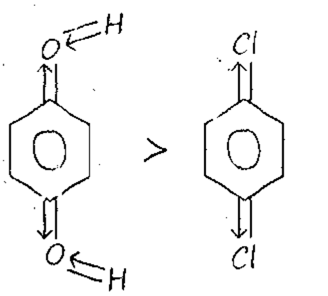


2. $CH_3-Cl > CH_3-F$ ($q \times d$) $C-Cl > C-F$
3. $CH_3-Cl > CH_2Cl_2 > CHCl_3 > CCl_4$
4. $CD_3F > CH_3F$ (D is more +ve than H)
5. $PCl_3F_2 < PF_3Cl_2$

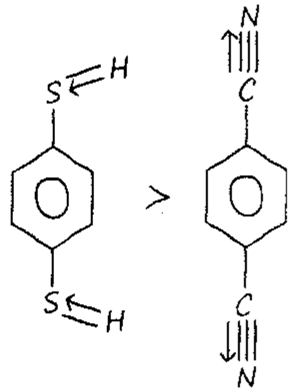
$\mu = 0$ $\mu \neq 0$



6.



$\mu = 0$ $\mu \neq 0$

7. 

M.O.T Bond order

Case 1: If $e^{\ominus}$s in a molecule ion

$8 \leq$ no. of $e^{\ominus} \leq 20$

	P	P	P	D	P
$\boxed{8}$	$\boxed{9}$	$\boxed{10}$	$\boxed{11}$	$\boxed{12}$	$\boxed{13}$
0	0.5	1	1.5	2	2.5

3

D $\boxed{14}$

P	P	P	D	P	
$\boxed{15}$	$\boxed{16}$	$\boxed{17}$	$\boxed{18}$	$\boxed{19}$	$\boxed{20}$
2.5	2	1.5	1	0.5	0

Case 2: If no. of $e^{\ominus}$s ≤ 8

[BABA] $B.O = \left(\frac{N_b - N_a}{2}\right)$

1	2	3
H_2	H_2^+	H_2^-
2	1	3
2	1	2(1)
BABA	BABA	BABA
$B.O = \frac{2-0}{2} = 1$	$B.O = \frac{1-0}{2} = 0.5$	$B.O = \frac{2-1}{2} = \frac{1}{2} = 0.5$

1. Stability $\propto$ B.O

   If B.O is same, then last $e^{\ominus}$ in B.M.O is stable.

   ①>②>③

2. B.E $\propto$ B.O $\propto \frac{1}{B.L}$

   If no. of $e^{\ominus}$s = even (except 10 and 16) $\rightarrow$ dia

3. If no. of $e^{\ominus}$s = odd $\longrightarrow$ para

Q. Find B.O and Magnetic nature

B_2	$10e^{\ominus}$	1	P	B_2	$10e^{\ominus}$	1	P
B_2^-	$11e^{\ominus}$	1.5	P	B_2^+	$9e^{\ominus}$	0.5	P
② $\pi \leftarrow \boxed{C_2}$	$12e^{\ominus}$	2	D	C_2^-	$13e^{\ominus}$	2.5	P
C_2^+	$11e^{\ominus}$	1.5	P	N_2	$14e^{\ominus}$	3	D
O_2^+	$15e^{\ominus}$	2.5	P	O_2	$16e^{\ominus}$	2	P
O_2^-	$17e^{\ominus}$	1.5	P	F_2	$18e^{\ominus}$	1	D
O_2^{2-}	$18e^{\ominus}$	1	D	NO	$15e^{\ominus}$	2.5	P
O_2^{2+}	$14e^{\ominus}$	3	D	NO^+	$14e^{\ominus}$	3	D
F_2^+	$17e^{\ominus}$	1.5	P	CO	$14e^{\ominus}$	3	D
Li_2	$6e^{\ominus}$		D				

[CO^+ 13
B.O=3.5 P]

$\overset{2}{\cancel{B}}\overset{2}{\cancel{A}}\overset{2}{B}A$

$B.O = \frac{2}{2} = 1$

Q. Which of the following would have a permanent dipole moment?

(A) BF_3 (B) SiF_4

$6-4=2e^{\ominus}=1LP$

(C) SF_4 (D) XeF_4

Q. Compare covalent character.

MF < MCl < MBr < MI

Q. Which is paramagnetic?

(A) NO^+	(B) N_2^+	(C) CO	(D) C_2
$14e^{\ominus}$	$13e^{\ominus}$	$14e^{\ominus}$	$12e^{\ominus}$
D	P	D	D

Q. Which of the following two are isostructural?

(A) XeF_2 & $IF_2^{\ominus}$

(5)T.B.P (5)T.B.P

(B) NH_3 & BF_3

3BP+1LP 3BP+0LP

= 4 Tetra = 3 Trigonal planar

(C) CO_3^{2-} & SO_3^{2-}

3BP+0LP 3BP+1LP

= 3 Trigonal planar = 4 Tetrahedral

(D) PCl_5 & ICl_5

T.B.P 5BP+1LP = 6 octahedral

Q. Which species does not exist?

(A) Be_2^+ (B) Be_2 (C) B_2 (D) N_2

$7e^{\ominus}$ $8e^{\ominus}$ $10e^{\ominus}$ $14e^{\ominus}$

B.O = 0

Q. In which molecule central atom has sp^2?

(A) $BeCl_2$ (B) BF_3

2BP+0LP 3BP+0LP

2=sp $3sp^2$

(C) C_2H_2 (D) NH_3

CH≡CH 3BP+1LP

sp sp $= 4sp^3$

Q. Compare bond length

$N_2^{\ominus}$ N_2 N_2^{2-} B.O $N_2 > N_2^- > N_2^{2-}$

15 2.5 14 3 16 2 B.L $N_2 < N_2^- < N_2^{2-}$

Q. Compare covalent character.

$\overset{+}{Li}Cl < \overset{2+}{Be}Cl_2 < \overset{3+}{Al}Cl_3 < \overset{4+}{C}Cl_4$

Q. In which molecule central atom has sp^3d?

(A) XeF_2 (B) H_3O

2BP+3LP 3BP+1LP

(C) XeF_4 (D) XeF_6

4BP+2LP 6BP+1LP

3BP+1LP = 4

Q. In chemical change $PCl_3 \longrightarrow PCl_5$

Hybridisation of P changes from?

sp^3 sp^3d

Q. Which has linear shape but not sp hybridisation

(A) XeF_2 (B) $I_3^{\ominus}$

2BP+3LP 2BP+3LP

Linear Linear

5 sp^3d 5 sp^3d

(C) CO_2 (D) Both A and B

2BP+0LP

2 Linear

sp

3 Hydrogen

M.O.P OF H_2

1. Lab Methods

$$Zn \xrightarrow{H^+} Zn^{2+} + H_2$$

$$Zn \xrightarrow{NaOH} \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

2. Commercial Methods

(a) Electrolysis of acidified water

$$2H_2O(\ell) \xrightarrow[H^+]{Electro} 2H_2 + O_2$$

(b) For high purity H_2 (> 99.95%)

$$Ba(OH)_2(aq) \xrightarrow{Electro}$$

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$$

$$H_2O \longrightarrow H^+ + OH^-$$

$$4H^+ + 4e^{\ominus} \longrightarrow 2H_2$$

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

(c) It is obtained as by product in the production of NaOH & Cl_2 by electrolysis of Brine solution.

$NaCl(aq)$

$NaCl \longrightarrow Na^+ + \boxed{Cl^-}$

$H_2O \longrightarrow \boxed{H^+} + \bar{O}H$

at cathode $H^+ + e^{\ominus} \longrightarrow \frac{1}{2}H_2\uparrow$

at anode $Cl^- \longrightarrow e^{\ominus} + \frac{1}{2}Cl_2\uparrow$

(d) Reaction of steam on hydrocarbon & coke

$$C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n+1)H_2$$

$$CH_4 + H_2O \xrightarrow[Ni]{1270\ K} CO + 3H_2 \quad \Delta H = +ve$$

Steam methane reforming reaction

CO & $H_2 \Longrightarrow$ Syn gas

$$CO + 2H_2 \xrightarrow[\substack{200-300\ atm \\ 300-400°C}]{(ZnO+Cr_2O_3)} CH_3OH$$

Coal gasification reaction

$$C + H_2O \xrightarrow{1270K} CO + H_2 \quad \Delta H = +ve$$

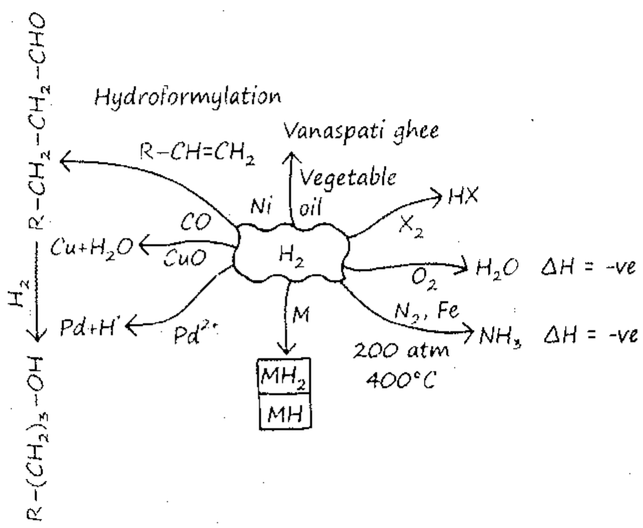
Water gas shift reaction

$$CO + H_2O \xrightarrow[Fe_2O_3.Cr_2O_3]{400°C} CO_2 + H_2 \quad \Delta H = -ve$$

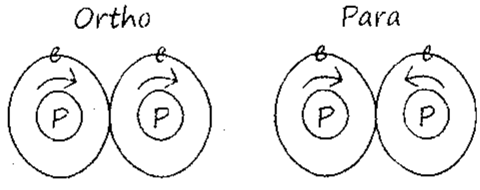
Physical prop of H_2

1. It is colourless, tasteless, odourless, combustible gas.
2. It is lighter than air.
3. Insoluble in H_2O.

Chemical prop



Ortho and para Hydrogen



P O P

1. Also known as nuclear spin isomers
2. Net spin para $\Rightarrow$ 0
   ortho $\Rightarrow$ double
3.

T	Ortho	Para
0K	–	100%
at liquefaction temp	50%	50%
at room temp or high temp	75% (3	25% : 1)

4. Chemical prop are same
5. Physical prop different

MP & BP O > P

Hydrides
- → Metallic Hydride: $TiH_{2.87}$ (d-block element)
- → Ionic Hydride: s-block elements except LiH, BeH_2, MgH_2
- → Covalent hydride, P-block
  - → Electron deficient (octet incomplete) B_2H_6 (13th)
  - → Electron precise (octet complete) CH_4 (14th)
  - → Electron Rich (octet comp but central atom has some L.P) $\ddot{N}H_3$

  15 & 16, 17 group

$$\boxed{\begin{array}{l}\text{Electrical conductance}\\ \text{I.H > M.H > C.H}\end{array}}$$

Water Chemical Reaction

1. Amphoteric nature

$$H_2O \xrightarrow{NH_3} NH_4^+ + OH^-$$

$$H_2O \xrightarrow{H_2S} H_3O^+ + HS^-$$

2. Redox reaction

$$H_2O \xrightarrow{Na} \overset{+1}{NaOH} + H_2$$

$$H_2O \xrightarrow{\overset{0}{F_2}} \overset{-1}{HF} + O_2$$

$$H_2O \xrightarrow{CO_2} C_6H_{12}O_6 + H_2O + O_2$$

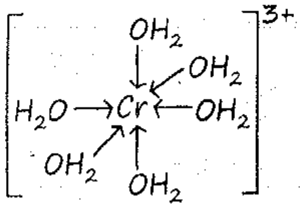
3. Autoprotolysis reaction

$$H_2O + H_2O \rightleftharpoons HO^{\ominus} + H_3O^+$$

4. Hydrated H_2O

(a) Coordinated H_2O

$[Cr(H_2O)_6]Cl_3$



$3Cl^-$

(b) Hydrogen bonded

$[Cu(H_2O)_4]SO_4 \overset{H.B}{\leftarrow} \cdot H_2O$

(c) Interstitial H_2O ; $BaCl_2.2H_2O$

5. Hydrolysis reaction

(a) $P_4O_{10} + H_2O \longrightarrow H_3PO_4$

(b) $SiCl_4 + H_2O \longrightarrow SiO_2 + HCl$

(c) $N^{3-} + H_2O \longrightarrow NH_3 + OH^-$

Hardness of H_2O

H_2O

- Hara water does not give Lather with soap
- Soft water gives Lather with soap

$$2C_{17}H_{35}COONa + M^{2+} \longrightarrow (C_{17}H_{35}COO)_2M\downarrow + 2Na^+$$

Sodium Stearate (M=Ca, Mg)

Hardness

- Temporary due to presence of Ca & Mg bicarbonates
- Permanent due to presence of Ca & Mg sulphates and chloride

B	Sc
T	P

Removal of Hardness

1. By boiling (for removal of temp hardness)

$$Ca(HCO_3)_2 \xrightarrow{Boil} CaCO_3\downarrow + CO_2\uparrow + H_2O$$

$$Mg(HCO_3)_2 \xrightarrow{Boil} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

2. Clark's method

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

For removal of permanent Hardness

1. By washing soda (Na_2CO_3)

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2NaCl$$

$$MSO_4 + Na_2CO_3 \longrightarrow MCO_3\downarrow + Na_2SO_4$$

(M = Ca & Mg)

2. Calgon's method

$Na_6P_6O_{18}$ $(NaPO_3)_6$

Sodium hexameta phosphate

$$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow 2Na^+ + [Na_2MP_6O_{18}]^{2-}$$

3. Zeolite/permutit process

$$\underbrace{NaAlSiO_4} \longrightarrow NaZ$$

$$2NaZ + M^{2+} \longrightarrow MZ_2 + 2Na^+$$

4. Synthetic resin method

$$RSO_3H \longrightarrow RNa$$

$$2RNa + M^{2+} \longrightarrow MR_2 + 2Na^+$$

Ion exchange process

- Cation exchange
- Anion exchange

Cation exchange:

$$R{-}H + M^{2+} \longrightarrow MR_2 + H^+$$

Anion exchange:

$$RNH_2 + H_2O \longrightarrow RNH_3^+\bar{O}H$$

$$RNH_3^+\bar{O}H + X^-$$

$$\downarrow$$

$$RNH_3^+X^- + \bar{O}H$$

$\bar{O}H$ exchange for

Cl^-, HCO_3^-, SO_4^{2-}

PPm

$$PPm = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 10^6$$

xPPm $\Rightarrow$ x gm solute is present in 10^6 gm H_2O

x gm solute is present in 10^6 mL H_2O

Hydrogen peroxide

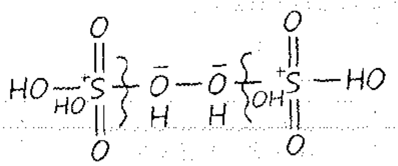
1. From $BaO_2.8H_2O$

$$BaO_2.8H_2O \xrightarrow{H_2SO_4} BaSO_4 + H_2O_2 + 8H_2O$$

$$Ba\boxed{O_2 + H_2}SO_4$$

2. From electrolysis of conc H_2SO_4

$$2HSO_4^- \xrightarrow{electro} H_2S_2O_8 + 2e$$

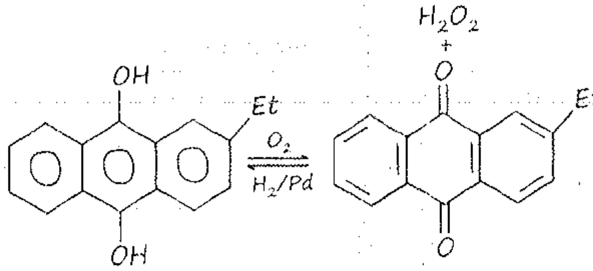


$$H_2S_2O_8 \xrightarrow{H_2O} 2H_2SO_4 + \boxed{H_2O_2}$$

Lab method for D_2O_2

$$K_2S_2O_8 + D_2O \longrightarrow KDSO_4 + \boxed{D_2O_2}$$

3. Industrial method



2-Ethylanthraquinol 2-Ethylanthraquinone

Volumetric strength of H_2O_2

'10' V H_2O_2

1 L H_2O_2 solution gives 10L O_2 at STP

According to the reaction:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

1. [V.S = 11.2 × M]

2. [V.S = 5.6 × N]

3. [Strength (g/L) = $\frac{68}{22.7}$ × V.S]

4. $\% \frac{W}{V} = \frac{S}{10}$

Chemical prop of H_2O_2 (Perhydrol)

Case 1 : Acts as an O.A

1. In A.M (Acidic Medium)

$$Fe^{2+} + H_2\overset{-1}{O_2} \xrightarrow{H^+} Fe^{3+} + H_2\overset{-2}{O}$$

$$S^{2-} + H_2\overset{-1}{O_2} \xrightarrow{H^+} \overset{+6}{S}O_4^{2-} + H_2\overset{-2}{O}$$

2. In B.M (Basic Medium)

$$Fe^{2+} + H_2\overset{-1}{O_2} \longrightarrow Fe^{3+} + \overset{-2}{O}H^{\ominus}$$

$$Mn^{2+} + H_2\overset{-1}{O_2} \longrightarrow Mn^{4+} + \overset{-2}{O}H^{\ominus}$$

Case 2 : Acts as a R.A

1. In A.M (Acidic Medium)

$$\overset{+7}{Mn}O_4^{\ominus} + H_2\overset{-1}{O_2} \xrightarrow{H^+} Mn^{2+} + \overset{0}{O_2}$$

$$HO\overset{+1}{Cl} + H_2O_2 \xrightarrow{H^+} H\overset{-1}{Cl} + \overset{0}{O_2} + H_2O$$

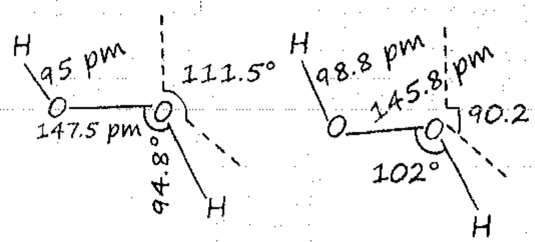
2. In B.M (Basic Medium)

$$\overset{+7}{Mn}O_4^{\ominus} + H_2O_2 \longrightarrow \overset{+4}{Mn}O_2 + \overset{0}{O_2}$$

$$\overset{0}{I_2} + H_2O_2 \longrightarrow \overset{-1}{I}^{\ominus} + \overset{0}{O_2}$$

Structure

Open book structure



Gas phase Solid phase (at 110K)

Bleaching action of H_2O_2

Oxidative bleaching

$$H_2O_2 \longrightarrow H_2O + [O]$$

Coloured matter $\xrightarrow{[O]}$ colourless (permanent)

D_2O

$$CaC_2 + D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \longrightarrow D_2SO_4$$

$$Al_4C_3 + D_2O \longrightarrow CD_4 + Al(OD)_3$$

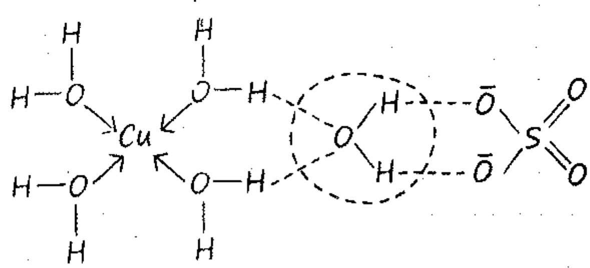
Practice

Q. PH_5 does not exist why?

High value of Δ_aH (Heat of atomisation) & $\Delta_{eg}H$ (electron gain enthalpy) of hydrogen.

Q. How many hydrogen bonded H_2O molecules are associated in $CuSO_4.5H_2O$ (Blue vitriol)?

Ans. 1



Q. Find strength of 10 V solution of H_2O_2 $\left(\frac{\%W}{V}\right)$

$V.S = 10$

$$(S)\text{strength } (g/L) = \frac{68}{22.7} \times 10$$

$$= 30$$

$$\frac{\%W}{V} = \frac{S}{10} = \frac{30}{10} = 3$$

Q. Compare B.D.E

H_2, D_2, F_2

$F_2 < H_2 < D_2$

Q. Compare reducing prop?

$NaH \quad MgH_2 \quad H_2O$

$H_2O < MgH_2 < NaH$

4 s-Block

Alkali Metals

Size	Li	I.E
Metallic character	Na	E.N
Ionic nature of compounds	K	M.P
Softness	Rb	B.P
	Cs	
increases ↓		decreases ↓

Density Li < K < Na < Rb < Cs

Chemical property:-

1. Reaction with O_2

(a) $M + O_2 \longrightarrow M_2O$

M = Li (some peroxide, (Li_2O_2) also)

(b) $M + O_2 \longrightarrow M_2O_2$

M = Na (some superoxide also NaO_2)

(c) $M + O_2 \longrightarrow MO_2$

(M = K, Rb, Cs)

Stability $M_2O > M_2O_2 > MO_2$

Oxidising power $M_2O < M_2O_2 < MO_2$

Hydrolysis of peroxides & superoxides

$M_2O_2 + H_2O \xrightarrow[\text{dil } H^+]{} H_2O_2 + 2MOH$

$2MO_2 + 2H_2O \xrightarrow[H^+]{\text{dil}} 2MOH + H_2O_2 + O_2$

Oxides

Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O ↓ Basicity & solubility increases

Ionic Radii $\underset{(g)}{Li^+} < \underset{(g)}{Na^+} < \underset{(g)}{K^+} < \underset{(g)}{Rb^+} < \underset{(g)}{Cs^+}$

Hydrated Radii $\underset{(aq)}{Li^+} > \underset{(aq)}{Na^+} > \underset{(aq)}{K^+} > \underset{(aq)}{Rb^+} > \underset{(aq)}{Cs^+}$

2. Reaction with H_2O

$M + H_2O \longrightarrow MOH + \frac{1}{2}H_2 + \text{Energy}$

LiOH, NaOH, KOH, RbOH, CsOH ↓ Basicity & solubility Increases

3. Reaction with N_2

$Li + N_2 \longrightarrow Li_3^+N^{3-} \xrightarrow[H^+\ \bar{O}H]{H_2O} LiOH + NH_3$

4. Reaction with H_2

$M + H_2 \longrightarrow MH$

LiH, NaH, KH, RbH, CsH ↓ Stability decreases

5. Reaction with aq NH_3

$M + (x + y)\, NH_3 \longrightarrow [M(NH_3)_x]^+ + [e^{\ominus}(NH_3)_y]$

Solvated electrons

Reducing agent

Paramagnetic

Conducting

Blue colour

When conc increases Paramagnetic $\longrightarrow$ diamagnetic

Blue $\longrightarrow$ Bronze

On standing

$M^+(am) + e^\ominus + NH_3(l) \longrightarrow \underset{\text{amide}}{MNH_2} + H_2\uparrow$

6. Reaction with dry NH_3

$NH_3 \xrightarrow{Li} Li_2NH + H_2$ — Lithium imide (NH^{2-})

$NH_3 \xrightarrow{M} MNH_2 + H_2$ — Metal amide (NH_2^-)

7. Sulphates (M_2SO_4)

Li_2SO_4 | Solubility & thermal Stability

Na_2SO_4

K_2SO_4

Rb_2SO_4

Cs_2SO_4 $\downarrow$ Increases

Li_2SO_4 is insoluble

$Li_2SO_4 \xrightarrow{\Delta} Li_2O + SO_3$

$M_2SO_4 \xrightarrow{\Delta} X$

(M = Na, K, Rb, Cs)

8. Nitrates (MNO_3)

$LiNO_3$ | Solubility & thermal Stability

$NaNO_3$

KNO_3

$RbNO_3$

$CsNO_3$ $\downarrow$ Increases

All nitrates are soluble

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

$MNO_3 \xrightarrow{\Delta} MNO_2 + O_2$

(M = Na, K, Rb, Cs)

9. Carbonates (M_2CO_3)

Li_2CO_3 | Solubility & thermal Stability

Na_2CO_3

K_2CO_3

Rb_2CO_3

Cs_2CO_3 $\downarrow$ Increases

Li_2CO_3 is insoluble

$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$

$M_2CO_3 \xrightarrow{\Delta} X$

(M = Na, K, Rb, Cs)

10. Bicarbonates ($MHCO_3$)

$LiHCO_3$ | Solubility & thermal Stability

$NaHCO_3$

$KHCO_3$

$RbHCO_3$

$CsHCO_3$ $\downarrow$ Increases

$LiHCO_3$ does not exist as solid solution

Rest all exist as solid $MHCO_3$

(M = Na, K, Rb, Cs)

11. Halides (MX)

M.P & B.P $\quad F > Cl > Br > I$

Covalent character $\quad LiF < LiCl < LiBr < LiI$

$\boxed{LiCl.2H_2O}$

(Rest all chlorides do not form hydrates)

Solubility $\quad BeF_2 \longrightarrow BeI_2$

C.C L to R$\uparrow$

Solubility L to R$\downarrow$

$AgF \longrightarrow AgI$

C.C L to R$\uparrow$

Solubility L to R$\downarrow$

Some Important Comp of Na

1. Sodium carbonate (Na_2CO_3)

Solvay ammonia process

$$NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

$$\downarrow CO_2 + H_2O$$

$$NaHCO_3 + NH_4Cl \xrightarrow{\overset{+\ -}{NaCl}} NH_4^+HCO_3^-$$

$$NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

$$NH_4Cl \xrightarrow{Ca(OH)_2} NH_3 + CaCl_2 + H_2O$$

Solvay ammonia process is not used for preparation of K_2CO_3 due to more solubility of $KHCO_3$

Prop

(a) Hydrated form is called washing soda $Na_2CO_3.10H_2O$

(b) White crystalline solid $Na_2CO_3.10H_2O$

(c) Heating effect (Glauber's Salt)

$$Na_2CO_3.10H_2O \xrightarrow{373\ K} Na_2CO_3.H_2O + 9H_2O$$

$$\downarrow T > 373\ K$$

$$Na_2CO_3 + H_2O$$

Soda ash

2. Sodium hydroxide (NaOH)

Castner-Kellner cell

Brine solution (aq NaCl)

$Hg \longrightarrow$ cathode

$C \longrightarrow$ anode

$NaCl \longrightarrow \boxed{Na^+} + \boxed{Cl^-}$

$H_2O \longrightarrow H^+ + OH^-$

At Cathode

$$Na^+ + e^{\ominus} \longrightarrow Na \xrightarrow{Hg} Na(Hg)$$

$$\downarrow H_2O$$

$$NaOH + H_2 + Hg$$

At Anode

$$Cl^{\ominus} \longrightarrow \frac{1}{2}Cl_2 + e^{\ominus}$$

Prop

(a) White solid

(b) Melts at 591 K

(c) Strong alkaline solution

3. **Sodium hydrogen carbonate ($NaHCO_3$) (Baking soda)**

MOP $Na_2CO_3 + CO_2 + H_2O \longrightarrow NaHCO_3$

Property:-

(a) $NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

(b) Mild antiseptic

(c) Fire extinguishers

4. **NaCl (Common salt)**

$$\text{Crude salt} \xrightarrow{H_2O} \text{filter}$$

$$\downarrow HCl$$

$$NaCl$$

Flame Test

Li	Na	K	Rb	Cs
Crimson red	Yellow	Violet	Red violet	Blue
Cr	Y	Vi	Re	Bablu

Practice

Q. LiF & CsI are very less soluble why?

LiF $\longrightarrow$ due to High L.E

CsI $\longrightarrow$ due to Less hydration of Cs^+

Q. Find products

(a) $Na + H_2O \longrightarrow NaOH + H_2 + \text{Energy}$

(b) $Na + O_2 \longrightarrow Na_2O_2$

(c) $Na_2O_2 + H_2O \longrightarrow NaOH + H_2O_2$

Q. Prepare Na from NaCl

Molten NaCl

Down's cell

At cathode $Na^+ + e^\ominus \longrightarrow Na$

At anode $Cl^\ominus \longrightarrow \frac{1}{2}Cl_2 + e^\ominus$

Q. Compare Ionic mobility in aq solution

$Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs^+(aq)$

Alkaline earth metals

Size, metallic charac, Ionic nature of compounds, softness		I.E & E.N
↓	1 Be	↓
	2 Mg	
	3 Ca	
	4 Sr	
Increase	5 Ba	Decreases

MP (1) > (3) > (4) > (5) > (2)

BP (1) > (5) > (3) > (4) > (2)

Density (5) > (4) > (1) > (2) > (3)

M.P (Madhya pradesh) ko

B.P (Bhopal)

Density (Denge)

Chemical prop

1. Reaction with O_2 (max covalent charac)

powdered form

$Be \xrightarrow{O_2} BeO$ } Amphoteric

$Mg \xrightarrow{O_2} MgO$

$Ca \xrightarrow{O_2} CaO$

$Sr \xrightarrow{O_2} SrO$

$Ba \xrightarrow{O_2} BaO$

} Basic Ionic

Oxide + $H_2O \longrightarrow$ Hydroxide

$MO + H_2O \longrightarrow M(OH)_2$

2. Reaction with H_2O

$Be \xrightarrow[H_2O]{steam} BeO + H_2$

$Mg \xrightarrow{H_2O} MgO + H_2$

$Mg \xrightarrow{H_2O} Mg(OH)_2 + H_2$

$M \xrightarrow{H_2O} M(OH)_2 + H_2$

Hydroxides

Ampho ⟵ $Be(OH)_2$

Basic $\begin{cases} Mg(OH)_2 \\ Ca(OH)_2 \\ Sr(OH)_2 \\ Ba(OH)_2 \end{cases}$ Solubility, Thermal stability & Basic charac ↓ Increases

$BeCl_2.4H_2O$

✓ $Be(OH)_2 \xrightarrow[2H_2O]{2HCl} [\overset{+2}{Be}(H_2O)_4]Cl_2$

$Be\begin{matrix} OH\ H)Cl \\ OH\ H)Cl \end{matrix}$ $[Be(\cancel{OH})_4]Cl_2$ (+6)

✓ $Be(OH)_2 \xrightarrow{2NaOH} Na_2[\overset{+2}{Be}(OH)_4]$

Beryllate ion

3. Reaction with N_2

$M + N_2 \longrightarrow \overset{+2}{M_3}\overset{-3}{N_2} \xrightarrow{H_2O} NH_3 + M(OH)_2$

M = all alkaline earth metals

4. Reaction with H_2

$M + H_2 \longrightarrow MH_2$ M = Mg, Ca, Sr, Ba ($M \neq Be$)

$BeCl_2 + LiAlH_4 \longrightarrow BeH_2 + LiCl + AlCl_3$

$(BeH_2)_n$ & $(MgH_2)_n$ are polymeric covalent hydride

Rest all MH_2 are ionic in nature.

5. Reaction with aq. NH_3

$M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^{2+} + 2[e^\ominus(NH_3)_y]$

Blue colour
Conducting nature
Good R.A
Paramagnetic

} Conc^n↑
Blue ⟶ Bronze
Paramagnetic ⟶ diamagnetic

6. **Reaction with dry NH_3**

$M + \text{dry } NH_3 \longrightarrow M_3N_2 + H_2$

$\left[\overset{2+}{M_3}\overset{3-}{N_2} \xrightarrow[H^+\ OH^-]{H_2O} M(OH)_2 + NH_3\uparrow\right]$

7. **Sulphates (MSO_4)**

Thermal stability (T.S)		Solubility
	$BeSO_4$	
	$MgSO_4$	
	$CaSO_4$	
	$SrSO_4$	
Increases ↓	$BaSO_4$	↓ Decreases

$MSO_4 \xrightarrow{\Delta} MO + SO_2 + O_2$

8. **Nitrates $M(NO_3)_2$**

T.S		Solubility
	$Be(NO_3)_2$	
	$Mg(NO_3)_2$	
	$Ca(NO_3)_2$	
	$Sr(NO_3)_2$	
Increases ↓	$Ba(NO_3)_2$	↓ Decreases

$M(NO_3)_2 \xrightarrow{\Delta} MO + NO_2 + O_2$

9. **Carbonates (MCO_3)**

T.S		Solubility
	$BeCO_3$	
	$MgCO_3$	
	$CaCO_3$	
	$SrCO_3$	
Increases ↓	$BaCO_3$	↓ Decreases

$MCO_3 \xrightarrow{\Delta} MO + CO_2$

10. **Bicarbonates $M(HCO_3)_2$**

All bicarbonates exist in sol^n

$M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + CO_2 + H_2O$

Note:

5 bicarbonates exist in solid form

$NaHCO_3$

$KHCO_3$

$RbHCO_3$

$CsHCO_3$

NH_4HCO_3

11. **Halides**

$M + X_2 \longrightarrow MX_2$

Best method for BeF_2

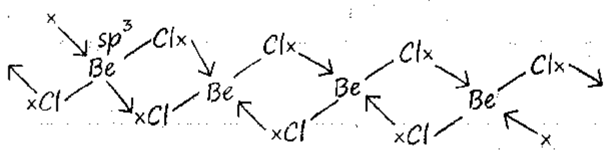
$(NH_4)_2BeF_4 \xrightarrow{\Delta} BeF_2 + 2NH_4F$

Best method for $BeCl_2$

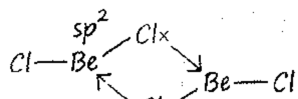
$BeO + C + Cl_2 \xrightarrow{600-800K} BeCl_2 + CO$

Structures of $BeCl_2$

(a) In solid phase $(BeCl_2)_n$



(b) In vapour phase $(BeCl_2)_2$



(c) When T is nearly 1200K

$BeCl_2$ $\quad \underset{sp}{Cl—Be—Cl}$

$BeCl_2 \cdot 4H_2O$

$MgCl_2 \cdot xH_2O$ $\quad x = 6, 8$

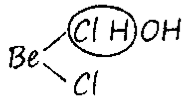
$CaCl_2 \cdot 6H_2O$

$SrCl_2 \cdot 6H_2O$

$BaCl_2 \cdot 2H_2O$

1. Heating of $BeCl_2 \cdot 4H_2O$

$$BeCl_2 \cdot 4H_2O \xrightarrow{\Delta} BeCl_2 \cdot H_2O + 3H_2O$$



$$\downarrow \Delta$$

$Be(OH)Cl$

hydroxy chloride

2. Heating of $MgCl_2 \cdot 6H_2O$

$$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgCl_2 \cdot 2H_2O + 4H_2O$$

$$\downarrow \Delta$$

$$MgO \xleftarrow{\Delta} Mg(OH)Cl + H_2O$$

$$MgCl_2 \cdot 6H_2O \xrightarrow[HCl]{\Delta/dry} MgCl_2 + 6H_2O$$

Some Imp. comp. of Ca

1. Quick lime (CaO)

MOP (a) From limestone ($CaCO_3$)

$$CaCO_3 \xrightarrow{1070 \text{ to } 1270K} CaO + CO_2$$

Prop (a) White amorphous solid

(b) High M.P

(c) It absorbs moisture & CO_2 from atmosphere

Slaking of lime

$$\underset{\text{lump of lime}}{CaO} + H_2O \longrightarrow \underset{\text{slaked lime}}{Ca(OH)_2}$$

$$CaO + CO_2 \longrightarrow CaCO_3$$

(d) It is basic in nature

$$CaO + SiO_2 \longrightarrow \underset{\text{Calcium silicate}}{CaSiO_3}$$

$$CaO + P_4O_{10} \longrightarrow \underset{\text{Thomas slag}}{Ca_3(PO_4)_2}$$

2. Slaked lime $Ca(OH)_2$

MOP (a) $CaO + H_2O \longrightarrow Ca(OH)_2$

Prop (a) White amorphous powder

(b) aq sol^n is called lime water

(c) Suspension of slaked lime is called milk of lime

(d) When CO_2 is passed in lime water, milkiness appears.

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{}{\overset{\text{milky}}{CaCO_3\downarrow}} + H_2O$$

Milkiness disappears when excess CO_2 & H_2O is passed.

$$CaCO_3 + CO_2 + H_2O \longrightarrow \overset{\text{soluble}}{Ca(HCO_3)_2}$$

(e) $Ca(OH)_2 + Cl_2 \longrightarrow$

$$CaCl_2 + \underset{\substack{\text{Calcium} \\ \text{hypochlorite}}}{Ca(OCl)_2} + H_2O$$

$\boxed{CaOCl_2}$

$Ca^{2+}(\overset{+1}{OCl})^- \longrightarrow +1$

$Cl^- \longrightarrow -1$

3. Lime stone ($CaCO_3$)

MOP (a) $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

Excess $CO_2 + H_2O$ should be avoided

(b) $Ca\boxed{Cl_2 + Na_2}CO_3 \longrightarrow CaCO_3 + 2NaCl$

Prop (a) White fluffy powder

(b) Heating effect

$$CaCO_3 \xrightarrow{1200\ K} CaO + CO_2$$

(c) Rxn with HCl & H_2SO_4

$$Ca^{2+}CO_3^{2-} \xrightarrow{H^+Cl^-} CaCl_2 + CO_2 + H_2O$$

$$\downarrow H_2^+SO_4^{2-}$$

$$CaSO_4 + CO_2 + H_2O$$

4. **Plaster of paris (POP) $CaSO_4 \cdot \frac{1}{2} H_2O$**

$$\text{MOP} \quad \underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} \xrightarrow{393\ K} \underset{\text{POP}}{CaSO_4 \cdot \tfrac{1}{2}H_2O}$$

$$\downarrow T > 393K$$

$$CaO + SO_2 + O_2 \xrightarrow{\text{strong}} \underset{\text{Dead burnt plaster}}{CaSO_4}$$

Flame Test

Be & Mg do not show flame test

Ca	Sr	Ba
Brick	Crimson	apple
Red	Red	Green

Name	Formula
1. Indian salt petre	KNO_3
2. Chile salt petre	$NaNO_3$
3. Milk of magnesia	$Mg(OH)_2$
4. Caustic soda	$NaOH$
5. Caustic potash	KOH
6. Plaster of paris	$CaSO_4 \cdot \frac{1}{2}H_2O$
7. Gypsum	$CaSO_4 \cdot 2H_2O$
8. Dead burnt plaster	$CaSO_4$
9. Caliche	$NaNO_3 + NaIO_3$
10. Epsom's salt	$MgSO_4 \cdot 7H_2O$
11. Glauber's salt	$Na_2SO_4 \cdot 10H_2O$
12. Slaked lime	$Ca(OH)_2$
13. Lime stone (Marble)	$CaCO_3$
14. Quick lime	CaO
15. Soda ash	Na_2CO_3
16. Washing soda	$Na_2CO_3 \cdot 10H_2O$
17. Bleaching powder	$CaOCl_2$
18. Brine	$aqNaCl$
19. Nitrolim	$CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2 + C$
20. Baking soda	$NaHCO_3$

Practice

Q. (a) BeO is almost insoluble but $BeSO_4$ is soluble in H_2O?

(b) BaO is soluble but $BaSO_4$ is insoluble in H_2O?

For solubility HE > LE

For insolubility HE < LE

Q. Compare hydrated radii

$$Be^{2+}_{(aq)} > Mg^{2+}_{(aq)} > Ca^{2+}_{(aq)} > Sr^{2+}_{(aq)} > Ba^{2+}_{(aq)}$$

Q. Compare solubility

$MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

due to HE > LE

Q. Which comp is ionic in nature?

(A) BeH_2 (B) MgH_2

✓(C) CaH_2 (D) $BeCl_2$

Hydrolith

$$MH \xrightarrow{H_2O} MOH + H_2\uparrow$$

$$MH_2 \xrightarrow{H_2O} M(OH)_2 + H_2\uparrow$$

5 p-Block (Boron Family)

Density		B.P
	B	
	Al	
	Ga	
	In	
Increases ↓	Tl	↓ Decreases

Exceptions

1. **Atomic Radius**

   B < Ga < Al < In < Tl

   due to poor screening of $3d^{10}$ e^{θ} in Ga

2. **E.N**

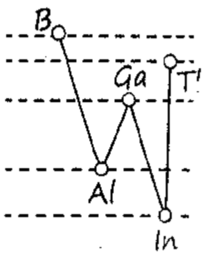
   Al < Ga < In < Tl < B

3. **M.P**

   B > Al > Ga < In < Tl

   B > Al > Tl > In > Ga

4. **Ionisation energy (I.E)**



B > Tl > Ga > Al > In

Tl > In due to L.C

Ga > Al due to poor screening of $3d^{10}e^{\ominus}$

Chemical Properties

1. **Reactivity towards air**

   $E + O_2 \longrightarrow E_2O_3$

   $E + N_2 \longrightarrow EN$

   (1) B does not react in crystalline form

   (2) Al forms very thin oxide layer (Al_2O_3)

   (3) Amorphous B and Al can form oxides and nitrides

B_2O_3

Al_2O_3

$\overset{+3}{Ga_2O_3}$ $\quad$ $\overset{+1}{Ga_2O}$

$\overset{+3}{In_2O_3}$ $\quad$ $\overset{+1}{In_2O}$

$\overset{+3}{Tl_2O_3}$ $\quad$ $\overset{+1}{Tl_2O}$

Stability of +3 O·N decreases down the group

Inert pair effect

ns^2 $e^{\ominus}s$ do not take part in bond formation

B $1s^2 2s^2 2p^1$

$Tl \longleftarrow \underline{6s^2}$ $6p^1$

f.d

Stability of +1 O·N increases down the group

$$\text{Decreases}\downarrow\begin{vmatrix} Ga^{3+} & Ga^{+1} \\ In^{3+} & In^{+1} \\ Tl^{3+} & Tl^{+1} \end{vmatrix}\downarrow\text{Increases} \qquad \begin{bmatrix} Ga^{3+} > Ga^{+1} \\ In^{3+} > In^{+1} \\ Tl^{3+} < Tl^{+1} \end{bmatrix}$$

Oxides of B — Acidic

Al, Ga — Amphoteric

In, Tl — Basic

2. **Rxn with acid and alkalies**

   B does not react

   $Al \xrightarrow{\text{dil HCl}} AlCl_3 + H_2$

   Sodium metaaluminate

   $Al \xrightarrow{\text{aq NaOH}} NaAlO_2 + H_2$

   $\downarrow$ NaOH

   $Na[Al(OH)_4]$

   Sodium tetrahydroxoaluminate (III)

3. **Reactivity towards Halogen**

   $E + X_2 \longrightarrow \overset{+3}{EX_3} / \overset{+1}{EX}$ $\qquad$ Except ($T\ell I_3$)

   Stability

   (1) +3 Halides decreases down the group

   (2) +1 Halides increases down the group

Q. Compare Reducing power

(1) $GaCl_3$ & $GaCl$

Stability $Ga^{+3} > Ga^{+1}$

$$\underset{\text{Less stable}}{Ga^{+1}} \xrightarrow[OX]{} \underset{\text{More stable}}{Ga^{+3}}$$

GaCl is better reducing agent than $GaCl_3$.

Q. Compare Oxidising power

(2) $TlCl_3$ & $TlCl$

$Tl^{3+} < Tl^{+1}$

$$\underset{\text{Less stable}}{Tl^{3+}} \xrightarrow{Red^n} \underset{\text{More stable}}{Tl^{+1}}$$

$TlCl_3$ is better O.A than TlCl.

Some Imp. comp. of Boron

1. **Borax #** Tincal or suhaga

Borax $Na_2B_4O_7 \cdot 10H_2O$

Jeweller's borax $Na_2B_4O_7 \cdot 5H_2O$

Borax glass $Na_2B_4O_7$ (Sodium tetraborate)

MOP

(1) From colemanite

$$Ca_2B_6O_{11} + Na_2CO_3 \rightarrow Na_2B_4O_7 + NaBO_2 + CaCO_3$$

$$NaBO_2 \xrightarrow{CO_2} Na_2B_4O_7 + Na_2CO_3$$

Prop

(1) Borax $^{aq}sol^n$ is alkaline in nature

$$\underset{(WA + SB)}{Na_2B_4O_7} + H_2O \rightarrow \underset{SB}{NaOH} + \underset{WA}{H_3BO_3}$$

(2) Borax can act as acidic buffer

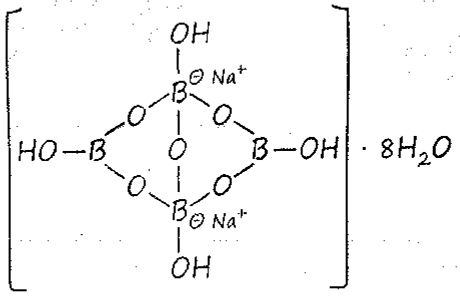
(3) Heating effect

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7$$

$$\xrightarrow{\Delta} \underbrace{\underset{\text{Sodium metaborate}}{NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Glassy bead}}$$

(4) Structure $Na_2B_4O_7 \cdot 10H_2O$

$$Na_2^+[B_4O_5(OH)_4]^{2-} \cdot 8H_2O$$



(1) Hybridisation of B $\Rightarrow sp^2$ & sp^3

(2) Total B—O—B Bonds = 5

(3) Total B—O bonds = 14

(4) Total L.P = 34

2. **H_3BO_3 (Boric acid)**

MOP

(1) From borax

$$Na_2B_4O_7 \xrightarrow{aq\ HCl} NaCl + H_3BO_3$$

$$Na_2B_4O_7 \xrightarrow{aq\ H_2SO_4} Na_2SO_4 + H_3BO_3$$

$$H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

(2) From boron trihalides

X = Cl, Br, I

$$BX_3 \xrightarrow{H_2O} H_3BO_3 + HX$$

$$B \begin{cases} \boxed{X\ \ H}\,OH \\ \boxed{X\ \ H}\,OH \\ \boxed{X\ \ H}\,OH \end{cases}$$

$$BH_3 \xrightarrow{H_2O} HBF_4 + H_3BO_3$$

$[H_2\ddot{O} \longrightarrow BF_3]$

(3) From diborane

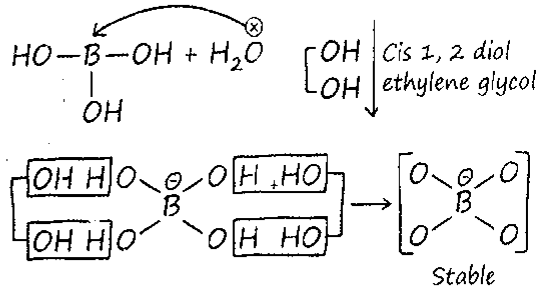
$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2\uparrow$$

$$HO\boxed{H\ H}-B-\boxed{H\ H}OH$$
$$\quad\quad\quad |$$
$$\quad\quad\boxed{H\ H}OH$$

Prop

(1) It is a weak monobasic non protic Lewis acid

$$H_3BO_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+\uparrow$$

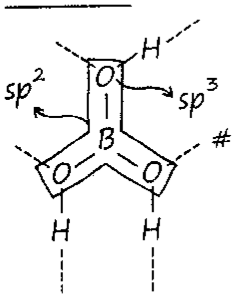


(2) Heating effect

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100°C} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{150°C} \underset{\text{Tetraboric acid}}{H_2B_4O_7}$$

$$H_2B_4O_7 \xrightarrow{\text{Strong Heating}} \underset{\text{Boron sesqueoxide}}{B_2O_3}$$

(3) Structure



Inter Molecular
Hydrogen Bonding

3. B_2H_6 (Diborane)

MOP

(1) From BF_3

(a) $BF_3 + LiAlH_4 \longrightarrow B_2H_6 + LiF + AlF_3$

(b) $BF_3 + NaH \xrightarrow{450\ K} NaF + B_2H_6$

(2) From $NaBH_4$

$$\underbrace{NaBH_4}_{BH_3 + NaH} + I_2 \longrightarrow H_2 + NaI + B_2H_6$$

Prop

(1) Rxn with O_2

$$B_2H_6 + O_2 \longrightarrow B_2O_3 + H_2O \quad \Delta H = -ve$$

(2) Rxn with H_2O

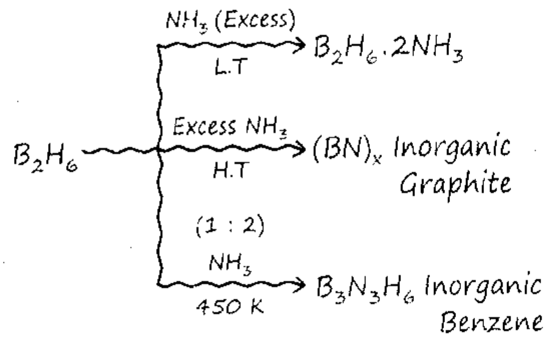
$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2\uparrow$$

(3) Rxn with metal hydride (MH)

M = Li or Na

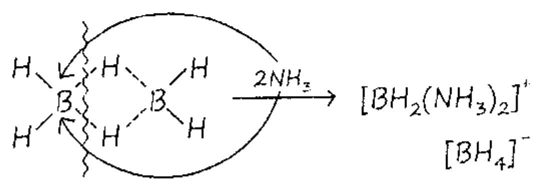
$$MH + B_2H_6 \longrightarrow M^+[BH_4]^-$$

(4) Rxn with NH_3 #



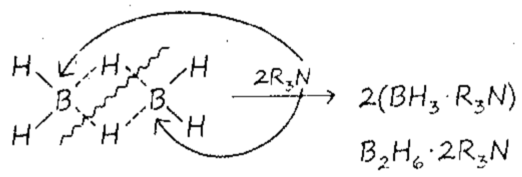
(5) Rxn with NH_3, 1° amine (RNH_2), 2° amine (R_2NH)

(Unsymmetrical bond breaking)



(6) Rxn with 3° amine (R_3N) & CO.

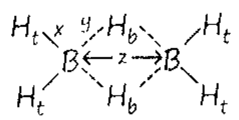
(Symmetrical bond breaking)



$$B_2H_6 \xrightarrow{2CO} (B_2H_6\cdot 2CO)$$

(7) **Structure of B_2H_6 #**

$$2BH_3 \longrightarrow B_2H_6$$



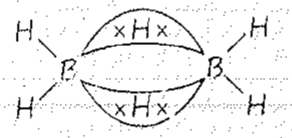
(a) $B—H_t \Rightarrow 2C - 2e^{\ominus}$ ④

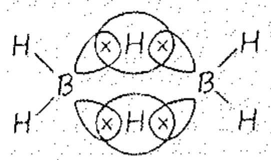
(b) $B---H_b---B \Rightarrow 3C - 2e^{\ominus}$ ②

Banana Bond

(c) BH_3 B_2H_6

sp^2 sp^3

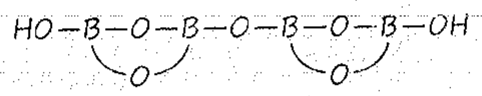
(d) 

(e) 

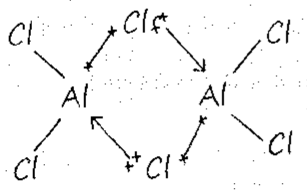
(f) Bond length $x < y < z$

Some Imp. Points of Boron Family

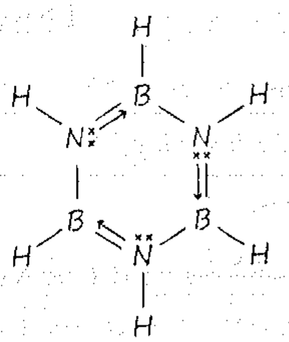
1. Structure of $H_2B_4O_7$ (Tetraboric acid)



2. Structure of Al_2Cl_6



3. Structure of $B_3N_3H_6$



\# Aromatic

\# More reactive than C_6H_6

4. Borax bead test

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{NaBO_2 + B_2O_3}_{\text{Glassy bead}}$$

$$MO + B_2O_3 \longrightarrow \text{Metaborates}$$

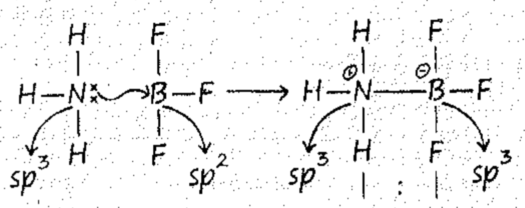
$$M(BO_2)_2$$

$$Cr_2O_3 + B_2O_3 \longrightarrow Cr(BO_2)_3$$

Metaborates of

Cr	Mn	Fe	Co	Ni	Cu
Green	Pink	Green	Blue	Brown	Blue
Gopal	prasad	Gupta ki	badi	barbaad	Biwi

5. Rxn of NH_3 with BF_3



adduct or Complex

6. Occurance of B

H_3BO_3 Orthoboric acid

$Na_2B_4O_7 \cdot 10H_2O$ Borax

$Na_2B_4O_7 \cdot 4H_2O$ Kernite

7. Occurance of Al

$\boxed{O > Si > Al}$

$Al_2O_3 \cdot 2H_2O$ Bauxite

Na_3AlF_6 Cryolite

8. Hydrolysis of BCl_3 and $AlCl_3$

$$BCl_3 \xrightarrow{H_2O} B(OH)_3 \xrightarrow{H_2O} [B(OH)_4]^{\ominus}$$

$$AlCl_3 \xrightarrow{H_2O} [Al(H_2O)_6]^{3+}$$

9. Acidic strength of trihalides of B

$[BF_3 < BCl_3 < BBr_3 < BI_3]$

2p-2p   2p-3p   2p-4p   2p-5p

Practice

Q. Boron is unable to form BF_6^{3-}, why?

due to non availability of vacant 'd' orbitals.

Q. White fumes appear around the bottle of anhydrous $AlCl_3$, why?

$$AlCl_3 \xrightarrow[\text{Moisture}]{H_2O} HCl$$

Q. $E^{\circ}_{Al^{3+}/Al} = -1.66$ V

$E^{\circ}_{Tl^{3+}/Tl} = +1.26$

Compare

(a) electropositive charac of Al & Tl

(b) oxidising power of Al^{3+} and Tl^{3+}

$E^{\circ}_{R}\downarrow$ $E \cdot P\uparrow$ $E \cdot P$ $Al > Tl$

$O \cdot P$ $Tl^{3+} > Al^{3+}$

Q. Why H_3BO_3 is a weak acid?

Because it is a non protic acid

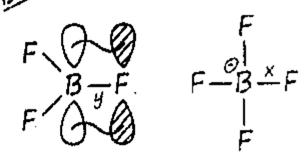
$H_3BO_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$

Q. Compare stability

${}^{3+}BCl_3 > {}^{3+}TlCl_3$

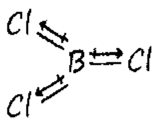
Q. Compare Bond length B—F

B.B BF_3 $\quad$ $BF_4^{\ominus}$ No B.B



$\boxed{x > y}$

Q. BCl_3 is non polar why?



3 BP + 0 LP

$\boxed{D.M = 0}$

Q. $AlF_3 + \underset{}{\overset{\text{Covalent}}{HF}} \longrightarrow$ No Rxn

$AlF_3 + \overset{+\ -}{\underset{\text{Ionic}}{NaF}} \longrightarrow Na[AlF_4]$ why?

$\big\downarrow BF_3$

AlF_3

Q. Identify acidic basic and Amphoteric oxides.

Am	Ac	Am	B	B
Al_2O_3,	B_2O_3,	Ga_2O_3,	Tl_2O_3,	In_2O_3

Q. $\underset{\text{Metal Al}}{X} \xrightarrow{NaOH} \overset{Al(OH)_3}{A} \xrightarrow[\text{White ppt}]{\Delta} D\ Al_2O_3$

$A \xrightarrow{\text{dil HCl}} \underset{AlCl_3}{C}$

$A \xrightarrow{\text{Excess NaOH}}$ Soluble complex B $Na[Al(OH)_4]$

Q. Aq sol^n of Borax is alkaline why?

$Na_2B_4O_7 + H_2O \longrightarrow \overset{SB}{NaOH} + \underset{WA}{H_3BO_3}$

$\boxed{P^H > 7}$

6 p-Block (Carbon Family)

Size		B.P
	C	
	Si	
	Ge	
	Sn	
Increases ↓	Pb	↓ Decreases

Exceptions

1. M.P & I.E

$C > Si > Ge > Pb > Sn$

↓

due to L.C

2. Density

$Si < C < Ge < Sn < Pb$

3. E.N

$Si \approx Ge \approx Sn < Pb < C$

#Catenation# Self linking prop

$C > Si > Ge \approx Sn$

Pb does not show catenation due to bigger size.

Chemical Prop

1. Reactivity towards oxygen #

$E + O_2 \longrightarrow \overset{+2}{EO} \ \& \ \overset{+4}{EO_2}$

Neutral	$\boxed{CO}$	CO_2	
Exist at High Temp ←	SiO	SiO_2	Acidic
	GeO	GeO_2	
	SnO	SnO_2	Amphoteric
	PbO	PbO_2	

Acidic strength $EO_2 > EO$

2. Reactivity towards H_2O

$C, Si, Ge \xrightarrow{H_2O}$ No Rxn

$\underset{\text{Steam}}{Sn + H_2O} \longrightarrow SnO_2 + H_2\uparrow$

$Pb + H_2O \longrightarrow$ No Rxn

due to formation of protective film of oxide (PbO)

3. Reactivity towards X_2

$E + X_2 \longrightarrow \overset{+4}{EX_4} \ \& \ \overset{+2}{EX_2}$ (E = Ge, Sn, Pb)

Stability

$\overset{+4}{E}$ Top to bottom decreases

$\overset{+2}{E}$ Top to bottom increases

due to inert pair effect

#

Stability decreases ↓	Ge^{+4}	Ge^{+2}	↓ Stability Increases
	Sn^{+4}	Sn^{2+}	
	Pb^{+4}	Pb^{2+}	

$\left.\begin{array}{l} Ge^{+4} > Ge^{2+} \\ Sn^{4+} > Sn^{2+} \end{array}\right\} Pb^{2+} > Pb^{4+}$

$\overset{+4}{Si}F_6^{2-}$, $\overset{+4}{Ge}Cl_6^{2-}$ $[\overset{+4}{Sn}(OH)_6]^{2-}$

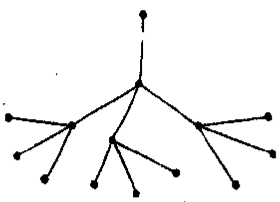
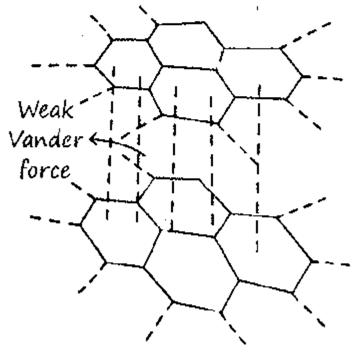
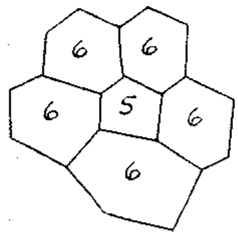
Exist due to vacant 'd' orbitals.

$[SiCl_6]^{2-}$ does not exist due to bigger size of Cl.

PbI_4 does not exist due to I.P.E.

PbF_4 & SnF_4 are ionic in nature.

Allotropes of Carbon

Diamond	Graphite	Fullerenes
1. 3D network solid	1. Layered struc & Layers are held together by weak vander waal forces	1. $\text{Graphite} \xrightarrow[\text{arc}]{\text{electric}} \text{Fullerene}$ Buck ball struc. He or Ne C_{60}----C_{350} $C_{60} \longrightarrow$ Buck minster fullerene (Soccer ball)
2. sp^3	2. sp^2	2. sp^2
3. Non aromatic	3. Aromatic	3. Aromatic
4. dangling Bonds are present	4. dangling bonds are present	4. No dangling bond
5. Good thermal conductor but poor electrical conduetor	5. Good conductor of heat and electricity	5. Good thermal and electrical conductor.
6. Diamond 	6. Graphite 	6. C_{60}  6 Membered Rings = 20 5 Membered Rings = 12
7. abrasive, hardest subs on earth	7. Lubricant, soft, slippery	7. $C_{70} \rightarrow$ Rugby ball

Other forms of elemental Carbon

1. Carbon black
2. Coke
3. Charcoal

These are impure form of Graphite or fullerenes

$$\text{Hydrocarbon} \xrightarrow[\text{Supply of air}/\Delta]{\text{In limited}} \text{Carbon black}$$

$$\text{Wood or coal} \xrightarrow[\text{air}/\Delta]{\text{In absence of}} \text{Coke or Charcoal}$$

Some Imp. Comp. of Carbon

1. CO (Carbon mono oxide)

M.O.P

(1) $2C + O_2 \longrightarrow 2CO$

limited suppy

(2) <u>Lab method</u>

$$HCOOH \xrightarrow[\text{Conc } H_2SO_4]{100°C} CO + H_2O$$

(3) Industrial method

$$C + \underset{H_2O}{Steam} \longrightarrow \underbrace{CO + H_2}_{\text{Syn gas or Water gas}}$$

$$C + air \longrightarrow \underbrace{CO + N_2}_{\text{Producer gas}}$$

Prop #

(1) Colourless, odourless, neutral, poisonous gas.

(2) It is a powerful reducing agent

$$\overset{+3}{Fe_2O_3} + 3\overset{+2}{CO} \xrightarrow{\Delta} 2\overset{0}{Fe} + 3\overset{+4}{CO_2}$$

$$\overset{+2}{ZnO} + \overset{+2}{CO} \xrightarrow{\Delta} \overset{0}{Zn} + \overset{+4}{CO_2}$$

Struc of CO

$$\overset{-}{C} \equiv \overset{+}{O} \qquad C \equiv O$$

1σ, 2π, 2 L.P

B·O = 3

2. Carbon dioxide (CO_2)

MOP

(1) $\underset{(Excess)}{C + O_2} \longrightarrow CO_2$

(2) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

(3) Lab method

$$\overset{2+\,2-}{CaCO_3} + 2\overset{+\,-}{HCl} \longrightarrow CaCl_2 + CO_2 + H_2O$$

(4) Industrial method

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

Prop of CO_2

(1) It is colourless, odourless acidic gas

(2) Solid $CO_2 \longrightarrow$ dry ice

(3) Dissolve in H_2O to form H_2CO_3

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$H_2CO_3 \mid HCO_3^-$ Buffer sol^n

Which maintain the pH of blood

(4) Photosynthesis

$$6CO_2 + 12H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

Struc

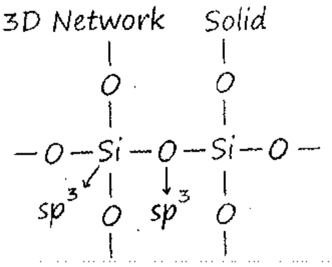
$$O = C = O \longleftrightarrow \overset{-}{O} - C \equiv \overset{+}{O} \longleftrightarrow \overset{+}{O} \equiv C - O^-$$

B·O = 2

2σ, 2π, 4 L.P

Some Imp. Comp of Silicon

1. SiO_2 or $(SiO_2)_n$



Prop

(1) Rxn with HF

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 \xrightarrow{\text{Excess HF}} H_2SiF_6 \text{ (Soluble)}$$

(2) Rxn with NaOH

$$SiO_2 + NaOH \longrightarrow \underset{\text{Sodium Silicate}}{Na_2SiO_3} + H_2O$$

(3) $SiO_2 \longrightarrow$ Crystalline quartz

$SiO_2 \longrightarrow$ Amorphous Silica

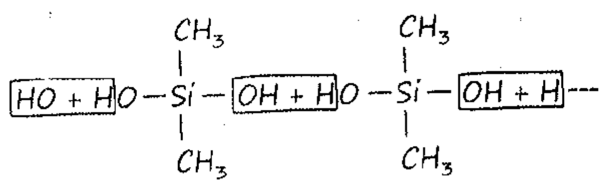
2. Silicones # $[R_2SiO]_n$

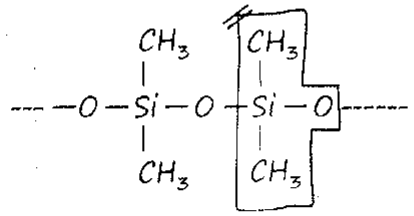
Organo silicon polymer

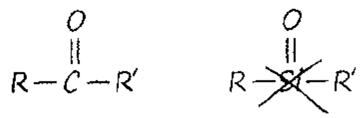
R = alkyl & aryl $[R_nSiCl_{4-n}]$

$$2CH_3Cl + Si \xrightarrow[300°C]{Cu} (CH_3)_2SiCl_2$$

$$(CH_3)_2SiCl_2 \xrightarrow{2H_2O} (CH_3)_2Si(OH)_2$$

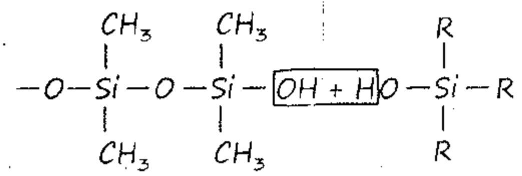


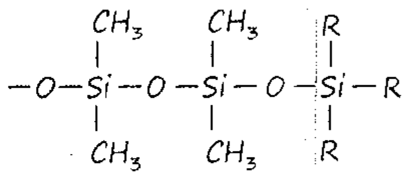




\# Polymer chain can be controlled by adding R_3SiCl

$$R_3SiCl \xrightarrow{H_2O} R_3Si(OH)$$

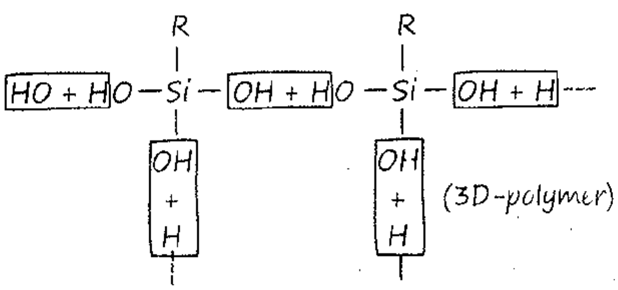




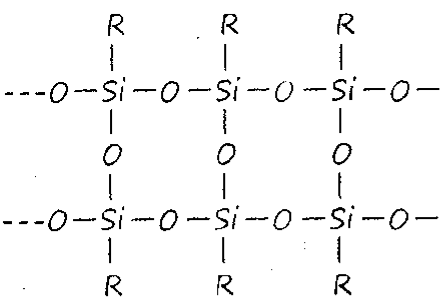
\# $R_3SiCl \xrightarrow{H_2O} R_3SiOH$

$$R_3Si\boxed{OH + H}OSiR_3 \longrightarrow \underset{\text{dimer}}{R_3Si{-}O{-}SiR_3}$$

$$RSiCl_3 \xrightarrow{3H_2O} RSi(OH)_3$$



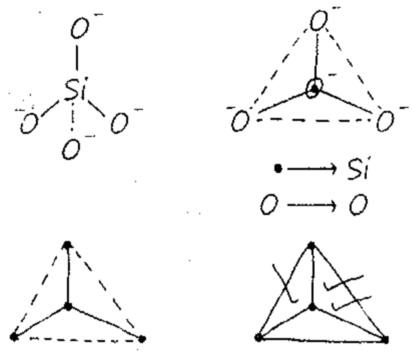
(3D-polymer)



$$CH_3Cl + Si \xrightarrow[\text{Powder}]{Cu} \begin{cases} (CH_3)_4Si \\ (CH_3)_3SiCl \\ (CH_3)_2SiCl_2 \\ CH_3SiCl_3 \end{cases}$$

3. Silicates

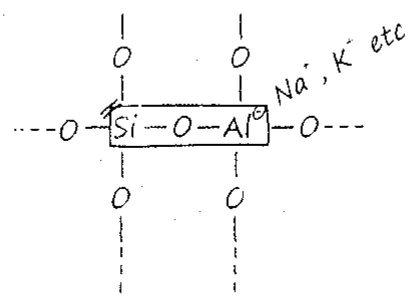
Silicates have SiO_4^{4-} unit



Silicates	Gen. formula	Sharing of 'O' atom
Orthosilicate	SiO_4^{4-}	0
Pyrosilicate	$Si_2O_7^{6-}$	1
Chain or cyclic silicate	$(SiO_3)_n^{2n-}$	2
2D	$(Si_2O_5)_n^{2n-}$	3
3D	$(SiO_2)_n$	4

4. Zeolites

Honeycomb like structure



$\boxed{\text{ZSM-5}}$

$$\underset{ROH}{\text{Alcohol}} \xrightarrow{ZSM-5} \underset{(CH_2)_n}{\text{Gasoline}}$$

\# Used to remove hardness

\# Used in petrochemical industries

Some Imp. points of Carbon family

(1) Hydrolysis of $SiCl_4$

$SiCl_4 \xrightarrow{4H_2O} Si(OH)_4 + HCl$

Silicic acid

(2) Carbon has unique ability to form multiple bonds ($C=C$, $C=O$, $C\equiv N$) due to small size & high E.N.

(3) GeX_4 is more stable than GeX_2 due to stability of $Ge^{+4} > Ge^{2+}$ due to inert pair effect.

(4) PbX_2 is more stable than PbX_4 due to stability of $Pb^{2+} > Pb^{4+}$ due to inert pair effect.

(5) $\underline{Si}F_6^{2-}$, $\underline{Ge}Cl_6^{2-}$, $[\underline{Sn}(OH)_6]^{2-}$

sp^3d^2 sp^3d^2 sp^3d^2

Practice

Q. CCl_4 does not hydrolyse, while $SiCl_4$ does, why?

availability of vacant 'd' orbitals

$CCl_4 \xrightarrow{H_2O}$ No Rxn

$SiCl_4 \xrightarrow{H_2O} Si(OH)_4$

Q. Find acidic, amphoteric & basic oxides?

$\boxed{CO}$	$\boxed{CO_2, SiO_2}$	$\boxed{PbO, SnO}$
Neutral	Acidic	Amphoteric

Q. Thermodynamically most stable allotrope of C is ______

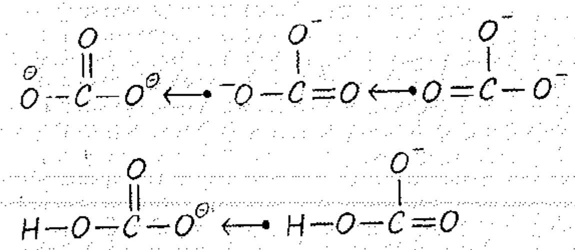
Graphite

$G > F > D$

Q. $\overset{+4}{Pb}Cl_4 \xrightarrow{\Delta} \overset{+2}{Pb}Cl_2 + Cl_2$

Less stable   more stable

Q. Draw Resonating struc of CO_3^{2-} & HCO_3^-



Nitrogen family

E.N ↓ decreases; Size & B.P ↓ increases

N
P
As
Sb
Bi

Exception M.P

$N < P < As > Sb > Bi$

$N < P < Bi < Sb < As$

[MP $\propto$ C.L.E]

Oxidation number

+5 & +3

Stability of +5 O·N decreases down the group

Stability of +3 O·N increases down the group

Due to I.P.E

Stability	Stability	Stability
As^{+5}	As^{+3}	$As^{+5} > As^{+3}$
Sb^{+5}	Sb^{+3}	$Sb^{+5} > Sb^{3+}$
Bi^{+5}	Bi^{+3}	$Bi^{+5} < Bi^{3+}$
Decreases ↓	Increases ↓	

7 p-Block (N + O Family)

NITROGEN FAMILY

Chemical properties:

1. Reactivity towards Hydrogen

(EH_3) Bond energy & Thermal stability & Lewis Basic strength & Bond angle ↓ decreases	$\ddot{N}H_3$, $\ddot{P}H_3$, $\ddot{A}sH_3$, $\ddot{S}bH_3$, $\ddot{B}iH_3$	reducing character ↓ Increases

Exceptions

due to Inter molecular H-Bonding (for NH_3)

1. B.P # $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$
2. M.P # $PH_3 < AsH_3 < SbH_3 < BiH_3 < NH_3$

Hybridisation

$\ddot{N}H_3$ $\underbrace{[PH_3, AsH_3, SbH_3, BiH_3]}_{\text{No hybridisation acc}^n \text{ to drago's Rule}}$

sp^3

2. Reactivity towards Oxygen

$\overset{+3}{E}_2O_3$, $\overset{+5}{E}_2O_5$

Acidic strength

E_2O_3		E_2O_5
N_2O_3		N_2O_5
P_2O_3	Acidic strength decreases ↓	P_2O_5
As_2O_3		As_2O_5
Sb_2O_3		Sb_2O_5
Bi_2O_3		Bi_2O_5

$\overset{+3}{E}_2O_3 < \overset{+5}{E}_2O_5$

N_2O_3, P_2O_3, As_2O_3, Sb_2O_3, Bi_2O_3

Acidic (N_2O_3, P_2O_3) Amphoteric (As_2O_3, Sb_2O_3) Basic (Bi_2O_3)

3. Reactivity towards Halogen $\overset{+3}{E}X_3$, $\overset{+5}{E}X_5$

covalent charac # Fajan's rule

C.C $NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$

C.C $\overset{+5}{E}X_5 > \overset{+3}{E}X_3$

4. Reactivity towards Metals.

$\overset{+2}{M}_3\overset{-3}{E}_2$ – 3 Oxidation state

Ca_3N_2 Calcium nitride

Ca_3P_2 Calcium phosphide

Some Imp. comp. of Nitrogen

1. Dinitrogen (N_2)

M.O.P. (1) $NH_4^+Cl^- + Na^+NO_2^- \rightarrow NaCl + N_2\uparrow + 2H_2O$

$NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$

(2) $\underset{\text{Ammonium dichromate}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{Green}}{Cr_2O_3}\downarrow + N_2\uparrow + 4H_2O$

(3) For very N_2

(N_3^-) $\overset{-}{N}=\overset{+}{N}=\overset{-}{N}$

Azide $\xrightarrow{\Delta} M + N_2\uparrow$

$2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$

$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

Property:

1. N_2 is inert at room temp due to High Bond diss. energy ($N\equiv N$)
2. Rxn with N_2

$M + N_2 \xrightarrow{\Delta}$ Metal nitride $\xrightarrow{H_2O}$ $NH_3\uparrow$ + Hydroxide

$Li + N_2 \xrightarrow{\Delta} Li_3N \xrightarrow{H_2O} LiOH + NH_3$

$Mg + N_2 \longrightarrow Mg_3N_2 \xrightarrow{H_2O} Mg(OH)_2 + NH_3$

3. Haber's process

$N_{2(g)} + 3H_{2(g)} \underset{}{\overset{773\text{ K}}{\rightleftharpoons}} \overset{2}{2}NH_{3(g)} + \text{Heat}$

Fav. cond^n for NH_3 production

Low Temp, High pressure

4. Birkland Eyde process

Heat + $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

Fav. cond^n for NO production

High temp, not affected by pressure

Ammonia (NH_3)

M.O.P 1. From Urea

$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + CO_2 + H_2O$

2. From ammonium salts

(a) $NH_4^+Cl^- + NaOH^- \longrightarrow \underset{(aq.\ NH_3)}{NH_4OH} + NaCl$

(b) $(NH_4^+)_2SO_4^{2-} + Ca^{2+}(OH^-)_2 \longrightarrow 2NH_4OH + CaSO_4$

3. Haber's process

Prop

1. Colourless, Pungent smelling gas
2. Rxn with metal salt

(a) $Zn^{2+}SO_4^{2-} + 2NH_4^+OH^- \longrightarrow \underset{\text{white}}{Zn(OH)_2\downarrow} + (NH_4)_2SO_4$

(b) $FeCl_3 + NH_4OH \longrightarrow \underset{\text{Brown}}{Fe_2O_3 . xH_2O\downarrow} + NH_4Cl$

3. Complex formation

(a) $\underset{\text{White}}{AgCl} + 2NH_4OH \longrightarrow \underset{\text{Colourless}}{[Ag(NH_3)_2]Cl}$ Tollen's reagent

(b) $\underset{\text{Blue}}{CuSO_4} + 4NH_4OH \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]SO_4}$ Schwittzer's reagent

Nitric acid (HNO_3)

M.O.P 1. $NaNO_3 \mid KNO_3 \xrightarrow{H_2SO_4} HNO_3 + NaHSO_4$ or $KHSO_4$

2. Ostwald process

$\underset{\text{(from air)}}{4NH_3 + 5O_2} \xrightarrow[500\ K,\ 9\ bar]{Pt/Rh} 4NO + 6H_2O$

$4NO \longrightarrow NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$

$HNO_2 \xrightarrow{\Delta} NO + HNO_3$

3. Birkland Eyde process

$N_2 + O_2 \rightleftharpoons 2NO \xrightarrow{O_2} NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$

$HNO_2 \xrightarrow{\Delta} NO + HNO_3$

ΔH = +ve

Prop

1. Rxn with non metals

IPS Carbon

$I_2 \xrightarrow{HNO_3} HIO_3 + NO_2 + H_2O$

$P_4 \xrightarrow{HNO_3} H_3PO_4 + NO_2 + H_2O$

$S_8 \xrightarrow{HNO_3} H_2SO_4 + NO_2 + H_2O$

$C \xrightarrow{HNO_3} CO_2 + H_2O + NO_2$

2. Rxn with Metals

$Zn + 4conc.\ HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

$4Zn + 10dil.\ HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

$Cu + 4conc.\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$

$3Cu + 8dil.\ HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

3. Brown ring Test (for NO_3^-)

$\overset{+5}{N}O_3^- + Fe^{2+} \xrightarrow{H^+} Fe^{3+} + \overset{+2}{N}O + H_2O$

$[Fe(H_2O)_6]^{2+} \xrightarrow{NO} [\overset{+1}{Fe}(H_2O)_5\overset{+1}{N}O]^{2+} + H_2O$

Brown ring Complex

$x + 5 \times 0 + 1 = 2$

$\boxed{x = 1}$

4. Rxn of Au & Pt with aqua regia

(Conc HNO_3 + Conc HCl)

1 : 3

$HNO_3 + HCl \longrightarrow NOCl + H_2O + [Cl]$

$Au + [Cl] \longrightarrow AuCl_3 \xrightarrow{HCl} H[\overset{+3}{Au}Cl_4]$

Aurochloric acid

$Pt + [Cl] \longrightarrow PtCl_4 \xrightarrow{HCl} H_2[\overset{+4}{Pt}Cl_6]$

Hexachloro Platinic acid

Oxides of Nitrogen

1. $\overset{+1}{N_2O}$ (Nitrous oxide)

\# O.N = +1

\# Colourless, neutral gas (laughing gas)

\# Struc # $N \equiv N \rightarrow O$ or

$$:N \equiv \overset{+}{N} - \overset{-}{\ddot{O}}:\ \text{(Diamagnetic)}$$

\# M.O.P $\underset{\text{Ammonium nitrate}}{NH_4NO_3} \xrightarrow{\Delta} N_2O + 2H_2O$

2. $\overset{+2}{NO}$ (Nitric oxide)

\# O.N = +2

\# Colourless, neutral gas

\# struc # $:\dot{N} = \ddot{O}:$ (Paramagnetic)

\# M.O.P

$$\underset{\text{Sodium nitrite}}{2NaNO_2} + 2FeSO_4 \xrightarrow{3H_2SO_4} Fe_2(SO_4)_3 + 2NaHSO_4 + 2NO + 2H_2O$$

3. $\overset{+3}{N_2O_3}$ (Nitrogen sesqui oxide)

\# O.N = +3

\# Blue solid, acidic

\# struc # $\ddot{O}=\ddot{N}-\ddot{O}-\ddot{N}=\ddot{O}$

(Diamagnetic)

or $\overset{O}{\overset{\|}{N}} - \overset{O}{\overset{\|}{N}} \rightarrow O$ or $:\ddot{O}=\ddot{N}-\overset{+}{N}(-\ddot{O}:^-)=\ddot{O}$

\# M.O.P #

$$2NO + \underset{(NO_2)}{N_2O_4} \xrightarrow{250\ K} 2N_2O_3$$

4. $\overset{+4}{NO_2}$ (nitrogen dioxide)

\# O.N = +4

\# Brown acidic gas

\# struc # $O=\dot{N}\longrightarrow O$ or $O=\overset{\bullet}{\underset{+}{N}}-O^-$

(Para)

\# M.O.P

Metal nitrate $\xrightarrow{\Delta}$ $MO + NO_2 + O_2$

M = Alkaline earth metal, Pb, Zn, Cu, Li

$$2Pb(NO_3)_2 \xrightarrow{400°C} 2PbO + 4NO_2 + O_2$$

5. $\overset{+4}{N_2O_4}$ (di Nitrogen tetra oxide)

\# O.N = +4

\# Colourless acidic solid/liq.

\# struc # $O \leftarrow \overset{O}{\overset{\|}{N}} - \overset{O}{\overset{\|}{N}} \rightarrow O$ or $\overset{-}{O} - \underset{+}{\overset{O}{\overset{\|}{N}}} - \underset{+}{\overset{O}{\overset{\|}{N}}} \rightarrow \overset{-}{O}$

\# M.O.P # $\underset{\text{Brown}}{2NO_2} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \underset{\text{Colourless}}{N_2O_4}$

6. $\overset{+5}{N_2O_5}$ (dinitrogen penta oxide)

\# O.N = +5

\# Colourless acidic solid

\# struc # $O \leftarrow \overset{O}{\overset{\|}{N}} - O - \overset{O}{\overset{\|}{N}} \rightarrow O$

or $\overset{-}{O} - \underset{+}{\overset{O}{\overset{\|}{N}}} - O - \underset{+}{\overset{O}{\overset{\|}{N}}} - \overset{-}{O}$

\# M.O.P

$$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$$

\# Solid $N_2O_5 \Longrightarrow \underset{sp}{NO_2^+}\ \underset{sp^2}{NO_3^-}$

Phosphorus

White phosphorus

M.O.P 1. From thomas slag

$$Ca_3(PO_4)_2 + SiO_2 \longrightarrow CaSiO_3 + P_4O_{10}$$

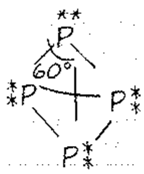
$$P_4O_{10} \xrightarrow{\text{Coke} + \Delta} \underset{\text{White}}{P_4} + CO$$

Prop

1. White waxy solid
2. Insoluble in H_2O but soluble in CS_2
3. Glows in dark
4. Kept under water

Structure

P_4 (White)



(a) sp^3

(b) Trigonal pyramid

(c) $\angle PPP = 60$

(d) Total P - P Bond = 6

(e) L.p = 4

Chemical Rxns

1. Rxn with alkali

$$\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow \overset{-3}{P}H_3 + 3NaH_2\overset{-1}{P}O_2$$

Sodium Hypo Phosphite

Dispropor.

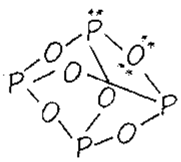
2. Rxn with oxygen

$$\underset{(air)}{P_4 + O_2} \xrightarrow{Limited} P_4O_6$$

$$\underset{(Excess)}{P_4 + 5O_2} \longrightarrow P_4O_{10}$$

Struc

1. P_4O_6



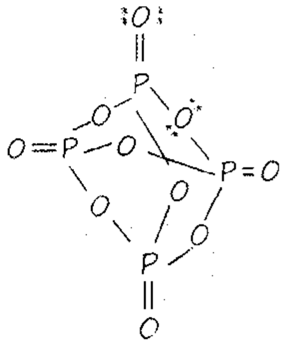
Sigma Bond = 12

π Bond = 0

L.p = 16

Hybridisation of P = sp^3

2. P_4O_{10}



Sigma Bonds = 16

π Bond = 4

Hybri of P = sp^3

$P_\pi - d_\pi$ Bonds = 4

L.p = 20

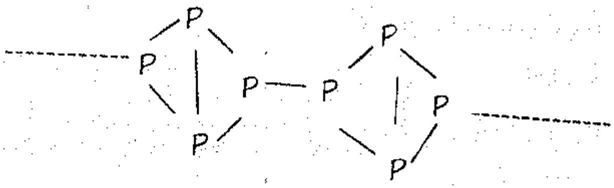
Red Phosphorus

M.O.P # White $P_4 \xrightarrow{300°C}$ Red P_4

Prop

1. non poisonous in nature
2. does not glow in dark
3. Insoluble in both H_2O & CS_2

Structure # Polymeric form



Black Phosphorus

$$\text{Red } P_4 \xrightarrow{530°C} \alpha\text{-Black (Rhombic)}$$

$$\text{Red } P_4 \xrightarrow{200°C} \beta\text{-Black (Monoclinic)}$$

Reactivity W > R > B

Stability W < R < B

Phosphorus (PH_3)

M.O.P #

1. From Ca_3P_2 (Calcium phosphide)

$$\overset{2+}{Ca_3}\overset{3-}{P_2} \xrightarrow[H^+OH^-]{H_2O} Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 \xrightarrow{H^+Cl^-} CaCl_2 + PH_3$$

2. Lab Method

$$\underset{White}{P_4} + 3NaOH + 3H_2O \xrightarrow[\text{atm of } CO_2]{\text{In Inert}} PH_3 + 3NaH_2PO_2$$

Prop

1. Colourless gas
2. Poisonous in nature
3. Basic in nature

$$PH_3 + HBr \longrightarrow PH_4^+Br^-$$

$$PH_3 \xrightarrow{HI} PH_4^+I^-$$

4. Rxn with metal salts

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

Black

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

5. Rotten fish smell
6. non inflammable when pure, but becomes inflammable in presence of P_2H_4 or P_4 vapours.

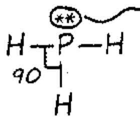
7. For purification of PH_3

$$\underset{\text{(Impure)}}{PH_3} + HI \longrightarrow PH_4I \xrightarrow{KOH} KI + H_2O + \underset{\text{Pure}}{PH_3}$$

8. It explodes in presence of O.A like HNO_3, Cl_2 & Br_2 vap

9. $PH_3 \xrightarrow[h\nu]{H_2O} \underset{\text{Red}}{P_4} + H_2$

10. Hybridisation of P
No hybridisation acc^n to drago's rule



Halides of Phosphorus

PCl_3 #

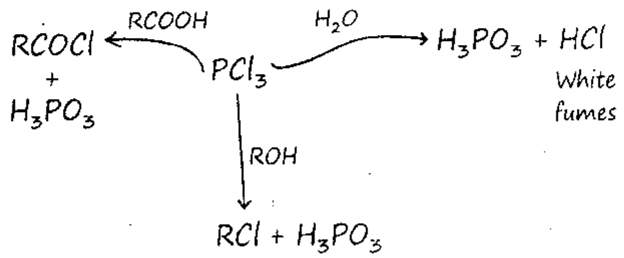
M.O.P # 1. $P_4 + 6Cl_2 \xrightarrow{dry} 4PCl_3$

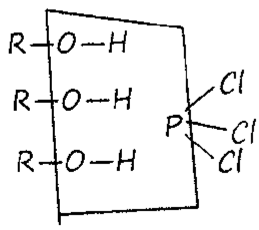
2. $P_4 + \underset{\text{Thionyl Chloride}}{8SOCl_2} \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

Cl—S—S—Cl
③ ② ② ③
10L.P

Prop. # 1. Colourless oily liq

2.





3. sp^3, Trigonal Pyramidal

Halides of Phosphorus

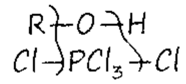
PCl_5 #

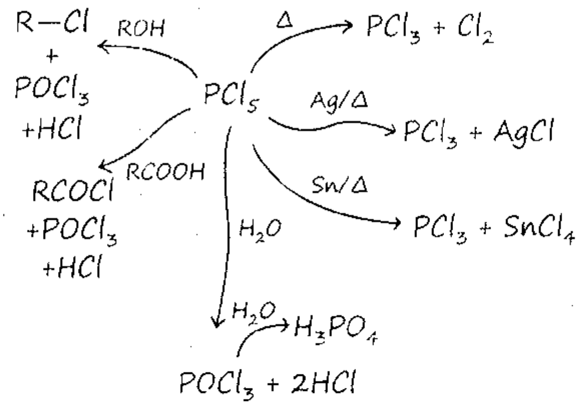
M.O.P # 1. $P_4 + 10Cl_2 \xrightarrow{dry} 4PCl_5$

2. $P_4 + \underset{\text{(Sulphuryl Chloride)}}{10SO_2Cl_2} \longrightarrow 4PCl_5 + 10SO_2$

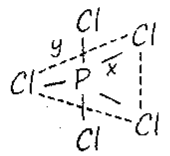
Prop. # 1. Yellowish powder

2.





3. Struc



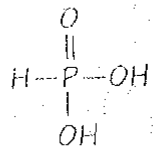
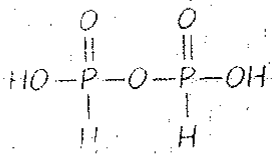
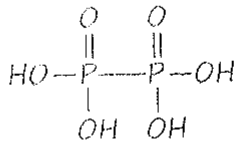
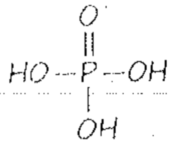
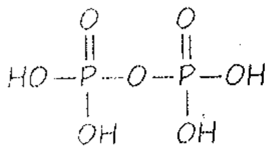
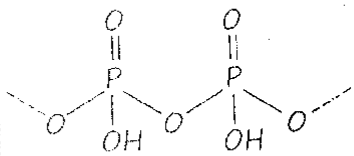
T.B.P (sp^3d)
B.L y > x

4. Solid PCl_5

PCl_4^+ PCl_6^-
sp^3 sp^3d^2

Oxyacids of phosphorus

Name	Formula	Structure	M.O.P	Basicity
(1) Hypophosphorous acid (Phosphinic acid)	$\overset{+1}{H_3PO_2}$	$H-\overset{\overset{O}{\parallel}}{\underset{\underset{H}{\vert}}{P}}-OH$	White $\overset{0}{P_4}$ + NaOH $\downarrow$ $\overset{-3}{PH_3} + NaH_2\overset{+1}{P}O_2 \xrightarrow{H^+} H_3PO_2$	1

(2) Ortho phosphorous acid (Phosphonic acid)	$H_3\overset{+3}{P}O_3$		$P_2O_3 + H_2O \rightarrow H_3PO_3$	2
(3) Pyro phosphorous acid	$H_4\overset{+3}{P_2}O_5$		$PCl_3 + H_3PO_3 + H_2O \rightarrow H_4P_2O_5$	2
(4) Hypophosphoric acid	$H_4\overset{+4}{P_2}O_6$ $4 + 2x - 12 = 0$ $x = 4$		Red P_4 + NaOH $\downarrow$ $H_4P_2O_6$	4
(5) Ortho phosphoric acid	$H_3\overset{+5}{P}O_4$		$P_2O_5 + H_2O \rightarrow H_3PO_4$	3
(6) Pyro phosphoric acid	$H_4\overset{+5}{P_2}O_7$		$2H_3PO_4 \xrightarrow{\Delta} H_4P_2O_7$	4
(7) Poly meta phosphoric acid	$(HPO_3)_n$		$H_3PO_3 + Br_2$	–

Some Imp. points of N-family

1. Dispro of H_3PO_3

$$4H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$$

2. Rxn of $AgNO_3$ with H_3PO_2

$$4\overset{+1}{Ag}NO_3 + H_3\overset{+1}{P}O_2 + 2H_2O \longrightarrow H_3\overset{+5}{P}O_4 + 4\overset{0}{Ag} + 4HNO_3$$

3. Hydrolysis of trichlorides

$$NCl_3 \xrightarrow{H_2O} NH_3 + HOCl$$

$$PCl_3 \xrightarrow{H_2O} H_3PO_3 + \underset{\text{White fumes}}{HCl}$$

$$AsCl_3 \xrightarrow{H_2O} As_2O_3 + HCl$$

$$SbCl_3 \xrightarrow{H_2O} SbOCl + HCl$$

$$BiCl_3 \xrightarrow{H_2O} BiOCl + HCl$$

Pearl white
Bismuth oxy chloride

4. Nitrolim $CaC_2 + N_2$

$$\underset{\text{Calcium Carbide}}{CaC_2} + N_2 \longrightarrow \underset{\text{Calcium Cyanamide}}{CaCN_2} + C$$

$$CaCN_2 \xrightarrow{H_2O} CaCO_3 + NH_3\uparrow$$

5. Solid PCl_5 exist as a dimer

$\underset{sp^3}{[PCl_4]^+}$ $\underset{sp^3d^2}{[PCl_6]^-}$

6. Solid PBr_5 exists as $\underset{sp^3}{[PBr_4]^+}$ Br^-

7. Solid N_2O_5 exist as Nitronium nitrate

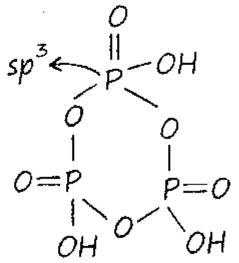
$\underset{sp}{NO_2^+}$ $\underset{sp^2}{NO_3^-}$

8. Holme's signal

$CaC_2 + Ca_3P_2$

9. Structure of $(HPO_3)_3$

Cyclic trimeric metaphosphoric acid



σ Bonds = 15

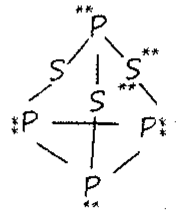
π Bonds = 3

P—O Bonds = 9

$p\pi$-$d\pi$ Bonds = 3

P—O—P Bonds = 3

10. Structure of P_4S_3



σ Bonds = 9

π Bonds = 0

L.p = 10

11. Ammonia can be dried over quick lime (CaO)

12. Rxn of NH_3 with Cl_2

$$\underset{\text{(Excess)}}{NH_3 + Cl_2} \longrightarrow NCl_3 + HCl$$

$$\underset{\text{(excess)}}{NH_3} + Cl_2 \longrightarrow NH_4Cl + N_2$$

13. Rxn of NH_3 with $CaOCl_2$

$$NH_3 + CaOCl_2 \longrightarrow N_2\uparrow$$

14. Rxn of NH_2OH with HNO_2

$$NH_2OH + HNO_2 \longrightarrow \boxed{N_2O}$$

15. Acid Anhydride concept

Acid	Anhy
$2HNO_3$	N_2O_5
$2HNO_2$	N_2O_3
$HNO_2 + HNO_3$	$N_2O_4 \rightarrow NO_2$

16. N does not form pentahalides due to non availability of vacant 'd' orbitals.

17. All trihalides of N except NF_3 are unstable. Only NF_3 is stable due to great extent of overlapping.

18. All trihalides except BiF_3 are covalent in nature, BiF_3 is ionic due to Fajan's rule.

19. $BiCl_5$ does not exist due to I.P.E

20. Cr & Al do not react with HNO_3 due to formation of passive film of oxide Cr_2O_3 Al_2O_3

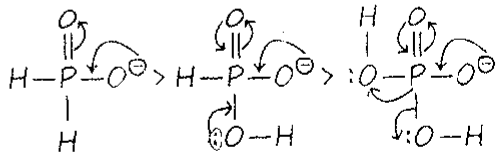
Practice

Q. Compare acidic strength

H_3PO_2 , H_3PO_3 , H_3PO_4

$$\overset{+1}{H_3PO_2} > \overset{+3}{H_3PO_3} > \overset{+5}{H_3PO_4}$$

Stability



Q. Why does $R_3P = O$ exist but $R_3N = O$ does not?

due to non availability of vacant 'd' orbitals in N

Q. N show catenation less than P?

$\ddot{N}$-$\ddot{N}$ due to LP-LP repulsion in N

Q $PCl_5 + D_2O \longrightarrow D_3PO_4 + DCl$

Oxygen Family

Size & MP & BP & density ↓	O, S, Se, Te, Po	I.E & E.N ↓
Increases		decreases

Electron affinity (E_A):

$S > Se > Te > PO > O$ due to compact Nature

Oxidation No.

+4 & +6

Stability of +6 O.N decreases

+4 O.N increases

Stability ↓	Stability ↓
Se^{+6}	Se^{+4}
Te^{+6}	Te^{+4}
PO^{+6}	PO^{+4}
decreases	Increases

due to I.P.E

Stability

$Se^{+6} > Se^{4+}$; $Te^{+6} > Te^{+4}$

$PO^{+6} < PO^{4+}$

O.N of oxygen

O_2		zero
O^{2-}	Oxide	-2
O_2^{2-}	Peroxide	-1
O_2^-	Superoxide	$-1/2$
$O_2^+[AsF_6]^-$		$+1/2$
KO_3		$-1/3$
OF_2		$+2$
O_2F_2		$+1$

Prop

1. Reactivity Towards Hydrogen

B.E & T.S & Bond angle		Acidic strength & Reducing Nature & Bond length
↓	H_2O	↓
	H_2S	
	H_2S_e	
	H_2T_e	
	H_2P_o	
decreases		Increases

(B.P & M.P) due to intermolecular H-Bonding

$H_2S < H_2Se < H_2Te < H_2PO < \boxed{H_2O}$

2. Reactivity towards oxygen

Oxidising power Increases ↓			O.P Increases ↓
	EO_2	EO_3	
	O_3	–	
	SO_2	SO_3	
	SeO_2	SeO_3	
	TeO_2	TeO_3	
	PoO_2	PoO_3	

O.P $EO_3 > EO_2$

3. Reactivity towards halogen

EX_4 EX_6

Covalent charac. $EX_6 > EX_4$

(Fajan's rule)

Small cation, Bigger anion.

Some Imp. comp. of oxygen

1. Dioxygen #

M.O.P

1. $MNO_3 \xrightarrow{\Delta} M_2O + NO_2 + O_2$

$M = Li$

$MNO_3 \xrightarrow{\Delta} MNO_2 + O_2$

M = all alkali except Li

$M(NO_3)_2 \longrightarrow MO + NO_2 + O_2$

M = all alkaline earth metal Zn, Cu, Pb

2. $KClO_3 \xrightarrow{\Delta} KCl + O_2$

3. $KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

Purple Green Brown

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

Orange-Red Yellow green

5. $Pb_3O_4 \xrightarrow{\Delta} PbO + O_2$

minium or Red Lead or sindoor — Litharge

6. $H_2O_2 \xrightarrow{\Delta} H_2O + O_2$

7. $Ag_2O \xrightarrow{\Delta} Ag + O_2$

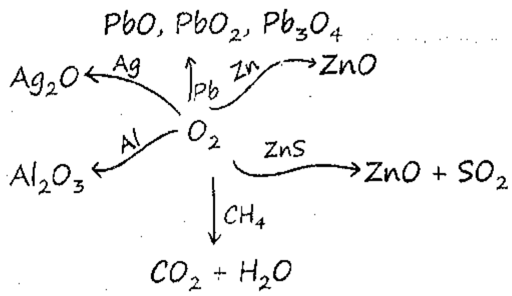
$HgO \xrightarrow{\Delta} Hg + O_2$

8. Electro of H_2O

Cathode $4H^+ + 4e^{\ominus} \longrightarrow 2H_2$

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

Prop. of dioxygen



\# Colourless paramagnetic gas (two unparied e's),

B.O = 2

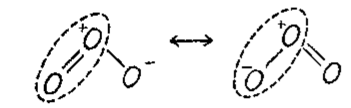
O_3 (Ozone)

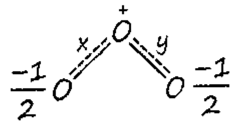
M.O.P 1. $3O_2 \underset{\text{discharge}}{\overset{\text{electric}}{\rightleftharpoons}} 2O_3$

Prop

1. O_3 is pale blue gas, dark blue liq, violet black solid

2. Struc





B.L $x = y$

B.O $= \frac{3}{2} = 1.5$

3. Chemical Rxn

O_3 is a powerful O.A

$2O_3 \rightarrow 3O_2$
$\Delta S > 0$
$\Delta H < 0$
$\Delta G < 0$

$O_3 \longrightarrow O_2 + [O]$

$O_3 \xrightarrow{PbS} PbSO_4 + O_2$

$O_3 \xrightarrow[H_2O]{KI} I_2 + KOH + O_2$

$O_3 \xrightarrow{NO} O_2 + NO_2$

$O_3 \xrightarrow{Pb} PbO + O_2$

$O_3 \xrightarrow{SO_2} O_2 + SO_3$

Allotropes of S

α-Sulphur # It is formed by evaporating the sol^n of S in CS_2.

$$(S_8)\ \alpha \underset{}{\overset{96^\circ C}{\rightleftharpoons}} \beta\ (S_8)$$

(96°C → Transition Temp)

Rhombic	Monoclinic
Yellow	colourless

(1) at 96°C	Both are stable
(2) T < 96°C	α stable
(3) T > 96°C	β stable

Some Imp. comp. of oxygen

SO_2

M.O.P 1. $S + O_2 \longrightarrow SO_2$

2. Lab Method

$SO_3^{2-} + H^+ \longrightarrow H_2SO_3 \longrightarrow SO_2 + H_2O$

3. Industrial method

$\overset{+2}{Fe}\,^{-1}S_2 + O_2 \longrightarrow \overset{+3}{Fe_2}O_3 + SO_2$

4. $Cu + \text{Conc } H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

Prop

1. Colourless gas
2. Pungent smell
3. Soluble in H_2O
4. liq at Room temp

SO_2

Chemical Rxns

$\overset{+4}{SO_2} \xrightarrow[H^+]{\overset{+6}{K_2Cr_2O_7}} \overset{+6}{K_2SO_4} + H_2O + \overset{+3}{Cr_2}\overset{+6}{(SO_4)_3}$

$SO_2 \xrightarrow[H_2O]{\overset{+7}{KMnO_4}} \overset{+2}{Mn}\overset{+6}{SO_4} + H_2\overset{+6}{SO_4} + K_2\overset{+6}{SO_4}$

$SO_2 \xrightarrow[H_2O]{Fe^{3+}} Fe^{2+} + SO_4^{2-} + H^+$

$SO_2 \xrightarrow[V_2O_5]{O_2} SO_3$

$SO_2 \xrightarrow{H_2S} S + H_2O$

$SO_2 \xrightarrow{NaOH} Na_2SO_3 \xrightarrow[SO_2 + H_2O]{Excess} NaHSO_3$

$SO_2 \xrightarrow{O_2} SO_3$

$SO_2 \xrightarrow[Charcoal]{Cl_2} \underset{SO_2Cl_2}{(A)} \xrightarrow{\text{White } P_4} \underset{\text{Oxide } SO_2}{(B)} + \underset{PCl_5}{(C)} \xrightarrow{H_2O} (D)\ H_3PO_4$

Some Imp. comp. of Sulphur

SO_2

\# SO_2 acts as bleaching agent

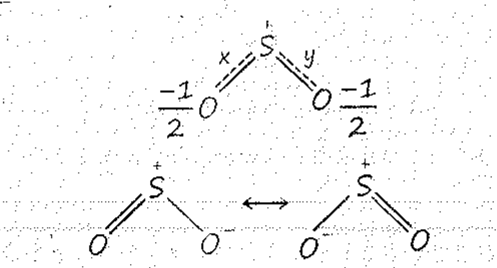
$SO_2 + H_2O \longrightarrow H_2SO_4 + [H]$

$[H]$ + Coloured matter $\longrightarrow$ Colourless $[O]$

\# Reductive bleaching

\# Temporary bleaching

Struc.



Bent shape, B.O = 1.5, B.L $\Rightarrow x = y$

H_2SO_4 King of chemicals

Prop

Chemical Rxns

$H_2SO_4 \xrightarrow{MX} MHSO_4 + HX$

$H_2SO_4 \xrightarrow{MX_2} M_2SO_4 + HX$

$H_2SO_4 \xrightarrow{PCl_5} POCl_3 + SO_2Cl_2 + HCl$

$H_2SO_4 \xrightarrow{S} SO_2 + H_2O$

$H_2SO_4 \xrightarrow{KI} I_2 + SO_2 + H_2O$

$H_2SO_4 \xrightarrow{C} CO_2 + SO_2 + H_2O$

$H_2SO_4 \xrightarrow{\text{Sucrose } C_{12}H_{22}O_{11}} 12C + 11\ H_2O$ (Charring of sugar)

$Na_2S_2O_3$ Sodium thio sulphate

$[Na_2S_2O_3 \cdot 5H_2O$ (Hypo)$]$

M.O.P 1. $S + Na_2SO_3 \longrightarrow Na_2S_2O_3$

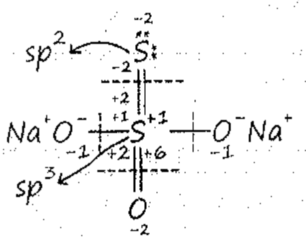
2. $\overset{0}{S} + NaOH \longrightarrow Na_2\overset{-2}{S} + Na_2\overset{+2}{S_2}O_3$

(Dispropor. Rxn)

3. $I_2 + Na_2S + Na_2SO_3 \longrightarrow NaI + Na_2S_2O_3$

Prop

1. Structure



$H_2SO_4 \longrightarrow H_2S_2O_3 \longrightarrow Na_2S_2O_3$

$Na_2S_2O_3$ (Sodium thiosulphate)

Chemical Rxns

$Na_2S_2O_3 \xrightarrow{Cl_2,\ H_2O} NaHSO_4 + HCl$ Antichlor

$Na_2S_2O_3 \xrightarrow{I_2} NaI + Na_2S_4O_6$

$Na_2S_2O_3 \xrightarrow{AgBr} NaBr + Na_3[Ag^{+1}(S_2O_3)_2]$

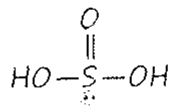
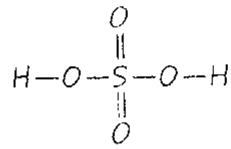
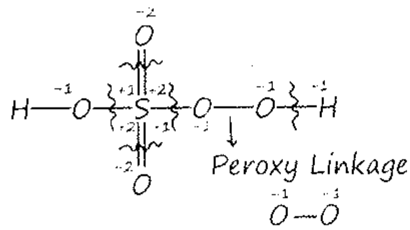
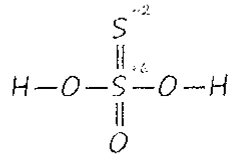
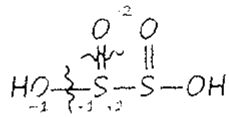
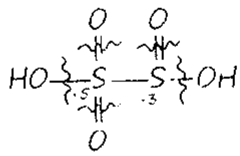
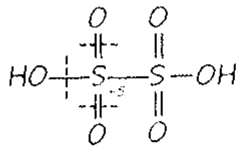
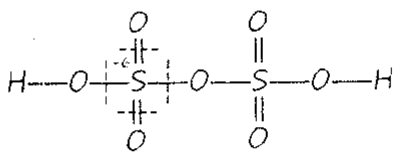
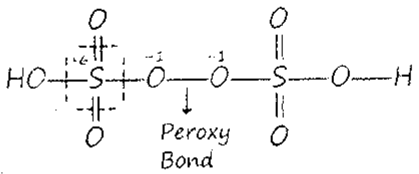
Sodium argento thiosulphate.

fixer in photography

$Na_2S_2O_3 \xrightarrow{AgNO_3} \underset{\text{White}}{Ag_2S_2O_3\downarrow} + NaNO_3$

$Ag_2S_2O_3 \xrightarrow{H_2O} \underset{\text{Black}}{Ag_2S\downarrow} + H_2SO_4$

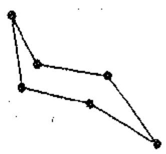
Oxyacids of Sulphur

Formula	O.N	Name	Structure
(1) H_2SO_3	+4	Sulphurous acid	
(2) H_2SO_4	+6	Sulphuric acid	
(3) H_2SO_5	+6	Caro's acid or peroxo mono sulphuric acid	
(4) $H_2S_2O_3$	−2 & +6	Thiosulphuric acid	
(5) $H_2S_2O_4$	+3	dithionous acid	
(6) $H_2S_2O_5$	+5 & +3	Pyrosulphurous acid	
(7) $H_2S_2O_6$	+5	Dithionic acid	
(8) $H_2S_2O_7$	+6	Oleum or pyrosulphuric acid	
(9) $H_2S_2O_8$	+6	Marshall's acid or peroxo disulphuric acid	

Some Imp. points of chalcogens

1. OF_6 does not exist due to absence of vacant 'd' orbitals.
2. All hexahalides of S are unstable except SF_6
3. SF_6 does not hydrolyse
4. $\overset{+1}{Se_2Cl_2} \longrightarrow \overset{+4}{SeCl_4} + \overset{0}{Se}$
   Dispropor
5. Struc of S_8, S_6
   S_8 Puckered Ring
   Crown shape

   S_6 Chair form



   S_2 paramagnetic just like O_2
   Exist at 1000 K
6. Tailing of Hg # Disturbance of $\overrightarrow{\text{Menis}}$ $\overleftarrow{\text{cus}}$ of Hg by passing ozone
   $Hg + O_3 \longrightarrow Hg_2O + O_2$
7. Estimation of ozone ÷
   $KI + H_2O + O_3 \longrightarrow I_2 + KOH + O_2$
   $I_2 + Na_2S_2O_3 \longrightarrow NaI + Na_2S_2O_3$
8. SO_2 turns lime water milky
   $SO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milky}}{CaSO_3}$
   $CaSO_3 + \underset{\text{(Excess)}}{SO_2} + H_2O \longrightarrow \underset{\text{Soluble}}{Ca(HSO_3)_2}$

Practice

Q. H_2O is liq, while H_2S is gas why?

Due to intermolecular H Bonding in H_2O.

Q. Which of the following does not react with oxygen directly?

(A) Zn (B) Ti

(C) Pt (D) Fe

Au & Pt Noble metal

Q. Which is mixed oxide?

(A) Mn_2O_7 (B) PbO_2

(C) Fe_3O_4 (D) ZnO

Oxide
- Simple
  - Acidic $[\overset{+7}{Mn_2O_7}, \overset{+6}{CrO_3}]$ (Acidic oxide)
  - Basic (CrO)
  - Ampho (V_2O_5)
- Neutral
- Mixed
  - Fe_3O_4 $(\overset{+2}{FeO} \cdot \overset{+3}{Fe_2O_3})$
  - Pb_3O_4 $(2\overset{+2}{PbO} \cdot \overset{+4}{PbO_2})$

Q. $Al_2O_3 \xrightarrow[H_2O]{HCl} [Al(H_2O)_6]^{3+} + Cl^{\ominus}$

$Al_2O_3 \xrightarrow{NaOH/H_2O} Na_3[Al(OH)_6]$

8 Halogens

Size, BP, MP, density	F, Cl, Br, I	I.E, EN
Increases ↓		↓ Decreases

Exception:-

Electron gain enthalpy

due to vacant 'd' orbitals $Cl > F > Br > I$

F_2 Yellow gas

Cl_2 Greenish yellow gas

Br_2 Reddish brown liq

I_2 Violet black solid

1. Oxidising power

$F_2 > Cl_2 > Br_2 > I_2$

2. Exception — due to L.p-L.p repulsion

B.D.E $Cl_2 > Br_2 > F_2 > I_2$

Chemical Prop

1. Reactivity towards Hydrogen

Acidic strength & Reducing power & Bond length		B.D.E & T.S & Stability
	HF	
	HCl	
	HBr	
	HI	
Increases ↓		↓ Decreases

Exception — due to inter. H Bonding

(1) B.P $HCl < HBr < HI < HF$

(2) M.P $HCl < HBr < HF < HI$

2. Reactivity towards Metals

$MX \quad MX_2 \quad MX_3$ ....

$MX \quad MX_2$

C·C $MX_2 > MX$ (Fajan's rule)

C·C $LiF < LiCl < LiBr < LiI$

C·C $LiF > NaF > KF > RbF > CsF$

Solubility of silver halides

AgF	> AgCl	> AgBr	> AgI
Soluble	White ppt	Pale yellow ppt	Yellow ppt

3. Reactivity of halogen with other halogens

Inter halogen comp $\overset{+1}{XX'} \quad \overset{+3}{XX'_3} \quad \overset{+5}{XX'_5} \quad \overset{+7}{XX'_7}$

$X \longrightarrow$ Bigger size

$X' \longrightarrow$ Small size

Inter halogen comp are usually more reactive than halogens

$XX' > X_2$

Some Imp. Comp. of Cl

Cl_2

M.O.P

1. From pyrolusite

(a) $\overset{+4}{MnO_2} + 4H\overset{-1}{Cl} \longrightarrow \overset{+2}{MnCl_2} + \overset{0}{Cl_2} + 2H_2O$

(b) $\underline{MnO_2} + \underbrace{4NaCl + 4H_2SO_4}_{\underline{HCl} + NaHSO_4}$

$\longrightarrow MnCl_2 + Cl_2 + 2H_2O + 4NaHSO_4$

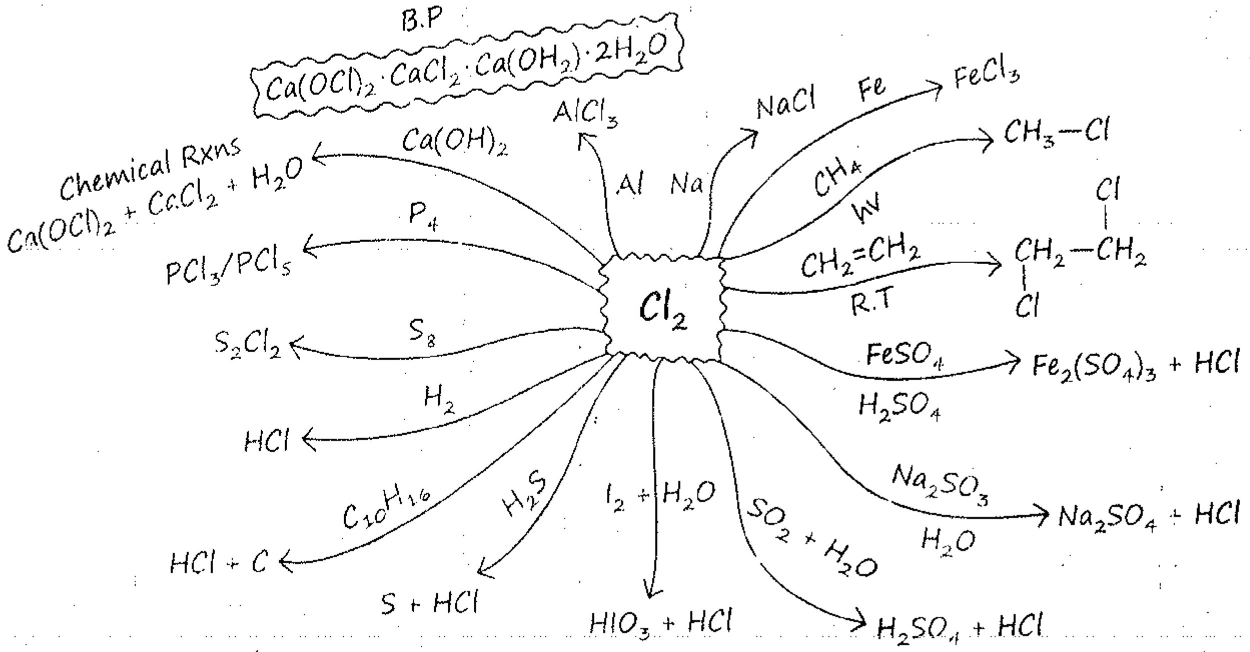
2. Deacon's process

$$4HCl + O_2 \xrightarrow[723\ K]{CuCl_2} 2Cl_2 + 2H_2O$$

3. Electrolysis of Molten NaCl

At cathode: $Na^+ + e^{\ominus} \longrightarrow Na_{(s)}$

At anode: $Cl^{\ominus} \longrightarrow \frac{1}{2}Cl_2\uparrow + e^{\ominus}$



2. Rxn with NH_3

$$3Cl_2 + \underset{\text{(Excess)}}{8NH_3} \longrightarrow 6NH_4Cl + N_2$$

$$\underset{\text{Excess}}{3Cl_2} + NH_3 \longrightarrow \underset{\text{Explosive}}{NCl_3} + HCl$$

3. Rxn with alkali

$$2\overset{0}{X_2} + \underset{\text{(Cold \& dil)}}{NaOH} \longrightarrow \underset{\text{Sodium halide}}{Na\overset{-1}{X}} + H_2O + \underset{\text{Sodium hypohalite}}{Na\overset{+1}{X}O}$$

$$3\overset{0}{X_2} + \underset{\text{Hot \& conc.}}{6NaOH} \longrightarrow \underset{\text{Sodium halide}}{5Na\overset{-1}{X}} + 3H_2O + \underset{\text{Sodium halate}}{Na\overset{+5}{X}O_3}$$

$\boxed{X = Cl, Br, I}$

Dispropor Rxn

4. Bleaching prop #

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$\downarrow$$

$$HCl + [O]$$

$$\downarrow \text{Coloured}$$

Colourless

\# oxidative bleaching

\# permanent bleaching

2. HCl

M.O.P

(1) $NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$

$NaCl + NaHSO_4 \xrightarrow{823\ K} Na_2SO_4 + HCl$

Prop

(1) $NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl}$

(2) $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$

$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$

$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O$

(3) Rxn of Au and Pt with aq. regia

Aq regia $\begin{pmatrix} HNO_3 + HCl \\ 1 : 3 \end{pmatrix}$

$$\overset{0}{Au} + H\overset{+5}{N}O_3 + 4HCl \rightarrow H\overset{+3}{Au}Cl_4 + \overset{+2}{N}O + 2H_2O$$

$$3\overset{0}{Pt} + 4H\overset{+5}{N}O_3 + 18HCl \rightarrow 3H_2\overset{+4}{Pt}Cl_6 + 4\overset{+2}{N}O + 8H_2O$$

(4) Rxn of Fe with HCl

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

Oxy acids of Chlorine

Formula	Name	Structure	O.N
Halic (I) acid $HClO$	Hypo chlorous acid	$Cl-OH$	+1
Halic (III) acid $HClO_2$	Chlorous acid	$O=Cl-OH$	+3
Halic (V) acid $HClO_3$	Chloric acid	$O=\overset{\overset{\displaystyle O}{\Vert}}{Cl}-OH$	+5
Halic (VII) acid $HClO_4$	Perchloric acid	$O=\underset{\underset{\displaystyle O}{\Vert}}{\overset{\overset{\displaystyle O}{\Vert}}{Cl}}-OH$	+7

Some Imp. points of Halogens

1. <u>Occurence</u>

$F \rightsquigarrow$ Fluoroapatite $3Ca_3(PO_4)_2 \cdot CaF_2$

$F \rightsquigarrow$ Fluorspar CaF_2

$F \rightsquigarrow$ Cryolite Na_3AlF_6

$Cl \rightsquigarrow$ Chloroapatite, $3Ca_3(PO_4)_2 \cdot CaCl_2$

$Cl \rightsquigarrow$ Common salt $NaCl$

$Cl \rightsquigarrow$ Carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$

$Br \longrightarrow$ Sea Water

$I \longrightarrow$ Caliche
($NaNO_3 + NaIO_3$)

2. Non metal displacement Rxn

I

Br

Cl

F

$F_2 \xrightarrow{KI} I_2 + KF$

$F_2 \xrightarrow{KBr} Br_2 + KF$

$F_2 \xrightarrow{KCl} Cl_2 + KF$

$Cl_2 \xrightarrow{KF} X$

$Cl_2 \xrightarrow{KBr} Br_2 + KCl$

$Cl_2 \xrightarrow{KI} I_2 + KCl$

$Br_2 \xrightarrow{KF} X$

$Br_2 \xrightarrow{KCl} X$

$Br_2 \xrightarrow{KI} I_2 + KBr$

$I_2 \xrightarrow{KF} X$

$I_2 \xrightarrow{KCl} X$

$I_2 \xrightarrow{KBr} X$

$I_2 + KI \downarrow KI_3$

3. Rxn of F_2 with alkali

$F_2 + NaOH \longrightarrow NaF + H_2O + OF_2$
(Cold & dil)

$F_2 + NaOH \longrightarrow NaF + H_2O + O_2$
(Hot & conc)

4. Rxn of F_2 & Cl_2 with H_2O

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

$F_2 + H_2O \longrightarrow HF + O_2 + O_3$

5. Rxn of NH_3 with $NaOCl$

$NH_3 + NaOCl \longrightarrow Cl_2 + NaOH + NH_2 - NH_2$

6. Rxn of Cl_2 with H_2O_2

$$\boxed{Cl_2 + H_2}O_2 \longrightarrow O_2 + 2HCl$$

7. Rxn of HF with SiO_2 (Etching of glass)
(Excess)

$$HF + SiO_2 \longrightarrow H_2SiF_6$$

8. Heating of $HClO_3$

$$HClO_3 \xrightarrow{T > 375\ K} ClO_2 + O_2 + H_2O$$

9. Rxn of I_2O_5 with CO

$$I_2O_5 + CO \longrightarrow I_2 + CO_2$$

$\downarrow Na_2S_2O_3$

$$NaI + Na_2S_4O_6$$

10. Rxn of Cl_2O_6 with HF

$$Cl_2O_6 + HF \longrightarrow [ClO_2]^+F^- + HClO_4$$

11. Purification of Br_2

$$\text{Impure } Br_2 + Na_2CO_3 \longrightarrow NaBr + NaBrO_3 + CO_2$$

$\downarrow H_2SO_4$

Br_2
Pure

12. **Structures**

(a) KI_3 $K^+(I^- \rightarrow I - I)$

$K^+I_3^-$ $I^{\ominus} \rightarrow I - I$

(b) KHF_2

$K^+F^- \overset{x}{\cdots} H \overset{y}{—} F$

B.I. $\Rightarrow x = y$

(c) I_4O_9 $I^{3+} + 3IO_3^-$

(d) I_2O_4 $IO^+ + IO_3^-$

(e) $CsBr_3$

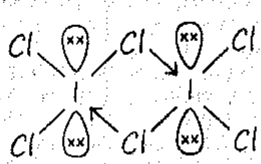
$\underbrace{Cs^+, Br^-, Br_2}$

(f) CsI_3

$\underbrace{Cs^+I_3^-}$

(g) ICl_3 dimer

I_2Cl_6
$I(sp^3d^2)$



planar molecule

13. Acidic strength, Thermal stability & oxidising power of oxyacids of Cl.

A.S $HClO_4 > HClO_3 > HClO_2 > HClO$
&
T.S

O.P $HClO_4 < HClO_3 < HClO_2 < HClO$

Practice

Q. Why is ICl more reactive than I_2?

Reactivity $ICl > I_2$

Q. Write the products formed

(a) $\overset{\delta+\ \delta-}{XX'} + H_2O \xrightarrow{H^+OH^-} XOH + HX'$

(b) $U + ClF_3 \longrightarrow UF_6 + ClF$

(c) $HI + O_2 \longrightarrow I_2 + H_2O$

Q. Find O·N of 'O' in

$\underline{O}_2F_2$, $\underline{O}F_2$

$2x - 2 = 0$ $\quad x - 2 = 0$
$x = +1$ $\quad x = +2$

Q. Unpaired $e^{\ominus}$ is present in which orbital in ClO_2

$7 - 4 = 3e^{\ominus} \longrightarrow 2e^{\ominus} + 1e^{\ominus}$

$\underline{Cl}O_2$

$\downarrow$ $\downarrow$

1 LP $\quad$ 1 UP$e^{\ominus}$
'd' orbital

9 Inert Gases

I.E & En		Size, B.P, M.P, density
	He	
	Ne	
	Ar	
	Kr	
	Xe	
	Rn	
Decreases ↓		↓ Increases

\# Electron gain enthalpy ΔH_{eg}

ΔH_{eg} = +ve for all noble gases

$Ne < Ar \approx Kr < Xe < Rn < He$

Electron affinity

1^{st} comp of Noble gas

$O_2^+[Pt\,F_6]^-$ 1^{st} I.E$(O_2) \approx 1^{st}$ I.E(Xe)

Red

$Xe^+[Pt\,F_6]^-$

Red

KrF_2 RnF_2

Fluorides of Xe

M.O.P #

1. $\underset{(g)\ (\text{Excess})}{Xe} + \underset{(g)}{F_2} \xrightarrow[1\ bar]{400°C} \underset{(s)}{XeF_2}$

2. $Xe + 2F_2 \xrightarrow[7\ bar]{600°C} \underset{(s)}{XeF_4}$
(1 : 5 ratio)

3. $Xe + 3F_2 \xrightarrow[60\text{-}70\ bar]{300°C} \underset{(s)}{XeF_6}$
(1 : 20 ratio)

Prop

1. **Hydrolysis**

$XeF_2 \xrightarrow{H_2O} Xe + O_2 + HF$

*** $\overset{+4}{XeF_4} \xrightarrow{H_2O} \overset{0}{Xe} + O_2 + HF + \overset{+6}{XeO_3}$

Disproportionation

** $XeF_6 \xrightarrow{H_2O} XeOF_4 + 2HF$

$\downarrow H_2O$

$XeO_3 \xleftarrow{H_2O} XeO_2F_2 + 2HF$

2. Rxn of Xenon fluorides with PF_5, SbF_5 and MF

$XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$

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

$XeF_6 + MF \longrightarrow M^+[XeF_7]^-$

M = Na, K, Rb, Cs

Li small size

Some Imp. Points of Noble Gases

1. Rxn of XeF_4 with O_2F_2

$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

2. He & Ne do not form clathrates due to small size
3. Solubility in H_2O increases from top to bottom
4. Ar is used in arc welding
5. Decay of Ra

$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}_2He^4$

6.

O·N	Comp of Xe	Hybridisation	Geometry	Shape	LP on Xe	Total L·P
+2	$\underline{Xe}F_2$	$sp^3d(2BP + 3LP)$	T·B·P	Linear	3	9
+4	$\underline{Xe}F_4$	$sp^3d^2(4BP + 2LP)$	Octahedral	sq planar	2	14
+4	$\underline{Xe}F_3^+$	$sp^3d(3BP + 2LP)$	T·B·P	T-shape	2	11
+6	$\underline{Xe}O_2F_2$	$sp^3d(4BP + 1LP)$	T·B·P	See-Saw	1	11
+6	XeO_3 (Explosive)	$sp^3(3BP + 1LP)$	Tetrahedral	Trigonal pyramidal	1	7

7. Rxn of XeO_3 with base

$$1+1+x-8=0 \quad x=+6$$

$$XeO_3 + NaOH \longrightarrow \overset{+6}{Na^+[HXeO_4]^-}$$

$$\downarrow NaOH \qquad 4+x-12=0 \quad x=+8$$

$$\overset{+8}{Na_4XeO_6} + \overset{0}{Xe} + O_2 + H_2O$$

8. Inert gases are least reactive due to high I.E, fully filled config & more +ve electron gain enthalpy.

9. Inert gases can be separated by adsorption and desorption on charcoal.

Practice

Q. Noble gases have very Low B.P why?

due to weak vanderwaal forces

Q. Why has it been difficult to study the chemistry of Rn?

due to small half life.

Q. Why is He used in diving apparatus?

because of Low solubility in blood.

10 d-Block

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

3d series	Sc	Ti	V	*Cr	Mn	Fe	Co	Ni	*Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
4d series	Y	Zr	Nb*	Mo*	Tc*	Ru*	Rh*	Pd*	Ag*	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10
5d series	La	Hf	Ta	W	Re	Os	Ir	Pt*	Au*	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

Prop

1. Size

(a) 3d series

$$\underbrace{Sc > Ti > V > Cr < Mn}_{\text{Zeff dominates over } \sigma} > \underbrace{Fe \approx Co \approx Ni}_{\text{Zeff overcomes } \sigma} < \underbrace{Cu < Zn}_{\sigma \text{ dominates over zeff}}$$

(b) Size $3d < \underbrace{4d \approx 5d}_{\text{due to L.C (poor screening of 4f } e^{\ominus}\text{s)}}$

3d Sc $\rightarrow$ Ti V

4d Y $\rightarrow$ Zr Nb

5d La $\rightarrow$ Hf Ta

57 72

Sc < Y < La } Ti < Zr ≈ Hf } V < Nb ≈ Ta

2. Ionisation Energy (I.E)

(a) 3d series

Sc Ti V Cr Mn Fe Co Ni Cu Zn

[Sc < V < Cr < Ti < Mn < Ni < Cu < Co < Fe < Zn]

(b) IE 5d > 3d > 4d

↓

due to L.C

3. M.P

(3d) Sc Ti V Cr Mn Fe Co Ni Cu Zn

Sc < Ti < V < Cr > Fe > Co > Ni > Mn > Cu > Zn

M.P [Zn < Cu < Mn < Ni < Co < Fe < Sc < Ti < V < Cr]

4. O.N

$\overset{+2}{Ti - Zn}$	$\overset{+3}{Sc - Ni}$	$\overset{+4}{Ti - Ni}$	$\overset{+5}{V - Mn}$	$\overset{+6}{Cr - Fe}$	$\overset{+7}{Mn}$
Tu zanti Hai ye	Sach nahi Hai	Tu nahi	Ve maahi	Kar fikar	Mere mann ki

[Cu^{+1}]

5. **Magnetic nature**

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

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

M.M = 0 (Diamagnetic)

MM ≠ 0 (Paramagnetic)

Cr^{3+} $\quad Cr \Rightarrow [Ar]\ 4s^1\ 3d^5$

$Cr^{3+} \Rightarrow [Ar]\ 4s^0\ 3d^3$

$\boxed{n = 3}$ $\quad$ | 1 | 1 | 1 | | |

$MM = \sqrt{3(3+2)} = \sqrt{15}$

Paramagnetic

6. **Complex formation tendency**

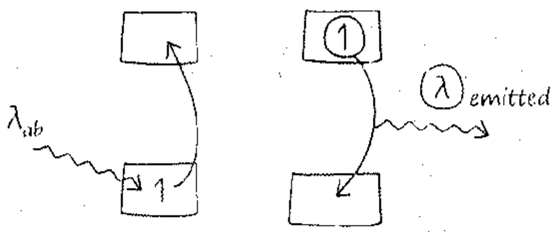
d-block elements form Large no. of complexes due to small size, high ionic charge & availability of d orbitals.

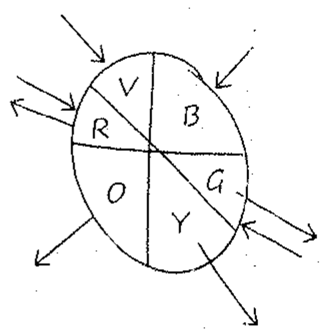
$[Ag(NH_3)_2]Cl$

$[Cu(NH_3)_4]SO_4$

$[Cu(H_2O)_4]SO_4 \cdot H_2O$

7. **Formation of coloured ion**





8. **Interstitial comp, formation**

I.C are formed when small atoms like H, C, N etc are trapped in the metal crystal lattice

TiC, $TiH_{1.7}$, Fe_3C etc

(1) Non stoichiometric

(2) Very hard

(3) High M.P than pure metal

(4) Chemically inert

(5) retain metallic conductivity

9. **Catalytic prop**

d-block elements are known for catalytic prop.

V_2O_5 in contact process

Fe in Haber's process

Ni in Hydrogenation

\# $I^{\ominus} + S_2O_8^{2-} \longrightarrow I_2 + SO_4^{2-}$

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

$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{2-}$ ✓

10. **Alloy formation**

Alloy ⇒ Alloy is Homo solid sol^n in which atoms are randomly distributed

Brass $\quad$ Cu + Zn

Bronze $\quad$ Cu + Sn

Some Imp. Compounds of d-block

1. $KMnO_4$ #

M.O.P

(1) Lab method

$Mn^{2+} + S_2O_8^{2-} \xrightarrow{H^+} MnO_4^{\ominus} + SO_4^{2-}$

(2) Commerical Method

(a) $MnO_2 \xrightarrow[\text{\& oxidised by air or } KNO_3]{\text{fused with KOH}} MnO_4^{2-}$

$MnO_4^{2-} \xrightarrow[\text{oxidation in alkaline medium}]{\text{Electrolytic}} MnO_4^-$

(b) $MnO_2 \xrightarrow[\text{\& oxidised by air or } KNO_3]{\text{fused with KOH}} MnO_4^{2-}$

$MnO_4^{2-} \xrightarrow{H^+} MnO_4^- + MnO_2$

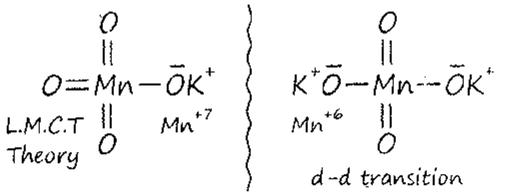
Prop

(1) Heating effect

$KMnO_4 \xrightarrow{513\ K} K_2MnO_4 + MnO_2 + O_2$

deep purple — Green — Brown

(2) Structure



(3) Chemical Rxn

$\overset{+7}{MnO_4^-} \xrightarrow{\text{Basic}} \overset{+6}{MnO_4^{2-}}$ $n^f = 1$

$\overset{+7}{MnO_4^-} \xrightarrow[\text{alkaline}]{\text{Neutral or}} \overset{+4}{MnO_2}$ $n^f = 3$

$\overset{+7}{MnO_4^-} \xrightarrow{\text{acidic}} Mn^{2+}$ $n^f = 5$

1	3	5
B	N	A

(1) In A.M

$MnO_4^- \longrightarrow Mn^{2+}$

ek $I^- \longrightarrow I_2$

OX $OX^{2-} \longrightarrow CO_2$

KO

fir $Fe^{2+} \longrightarrow Fe^{3+}$

Se $S^{2-} \longrightarrow S$

New $NO_2^- \longrightarrow NO_3^-$

song $SO_3^{2-} \longrightarrow SO_4^{2-}$

sunao $Sn^{2+} \longrightarrow Sn^{4+}$

$MnO_4^- + I^- \xrightarrow{H^+} Mn^{2+} + I_2$

2. In Neutral or Alkaline medium

$MnO_4^- \xrightarrow{H_2O} MnO_2$

ck $I^- \xrightarrow{H_2O} IO_3^-$

thi $S_2O_3^{2-} \xrightarrow{H_2O} SO_4^{2-}$

Manisha $Mn^{2+} \xrightarrow[\text{Catalyst } ZnSO_4 \text{ or } ZnO]{H_2O} MnO_2$

1. $K_2Cr_2O_7$ #

M.O.P # (1)

$\underset{\text{Chromite}}{FeCr_2O_4} \xrightarrow[O_2]{\text{Fused with } Na_2CO_3} \overset{\text{Yellow}}{Na_2CrO_4} + Fe_2O_3 + CO_2$

$\xrightarrow{H^+} Na_2Cr_2O_7 \xrightarrow{KCl} \underset{\text{Orange}}{K_2Cr_2O_7}$

Prop

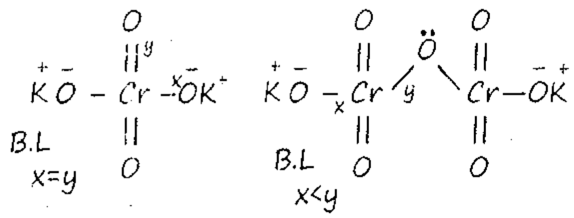
1. Heating effect

$\underset{\text{Orange}}{K_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{Yellow}}{K_2CrO_4} + \underset{\text{Green}}{Cr_2O_3} + O_2$

*2. $\underset{\text{Orange}}{\overset{+6}{Cr_2O_7^{2-}}} \underset{H^+}{\overset{^-OH}{\rightleftharpoons}} \underset{\text{Yellow}}{\overset{+6}{CrO_4^{2-}}}$

3. Struc

$K_2CrO_4 \leftarrow \text{LMCT} \rightarrow K_2Cr_2O_7$



4. $K_2Cr_2O_7$ acts as an O.A in acidic medium

$\overset{+6}{Cr_2O_7^{2-}} \xrightarrow{H^+} \overset{+3}{Cr^{3+}}$ $n^f = 6$

(3)X2=(6)

$\left[Cr_2O_7^{2-} + Fe^{2+} \xrightarrow{H^+} Fe^{3+} + Cr^{3+} \right]$

fir $Fe^{2+} \longrightarrow Fe^{3+}$

ek $I^{\ominus} \longrightarrow I_2$

Song $H_2S \longrightarrow S$

Sunao $Sn^{2+} \longrightarrow Sn^{4+}$

5. Chromyl chloride test

$$\text{Solid Ionic Chloride} \xrightarrow[\text{Conc } H_2SO_4]{\text{Solid } K_2Cr_2O_7} \underset{CrO_2Cl_2}{\text{Chromyl chloride Reddish brown vap.}}$$

$$CrO_2Cl_2 \xrightarrow{NaOH} \underset{\text{Yellow Sol}^n}{Na_2CrO_4} \xrightarrow{Pb(OAc)_2} \underset{\text{Yellow ppt}}{PbCrO_4}$$

$Pb-(O-\overset{\overset{O}{||}}{C}-CH_3)_2$

$Pb(OAC)_2$

Following chlorides do not give C.C.T (Chromyl chloride test)

$AgCl, SnCl_4, PbCl_4, Hg_2Cl_2$ & $HgCl_2$

Ag	Sn	Pb	Hg
aji	Suno	Pyar	Hogya

3. Green vitriol ($FeSO_4 \cdot 7H_2O$)

M.C.P (1) $Fe + H_2SO_4 \xrightarrow{H_2O} FeSO_4 \cdot 7H_2O$

<u>Heating effect</u>

$$FeSO_4 \cdot 7H_2O \xrightarrow{300°C} FeSO_4 + 7H_2O$$

$$FeSO_4 \xrightarrow{\text{Strong Heating}} Fe_2O_3 + SO_2 + SO_3$$

<u>M.O.P</u> $Zn \xrightarrow[H_2O]{H_2SO_4} ZnSO_4 \cdot 7H_2O$

$ZnO \xrightarrow[H_2O]{H_2SO_4} ZnSO_4 \cdot 7H_2O$

$ZnCO_3 \cdot Zn(OH)_2 \xrightarrow[H_2O]{H_2SO_4} ZnSO_4 \cdot 7H_2O$

Basic Zinc Carbonate

<u>Heating effect</u>

$$ZnSO_4 \cdot 7H_2O \xrightarrow{T<70°C} ZnSO_4 \cdot 6H_2O \xrightarrow{T>70°C} ZnSO_4 \cdot H_2O \xrightarrow{220°C} ZnSO_4 \xrightarrow{750°C} ZnO + SO_3$$

$$ZnSO_4 \xrightarrow{T>800°C} ZnO + SO_2 + O_2$$

3. Blue vitriol ($CuSO_4 \cdot 5H_2O$)

M.O.P 1. $Cu \xrightarrow{H_2SO_4} X$

2. $Cu \xrightarrow[H_2SO_4]{O_2} CuSO_4 \cdot 5H_2O$

3. $CuCO_3 \cdot Cu(OH)_2 \xrightarrow{H_2SO_4} CuSO_4 \cdot 5H_2O$

Basic Copper Carbonate

Structure # $CuSO_4 \cdot 5H_2O$

$[Cu(H_2O)_4]SO_4 \cdot H_2O$

<u>Heating effect</u>

$$\underset{\text{Blue}}{CuSO_4 \cdot 5H_2O} \xrightarrow[\text{exposure}]{\text{on}} \underset{\text{pale blue}}{CuSO_4 \cdot 3H_2O} \xrightarrow{100°C} \underset{\text{Bluish white}}{CuSO_4 \cdot H_2O} \xrightarrow{220°C} \underset{\text{white}}{CuSO_4} \xrightarrow{750°C} CuO + SO_3$$

$$CuSO_4 \xrightarrow{T>850°C} \underset{\text{Black}}{CuO} + SO_2 + O_2$$

<u>Chemical Rxn</u>

$$\underset{\text{(Excess)}}{CuSO_4} + Na_2S_2O_3 \longrightarrow \underset{\text{Sodium Cupro-thiosulphate}}{Na_4[\overset{+1}{Cu_6}(S_2O_3)_5]}$$

6. Philosophers wool (ZnO) or Chinese white

<u>M.O.P</u> 1. $Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$

2. $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

3. $ZnCO_3 \cdot Zn(OH)_2 \xrightarrow{\Delta} ZnO + CO_2 + H_2O$

4. $Zn(NO_3)_2 \xrightarrow{\Delta} ZnO + NO_2 + O_2$

Prop

1. ZnO is white when cold & yellow when hot (Due to crystal defect).
2. ZnO is an amphoteric oxide

$$ZnO \xrightarrow{HCl} Zn^{2+} | Cl_2^{-}$$

$$ZnO \xrightarrow{NaOH} Na_2^{+} | ZnO_2^{2-}$$

7. FeCl$_3$

M.O.P 1. $Fe + Cl_2 \longrightarrow \underset{\text{(Excess)}}{FeCl_3}$

Prop 1. $FeCl_3 + KSCN \longrightarrow \underset{\text{Blood red}}{Fe(SCN)_3}$

2. $FeCl_3 + K_4[Fe(CN)_6] \longrightarrow \overset{+3}{Fe_4}[\overset{+2}{Fe}(CN)_6]_3$

$\overset{+3}{Fe}[\overset{+2}{Fe}]$	prussian's blue
$\overset{2+}{Fe}[Fe^{3+}]$	Turbull's blue

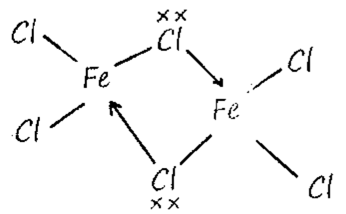
Prussian's blue
Iron (III) hexacyano-ferrate (II)

3. Heating effect

$FeCl_3 \xrightarrow{\Delta} FeCl_2 + Cl_2$

4. Struc.

$FeCl_3$ in solid form exist as dimer $(FeCl_3)_2$



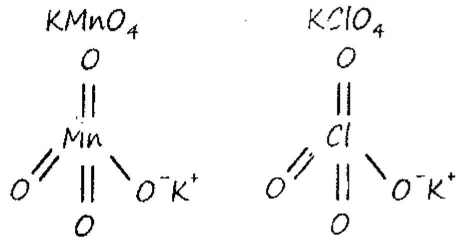
1. All Cu^{2+} halides are stable except iodide

$Cu^{2+} + I^{\ominus} \longrightarrow \overset{+1}{Cu_2}I_2 + I_2$

2. Many Cu^+ Comp are unstable in aq Sol^n.

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

(Stability) $Cu^{2+} > Cu^+$ due to more $-ve\ \Delta H^{hyd}$ which is greater than 2nd I.E.



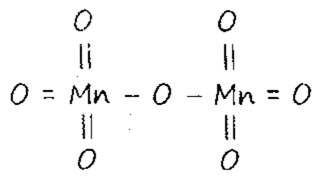
3. O.N of metal in most of the Carbonyls is zero $[Ni(CO)_4]$, $[Mn(CO)_5]$ $[Cr(CO)_6]$

$x + 0 = 0$

4. FeO_4^{2-} ion formed in alkaline media

$FeO_4^{2-} \longrightarrow Fe_2O_3 + O_2$

5. Highest fluride of Mn is $\overset{+4}{Mn}F_4$ while oxide is $\overset{+7}{Mn_2}F_7$



6. Oxidising power (O.P)

$\overset{+5}{V}O_2^- < \overset{+6}{Cr_2}O_7^{2-} < \overset{+7}{Mn}O_4^-$

7. Mn^{3+} & Co^{3+} are strong O.A while Ti^{2+}, V^{2+}, Cr^{2+} are strong R.A.

$Cr^{2+} + H^+ \xrightarrow{dil} Cr^{3+} + H_2\uparrow$

8. All metal except Sc form ionic MO.

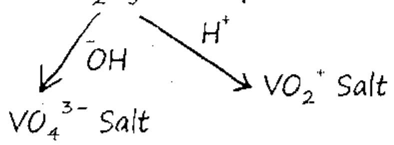
9. Higher O.N oxides are acidic in Nature

$Mn_2O_7 \rightarrow HMnO_4$ & $CrO_3 \rightarrow H_2CrO_4$ & $H_2Cr_2O_7$

10. V_2O_3 Basic

$\overset{+4}{V_2}O_4$ Less Basic $\xrightarrow{H^+} VO^{2+}$ Salt

$\overset{+5}{V_2}O_5$ Amphoteric



$x - 8 = -3$; $x = +5$;

11. Mn^{+7} halide does not exist, $\overset{+7}{Mn}O_3F$ exist.

12. CrO Basic, Cr_2O_3 Amphoteric

13. Cr^{+6} is less stable than Mo^{+6} & W^{+6} ; $(Cr_2O_7^{2-})$

Cr^{+6} is strong O.A while MOO_3 & WO_3 are not?

14. Sodium dichromate crystallises as $Na_2Cr_2O_7 \cdot 2H_2O$

15. Stability of VF_2 is due to Lower O.N VX_2 (X = Cl, Br, I)

16. Beyond Mn, no metal has trihalide except FeX_3 & CoF_3 (X = F, Cl, Br)

17. Halides of V^{5+} exist as VF_5, Cr^{+6} exist as CrF_6

other halides of V $\xrightarrow{\text{Hydrolysis}} VOX_3$

11

f-Block

Inner Transition Metal

Group (3)

Period 6 (1) Lanthanoids

$_{57}La$ ¦ $_{58}Ce$ Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb $_{71}Lu$

Group (3)

Period 7 (2) Actinoids

$_{89}Ac$ ¦ $_{90}Th$ Pa U Np Pu Am Cm Bk Cf Es Fm Md No $_{103}Lr$

1. Lanthanoids (1) E.C F-block ⇒ General E.C $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

Lanthanoids ⇒ $4f^{1-14}\,5d^{0-1}\,6s^2$

	La	$\boxed{Ce}$	Pr	Nd	Pm	Sm	Eu	$\boxed{Gd}$	Tb	Dy	Ho	Er	Tm	Yb	$\boxed{Lu}$
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
6S	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

(2) O.N

	+2	+3	4+	+4
	Eu^{2+}, Yb^{2+}	Most common	Ce	$\boxed{\text{Pr Nd Tb Dy}}$
	R.A	Ln^{3+}	MO_2	O.A

(3) Ionic Radii

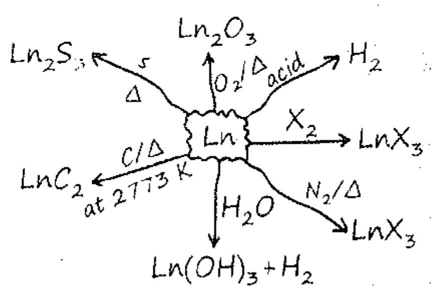
Ln^{3+} $La^{3+} > Ce^{3+} > Pr^{3+}$ ....> Lu^{3+}

Left to Right decreases due to increase in E.N.C owing to Lanthanoid contraction (poor screening of 4f $e^{\ominus}$s)

Screening order:

$s > p > d > f$

(4) Chemical Rxns



(5) General prop.

(1) All Ln are silvery white soft metals (but Sm is steel hard) due to strong metallic bond.

(2) Except La^{3+} and Lu^{3+} all M^{3+} ions are Coloured.

(3) Except f^0 type (La^{3+} & Ce^{+4} etc) type (Yb^{2+} & Lu^{3+} etc), all ions are paramagnetic

(4) Basicity of Ln decreases from L to R due to decrease in size

$La(OH)_3 \xrightarrow[\text{decreases}]{\text{Basicity}} Lu(OH)_3$

(5) Hardness ∝ atomic no.

(6) Alloys of Ln are called Mischmetals 95% Ln 5% Fe with some traces of S, C, Ca etc.

2. Actinoids

(1) **E.C** $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ $\boxed{Ac\ 5f^{1-14}\ 6d^{0-1}\ 7s^2}$

	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
5f	0	0	3	4	5	6	7	7	9	10	11	12	13	14	14
6d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
7S	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
(2) **O.N**		–	3	3	3	3	3	3	3	3	3	3	3	3	3
		4	4	4	4	4	4	4	4						
			5	5	5	5	5								
				6	6	6	6								
					7	7									

3. Size

L to R size decreases due to increase in ENC owing to Actinoide contraction (poor screering of 5f $e^{\ominus}$s)

4. General Charac

(1) All are paramag.

(2) All are silvery white metal.

(3) They get tarnished on exposure to alkali.

(4) All are radioactive (& At No 92 onward all elements are called transuranic element)

(5) They react with boiling water to form mix. of oxides & hydrides.

(6) All react with non metals at moderate temp.

(7) All react with HCl but effect with HNO_3 is small due to the formation of oxide Layer.

12

Metallurgy

The scientific and technological method used to extract metal from its ore is called Metallurgy

\# Minerals # The naturally occurring compounds of a metal (in earth's crust).

\# Ores # The minerals from which metal is extracted economically.

Ore ← $Al_2O_3 \cdot 2H_2O$ (Bauxite), $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (Clay) — Minerals

\# All ores are minerals but all minerals are not ores.

Metallurgy involves following steps

1. Crushing and grinding (Pulverisation) by Jaw mill or stamp mill
2. Conc^n of the ore
3. Isolation of metal from ore
4. Purification of metal, Pulverisation
6. Conc^n or dressing or benefaction

The removal of impurities (sand, clay etc.) from ore.

1. Gravity sep
2. Magnetic sep
3. Froth Floatation
4. Leaching

1. G.S or Hydraulic washing or Levigation.

(a) It is Based on diff Specific gravities of ore and gangue particles.

(b) An upward stream of running H_2O is used to wash the ore. The lighter gangue particles are washed away and heavier ore particles are left behind.

(c) Used for the conc^n of Fe_2O_3 (Haematite oxide ores).

2. Magnetic Separation Method

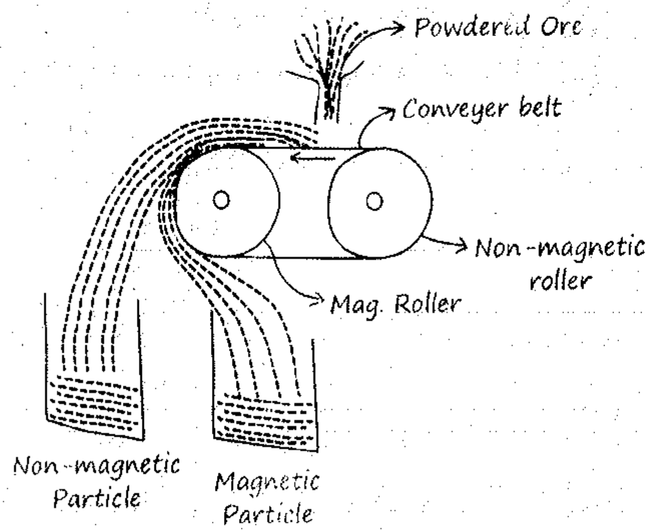
(1) It is based on diff magnetic prop of ore & gangue.

(2) Either ore or gangue particles are magnetic in nature.

(3) Used for the conc^n of

(a) Cassiterite (SnO_2) (non mag) Ore + Wolframite ($FeWO_4$) (mag) Impurity

(b) Rutile (TiO_2) Mag ore + Chlorapatite ($3Ca_3(PO_4)_2 \cdot CaCl_2$) Non mag impurity



3. Froth Floatation Method #

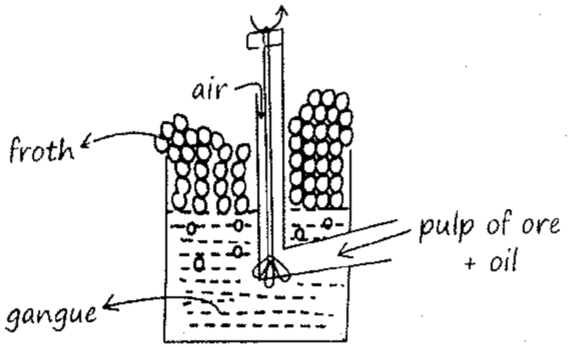
(1) It is based on diff. wetting prop of ore and gangue particles.

(2) Ore particles are wet by oils & gangue by water.

(3) Collectors & Froth stabilisers are added.

Collectors ⇒ Pine oil, Fatty acids & Xanthates

Froth stabilizers ⇒ Cresol & aniline



\# It is used for the con^n of sulphide ores

\# It is also used for the sep. of two sulphide ores

$$\cancel{\boxed{PbS + ZnS}} \xrightarrow[NaCN]{Depressant} \underset{\text{Sodium zinco cyanide}}{Na_2[Zn(CN)_4]}$$

4. Leaching #

(1) Alumina from Bauxite ore

Powdered ore

$$Al_2O_3 + SiO_2 + Fe_2O_3 + TiO_2$$

$\downarrow$ Conc NaOH/Δ

Soluble	Insoluble
$Al_2O_3 + SiO_2$	$Fe_2O_3 + TiO_2$

$$Al_2O_3 + NaOH + H_2O \xrightarrow[35\text{-}36\ bar]{200\text{-}250°C} \underset{\text{Sodium Aluminate}}{Na[Al(OH)_4]}$$

$$SiO_2 + NaOH \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3}$$

$$Na[Al(OH)_4] \xrightarrow{CO_2} Al_2O_3 \cdot xH_2O + NaHCO_3$$

$$Al_2O_3 \cdot xH_2O \xrightarrow{1470\ K} Al_2O_3$$

(2) Ag & Au

$$M + CN^{\ominus} + O_2 + H_2O \longrightarrow [M(CN_2)]^{\ominus} + \bar{O}H$$

$$[M(CN)_2]^{\ominus} + Zn \longrightarrow M + [Zn(CN)_4]^{2-}$$

$[M = Ag \ \& \ Au]$

Mac Arthur-forrest cyanide process.

Extraction of Metals

1. Zn from ZnS (Zinc blende) or (Sphalerite)

(1) Pulverisation

(2) F.F Method

(3) Isolation

(a) Roasting: Heating in presence of air at the temp below M.P of metal

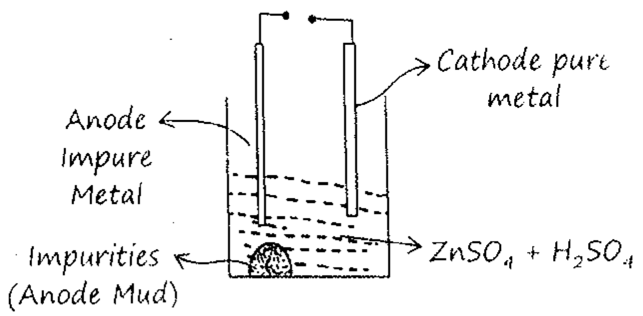
$$\underset{\text{More stable}}{ZnS + O_2} \xrightarrow[1200\ K]{\Delta} \underset{\text{Less Stable}}{ZnO + SO_2}$$

(b) Reduction by coke

Smelting

$$ZnO + \underset{(R.A)}{C} \xrightarrow{1400°C} \underset{\text{Impure Zn}}{Zn} + CO$$

(4) Purification by Electrolytic Refining



At anode $\underset{\text{Impure}}{Zn} \longrightarrow Zn^{2+} + 2e^{\ominus}$

At cathode $Zn^{+2} + 2e^{\ominus} \longrightarrow \underset{\text{Pure}}{Zn}$

2. Cu from $CuFeS_2$ (Chalcopyrite) or (Copper purite)

(1) Pulverisation

(2) F.F Method

(3) Isolation

(1) Roasting:

$$CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + FeS + SO_2$$

$$\text{Impurities}\begin{cases} S + O_2 \longrightarrow SO_2 & P_4 + O_2 \longrightarrow P_4O_{10} \\ As + O_2 \longrightarrow As_2O_3 & Sb + O_2 \longrightarrow Sb_2O_3 \end{cases}$$

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$

$FeS + O_2 \longrightarrow FeO$ (Basic impurities)

$\big\downarrow SiO_2$ (Acidic flux)

$FeSiO_3$ (Slag)

Matte $\{Cu_2S + FeS\}$

In Bessemer convertor

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$

$FeS + O_2 \longrightarrow FeO + SO_2$

$\big\downarrow SiO_2$

$FeSiO_3$

self Reduction process

$Cu_2O + Cu_2S \longrightarrow \underset{\text{Blister Cu}}{Cu} + SO_2$

(4) Purification by Electrolytic Refining

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

At anode:- Impure Cu

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

At cathode:- Pure Cu

Electrolyte:- $CuSO_4 + H_2SO_4$

Impurities:- Sb, Se, Te

$\underbrace{\text{Ag, Au, Pt etc.}}_{\text{Anode Mud}}$

Extraction of Cu from Low grade ore

Hydrometallurgy

$Cu \xrightarrow[\text{bacteria}]{\text{acid}} Cu^{2+}(aq)$

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

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

✓ $Cu^{2+} + \underset{\text{Scrap}}{Fe} \longrightarrow Fe^{2+} + Cu$

Extraction of Cu from Cu_2O

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$

Smelting $Cu_2O + \underset{\text{R.A}}{C} \longrightarrow Cu + CO_2$

3. **Ag from argentite** (Ag_2S)

(1) Pulverisation

(2) F.F Method

(3) Mac-Arthur-forrest cyanide process

$Ag_2S + NaCN + O_2 + H_2O \longrightarrow$

$Na[\overset{+1}{Ag}(CN)_2] + \bar{O}H + Na_2S$

$Na_2S \xrightarrow{O_2} Na_2SO_4$

$Na[Ag(CN)_2] \xrightarrow{\overset{0}{Zn}} \underset{\text{Impure}}{\overset{0}{Ag}} + Na_2[\overset{+2}{Zn}(CN)_4]$

(4) Purification # At anode # Impure Ag

At cathode # Pure Ag

Electrolyte # $AgNO_3 + HNO_2$

4. Au

(1) Pulverisation

(2) $\underset{\text{Leaching}}{Au + NaCN + O_2 + H_2O} \longrightarrow$

$Na[\overset{+1}{Au}(CN)_2] + \bar{O}H$

$\big\downarrow \overset{0}{Zn}$

$\underset{\text{Impure}}{\overset{0}{Au}} + Na_2[\overset{+2}{Zn}(CN)_4]$

Purification

At anode:- Impure Au

At cathode:- Pure Au

Electrolyte:- $AuCl_3 + HCl$

5. **Al from Bauxite** $\left(\begin{array}{l}Al\,O_x(OH)_{3-2x}\\ 0 < x < 1\end{array}\right)$ $(Al_2O_3 \cdot 2H_2O)$

(1) Pulverisation

(2) Leaching

Baeyer's process

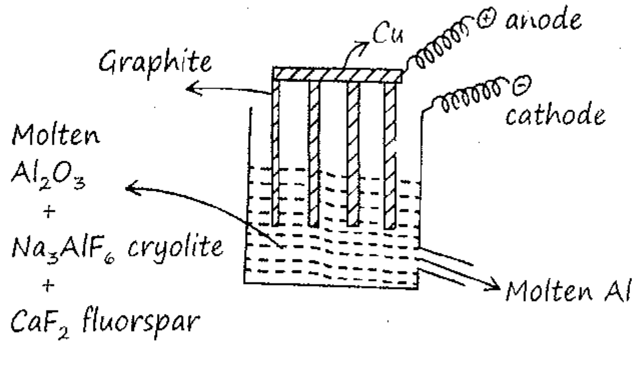
$Al_2O_3 + \underset{\text{(Excess)}}{NaOH} \longrightarrow Na[Al(OH)_4]$

$Al_2O_3 \xrightarrow{NaOH} Al(OH)_3$

$Na[Al(OH)_4] \xrightarrow{H^+} Al(OH)_3$

$Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 \xleftarrow{\Delta} Al(OH)_3$

(3) Hall-Heroult's process



<u>At Cathode</u>

$$Al^{3+} + 3e^{\ominus} \longrightarrow \underset{99\%\ \text{Pure}}{Al}$$

<u>At anode</u>

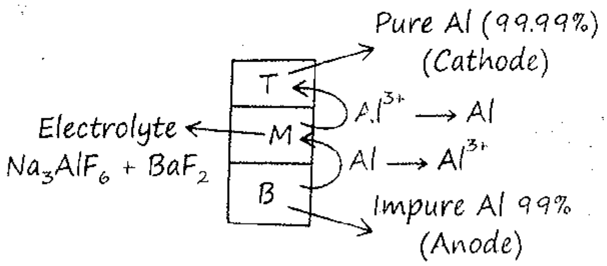
$$O^{2-} \longrightarrow O_2 \xrightarrow{C} CO, CO_2$$

\# To decrease M.P

\# To increase conductivity

(4) <u>Purification by Hoope's process</u>

\# it is a three Layer process



\# All three Layers have diff densities

6. Fe from Haematite (Fe_2O_3)

(1) Pulverisation

(2) Conc^n by Gravity sep method

(3) <u>Rxns</u> #

(1) Low temp zone (500-800 K)

$$\underset{RA}{Fe_2O_3 + CO} \longrightarrow Fe_3O_4 + CO_2$$

$$Fe_3O_4 \xrightarrow{CO} Fe + CO_2$$

$$Fe_2O_3 + CO \longrightarrow FeO + CO_2$$

(2) Medium temp zone (900-1600 K)

$$C + CO_2 \longrightarrow CO$$

$$FeO + CO \longrightarrow Fe + CO_2$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$\underset{\text{Basic flux}}{CaO} + \underset{\text{impurity acidic}}{SiO_2} \longrightarrow \underset{\text{slag}}{CaSiO_3}$$

(3) In High temp zone 2170 K

$$C + O_2 \longrightarrow CO_2$$

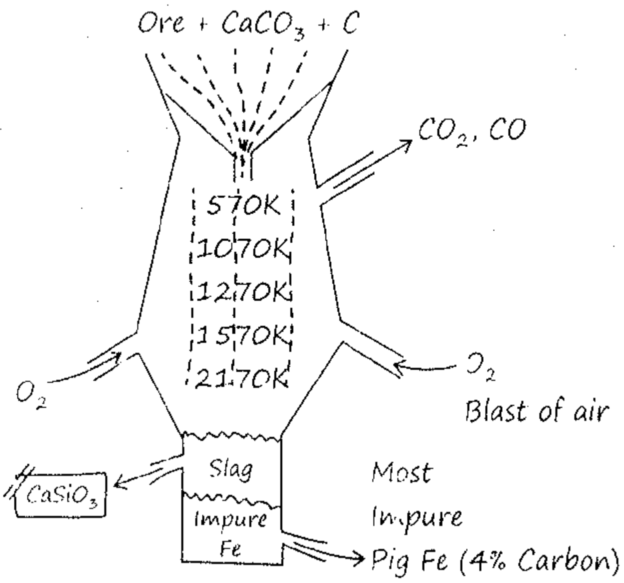
(4) Fe from Haematite (Fe_2O_3)

$$\underset{4\%C}{\text{Pig Fe}} \xrightarrow[\text{Hot air Blast}]{\text{Scrap Fe/C}} \underset{3\%C}{\text{Cast Fe}}$$

(P, S, Si, Mn etc)

Wrought iron is prepared by Heating of cast Fe in reverb. furnace lined with Fe_2O_3

$$Fe_2O_3 + C \longrightarrow Fe + CO$$



<u>Purification</u>

1. <u>Distillation</u> # (for Low Boiling metals like Zn & Hg)

   Impure metal is evaporated to obtain pure metal as distillate

2. <u>Liquation</u> # (for Low melting metal like Sn)

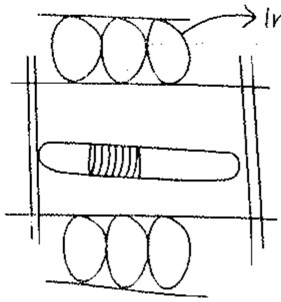
   Impure metal can be made to flow on slopping surface. In this way, metal is sep by impurities.

3. <u>Electrolytic refining</u>

   At anode # $\underset{\text{impure}}{M} \longrightarrow M^{n+} + ne^{\ominus}$

   At cathode # $M^{n+} + ne^{\ominus} \longrightarrow \underset{\text{pure}}{M}$

4. Zone refining (for Semi conductor & metals of High purity (like Si, Ge, B etc))



It is based on the princi that impurities are more soluble in melt than in solid state of the metal.

5. Vapour phase refining

(a) Mond's process for Ni

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

(b) Van-Arkel process for Ti & Zr

$$Zr + 2I_2 \xrightarrow{523\ K} ZrI_4 \xrightarrow{1800\ K} \underset{\text{pure}}{Zr + 2I_2}$$

13 Coordination Compound

Werner's Theory

1. Werner proposed the concept of primary valency and secondary valency
2. P.V is ionisable & it is equal to O.N of central metal atom/ion
3. S.V is non ionisable & it is equal to C.N of C.A or C.M.A

$K_4[\underline{Fe}(CN)_6]$ S.V = C.N = 6 x 1 = 6

$4 + x - 6 = 0$

$x = +2$ $\boxed{PV = 2}$

Rxn with Excess $AgNO_3$

$[\quad CN = 6] Cl^-_{x} \xrightarrow[Excess]{Ag^+NO_3} x\ AgCl$ White ppt

$COCl_3 \cdot 6NH_3 \xrightarrow[AgNO_3]{Excess} 3\ AgCl$

$[CO(NH_3)_6]Cl_3$

$COCl_3 \cdot 5NH_3 \xrightarrow[AgNO_3]{Excess} 2\ AgCl$

$[CO(NH_3)_5Cl]Cl_2$

$COCl_3 \cdot 4NH_3 \xrightarrow[AgNO_3]{Excess} 1\ AgCl$

$[CO(NH_3)_4Cl_2]Cl$

Q. Formula — Moles of AgCl ppt per mole of comp with excess $AgNO_3$

Formula	Moles of AgCl ppt per mole of comp with excess $AgNO_3$
$PdCl_2 \cdot 4NH_3$ $[Pd(NH_3)_4]Cl_2$	2
$NiCl_2 \cdot 6H_2O$ $[Ni(H_2O)_6]Cl_2$	2
$PtCl_4 \cdot 2HCl$ $H_2[PtCl_6]$	0
$PtCl_2 \cdot 2NH_3$ $[Pt(NH_3)_2Cl_2]$	0

Q. Compare conductivity of following comp.

Total ions

(A) $[Co(NH_3)_6]Cl_3$ 4 1:3 type Electrolyte

(B) $[CoCl(NH_3)_5]Cl_2$ 3 1:2 type Electrolyte

(C) $[CoCl_2(NH_3)_4]Cl$ 2 1:1 type Electrolyte

$\boxed{A > B > C}$

Q. Diff. b/w double salt and a complex

Double Salt	Complex
1. Retains identity in solid state but loses identity in sol^n	1. Retains identity in both solid as well as in sol^n
2. Completely dissociates into ions	2. Do not completely disso.
3. Give test of simple ions	3. Do not give test of simple ion
Exp: Carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ Mohr salt $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ Potash alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Exp: $K_4[Fe(CN)_6]$, $[Cr(H_2O)_6]Cl_3$

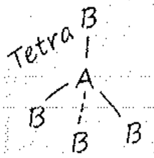
Some imp. Terms of C.C

$K_4[Fe(CN)_6]$

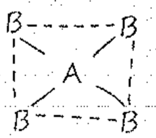
- K_4 → Counter ion
- $[Fe(CN)_6]$ → Coordination entity
- Fe → Central metal atom/ion, Lewis acid
- CN → ligand

Coordination Polyhedron

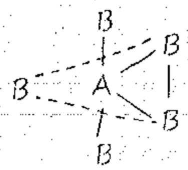
AB_4 Tetra



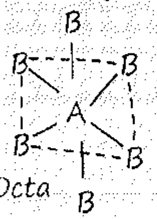
Sq planar



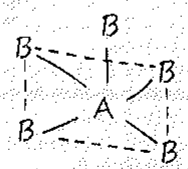
AB_5 T·B·P



AB_6



Octa



Square pyramidal

Homoleptic complex

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

Heteroleptic complex

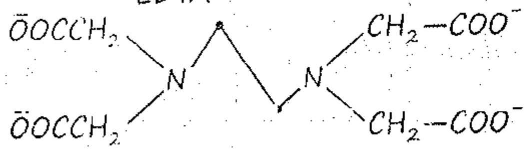
$[Ni(NH_3)_2Cl_2]$

Ligands

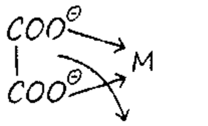
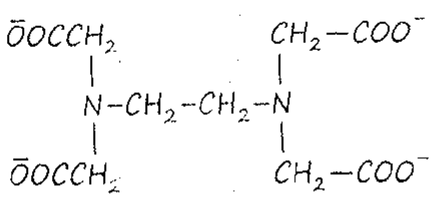
1. Ligands can be $1e^{\ominus}$ donor, $2e^{\ominus}$ donor (LP donor) and $\pi e^{\ominus}$ donor
2. Ligand is Lewis Base

Classification

1. **Based on charge**

+ve	–ve	Neutral
NO_2^+, $NH_3^+-NH_2$	X^-	NH_3
NO^+	$OH^{\ominus}$	H_2O
	OX^{2-} $\begin{pmatrix} COO^- \\ \vert \\ COO^- \end{pmatrix}$	CO
	$CN^{\ominus}$	NO
	$NO_2^{\ominus}$	Py 
	CO_3^{2-}	en $H_2N-CH_2-CH_2-NH_2$
	SO_4^{2-}	PPh_3
	$EDTA^{4-}$ 	CH_3-NH_2

2. **Based on donation**

Monodentate (1 atom donor)	didentate 2 donor atom	Polydentate Hexadentate (6 donor atom)	Ambidentate (2 donor atoms) but only one can donate at a time
$X^{\ominus}$, $OH^{\ominus}$, NO_2^{+}, NO^{+} $N^{+}H_3-NH_2$, CO, NO, Py CH_3-NH_2, NH_3, H_2O etc PPh_3	en CH_2-CH_2 (NH_2 NH_2) Ox^{2-} $COO^{\ominus}$ / $COO^{\ominus}$  Chelate	 $EDTA^{4-}$	$M \leftarrow NO_2^{\ominus}$ $M \leftarrow O^{\ominus}NO$ $M \leftarrow SCN^{\ominus}$ $M \leftarrow NCS^{\ominus}$

IUPAC Naming

Rules

1. Name of cation is written before anion.
2. Naming of ligand
   (a) Anionic Ligands ending with $e \rightarrow o$
   - $X^{\ominus}$ halido
   - $\bar{O}H$ hydroxido
   - OX^{2-} oxalato
   - $CN^{\ominus}$ cyanido etc

   (b) Neutral
   - $H_2O \longrightarrow$ aqua
   - $NH_3 \longrightarrow$ ammine
   - $CH_3-NH_2 \longrightarrow$ methyl amine
   - $CO \longrightarrow$ Carbonyl
   - $NO \longrightarrow$ Nitrosyl
   - $PPh_3 \longrightarrow$ triphenyl phosphine
   - en $\longrightarrow$ ethane-1, 2-diamine
   - Py $\longrightarrow$ Pyridine

   (c) +vely charged Ligand (Cationic Ligand)
   - -ium NO_2^{+} nitronium
   - NO^{+} nitrosonium
   - $^{+}NH_2-NH_2$ Hydrazinium
3. If prefixes mono, di, tri etc used for number of ligand has numerical prefix then bis, tris, tetrakis etc are used

   $[CoCl_2(en)_2]^{+}$

   bis-(ethane-1, 2-diamine)
4. Naming of C·M·A/ion

CMA	When CMA is neutral or positively charged complex	When CMA is –vely charged complex
Fe	iron	Ferrate
Co	cobalt	Cobaltate
Ni	nickel	nickelate
Pd	palladium	palladate
Pt	platinum	platinate
Cu	copper	Cuprate
Ag	silver	argentate
Au	gold	aurate
Zn	Zinc	Zincate

5. O·N of C·M·A / ion is writen just after naming of C·M·A /ion in Roman in paranthesis

Q. $[Cr(NH_3)_3(H_2O)_3]Cl_3$

triamminetriaquachromium (III) chloride

Q. $K_2[Zn(OH)_4]$

Potassium tetrahydroxidozincate (II)

Q. $Hg[Co(SCN)_4]$

Mercury (I) tetrathiocyanatocobaltate (III)

Q. $K_3[Al(OX)_3]$

Potassium trioxalatoaluminate (III)

Q. $[Ni(CO)_4]$

tetracarbonylnickel (O)

Q. $[CoCl_2(en)_2]$

dichlorido bis-(ethane-1, 2-diamine) Cobalt (III) ion

Q. $[Co(NH_3)_5(CO_3)]Cl$

Pentamminecarbonatocobalt(III) Chloride

Q. $[Co(en)_3]_2(SO_4)_3$

tris-(ethane-1, 2- diamine) cobalt (III) sulphate

Q. $[Ag(NH_3)_2][Ag(CN)_2]$

diamminesilver (I) dicyanidoargentate (I)

Q. $[Pt(NH_3)_4Cl(NO_2)]$

tetraamminechloridonitrito-N-platinum (II)

Q. $\overset{3-}{Fe_4}[Fe(CN)_6]_3^{4}$

iron (III) hexacyanidoferrate (II)

Isomerism

Structural Isomerism

1. Coordination isomers
2. Hydrate isomers
3. Linkage isomers
4. Ionization isomers

1. **Coordination iso #**

When cation & anion both are complex

$[Cr(NH_3)_6][Co(CN)_6]$

&

$[Co(NH_3)_6][Cr(CN)_6]$

2. **Hydrate iso**

When H_2O acts as ligand as well as water of crystallization

$[Cr(H_2O)_6]Cl_3$ & $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

3. **Linkage iso #**

When ambidentate Ligand is present

$[Co(NH_3)_5(NO_2)]Cl_2$

&

$[Co(NH_3)_5(ONO)]Cl_2$

4. **Ionisation isomers #**

Compounds which give diff ion in Sol^n

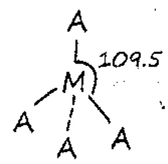
$[Co(NH_3)_5Br]\underbrace{SO_4}_{SO_4^{2-}}$ & $[Co(NH_3)_5SO_4]\underbrace{Br}_{Br^-}$

Stereo isomerism

1. **Geometrical isomerism #**

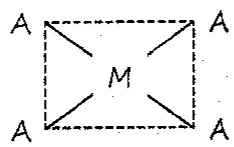
Case 1: In C·N = 4

(a) Tetrahedral Geometry



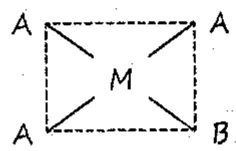
Does not Exhibit G.I

(b) In sq. planar Geo



$[MA_4]$ ✗

$[MA_3B]$ ✗



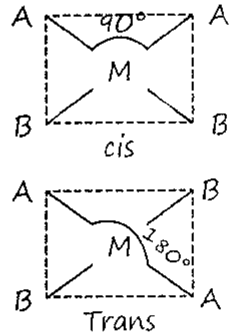
$[MA_2B_2]$ ✓ 2

$[MA_2BC]$ ✓ (2)

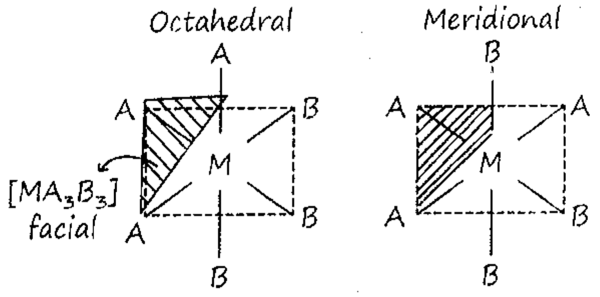
$[MABCD]$ ✓ (3)

$[M(AA)_2]$ X

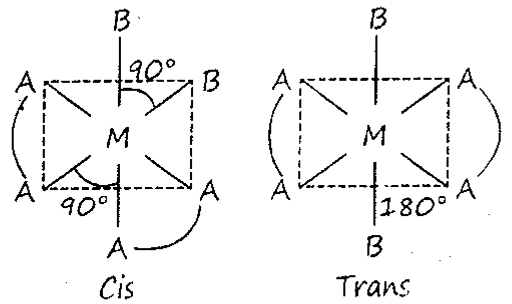
$[M(AB)_2]$ ✓ (2)



Case 2: In C·N = 6



$[M(AA)_2B_2]$

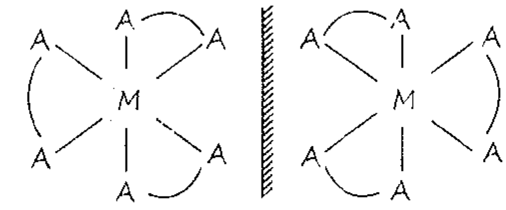


Complexes	No. of G·I
$[M A_4 B_2]$	2
$[M A_4 BC]$	2
$[M A_3 B_3]$	2
$[M A_3 B_2 C]$	3
$[M A_3 BCD]$	4
$[M A_2 B_2 C_2]$	5
$[M A_2 B_2 CD]$	6
$[M A_2 BC DE]$	9
$[M AB CD EF]$	15
$[M (AA)_2 B_2]$	2
$[M (AA)_2 BC]$	2
$[M (AB)_3]$	2

$\boxed{M(AA)_3}$

Does not Exhibit G.I.

2. *Optical isomerism* #



Enantiomer

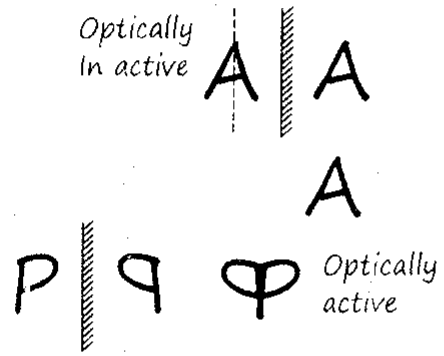
Case 1: In C·N = 4

O·I is not exhibited in

C·N = 4 Tetra x (unless four different ligands are present)

sq planar x

Enantiomer # non - superimposible mirror image



Case 2: In C·N = 6

Complexes	Enantiomer pair
$[M A_4 B_2]$	0
$[M A_4 BC]$	0
$[M A_3 B_3]$	0
$[M A_3 B_2 C]$	0
$[M A_3 BCD]$	1
$[M A_2B_2C_2]$	1
$[M A_2 B_2 CD]$	2
$[M A_2 BC DE]$	6
$[M AB CD EF]$	15
$[M(AA)_2B_2]$	1
$[M (AA)_2BC]$	1
$[M (AB)_3]$	2

$\boxed{M(AA)_3}$

Exhibits O.I

in C·N = 6

Stereo	G.I	Complexes	Enantiomer pair
2	2	$[MA_4B_2]$	0
2	2	$[MA_4BC]$	0
2	2	$[MA_3B_3]$	0
3	3	$[MA_3B_2C]$	0
5	4	$[MA_3BCD]$	1
6	5	$[MA_2B_2C_2]$	1
8	6	$[MA_2B_2CD]$	2
15	9	$[MA_2BCDE]$	6
30	15	$[MABCDEF]$	15
3	2	$[M(AA)_2B_2]$	1
3	2	$[M(AA)_2BC]$	1
4	2	$[M(AB)_3]$	2

$\boxed{M(AA)_3}$

Exhibits O.I
not G.I
OI ✓
GI X

Q. Identify which complex Exhibits G·I or O·I or both ?

1. $[Pt(NH_3)_2Cl(NO_2)]$ (C.N = 4 sq planar)

   $[MA_2BC]$ G·I ✓, O·I X

2. $[Pt(Gly)_2]$ Gly $H_2N-CH_2-COO^{\ominus}$

   $[M(AB)_2]$ G·I ✓, O·I X

3. $[Cu(en)_2]^{+2}$

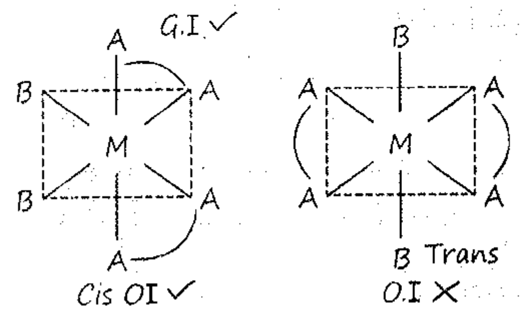
   $[M(AA)_2]$ G·I X, O·I X

4. $[Pt(H_2O)(NH_3)BrCl]$

   $[MABCD]$ G·I ✓, O·I X

5. $[Co(H_2O)_2(OX)_2]^-$

   $[M(AA)_2B_2]$



6. $[Co(H_2O)_2(NH_3)_2(OX)]^+$

   $[M(AA)B_2C_2]$ G·I ✓, O·I ✓

7. $[Zn(NH_3)_2Cl_2]$

   $[MA_2B_2]$ Tetra

   G·I X, O·I X

8. $[Fe(NH_3)_2(CN)_4]^-$

   $[MA_4B_2]$

   G·I ✓, O·I X

9. $[Co(NH_3)_5(NO_2)](NO_3)_2$

   $[MA_5B]$

   G·I X, O·I X

10. $[Co(en)_3]Cl_3$

    $[M(AA)_3]$

    G·I X, O·I ✓

Valence Bond theory

1. C.M.A./ion used (n − 1)d, ns, np or ns, np, nd for Bonding
2. Ligand will donate L.P to the vacant orbital of CMA/ion

3. Pairing occurs when strong field Ligands like NH_3, $CN^{\ominus}$, CO etc are present

Hybri	**Geo**
sp^3	Tetrahedral
dsp^2	Sq. planar
sp^3d	T.B.P
dsp^3	Sq. pyramidal
sp^3d^2	Octahedral
d^2sp^3	Octahedral

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

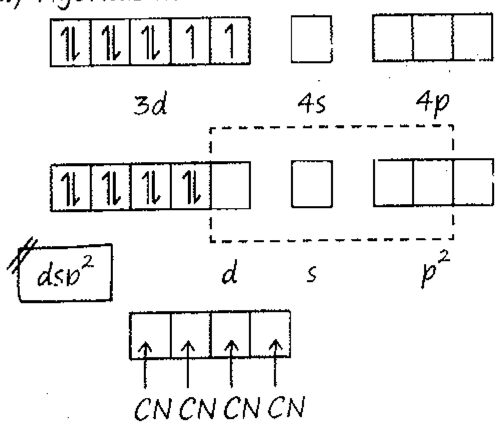
(a) $O \cdot N = +2$

(b) $C \cdot N = 4 \times 1 = 4$

(c) $E \cdot C\ Ni \Rightarrow [Ar]\ 4s^2 3d^3$

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

(d) Hybridisation



(e) Shape Sq planar

(f) Unpaired $e^{\ominus}s = 0$

$n = 0$

$\boxed{MM = 0}$ Diamagnetic

(g) $E \cdot A \cdot N = A \cdot N - O \cdot N + 2 \times C \cdot N$

$= 28 - 2 + 2 \times 4 = 26 + 8 = 34$

(h) Colour Colourless

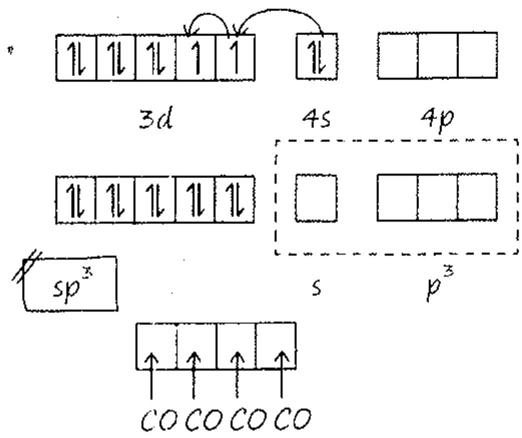
Q. $[Ni(CO)_4]$

(a) $O \cdot N = 0$

(b) $C \cdot N = 4 \times 1 = 4$

(c) $E \cdot C\ _{28}Ni \Rightarrow [Ar]\ 4s^2 3d^8$

(d) Hybridisation



(e) Shape Tetrahedral

(f) Unpaired $e^{\ominus}s = 0$

$n = 0$

$\boxed{MM = 0}$ Diamagnetic

(g) $E \cdot A \cdot N = A \cdot N - O \cdot N + 2 \times C \cdot N$

$= 28 - 0 + 2 \times 4 = 28 + 8 = 36$

(h) Colour Colourless

Q. $[Ni(Cl)_4]^{2-}$

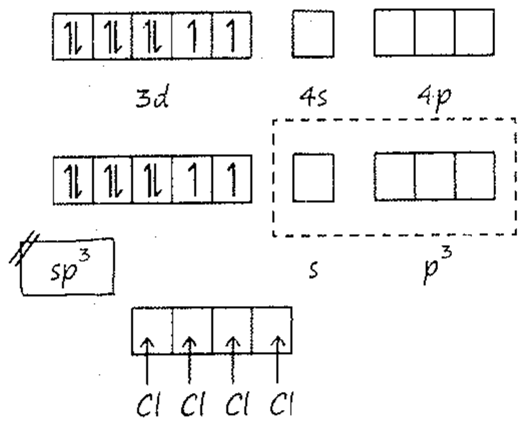
(a) $O \cdot N = +2$

(b) $C \cdot N = 4 \times 1 = 4$

(c) $E \cdot C\ _{28}Ni \Rightarrow [Ar]\ 4s^2 3d^8$

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

(d) Hybridisation



(e) Shape Tetrahedral

(f) Unpaired $e^{\ominus}s = 2$

$n = 2$

$MM = \sqrt{2(2+2)}$

$\boxed{MM = \sqrt{8}}$ Paramagnetic

(g) $E{\cdot}A{\cdot}N = A{\cdot}N - O{\cdot}N + 2 \times C{\cdot}N$

$= 28 - 2 + 2 \times 4 = 26 + 8 = 34$

(h) Colour Coloured

Q. $[Co(NH_3)_6]^{3-}$

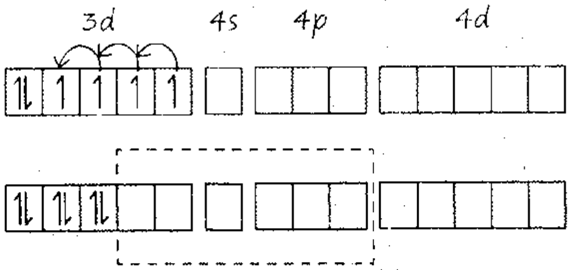
(a) $O{\cdot}N = +3$

(b) $C{\cdot}N = 6 \times 1 = 6$

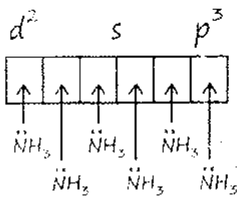
(c) $E{\cdot}C\ {}_{27}Co \Rightarrow [Ar]\ 4s^2 3d^7$

${}_{27}Co^{3-} \Rightarrow [Ar]\ 4s^0 3d^6$

(d) Hybridisation



$\boxed{d^2sp^3}$



(e) Shape Octahedral

(f) Unpaired $e^{\ominus}s = 0$

$n = 0$

$M{\cdot}M = 0$ Diamagnetic

(g) Colour Colourless

(h) HS/LS : Inner complex or Low spin complex or spin paired complex

(I) $E{\cdot}A{\cdot}N = 27 - 3 + 2 \times 6 = 24 + 12 = 36$

Q. $[CoF_6]^{3-}$

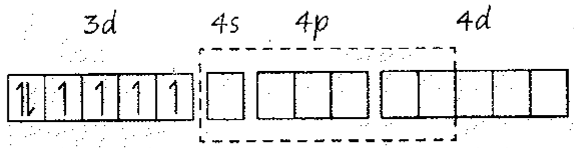
(a) $O{\cdot}N = +3$

(b) $C{\cdot}N = 6 \times 1 = 6$

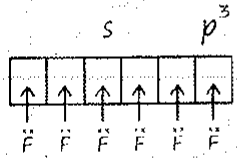
(c) $E{\cdot}C \Rightarrow {}_{27}Co \Rightarrow [Ar]\ 4s^2 3d^7$

${}_{27}Co^{3+} \Rightarrow [Ar]\ 4s^0 3d^6$

(d) Hybridisation



$\boxed{sp^3d^2}$



(e) Shape Octahedral

(f) Unpaired $e^{\ominus}s = 4$

$n = 4$

$M{\cdot}M = \sqrt{4(4+2)} = \sqrt{24}$ Paramag.

(g) Colour Coloured

(h) HS/LS : Outer complex or High spin complex or spin free complex

(I) $E{\cdot}A{\cdot}N = 27 - 3 + 2 \times 6 = 24 + 12 = 36$

Q. $[Ni(NH_3)_6]^{2+}$

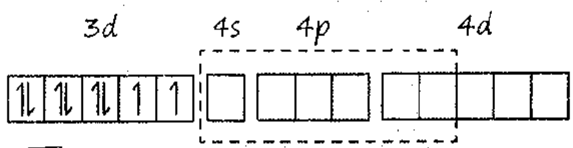
(a) $O{\cdot}N = +2$

(b) $C{\cdot}N = 6 \times 1 = 6$

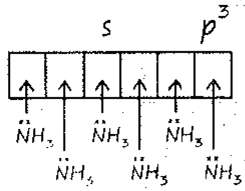
(c) $E{\cdot}C\ {}_{28}Ni \Rightarrow [Ar]\ 4s^2 3d^8$

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

(d) Hybridisation



$\boxed{sp^3d^2}$



(e) Shape Octahedral

(f) Unpaired $e^{\ominus}s = 2$

$n = 2$

$M{\cdot}M = \sqrt{2(2+2)} = \sqrt{8}$ Paramag.

(g) Colour Coloured

(h) HS/LS : Outer complex or High spin complex or spin free complex

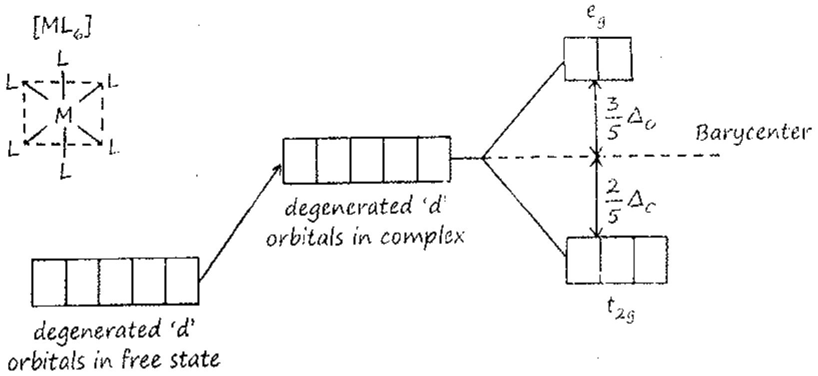
(I) $E{\cdot}A{\cdot}N = 28 - 2 + 2 \times 6 = 26 + 12 = 38$

1. Pt in C·N = 4 always sq planar also (Pd & Au)
2. $[Co(C_2O_4)_3]^{3-}$ is diamag d^2sp^3

C.F.T (Crystal Field Theory)

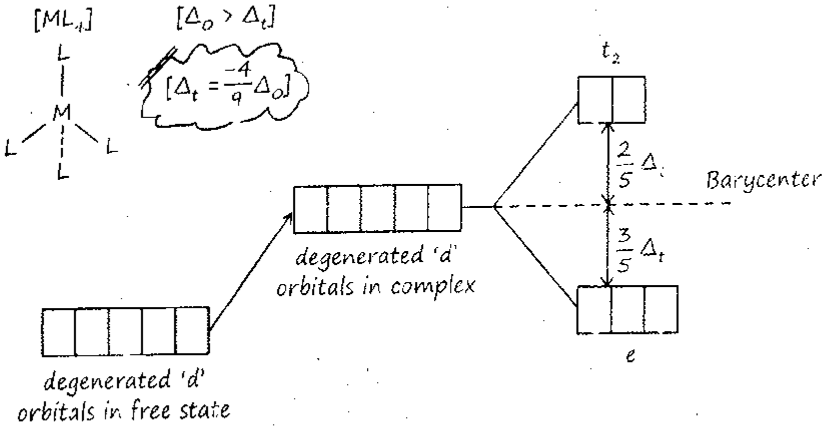
Case 1 : In octahedral field

$\Delta_o \Rightarrow$ C·F·S·E (Crystal field splitting energy)



Case 2 : In Tetrahedral field

$\Delta_t \Rightarrow$ C·F·S·E (Crystal field splitting energy)



Factors affecting C·F·S·E

1. C·F·S·E α C·N
2. CFSE $3d < 4d < 5d$
3. Geometry $\Delta_o > \Delta_t$ $\quad \Delta_t = \frac{-4}{9}\Delta_o$
4. <u>Nature of ligand</u>

   SFL CFSE ↑

   WFL CFSE ↓

*** Spectrochemical Series #**

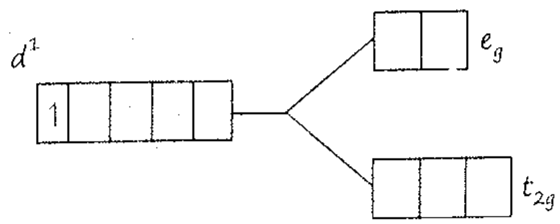
$I^{\ominus} < Br^{\ominus} < SCN^{\ominus} < Cl^{\ominus} < S^{2-} < F^{\ominus} < OH^{\ominus} < OX^{2-} < H_2O$

$< NCS^{\ominus} < EDTA^{4-} < NH_3 < en < NO_2^{\ominus} < CN^{\ominus} < CO$

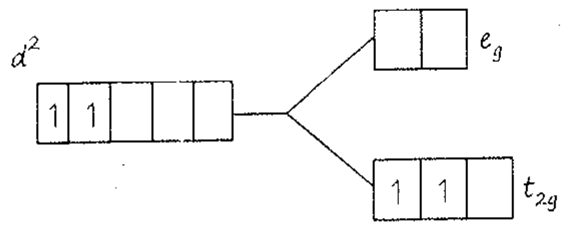
(C donor > N donor > O donor > X donor)

Calculation of C.F.S.E in octa field

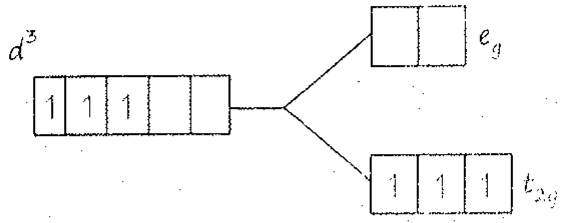
$CFSE = x \times (-0.4\ \Delta_o) + y \times (+0.6\ \Delta_o) + z \times P$



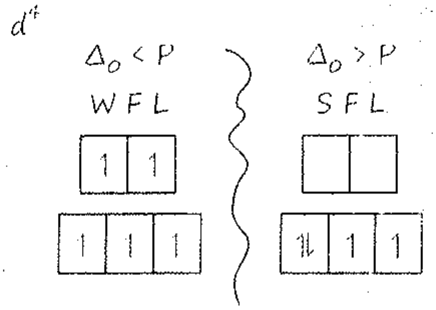
$CFSE = 1 \times (-0.4\ \Delta_o) + 0 + 0 = -0.4\ \Delta_o$



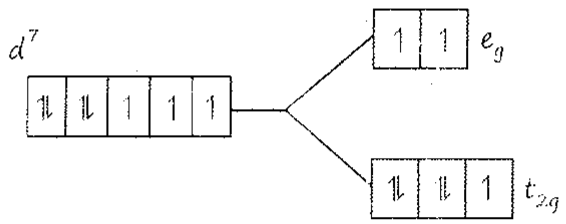
$CFSE = 2 \times (-0.4\ \Delta_o) + 0 + 0 = -0.8\ \Delta_o$



CFSE = 3 × (−0.4 Δ_o) + 0 + 0 = −1.2 Δ_o



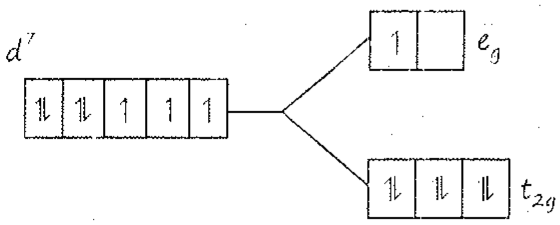
Case 1 : If $\Delta_o < P$ (W F L)



CFSE = 5 × (−0.4 Δ_o) + 2 × (+0.6 Δ_o) + 0

= −2 Δ_o + 1.2 Δ_o = −0.8 Δ_o

Case 2 : If $\Delta_o > P$ (S.F.L)

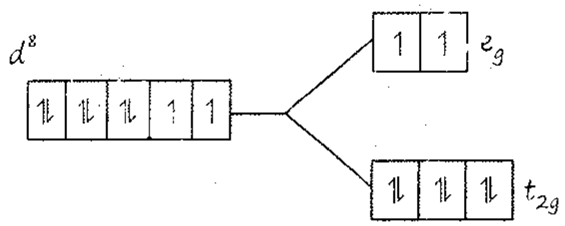


CFSE = 6 × (−0.4 Δ_o) + 1 × (+0.6 Δ_o) + 1 × P

= −2.4 Δ_o + 0.6 Δ_o + P

= −1.8 Δ_o + P

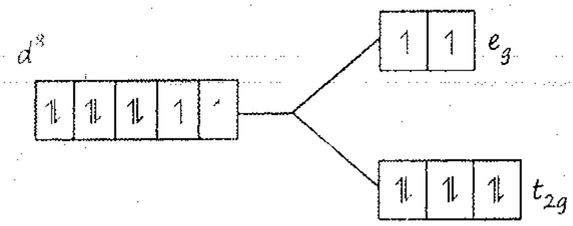
Case 1 : If $\Delta_o < P$ (W F L)



CFSE = 6 × (−0.4 Δ_o) + 2 × (+0.6 Δ_o) + 0

= −2.4 Δ_o + 1.2 Δ_o = −1.2 Δ_o

Case 2 : If $\Delta_o > P$ (S.F.L)

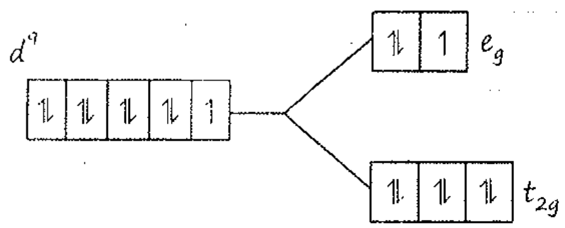


CFSE = 6 × (−0.4 Δ_o) + 2 × (+0.6 Δ_o) + 0 × P

= −2.4 Δ_o + 1.2 Δ_o

= −1.2 Δ_o

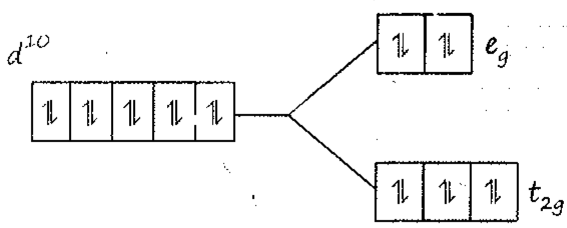
Either W.F.L or S.F.L



CFSE = 6 × (−0.4 Δ_o) + 3 × (+0.6 Δ_o) + 0

= −2.4 Δ_o + 1.8 Δ_o = −0.6 Δ_o

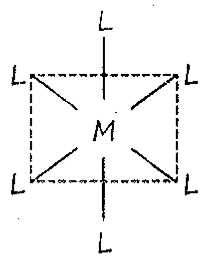
Either W.F.L or S.F.L



CFSE = 6 × (−0.4 Δ_o) + 4 × (+0.6 Δ_o) + 0

= −2.4 Δ_o + 2.4 Δ_o = 0

Jahn-Teller Distortion (J.T.D)

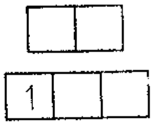


In symmetrical octahedral field, J.T.D is absent

Half filled

Fully filled

H.F + F.F

d^1  ✓

JTD is absent

~~d^3, d^5, d^6 WFL SFL d^8, d^{10}~~

~~3 5 6 8 10~~

d^2 ✓

d^3 ✗

d^4 ✓

d^5 (W.F.L) ✗

d^5 (S.F.L) ✓

d^6 (W.F.L) ✓

d^6 (S.F.L) ✗

d^7 ✓

d^8 ✗

d^9 ✓

d^{10} ✗

Q. Correct order of wavelength of absorption (λ_{ab}) in visible region

$[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(NO_2)_6]^{4-}$

(1) (2) (3)

C.F.S.E (1) < (2) < (3)

λ_{ab} (1) > (2) > (3)

Q. J.T.E is not observed in High spin complexes of

(A) d^4 (B) d^9

(C) d^7 ✓(D) d^8

Q. Δ_o for $[CoCl_6]^{4-}$ is 18,000 cm^{-1} find the CFSE of $[CoCl_4]^{2-}$?

$$\Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18000 = 8000\ cm^{-1}$$

Q. Arrange the order of CFSE

$[CrCl_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$

(1) (2) (3)

<u>CFSE</u> (1) < (3) < (2)

Organometallic comp

Comps in which metal is directly Bonded with Carbon.

O.M.C

Ionic: M & C ⇒ Ionic Bond

Covalent: M & C ⇒ Covalent
a) σ Bonded
b) π Bonded
c) σ & π Both

1. Ionic O.M.C #

$R^{\ominus} Li^{+}$, $CH_3-C\equiv C^{\ominus} Na^{+}$ etc

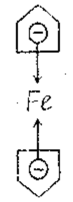
2. <u>Covalent O.M.C</u>

(1) <u>σ Bonded</u>

$\overset{\delta-}{R}-\overset{\delta+}{Mg}-\overset{\delta-}{X}$, $(CH_3)_4Sn$, Al_2Me_6 etc

(2) Ferrocene

$[Fe-(\eta^5-C_5H_5)_2]$



<u>Hapticity</u> no. of C in Ring

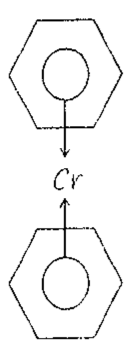
ON = +2

Fe

Bis-(η^5-cyclopentadienyl) iron (II)

3. <u>Dibenzene Chromium</u> #

$[Cr(\eta^6-C_6H_6)_2]$



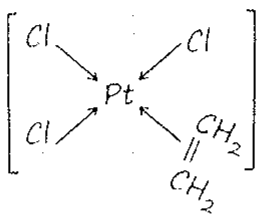
Bis (benzene) chromium (0)

O.N = 0

Cr

4. <u>Zeise's salt</u>

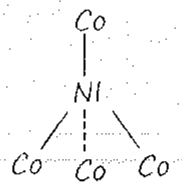
$K[Pt\,Cl_3(C_2H_4)]\cdot xH_2O$

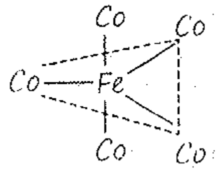


$\cdot xH_2O$

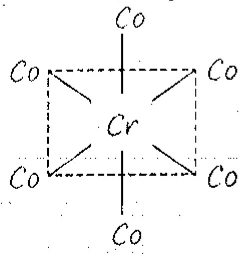
σ and π Both bonded

Metal Carbonyl #

$Ni(CO)_4$  sp^3

$Fe(CO)_5$  dsp^3 d_{z^2}

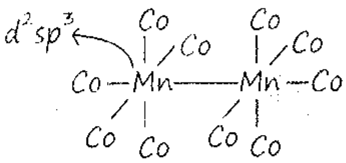
$Cr(Co)_6$



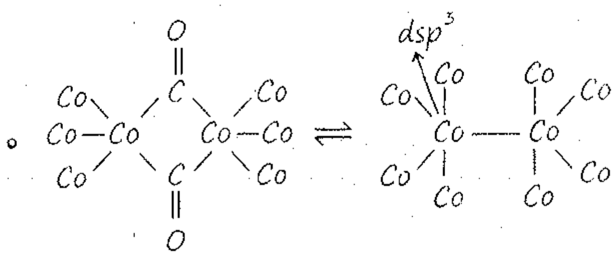
d^2sp^3

$d_{x^2-y^2}, d_{z^2}$

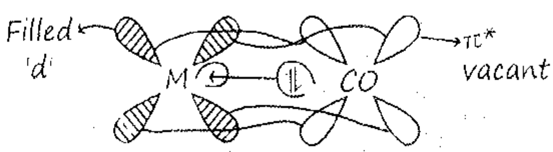
$Mn_2(Co)_{10}$



$Co_2(Co)_8$



Bonding in Metal carbonyls



1. M & C σ Bond is formed by donation of L.P of carbonyl carbon to the vacant 'd' orbital of metal.
2. M & C π Bond is formed by sidewise overlapping of M (filled 'd') & C (π* orbitals)
3. This bonding is known as synergic bonding & effect is called synergic effect & ligands are called π-acid ligands CO, CN^-, NO, PF_3 etc.
4. due to synergic bonding

   M & C B.O ↑ B.S ↑ B.L ↓

   C & O B.O ↓ B.S ↓ B.L ↑
5. Charge density on metal ↑

   M & C B.O ↑ B.S ↑ B.L ↓

   C & O B.O ↓ B.S ↓ B.L ↑

Q. If CO Bond length in CO is 1.128 Å then what is the value of CO Bond length in $Fe(CO)_5$?

(A) 1.15 Å (B) 1.128 Å

(C) 1.72 Å (D) 1.118 Å

Q. Compare CO Bond strength in

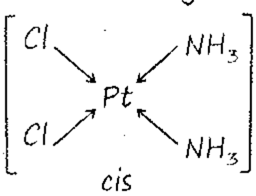
$[Mn(CO)_6]^+$, $[Cr(CO)_6]$, $[V(CO)_6]^-$

1 2 3

CO Bond strength $\boxed{1 > 2 > 3}$

Some Imp. points

1. Chlorophyll, Haemoglobin & Vitamin B_{12} are coordination complexes of Mg, Fe & Co respectively.
2. Anti cancer agent is cis platin

    $[Pt(NH_3)_2Cl_2]$

   cis
3. Wilkinson catalyst is used for hydrogenation of alkene $[Rh(PPh_3)_3Cl]$

   chloridotris-(triphenyl phosphine) rhodium (I)
4. Rxn of $CuSO_4$ with Excess KCN

   $$CuSO_4 + \underset{(Excess)}{KCN} \longrightarrow K_2SO_4 + K_3[\overset{+1}{Cu}(CN)_4] + \underset{(N\equiv C-C\equiv N)}{(CN)_2}$$
5. Chelate complexes are more stable than non chelate complex usually

   $[Fe(C_2O_4)_3]^{3-} > [FeCl_6]^{3-}$
6. O.N of metal in metal carbonyls may be –ve

   $K[CO(CO)_4]$

   $1 + x + 0 = 0$

   $\boxed{x = -1}$

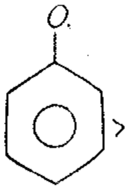
Organic Chemistry

Organic Chemistry

1 GOC

1. Nucleophilicity

$$Nu^- \propto \frac{1}{EN} \propto \frac{1}{Reso} \propto \frac{1}{Bulkiness.}$$

$CH_3-CH_2-O^-$ >  > $CH_3-\overset{O}{\overset{||}{C}}-O^-$ >

$Nu^- \propto LP \propto -ve$ charge $\propto$ size of C^- ↑

$F^- < Cl^- < Br^- < I^-$ [Polar protic solvent]

Polar Aprotic = $F^- > Cl^- > Br^- > I^-$.

2. Priority Order

A > M > H > I.

Aromatic mesomeric Hyperconjugation Inductive

3. Orders

+M:- $CH_2^- > NH^- > O^- > \ddot{N}H_2 > \ddot{O}H$

Activators

$> \ddot{O}CH_3 > \ddot{N}H-\overset{O}{\overset{||}{C}}-CH_3 > \ddot{O}-\overset{O}{\overset{||}{C}}-R$

$> :\ddot{F}: > :\ddot{Cl}: > :\ddot{Br}: > :\ddot{I}:$

+I:- $CH_2^- > NH^- > O^- > RCOO^- >$

3°Butyl > isopropyl > Et > Me

> T > D > H

−M:- $\overset{+}{C}H_2 > NO_2 > CN > SO_3H$

> CHO > COR > COOR > $CONH_2$

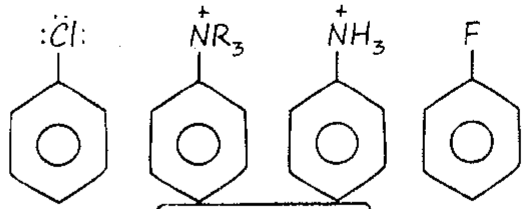
> COO^- Deactivators

−I:- $\overset{+}{N}F_3 > -\overset{+}{N}R_3 > -\overset{+}{N}H_3 > NO_2$

> CN > SO_3H > CHO > COR > COOH

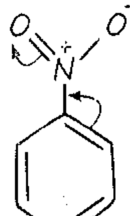
> COOR > Halogens > OCH_3 > OH >

≡ > NH_2 > Ph > =



(No d-orbital)

−I ✓ (Not−M)

 → Shows −M

+ With respect to group already present, it's **Meta** position is not affected by Meso or Reso effect.

Only Inductive!

+ Cyclic > Linear > Cross conjugation.
+ More equivalent ↑ Acidic Nature ↑ resonating structure of CB

Rules for Resonating Structure

Stability:- least stable: (++) or (−−) near

1. Octet complete.
2. Neutral structure > Charged ones.
3. More EN = −ve Charge
   Less EN = +ve Charge.
4. +ve & −ve charge near to each other

Bredt's Rule

1. At bridge head carbon, −ve is not accepted till total no. of carbon in the ring is 8. After 8-carbon sp^2 chalega:

$$-to = BI \propto \frac{1}{Reso}$$

Effect of Resonance

1. Max e^- density.
2. = to –
   BL ∝ Reso

Heat of hydrogenation $\propto \frac{1}{\text{Reso}} \propto \pi$ bond

Aromaticity ∝ Reso Energy ∝ Reso

α + M

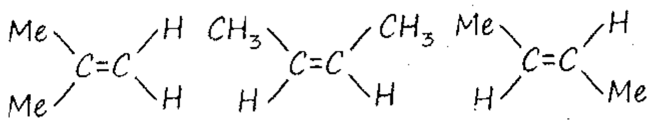
Stability Order

Conjugated   Isolated   Cumulated

HOH Order

Hyperconjugation   [H > O > T]

Alkane:– σ – π* overlap



Geminal   Cis   trans.

Stability: Geminal > Trans > Cis.

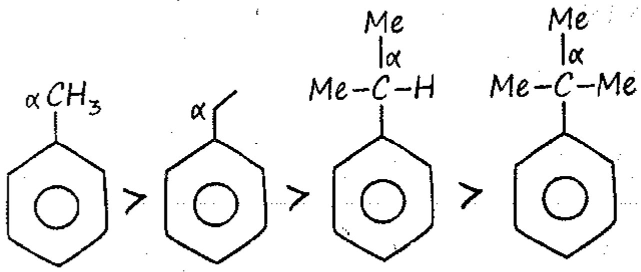
+ Heat of hydrogenation is energy required to convert double into single bond in a molecule.

Stability ↓   HOH ↑

Reactivity ∝ Stability

$\alpha(\alpha\text{–H}) \approx$ H-effect $\propto \frac{1}{\text{HOH.}}$

Reactivity of Benzene



αH = 3   αH = 2   αH = 1   αH = 0.

+ Reactivity ∝ αH

VIMP TRICK

D → Distance

N → Number

P → Power

Only inductive

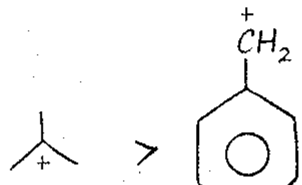
+ [redacted] (Stability)

Hyperconjugⁿ

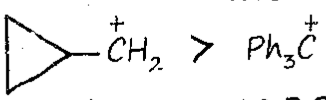
+ [redacted] (Stability)

α-H = 3   3 α D   3 α T

(Stability)



9 α H   4R.S.



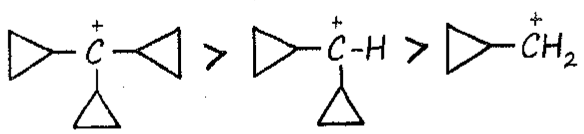
αH = 1   10 R.S.

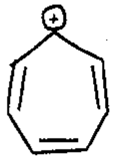
Dancing Reso

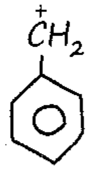
Very Stable C^+ Dancing Reso

Cyclopropyl Methyl Carbocation.

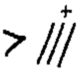
Stability Order of Carbocation

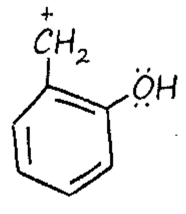
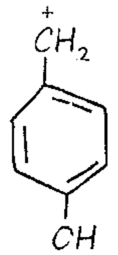


>  > Ph_3C^+ > Ph_2C^+

> $(CH_3)_3C^+$ >  > 

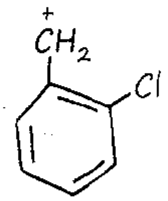
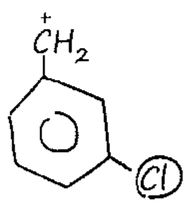
> $[CH_3]_2\overset{+}{C}H$ > $CH_3-\overset{+}{C}H_2$ > $\overset{+}{C}H_2$ > 

> 

+  <  **(Stability)**

-I Max.
+M $dist^n$ independent

-I Min
+ M.

+  < 

-I Max
-I > +M

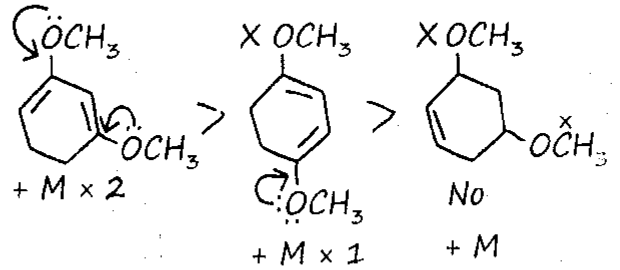
-I less
m-position
only inductive !

+ **Stability of C^+ and C^-**

$$C^+ \propto \frac{+M + I}{-M - I}$$

$$C^- \propto \frac{-M - I}{+M + I}$$

☞

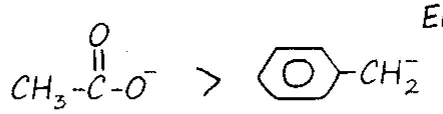


+M × 2 > +M × 1 > No +M

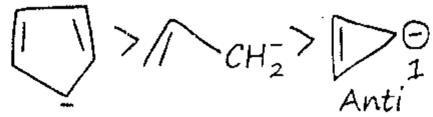
+ +I order

T > D > H.

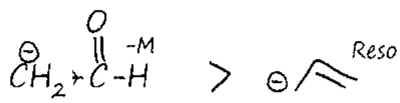
V.imp Examples

 Equivalent Reso.

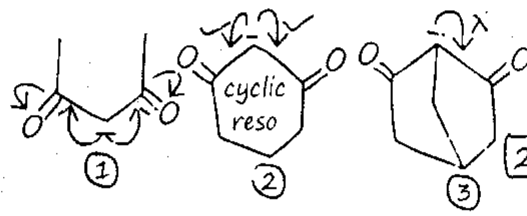
F_3C^- < Cl_3C^- d orbital Reso.



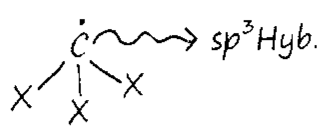
2 R.S. 1 R.S. 1 R.S. Anti aromatic ($4n\ \pi e^-$)



$\underset{-M}{H-\overset{O}{\overset{\|}{C}}}-\overset{-}{C}H-\underset{-M}{\overset{O}{\overset{\|}{C}}-H}$ > $CH_3-\overset{-}{C}H-\underset{-M}{\overset{O}{\overset{\|}{C}}-H}$

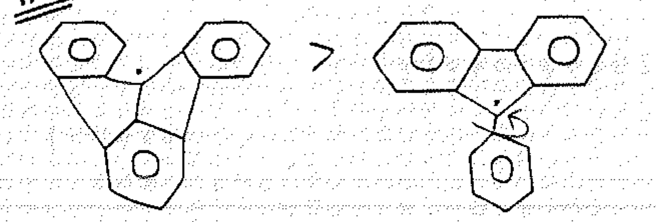


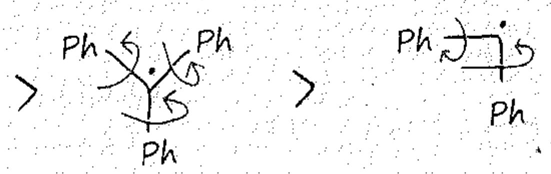
$\boxed{2>1>3}$

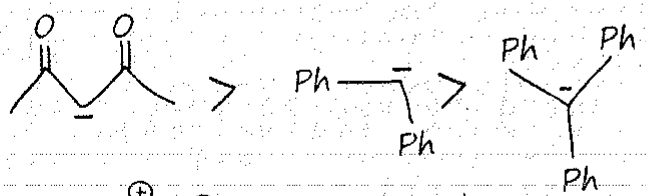


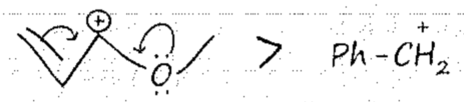
Ph_3C^+ > $Ph_2\overset{+}{C}H$ > $Ph\overset{+}{C}H_2$
$Ph_3\dot{C}$ > $Ph_2\dot{C}H$ > $Ph\dot{C}H_2$
☞ Ph_2CH^- > Ph_3C^- > $PhCH_2^-$

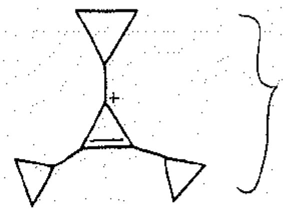
IIT











World Most Stable C^+.

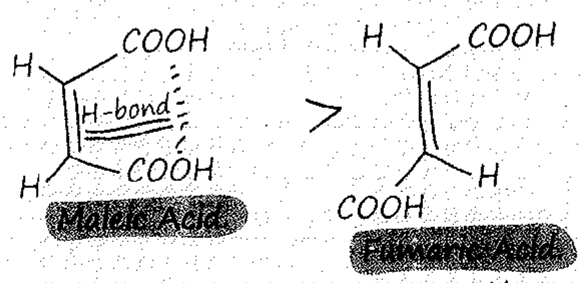
Theory	Acid	Base
1] Arrhenius. पानी (BADP)	$H^+(aq)$	$OH^-(aq)$
2] Bronsted-Lowry	Proton-donor $HCl \longrightarrow H^+ + Cl^-$	Proton acceptor $\ddot{N}H_3 + H^+ \longrightarrow NH_4^{\oplus}$
3] Lewis	L.P. Acceptor $NH_3 + H^+ \longrightarrow H-\overset{\ominus}{N}\rightarrow H$ (Base, Acid)	L.P. Donor

Acidic Nature of Carbon Acids

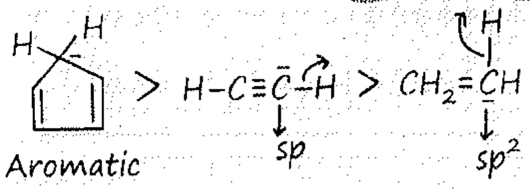
1> $\begin{array}{c} COOH \\ | \\ COOH \end{array}$ > H–COOH

2> HCOOH > Ph–COOH > CH_3–COOH

3>



4>



Ortho Effect } only in Benzoic not in Phenol

Repulsion b/w COOH & ortho group such that COOH goes out of plane & +M does not operate. ∴ Acidity ↑.

Substituted Ortho Benzoic Acids > Benzoic or (m & p-isomer) Acids.

(Acidic strength)

Basic nature of amine

① Aliphatic > Aromatic

$\ddot{N}H_3$ ① $R-\ddot{N}H_2$ ② $R-\underset{\cdot\cdot}{\overset{R}{\overset{|}{N}}}-H$ ③ $R-\underset{\cdot\cdot}{\overset{R}{\overset{|}{N}}}-R$ ④

If

Gas Phase (or non-polar solvent):-

$3° > 2° > 1° > NH_3$

Polar protic Solvent

R = CH_3.   R = Ethyl.

$2 > 1 > 3 > \ddot{N}H_3$ $2 > 3 > 1 > \ddot{N}H_3$

$$\text{Basicity} \propto \frac{1}{\text{Aromaticity}}$$ e^- density decreases

Basicity order

Guanidine > $R-\ddot{N}H_2$ > $\ddot{N}H_3$

> Aromatic amine > $R-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$

> $R-C\equiv\ddot{N}$

Guanidine:- $H_2\ddot{N}-\overset{\ddot{N}H_2}{\overset{|}{C}}=\ddot{N}H$

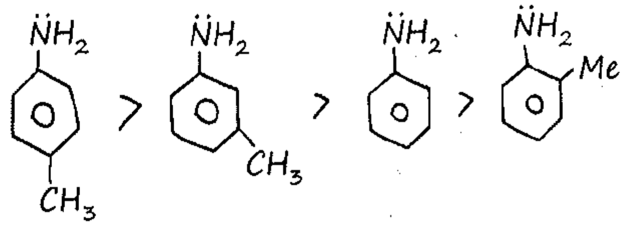
$$\text{Basicity} \propto \frac{1}{\text{Reso}} \propto \frac{1}{\text{E.N}}$$

[redacted]

There is no repulsion b/w para group & NH_3^+ so after L.P. donation it becomes more stable.

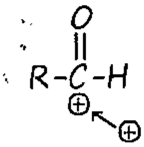
Para Amines > Ortho Amines.
(Basic strength)

$\boxed{P > m > o}$



Neet
Reactivity of RX $\propto$ C^+ Stability

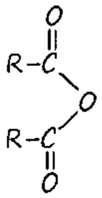
Neet
Reactivity of carbonyl compounds



$\oplus$ ↑ Reactivity ↑.

[redacted]

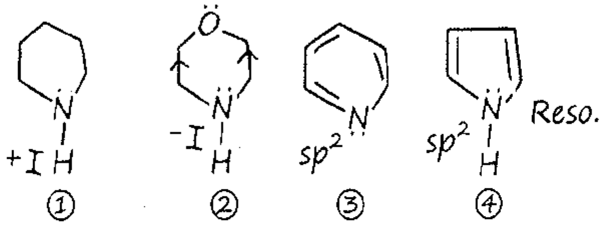
Acid anhydride :-



Acyl chloride:- $R-\overset{O}{\overset{\|}{C}}-Cl$

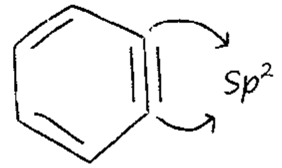
1° Amide
↓
$RCO\ddot{N}H_2$

Ester :- $R-\overset{O}{\overset{\|}{C}}-OR$.



K_b :- ① > ② > ③ > ④.

+



Rearrangement of carbocation

Migratory Aptitude:-

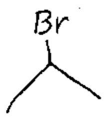
H > Ar > R.
Benzyl.

Reaction

Substitution Rx^n → Single bond

Addition Rx^n → // or /// bond involved

Markovnikov Rule	Anti Markovnikov Rule
Θve part of reagent goes to multiple bonded carbon bearing less "H"	Θve part goes to multiple bonded carbon bearing more "H"



(Peroxide)

2 Hydrocarbons

Name of reaction	Reagent	Function
1> Hydrogenation:- of alkene/alkyne	$\xrightarrow[Ni/Pt/Pd]{H_2}$ Raney Ni [Sabatier-Senderens Rx^n]	Alkane banao. Syn Addition
2> Reduction of alkyl halide to alkane	$\xrightarrow[(Zn + H^+)]{Zn + dil\ HCl}$	X- hatao H- lagao
3> Wurtz reaction I > Br > Cl > F	Na/Dry Ether (New C-C bond Form)	Free Radical banao aur higher Alkane banao $R^\bullet \rightarrow R-R$
4> Decarboxylation [R-COOH ⟶ R-H]	$\underset{3}{NaOH} + \underset{1}{CaO}$ (3 : 1) Acidic Δ Poison	COOH/COONa hatao "H" lagao. [All COOH Eliminated]
5> Kolbe's electrolysis of:- RCOONa (or RCOOK) (New C-C bond Form)	Cathode :- $H_2 \uparrow$ Anode :- Alkane (R–R) Sol^n = Basic [pH ↑]	Same like Wurtz Rx^n. Free Radical banao!
6> Halogenation:- of alkane F > Cl > Br > I	X_2 / hv In case of I_2 also use HIO_3 & HNO_3	"H" - Hatao "X" - lagao.
7> Isomerisation:- of alkane	Anhyd. $AlCl_3$ / HCl	Chain isomer banao.
8> Aromatisation of:- n-hexane or higher alkane	Cr_2O_3 or V_2O_5 Mo_2O_3	Aromatic Ring banao.
9> Fittig rxn of:- aryl iodide	Na - DE. Chlorobenzene ⟶ Ph – Ph	
10> Wurtz fittig rxn:- (Ar–X + R–x)	Na - DE. Chlorobenzene ⟶ Toluene + Ph – Ph	
11> Ullmann rxn:-	Cu - DE. Iodobenzene ⟶ Ph – Ph	

New C-C bond form

12> Corey-HOUSE syn:- Gilmann Reagent. (R_2CuLi)

$$R_2^-Cu^-Li^+ + R'-X \longrightarrow R-R'$$

If $3°R-X \Rightarrow$ Alkene.

13> Reduction of R-X:-

$Zn + HCl$
$Zn + CH_3COOH$
$Zn + NaOH$
$Zn - Cu + C_2H_5OH$
$Al - Hg/C_2H_5OH$

} X hatao H lagao

$H_2/Ni, Pt, Pd$

LAH (1°, 2°Rx) $\longrightarrow$ 1° - 2° R-H 3° = Alkene

SBH (2°, 3°Rx) $\longrightarrow$ 2° - 3° R-H 1° = No Rx^n

HI/Red P. ☹ $\longrightarrow$ X hatao H lagao

TPH (1°, 2°, 3°) $\longrightarrow$ FRS. X hatao H lagao

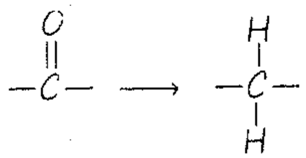
14> Grignard reagent:- R- MgX

$$R - X + Mg \xrightarrow{DE} R^- - \overset{+2}{Mg}\bar{X}$$

$$R^- - MgX \xrightarrow{H^+} R-H$$

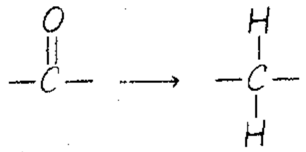
Acidic Medium

15> Clemmenson reduction:- $\frac{\text{Zn-Hg}}{\text{Conc. HCl}}$

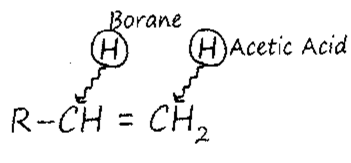


Basic Medium

16> Wolff-kishner reduction:- $\frac{NH_2NH_2}{NaOEt}$



17> HBO of Alkene:- B_2H_6/ THF
CH_3COOH/ 0°C



18> Hydrolysis of carbide:-

$Al_4C_3^{-4} + H_2O$
$Be_2C^{-4} + H_2O$
$Mg_2C^{-4} + H_2O$

} CH_4

$CaC_2^{-2} + H_2O \longrightarrow HC \equiv CH$

19> Nitration of alkane :- Conc. HNO_3 $R{-}H \xrightarrow{H\dot{O} + \dot{N}O_2} R{-}NO_2$

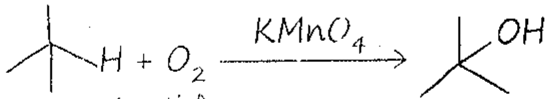
20> Sulphonation of alkane :- Conc. H_2SO_4 $R{-}H \xrightarrow{H\dot{O} + HS\dot{O}_3} R{-}SO_3H$

21> Combustion:- $C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \xrightarrow{\Delta} nCO_2 + (n+1)\, H_2O$

$CH_4 + \frac{1}{2} O_2 \xrightarrow[Ni]{\Delta} CO + 2H_2$
(partial) Syn gas.

$CH_4 + O_2 \xrightarrow[200°C]{Cu} CH_3 - OH$
(partial)

$CH_4 + O_2 \xrightarrow[200°C]{MbO} HCHO$
(partial)



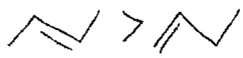
(partial)

22> Dehydration of alcohols:-

E_1 = Multi Step C^+ ✓

E_2 = Single Step [Anti Elim^n]

Conc. H_2SO_4
H_3PO_4 $KHSO_4$
$POCl_3$ /Pyridine

Rearrangement ✓
C^+ banega
Saytzeff Rule:- 
Jaha pr -OH laga hoga
Waha pr C^+ banakr rearrange
krke product likhna !

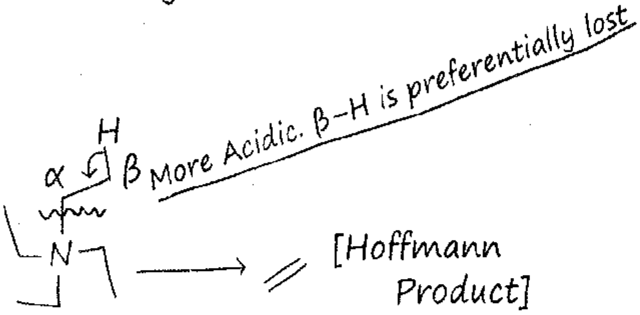
23> Dehydro-halogenation of haloalkane:- (R-X → Alkene)
(α, β- elimination)

Alc. KOH.
(Anti Elim^n)

Bad LG } Hoffmann
Bulky base } (Major)

24> Hoffmann elimination of quaternary ammonium hydroxide :-

Ag_2O/H_2O
(Anti Elimi^n)



25> Copes elimination of 3° N-Oxide:-

PAA
MCPBA [Syn Elim^n]
H_2O_2/Δ

Less Crowded β-H Eliminate
1st (Hoffmann Product)

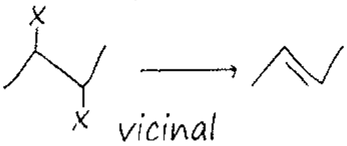
26> Partial reduction of non terminal alkynes:-

Lindlar's Catalyst
↳ H_2-Pd-$BaSO_4$
H_2-Pd-$CaCO_3$
H_2/Ni_2B (Nickel or Boride).
Cis Alkene

Birch Reduction
↳ Na or Li/Liq NH_3
Trans Alkene

27> Dehalogenation of vicinal-dihalide :- Free Radical banake Product likho....

Zn dust + CH_3OH or
NaI + Acetone (ether)
→ Anti elimination



vicinal dihalides convert to alkene.
Tetrahalides convert to alkyne.

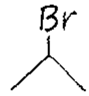
28> Addition of H_2 or alkene/Alkyne:-

Raney Ni, Pt/C, Pd/C, Rh/C, PtO_2 [Adam's Catalyst]

Alkene से Alkane
Alkyne से Alkane

29> Addition of HX:- [Rearrangement ✓]

MR* Alkene + HX ⟶ Alkyl halide. C^+ ✓
(MarkowniKoff Obey!)
Jidhar C^+ Stable hoga udhar X lagega.



(Major)

AMR Anti MarkowniKoff:- HBr/Peroxide

(Major)

30> Hydration of alkene:- $H^+ \longrightarrow C^{\ominus}$ Pr
C^+ ✓ MR*
$OH^- \longrightarrow$ Stable C^+ पर lagega.

31> Addition of X_2-CCl_4:-

Non classical C^+
Anti Addition
CAR, TAM. CSM, TSR.
NO^+Cl^- = Tilden Reagent

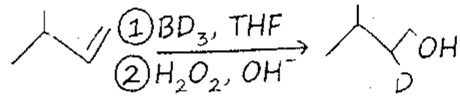
Vicinal dihalide banega.

32> Hydroboration oxidation(HBO) (**Syn addition**)
AMR No C^+

$$\frac{①\ BH_3/THF}{②\ H_2O_2/OH^-}$$

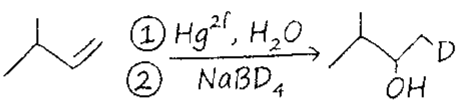
$CH_3COOH \rightarrow$ alkane

Less crowded pr OH^- uske Adjacent Ⓗ from BH_3



33> Oxymercuration demercuration (OMD) (**Anti addition**)
MR No C^+

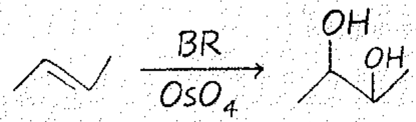
$$\frac{①\ Hg(OAc)_2\ H_2\overset{OH}{O}\text{-THF}}{②\ (Et_2O)\ NaB\underset{H}{H_4}\ (THF)}$$



More Crowded Pr OH^- (H_2O) uske adjacent H from R.A = $NaBH_4$

34> Bayer's reagent & OsO_4/pyridine/ $NaHSO_3$ [syn-addition]:-

+ BR = Cold alkaline dil $KMnO_4$
+ $OsO_4/Py/NaHSO_3$
+ Vicinal diol banega [1, 2-diol]

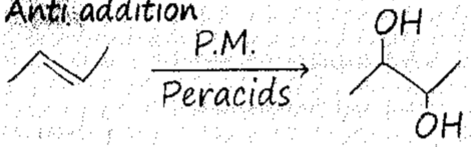


35> Peracids/prevost method (Anti addition) :-

$CH_3-\overset{O}{\overset{\|}{C}}-O-O-H/H_3O^+$

$\rightarrow I_2/CH_3-CO\bar{O}Ag^+$

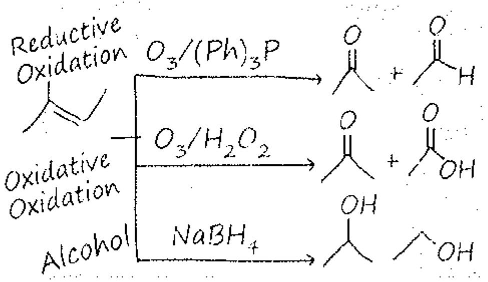
+ Vicinal diol banega
+ **Anti addition**



Syn
- $H_2/Pd/Pt$
- alk. $KMnO_4$
- OsO_4
- HBO

Anti
- Br_2/CCl_4
- $Br_2/H_2O/MeOH/NaCl$
- HOCl
- $RCOOH/H_3O^+$
- Prevost
- OMD

36> Ozonolysis:-



CH_3OH or $[O_3]$
CH_2Cl_2 (−78°)

Note:- $O_3/NaBH_4$ or LAH } gives Alcohol

//$_O$ Todo $-\overset{\|}{C}-$ lagao

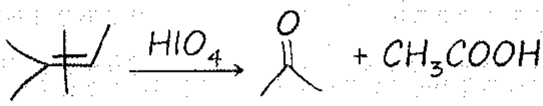
Oxidative Ozo:- $-COOH + -\overset{O}{\overset{\|}{C}}-$
↳ H_2O, H_2O_2, Ag_2O

Reductive Ozo:- $-CHO + -\overset{O}{\overset{\|}{C}}-$
↳ $Zn + H_2O$, $(CH_3)_2S$, $(Ph)_3P$, Zn + HCl/Acetic. Acid, Thiourea

37> Oxidation:-

+ Hot Conc. $KMnO_4/H^+/OH^-$
+ $K_2Cr_2O_7/\Delta + NaIO_4$
+ $HIO_4 + [CH_3COO]_4Pb$

Alkene से Acid Banao !



38> Wohl-zeigler:-
(Free-Radical)

+ NBS/CCl_4, hv (Br lgayega.)
+ SO_2Cl_2
+ Br_2 − 500°C
+ Cl_2 − 500°C

Only Allylic/Benzylic Sub^s.
Jaha Kahi pr $C^{\cdot}$ Stable hoga waha pr −Br lagega.

39> Rx^n with SeO_2:- Allylic −OH Add^n.

40> 1,1,1 tri-halo compound:-

$$H-C(Cl)_2-Cl + 6Ag + Cl-C(Cl)_2-H \longrightarrow H-C\equiv C-H + 6AgCl$$

41> Dehydrohalogenation:- (Anti Elimination)

Vicinal/Geminal dihalides $\longrightarrow$ Alkynes

i. Alc. KOH/Δ

ii. $NaNH_2$ or KNH_2 or $Na/liq\ NH_3$

If $NaNH_2$ use directly

3 — Terminal alkyne

2 — intermediate vinylic halide

} Moles Req.

42> Addition of Br_2/CCl_4 on alkyne:- Alkyne से Tetrahalide banao.

$$R-C\equiv C-R \longrightarrow R-CBr_2-CBr_2-R$$

43> Addition of $2H\overset{+}{O}\overset{-}{Cl}$:-

$$R-\overset{+}{C}\equiv\overset{-}{C}-R \xrightarrow{2H\overset{+}{O}\overset{-}{Cl}} R-C(OH)_2-CCl_2-R \longrightarrow R-\underset{\|}{\overset{O}{C}}-CCl_2-R$$

Jaha Stable C^+ waha $-\underset{\underset{O}{\|}}{C}-$ uske Adjacent Geminal dihalide.

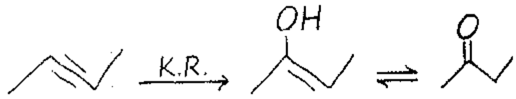
44> Addition of HBr:- Alkyne $\longrightarrow$ Vicinal or *Geminal dihalide. (Major) $\hookrightarrow :\ddot{Br} = +M$

45> Higher alkynes from Lower alkynes:-

$$HC\equiv \overset{\ominus}{C}H \xrightarrow[\diagup Br]{NaNH_2} HC\equiv C\diagup \xrightarrow[\diagup Br]{NaNH_2} \diagdown C\equiv C\diagup$$

46> Kucherov's rxn:- [$Nu^{\ominus}$ add^n rx^n]

$$\frac{60\%\ \text{or}\ 40\%\ \text{dil.}\ H_2SO_4}{1\%\ HgSO_4}$$



$-OH$ udhar lagega jaha more stable C^+.

47> Polymerisation:- Red-hot Fe or Cu Tube. or $Ni(CN)_2$

Alkyne से Aromatic Ring.

48> Tollen's or fehling Test:-

Terminal alkynes give (+)ve Test

Tollen's:- $[Ag(NH_3)_2]^+ \xrightarrow{///}$ White ppt of silver alkynide

Fehling:- $\left[aq.CuSO_4 + Na/K\ \text{tartarate}\right] \xrightarrow{///}$ Red ppt. of copper alkynide

$C_6H_6 = C_6D_6 = C_6T_6$

49> Nitration of benzene:- ($E^+ = NO_2^+$)

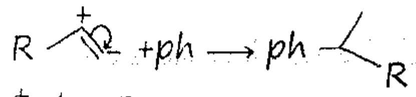
Conc. HNO_3 + conc. H_2SO_4 (1 : 2)
conc. HNO_3
Fuming HNO_3
$NO_2^+ BF_4^-$

$ph \longrightarrow ph\text{-}NO_2$
Oil of Mirbane

50> Friedel craft's alkylation:- ($E^+ = R^+$)

Anhydrous $AlCl_3$.
& other Lewis Acid.

$ph + R^+\text{-}X^- \longrightarrow ph\text{-}R$

HF / 0°C $\longrightarrow$ 

dil. H_2SO_4 $\longrightarrow \overset{+}{R} \{ \overset{-}{OH} + ph \longrightarrow ph\text{-}R$

51> Friedal craft's acylation:- ($E^+ = R\text{-}\overset{O}{\overset{\|}{C}}{}^{\oplus}$)

Anhydrous $AlCl_3$.

$ph + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}X \longrightarrow ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$

$ph + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \longrightarrow ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + R\text{-}COOH$

Ye uss dir^n. में Tutega jaha pr more stable C⁺ banega!

52> Halogenation:- ($E^+ = X^{\oplus}$)
($F_2 > Cl_2 > Br_2 > I_2$)

X_2 / Fe
X_2 / FeX_3

$ph \longrightarrow ph\text{-}X$

53> Sulphonation:- ($E^+ = SO_3$)
(Neutral E^+)
$C_6H_6 > C_6D_6 > C_6T_6$

i. conc. H_2SO_4
ii. oleum ($H_2S_2O_7$)

$ph \longrightarrow ph\text{-}SO_3H$

54> Oxidation of alkyl halide:-

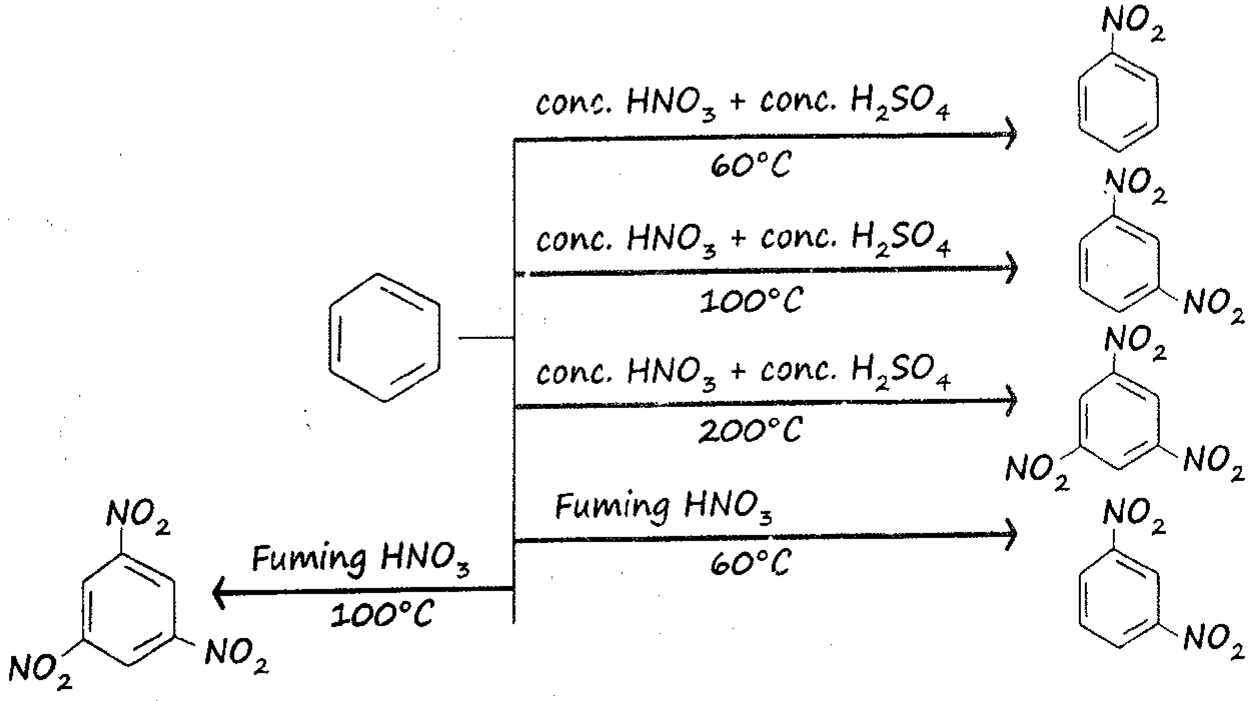
$KMnO_4$
$K_2Cr_2O_7$

$ph\text{-}R \longrightarrow ph\text{-}\boxed{COOH}$
Note:- α-H must be present

55> Rxn with fused NaOH:-

$ph \xrightarrow[\text{Condition}]{\text{Drastic}} ph\text{-}OH$

Benzene pr Good Leaving Group होना है!



56> Gattermann Koch reaction:- (1) $CO + HCl, AlCl_3$ ph $\longrightarrow$ ph-CHO

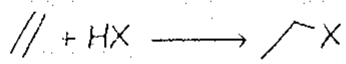
57> Gattermann aldehyde synthesis:- (1) $HCN + HCl, AlCl_3$ ph $\longrightarrow$ ph-CHO
(2) H_2O

3 Haloalkane and Haloarene

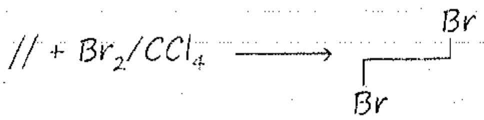
1) Halogenation of Alkane :-

$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + HCl$

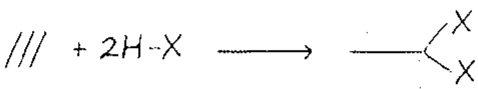
2) Addition of HX to Alkenes :-



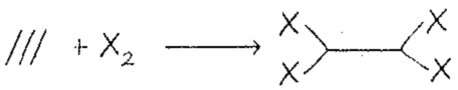
3) Addition of X_2/CCl_4 Alkene :-



4) Addition of HX to Alkyne :-



5) Addition of X_2 to Alkyne :-



6) Reaction with NBS :-

7) From Alcohols :-

R-OH $\xrightarrow{SOCl_2}$
- Py ✓ → S_N2
- $\boxed{R-Cl}$
- Py x → S_Ni

→ Darzen's Process

$\boxed{R-OH}$
- $\xrightarrow{PCl_5} R-Cl + POCl_3 + HCl$
- $\xrightarrow{PCl_3} R-Cl + H_3PO_3$
- $\xrightarrow{P + Br_2} R-Br + H_3PO_3$
- $\xrightarrow{P + I_2} R-I + H_3PO_3$

} S_N2

8) Reaction of Alcohol with HX :-

HI > HBr > HCl > HF

$R-OH + HX \longrightarrow R-X + H_2O$

$3° \rightarrow S_N1$ $1°/2° \rightarrow S_N1$ or S_N2

Lucas Reagent:- White Turbidity alcohol { → 3° ↑↑↑ ; → 2° ✓ ; → 1° X

9) Hunsdiecker- Borodin Reaction :-

Free Radical Mech^m.

$R-\overset{O}{\overset{\|}{C}}-OAg + Br_2 \xrightarrow{CCl_4} R-Br + AgBr + CO_2\uparrow$

COOAg hatao

$R = 1° > 2° > 3°$ "R" Ko "X" lagao!

Simonini RX^n :-

$2\ R-\overset{O}{\overset{\|}{C}}-OAg + I_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR + 2AgI + CO_2\uparrow$

10) Halide Exchange Method :-

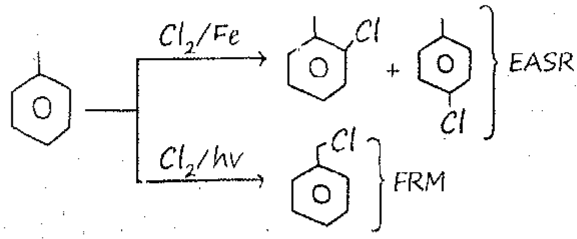
Finkelstein Rx^{n} :-

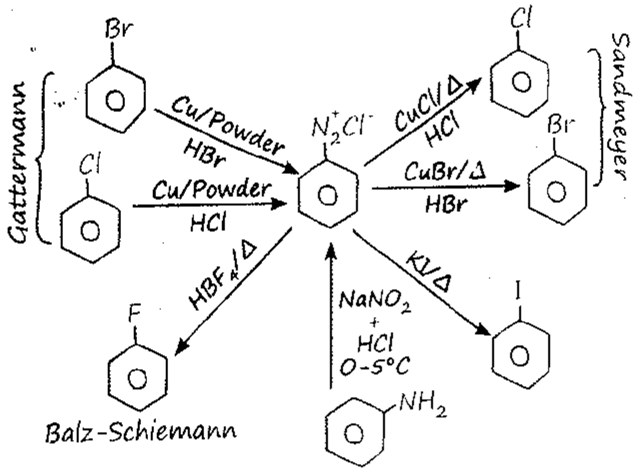
S_N2 $R-Cl + NaI \xrightarrow{Acetone} R-I + NaCl$

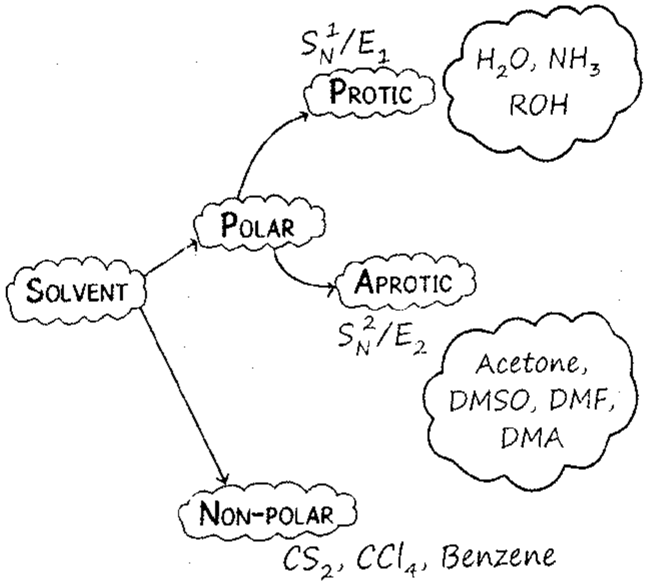
Swarts rx^n :-

S_N1 $R-Cl + AgF$ or $Hg_2F_2 \longrightarrow R-F + AgCl$

11) Aryl Halides :-



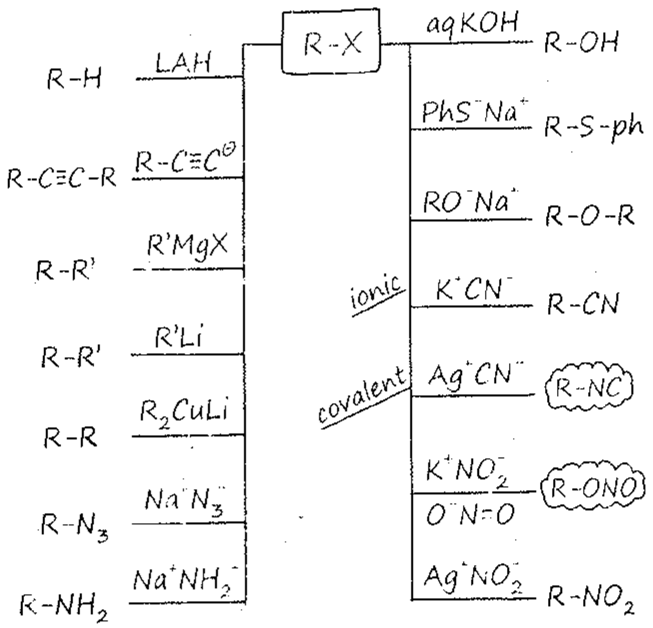




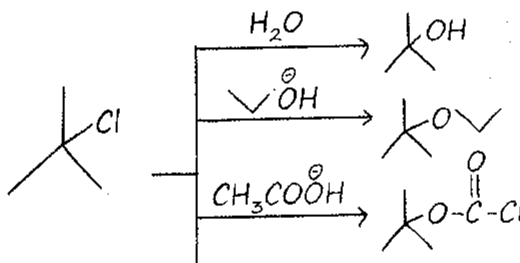
Note :-

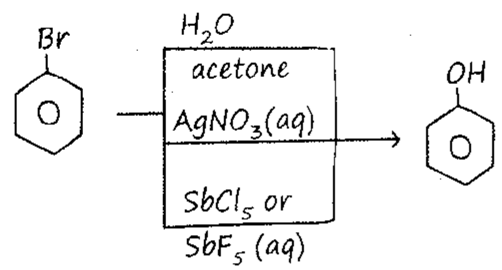
S_N^1	S_N^2
3°>2°>1°	1°>2°>>>>3°
C^+ ✓	C^+ α
Rate α [R-X]	Rate α [R-X][Nu]
Weak $Nu^\ominus$	Strong Nu^-
Polar Protic solvent	Polar Aprotic solvent

R-I > R-Br > R-Cl > R-F

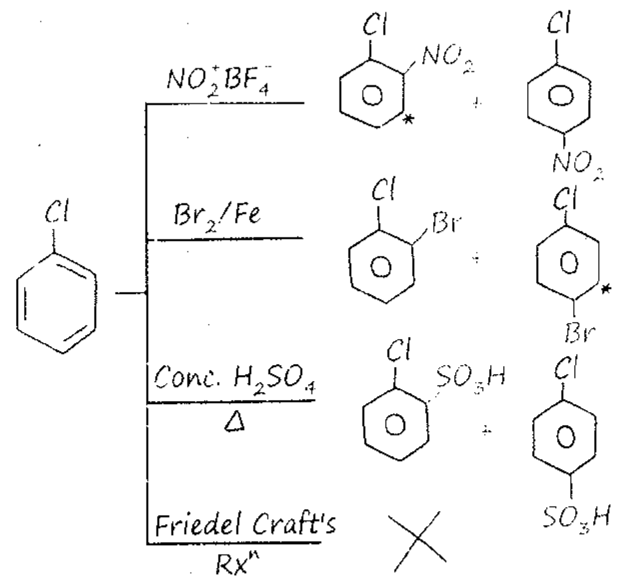


12) Solvolysis :- S_N1





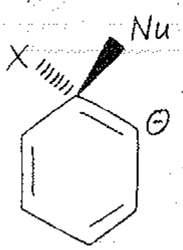
EASR :-



NASR :-

ADDITION- ELIMINATION

F > Cl > Br > I

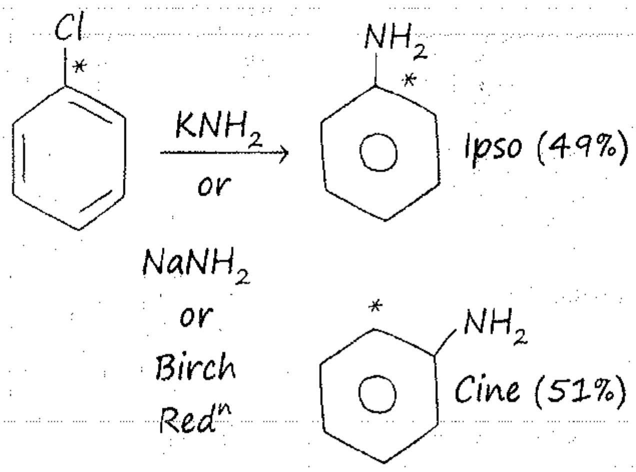


Meisenheimer Complex

+ Same as S_N2
+ Benzene must be connected to EWG.
+ "X" ko hatakr Nu^- ko lagao !

ELIMINATION- ADDITION

I > Br > Cl > F



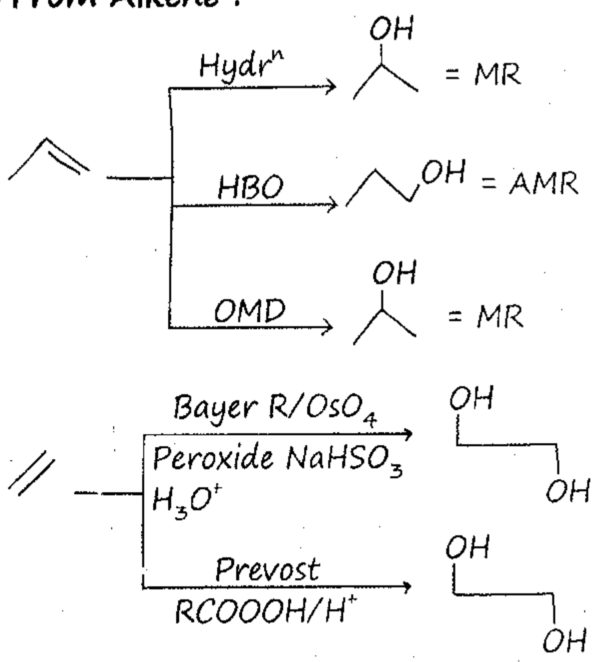
4 Alcohols, Phenols and Ethers

ALCOHOLS

① From Alkyl Halides :- $[S_N^1$ and $S_N^2]$

$$R-X + aq\ KOH \longrightarrow R-OH + KX$$

② From Alkene :-



③ Using Grignard Reagent :-

R^-Mg^+X $(Nu^-$ add$^n)$

$$H-\overset{\overset{O}{\|}}{C}-H \xrightarrow[+RMgX]{H_3O^+} R-CH_2-OH \quad [1° \text{ Alcohol}]$$

$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[+RMgX]{H_3O^+} R-\overset{\overset{R}{|}}{C}H-OH \quad [2° \text{ Alc.}]$$

$$R-\overset{\overset{O}{\|}}{C}-R \xrightarrow[+RMgX]{H_3O^+} R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH \quad [3° \text{ Alc.}]$$

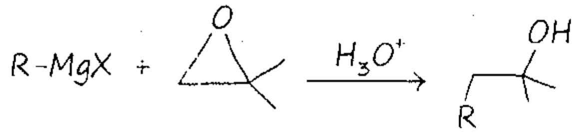
+ Ester :-

$$RO-\overset{\overset{O}{\|}}{C}-H \xrightarrow{RMgX} H-\overset{\overset{O}{\|}}{C}-R + ROMgX$$

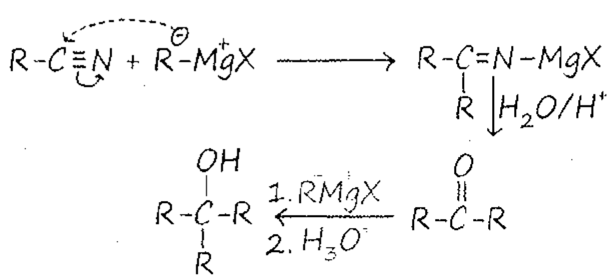
$$\downarrow RMgX$$

• always two Alcohol. $\left\{ ROH + R-\underset{\underset{R}{|}}{C}H-OH \right.$

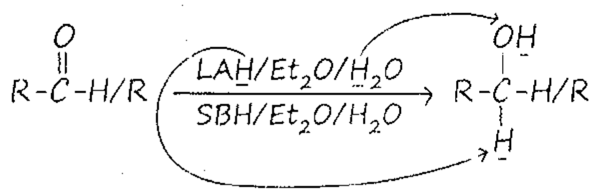
+ Epoxide :- $\boxed{S_N2}$ Cyclic Ethers are more reactive than normal ones!



+ CYANIDE :-

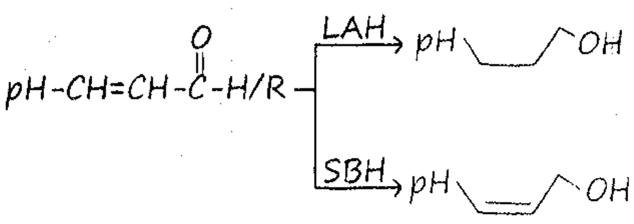


④ Reduction of Carbonyl Compounds :- Sodium boro hydride:- Acid halides only.



• LAH [Strong R.A.]

• Exceptionally reduce {cinnamyl cond^n}



Other Reducing Agents :-

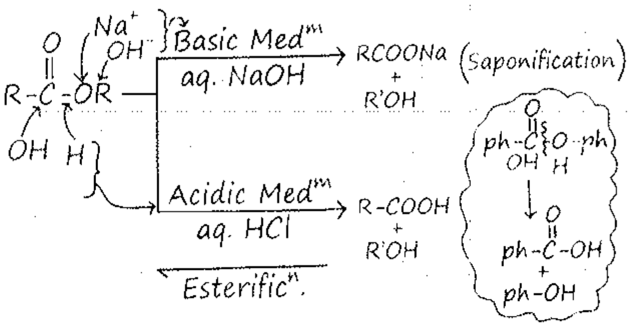
H_2/PtO_2 ⟶ Adam's Catalyst.

Na/EtOH ⟶ Bouevault Blanc Red^n.

Aluminium isopropoxide ⟶ MPV- Reduction.

	LAH	SBH	H_2-Pt, Ni, PtO_2	Na/EtOH	HBO	DiBAL-H
Ald	✔	✔	✔	✔	✔	✔
Ketone	✔	✔	✔	✔	✔	✔
Acid	✔	✘	✘	✔	✔	✔
Ester	✔	✘	✘	✔	✔	✔
Acid halide	✔	✔	✘	✔	✔	✔

(5) Hydrolysis of Esters :-

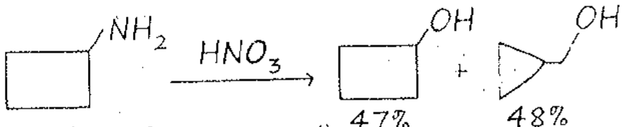


(6) From Aliphatic Pri Amine :-

$$R\text{-}NH_2 \xrightarrow[0^\circ\text{-}5^\circ C]{NaNO_2 + HCl} R\text{-}OH + N_2\uparrow + HCl$$

-NH_2 hatao C^+ banao aur waha pr -OH lagao jaha stable C^+ bana ho!

$$CH_3\text{-}NH_2 \xrightarrow{HNO_2} CH_3OH$$



(Demjanov Rearrangement)

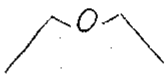
(7) Reaction with HX :-

HI > HBr > HCl > HF.

$$R\text{-}OH + HX \longrightarrow R\text{-}X + H_2O$$

(8) Dehydration of Alcohols :-

$$R\text{-}OH \xrightarrow[165^\circ\text{-}170^\circ C]{Conc.\ H_2SO_4} \text{//} \quad E_2 = 1^\circ Alc.,\ E_1 = 3^\circ/2^\circ Alc.$$

$$R\text{-}OH \xrightarrow[140^\circ C]{Conc.\ H_2SO_4}$$ 

(9) Esterification :-

$$CH_3\overset{*}{O}H + CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{18}{O}H \underset{}{\overset{H^+}{\rightleftharpoons}} C_2H_5\text{-}\overset{O}{\overset{\|}{C}}\overset{*}{O}CH_3 + H_2\overset{18}{O}$$

1° > 2° Alc > 3° Alc.

(10) Oxidation :-

1° Alcohol ⟶ Carboxylic Acid.
2° Alcohol ⟶ Ketone
3° Alcohol ⟶ No Rx^n

Strong oxidising agent :-

$KMnO_4$, $K_2Cr_2O_7$ } 1°Alc ⟶ Acid; 2°Alc ⟶ Ketone $\xrightarrow{\cancel{XX}}$ 2Acid

Mild O.A.:-

DND Collins = CrO_3 + Py + CH_2Cl_2
PCC Sarett = CrO_3 + Py + HCl
PDC Cornforth = Py + $Na_2Cr_2O_7$, $(Py)_2Cr_2O_7$
Swern = DMSO + $[COCl]_2$ + Et_3N
Ag_2CO_3
Cerric ammonium nitrate (CAN)

} 1°Alc → Aldehyde. 2°Alc → Ketone

* Jones:- CrO_3 + dil.H_2SO_4 + Acetone
1°Alc → Aldehyde → Acid   2°Alc → Ketone

* MnO_2 = Allylic/Benzylic -OH Oxidation
* Cu/300°C = 1°Alc → Ald., 3°Alc → Alkene
2°Alc → Ketone

Further oxidation of ketone:-
(Popoff's rule)

$-\overset{O}{\overset{\|}{C}}-O-$ उस Side पर रहेगा जहां पर less Carbon atom होंगे .

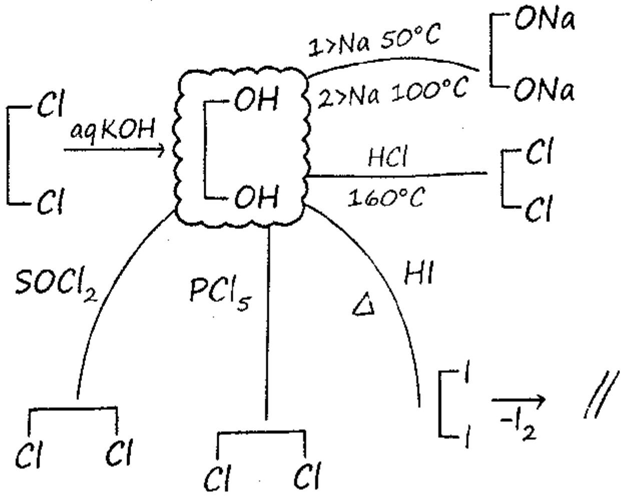
$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\}CH_2CH_3 \xrightarrow{K_2Cr_2O_7} CH_3\text{-}COOH +$$ 

Victor-meyer (RBC) test :-

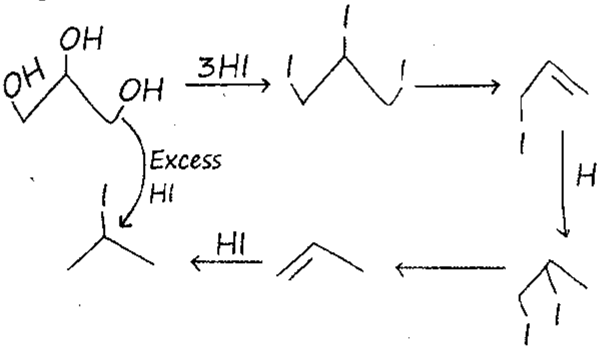
• P + I_2
• $AgNO_3$
• HNO_2
• NaOH.

1°Alc. → Nitrolic Acid salt (Red)
2°Alc. → pseudonitrole (Blue)
3°Alc. → Colorless

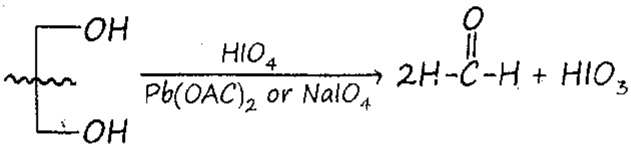
DIOLS



Glycerol :-

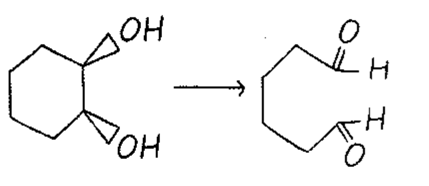


(1) Oxidation of DIOL :-

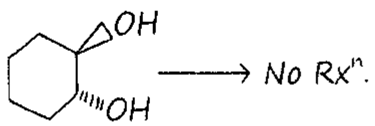


(2) Malaprade/Criegee RXN :-

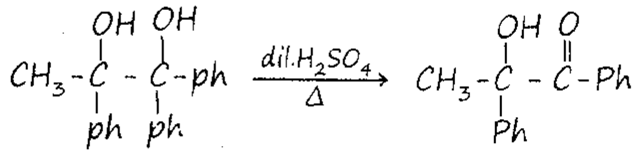
(1,2) Vicinal diol same same hone chahiye bond break Karo dono Ke beech Ka aur $\overset{O}{\parallel}$ $\overset{O}{\parallel}$ lagao!



Reagent:-
HIO_4
$NaIO_4$
$Pb(OAC)_2$

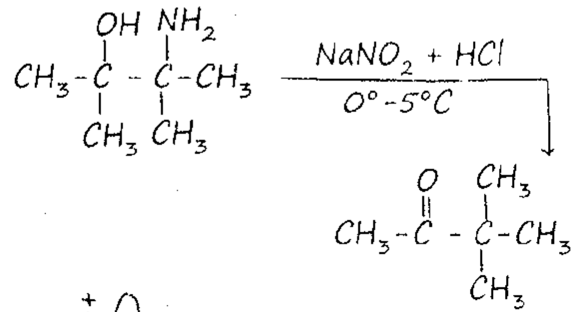


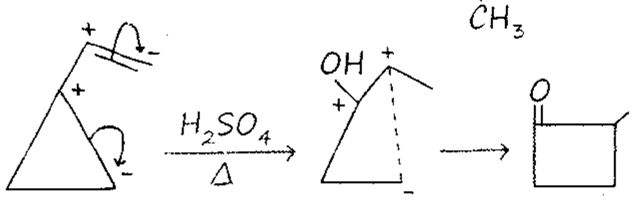
(1) Pinacol - Pinacolone Rearrangement :-



If the initially form C^+ is unstable it can undergo H > Ph > R shift & C^+ will be stabilised by +M of -OH Finally pinacolone is formed!

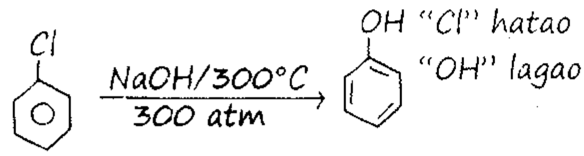
Pinacol - pinacolone type :-



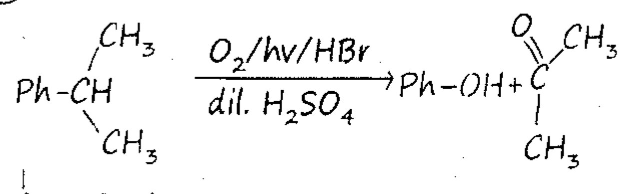


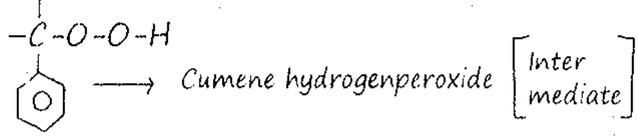
PHENOLS

(1) Dow's Process :-



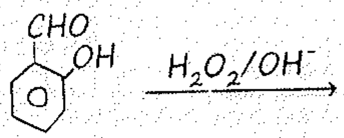
(2) From Cumene :-





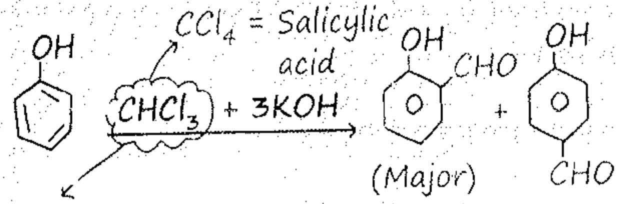
OH waha pr lagega jaha e^- density jyada hoga uske adjacent $\overset{O}{\parallel}$ lagado.

3) Dakin Process :-



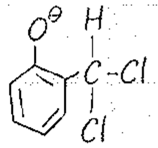
• -CHO ko -OH banado.

4) Reimer - Tiemann RXN :-

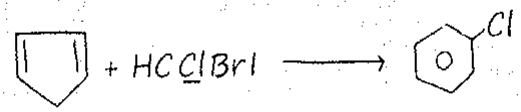


CO_2 = Kolbe's-Schmidt reaction [Salt of Salicylic acid]

• $:CCl_2$:- DCC [E^+] → (Singlet.)

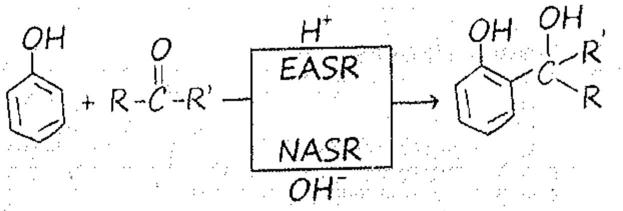
•  :- Intermediate.

Miscellaneous-Riemann-Tiemann reaction:-



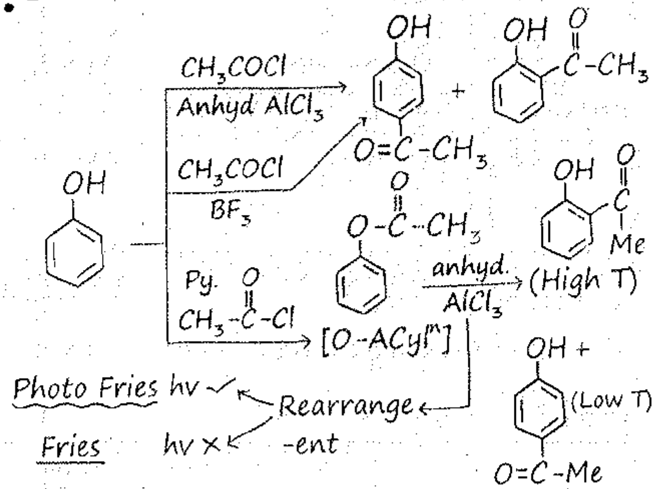
• Joh Bad L.G. hoga woh Benzene pr lagega.

5) Lederer - Manasse Reaction :-

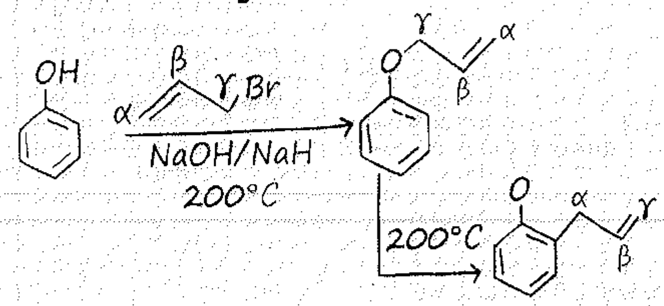


6) Friedel - Craft Acylation :-

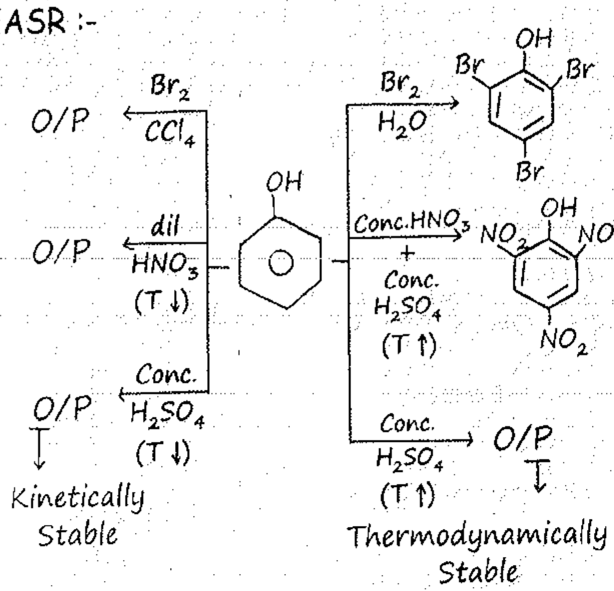
•



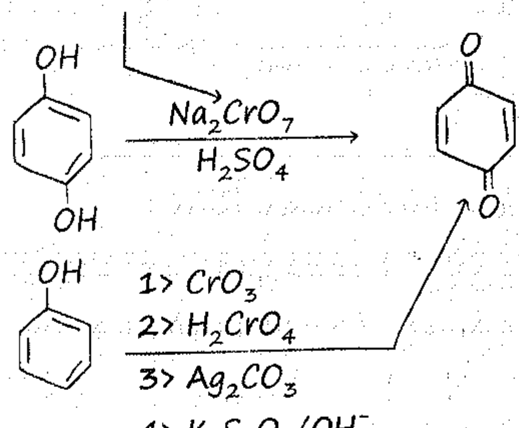
Claisen-rearrangement :-



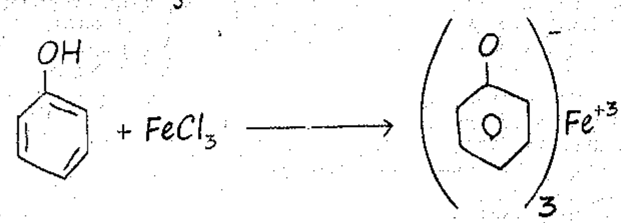
EASR :-



Elb's RXN (oxidation) :-



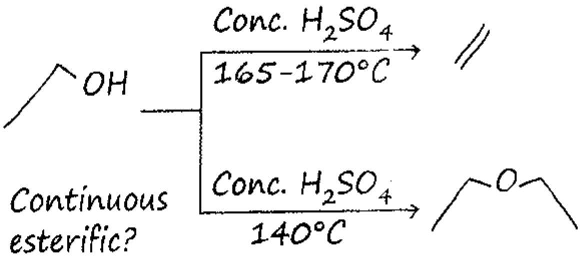
Rxn with $FeCl_3$:-



Violet Colour.

ETHERS

① Dehydration of Alcohols :-



- Continuous esterific?
- Intermolecular dehydration (SN^2)

② Williamson's Ether SYN :-

$$R-X \xrightarrow[S_N2]{R'-O^{\ominus}Na^{+}} R-O-R'$$

(1° Alkyl halide)

③ RXN with Diazomethane :-

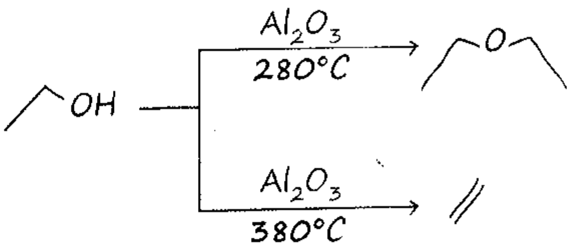
$$R-OH + \bar{C}H_2-\overset{+}{N}_2 \longrightarrow R-O-CH_3$$

(Methyl ether)

④ Alkoxymercuration :-

$$R-CH=CH_2 \xrightarrow[MR\ [No\ C^+]]{OMD(R'-OH)} R-\underset{\displaystyle OR'}{\underset{|}{C}H}-CH_3$$

⑤ RXN with Al_2O_3 or THO_2 :-



⑥ Dry Ag_2O :-

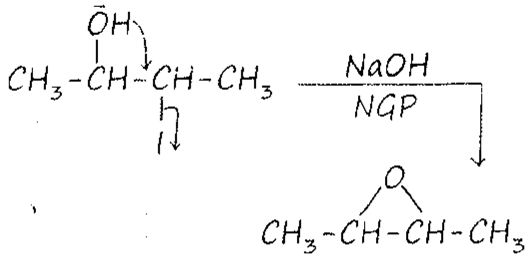
$$R-X \xrightarrow{dry\ Ag_2O} R-O-R$$

⑦ Addition of Alcohol to Alkene :-

$$R-\overset{+}{C}H=\overset{-}{C}H_2 \xrightarrow{R-CH_2-\bar{O}H} R-\overset{\displaystyle O-CH_2-R}{\overset{|}{C}H}-CH_3$$

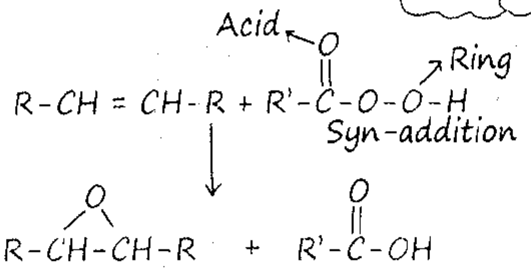
C^+ ✓

⑧ From Hydroxyl Halo Compounds :-



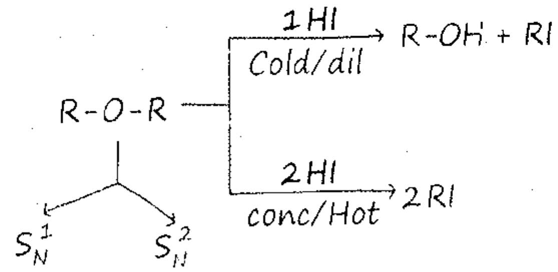
⑨ From Peracids :-

CSM TSR



Chemical property :-

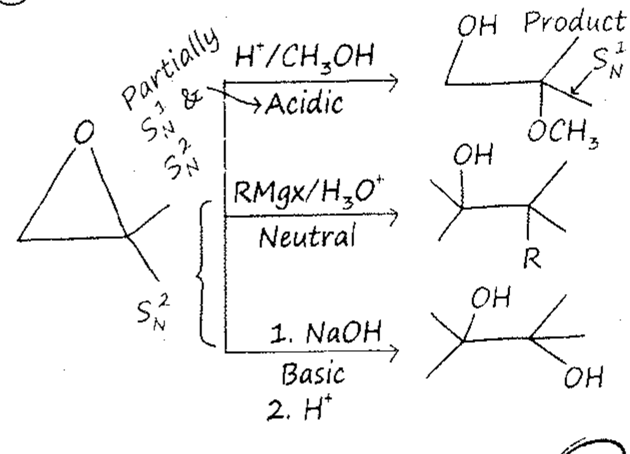
① Reaction with HI :-

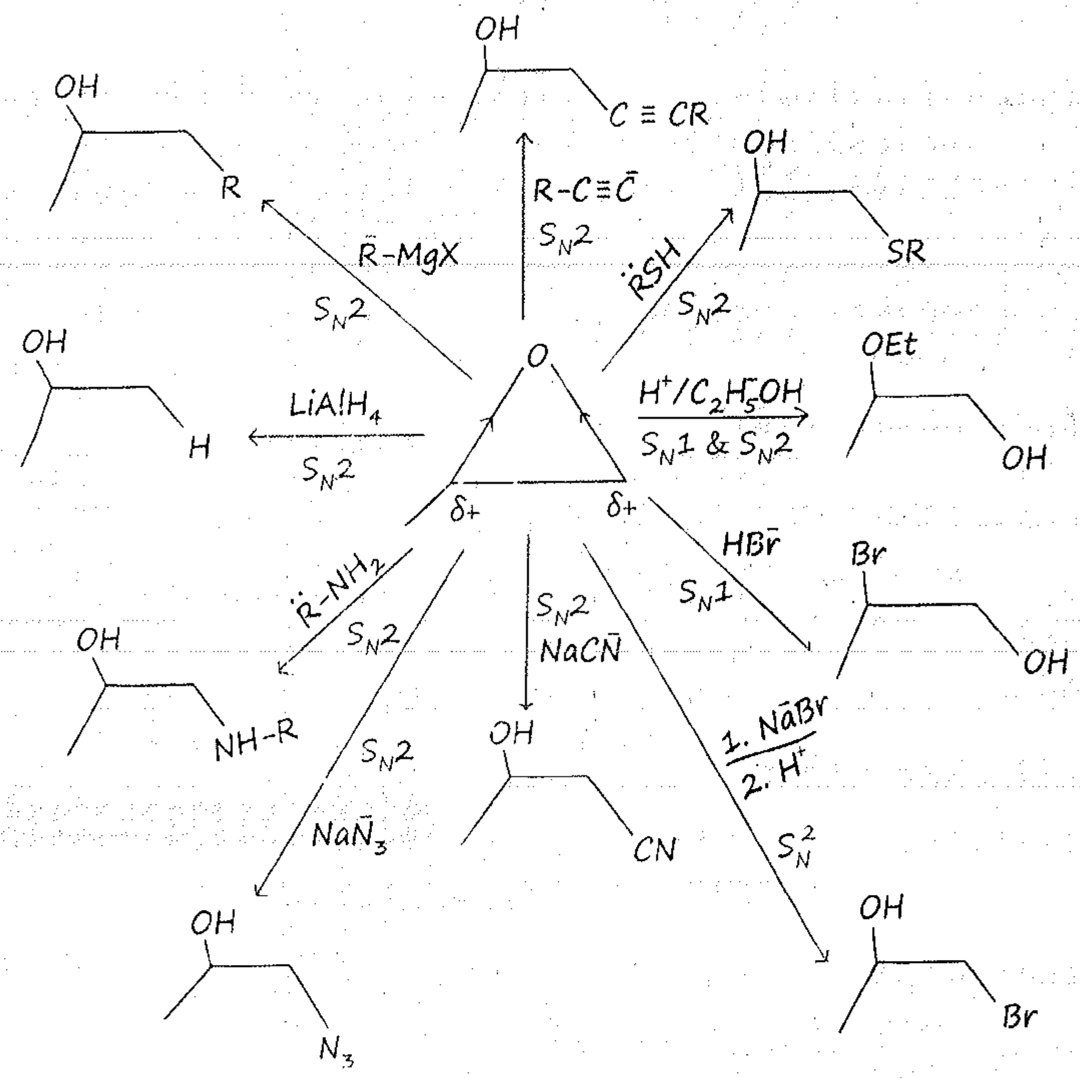


3° allyl, 1°, Methyl.
Benzyl

- S_N^1 :- I^- Udhar lagega jaha stable C^+ hoga aur H^+, O^- pr Ether Ke. aur S_N2 mein just inverse.

② Reaction with Oxirane :-




OH
C ≡ CR
R-C≡C̄
S_N2
OH
R
R̈-MgX
S_N2
OH
SR
R̈SH
S_N2
O
OEt
OH
H^+/C_2H_5OH
S_N1 & S_N2
OH
H
LiAlH$_4$
S_N2
δ+
δ+
HBr̄
S_N1
Br
OH
R̈-NH$_2$
S_N2
OH
NH-R
S_N2
NaCN̄
S_N2
NaN̄$_3$
OH
CN
1. NaB̄r
2. H$^+$
S_N2
OH
N$_3$
OH
Br

5 Aldehyde, Ketones & Carboxylic Acids

1) Oxidation of Alcohol :- Mop

Alcohol →
- $1° \xrightarrow{\text{Mild OA}}$ Aldehyde
- $2° \xrightarrow[\text{Jones}]{\text{reagent}}$ Ketone
- $3° \xrightarrow{[O]}$ X

2) Dehydrogenation of Alcohol :-

$(-H_2)$

Alcohol →
- $1° \xrightarrow{Cu/Ag,\ 300°C}$ Aldehyde
- $2° \xrightarrow{Cu/Ag,\ 300°C}$ Ketone
- $3° \xrightarrow{Cu/Ag,\ 300°C}$ Alkene

3) Ozonolysis of Alkene :-

$$R-CH=CR_2 \xrightarrow[-78°C]{O_3/Zn/H_2O} R-\overset{O}{\overset{\|}{C}}-H + R-\overset{O}{\overset{\|}{C}}-R$$

4) Kucherov + HBO :-

$$R-C\equiv C-H \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} R-\overset{OH}{\overset{|}{C}}=CH_2 \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-CH_3$$

$$R-C\equiv C-H \xrightarrow[\text{(Anti MR)}]{HBO} R-CH=\overset{OH}{\overset{|}{CH}} \rightleftharpoons R-CH_2-CHO$$

5) Rosenmund Reduction :-

"exclusively for aldehyde"

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Quinoline}]{H_2-Pd\ BaSO_4} R-\overset{O}{\overset{\|}{C}}-H$$

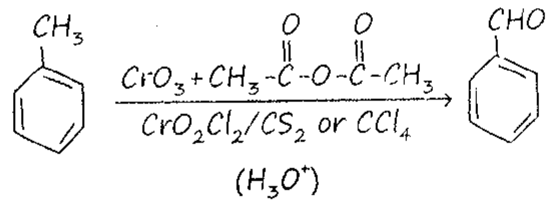
lindlar's Catalyst

Reactivity order:-

Acid halide > Alkyne > Aldehyde > Alkene > Ketone

6) Etard Reaction :-

* Aromatic Aldehydes.*



7) Stephen reduction - Aldehyde SYN:-

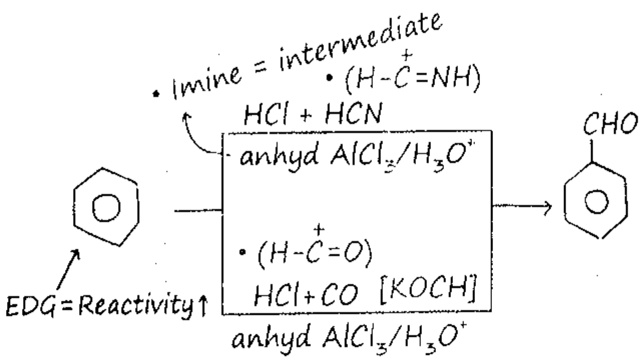
$$R-CN \xrightarrow{SnCl_2 + HCl} R-CHO$$

DND//or///

$$\left.\begin{array}{l} R-CN \\ RCOOH \\ RCOOR \\ RCOCl \end{array}\right\} \xrightarrow{DiBAL-H} R-CHO$$

EASR

8) Gattermann :-



9) Distillation of Ca^{2+} & Ba^{+2} Salts of COOH:-

$$(HCOO^-)_2 + Ca^{2+} \xrightarrow[-CaCO_3]{\text{Distillation}} H-\overset{O}{\overset{\|}{C}}-H$$

Chemical property :-

Nucleophilic. Addition Reaction:-

① Ald /Ketone
- $\xrightarrow{NH_3}$ Imine
- $\xrightarrow{NH_2-R}$ Schiff's base
- $\xrightarrow{NH-R_2}$ enamine
- $\xrightarrow{NR_3}$ ✗

Imine:- $R-C(H/R')=NH$

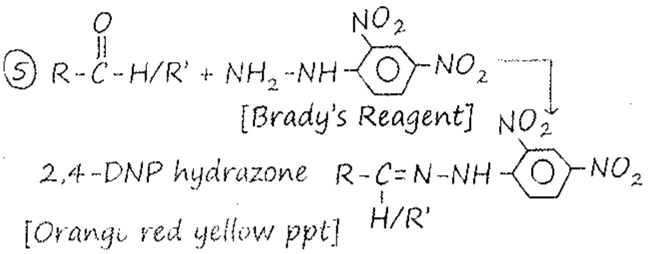
Schiff's base :- $R-C(H/R')=NR$

② $RCHO + NH_2OH \longrightarrow R-C(H)=N-OH$ (Aldoxime)

$RCOR + NH_2OH \longrightarrow R-C(R)=N-OH$ (Ketoxime)

③ $R-C(=O)-H + NH_2-NH_2 \longrightarrow R-C(H)=N-NH_2$ (Hydrazone)

④ $R-C(=O)-H + NH_2-NH-Ph \longrightarrow R-C(H)=N-NH-Ph$ (Phenyl hydrazone)

⑤ 

[Brady's Reagent]

2,4-DNP hydrazone

[Orange red yellow ppt]

Distinguish T

⑥ $R-C(=O)-H/R' + NH_2-NH-C(=O)-NH_2 \longrightarrow R-C(H/R')=N-NH-C(=O)-NH_2$

(Semicarbazide) (Semicarbazone)

⑦ $R-C(=O)-H/R' + HCN \xrightarrow[PH]{Alkaline} R-C(OH)(CN)-H/R'$ (Racemic Mix)

⑧ $R-C(=O)-H + NaHSO_3 \longrightarrow R-C(OH)(H)-S(=O)_2-ONa$ [White Crystal]

Only Aldehyde & Methyl Ketone

Distinguish T

⑨ ★

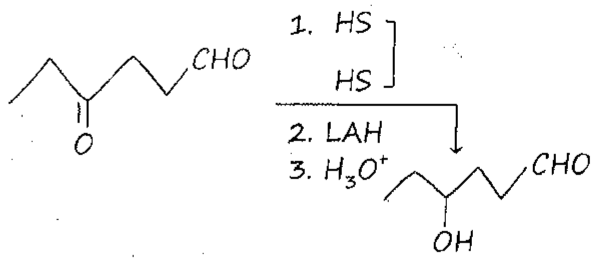
$R-C(=O)-H \xrightarrow{1eq\ R'OH} R-C(OH)(OR')-H$ (Hemiacetal)

$R-C(=O)-H \xrightarrow{2eq\ R'OH} R-C(OR')(OR')-H$ (Acetal)

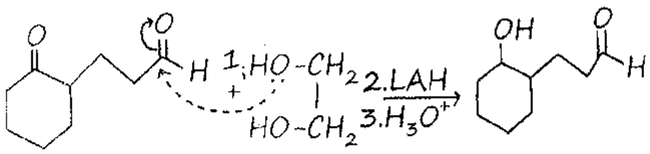
$R-C(=O^*)-R \xrightarrow{1eq\ ROH} R-C(^*OH)(OR')-R$ (Hemi Ketal)

$R-C(=O^*)-R \xrightarrow{2eq\ ROH} R-C(OR')(OR')-R$ (Ketal) $+ H_2O^*$

- **MOZINGO Rx^n**
  - Diols or thiols are used as protecting agents.



- Vicinal diols can be used as protecting groups in a compound if it has a multiple Fn groups & protect one of them.



Oxidation Rxn's :-

1> Rx^n with $K_2Cr_2O_7/H^+$ or $OH^-/KMnO_4$:-

$R-C(=O)-H \xrightarrow{K_2Cr_2O_7} R-COOH$

$R-C(=O)-H \xrightarrow[\Delta]{K_2Cr_2O_7/H^+ \text{ or } OH^-} R-COOH$

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{K_2Cr_2O_7} \text{No rx}^n$$

Not oxisidisable at normal condi^n
Req. Drastic Cond^n.

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\Delta]{K_2Cr_2O_7/H^+ \text{ or } OH^-} 2\ R-COOH$$

(1 "C" less)

Unsymmetrical Ketone

"Popoff's Rule"

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}} \vdots CH_2-CH_2-CH_3$$

A weaker base is a good L.G.

*** TOLLEN'S REAGENT:- (SILVER MIRROR TEST)**

Given by:- Aldehyde, Terminal Alkyne, Formic Acid, α-hydroxy Ketones.

Note:- Ketones ye test nai denge !

α-hydroxy Ketone:-

$$CH_3-\underset{OH}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-CH_3 + T.R. \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 + Ag\downarrow$$

Reagent:- Ammonical Silver Nitrate (O.A.)
$[Ag(NH_3)_2]^+\ NO_3^-$

*** HALOFORM TEST :-**

Given by:- $\boxed{CH_3-\overset{O}{\overset{\|}{C}}}-$ $\Rightarrow$ Aldehydes & Ketones having this group.

Reagent:- $NaOH + X_2$ (excess)

$$CH_3-\overset{O}{\overset{\|}{C}}-H/R + NaOH + I_2 \longrightarrow H/R-\overset{O}{\overset{\|}{C}}-ONa + CHI_3\downarrow$$

(iodoform)

* Bright yellow crystalline ppt.*

Note:-
COOH & its derivative inspite of having $CH_3-\overset{O}{\overset{\|}{C}}-$ not give test!
as we need more Acidic α-Hydrogen.

$\left\{ CH_3-\overset{O}{\overset{\|}{C}}-OH \right.$ ✗ ✓

*** BAYER-VILLIGER OXIDATION :-**

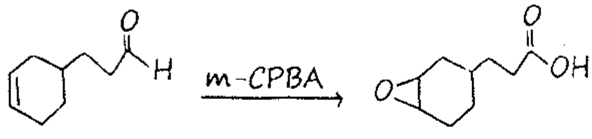
$$\underset{\text{(Ketones)}}{R-\overset{O}{\overset{\|}{C}}-R} \xrightarrow[\text{PAA, TFPAA, MCPBA, } H_2O_2/BF_3,\ H_2SO_5 \text{ (Caro's Acid)}]{\text{(Peracids)}} \underset{\text{(esters)}}{R-\overset{O}{\overset{\|}{C}}OR}$$

Migratory Aptitude:-

H > 3°alkyl > Cyclohexyl > 2°alkyl > Benzyl > Phenyl > 1° alkyl > CH_3

* Jo Migrate Karega uske baju men "O".

Cyclic Ketones $\Rightarrow$ Lactones.



//- bond react to Form Cyclic Ethers.

Reduction Rxn's :-

1> With LAH, SBH, H_2Pd :-

$$R-\boxed{\overset{O}{\overset{\|}{C}}}-H/R' \xrightarrow[2.\ H_2O/Ether]{1.\ LiAlH_4} R-\boxed{\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}}-H/R'$$

2> With HI/Red P :- 😈!

Baap of all R.A.

$$R-\boxed{\overset{O}{\overset{\|}{C}}}-H/R' \xrightarrow{HI/Red\ P} R-\boxed{\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}}-H/R'$$

3> Clemmensen Red^n :- (Acidic Medium).

$$R-\boxed{\overset{O}{\overset{\|}{C}}}-H/R' \xrightarrow[conc.\ HCl.]{Zn-Hg} R-\boxed{\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}}-H/R'$$

1 mole Aldehyde $\left.\right\}$ $4e^- \longleftarrow Zn$, $4H^+ \longleftarrow HCl$

intermediate:- Alcohol

Grp like NO_2, $-OC_2H_5$, $-OH$, $-//$ don't prefer C.M.R. respond to Acidic Med^m

4> Wolf-Kishner Red^n :-

$$R-\boxed{\overset{O}{\overset{\|}{C}}}-H/R' \xrightarrow[NaOEt/\underset{OH}{\underset{|}{C}H_2}-\underset{OH}{\underset{|}{C}H_2}]{NH_2-NH_2} R-\boxed{\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}}-H/R'$$

intermediate :- Hydrazone

Rxn's due to α-H :-

1> ALDOL Condensation :- (NAR)

$$2CH_3-\overset{O}{\overset{\|}{C}}-H/R' \xrightarrow{\text{Mild Base}} CH_3-\underset{H/R'}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-H/R' \text{ (Aldol)}$$

Mild Base: Bicarbonates, Hydroxides, Carbonates.

β-hydroxycarbonyl Compound

Polymeris^n → Resin

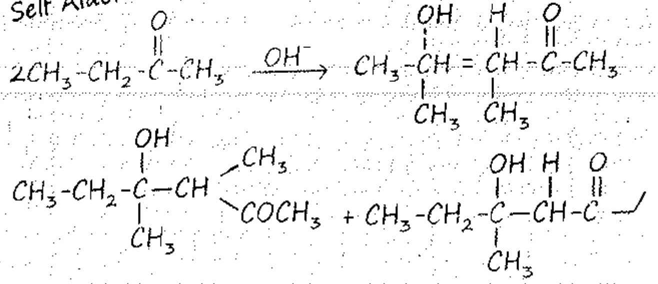
$$CH_3-\underset{H/R'}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-H/R' \longleftarrow \text{(heat)}$$

- **Cross/Mixed Aldol Condensation :-**

Major Product :- $Nu^{\ominus}$ = Ketone

Reagent = Aldehyde

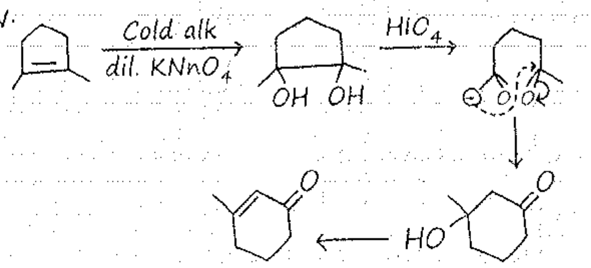
Self Aldol :-



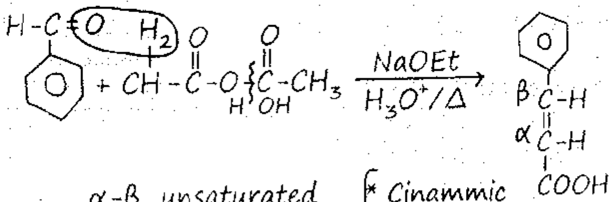
Intramolecular Aldol Condensation :-

Product :- Ring Size > Acidic "H" (Priority).

Jee Adv.



2> PERKIN Rx^n (Condensation) :- (NAR)

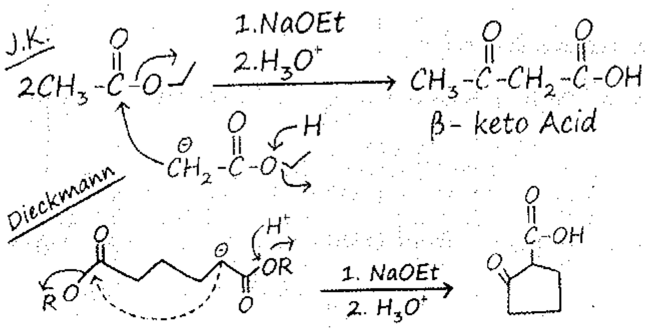


α-β unsaturated carboxylic acid. { * Cinammic acid. *

* Ar. Aldehyde with EWG. inc. Reactivity.

3> Claisen - Condensation :- (NSR)

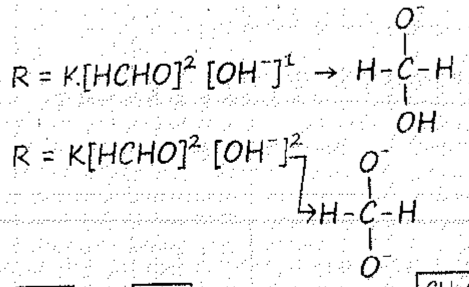
J.K.

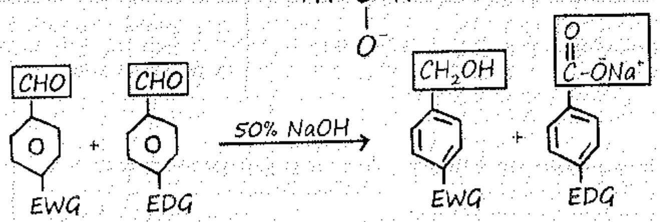


4> Cannizaro's Rx^n :- [Disproportionation Rx^n]

$$2H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{50\%\ NaOH} H-\overset{O}{\overset{\|}{C}}-ONa + CH_3OH$$

(No αH) Salt of COOH Acid

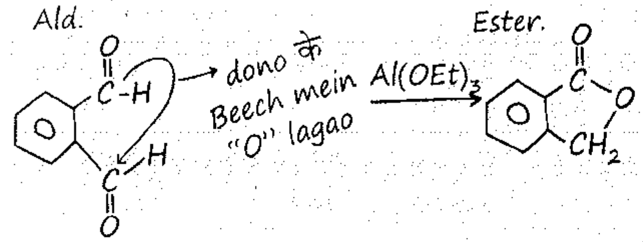




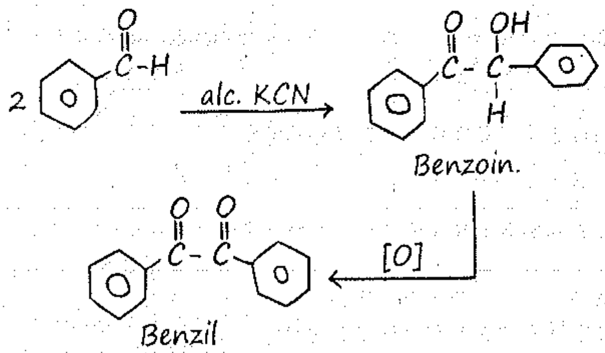
- **TiscnenKo Rx^n :-**

$$2R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{Al(OEt)_3} R-\overset{O}{\overset{\|}{C}}-\boxed{OCH_2R}$$

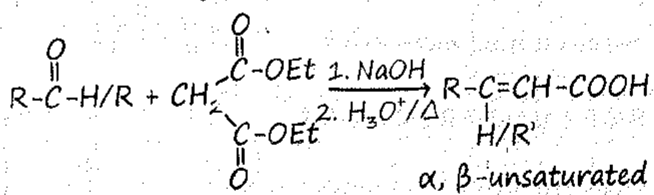
Ald. Ester.



5> Benzoin Condensation rx^n :-

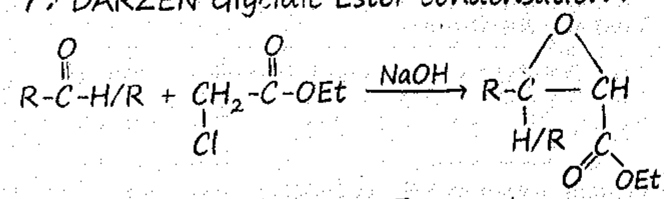


6> Knoevenagel rx^n. [Modified Aldol]



DEM. α, β-unsaturated Carboxylic acid.

7> DARZEN Glycidic Ester condensation :-



Epoxy ester.
(glycidic ester)

8 > Beckmann Rearrangement :-

$$CH_3-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{\ddot{N}H_2OH} CH_3-\overset{Ph}{\overset{|}{C}}=\ddot{N}-OH$$

Syn/anti.

$$\text{Anti} \xrightarrow{HCl,\ H_3PO_4,\ H_2SO_4,\ PCl_5,\ SOCl_2,\ Ph-SO_2Cl,\ \Delta} Ph-\overset{O}{\overset{\|}{C}}-NH-CH_3$$

$$\text{Syn.} \xrightarrow{HCl,\ H_3PO_4,\ H_2SO_4,\ PCl_5,\ SOCl_2,\ Ph-SO_2Cl,\ \Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH-Ph$$

9 > Wittig Rx^n :-

$$R-\overset{\boxed{O}}{\overset{\|}{C}}-H/R' + Ph_3\overset{+}{P}-\boxed{\overset{\ominus}{C}H_2} \longrightarrow R-\overset{\boxed{CH_2}}{\overset{\|}{C}}-H/R'$$

ylide

DISTINGUISH TEST : -

	1> Tollen's Reagent	2> Fehling	3> Benedict	4> Schiff.
Ketones	✗	✗	✗	✗
α-hydroxy Ketone	✓	✓	✓	✓
Terminal alkyne	✓	✓	✓	✓
HCOOH	✓	✓	✓	✓
Aromatic Acid	✓	✗	✗	✗
Aliphatic Acid	✓	✓	✓	✓

1> Tollen's Reagent :- $[Ag(NH_3)_2]^+ \longrightarrow$ Silver Mirror Test.

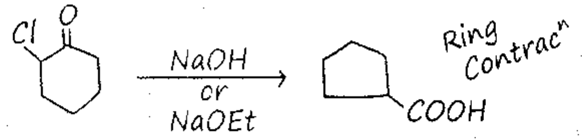
2> Tollen's Reagent :- (A) aq $CuSO_4 \longrightarrow$ Red ppt.
(B) Na/K Tartarate $\longrightarrow$ Rochells salt

3> Benedict Solution :- aq $CuSO_4$ + Na/K Citrate. + RCHO
Magenta (Pink)

4> Schiff's Reagent :- p-rosaniline hydrochloride

Carboxylic acids & it's derivative :-

1> Favorskii Rearrangement :-



2> Hell - Volhard - Zelinsky (HVZ) Rx^n :-

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[PBr_3 + Br_2]{Red\ P = Br_2/Cl_2} \underset{Br/Cl}{\underset{|}{C}H_2}-\overset{O}{\overset{\|}{C}}-OH$$

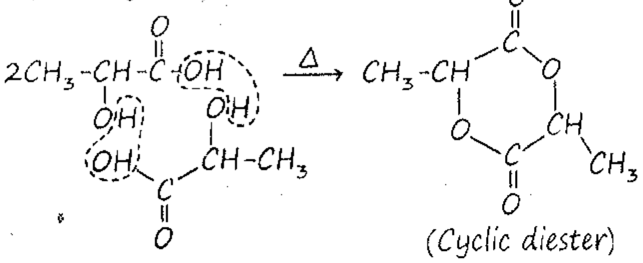
atleast 1 αH req.

α-halosubstituted Carboxylic acid.

Aromatic COOH not give HVZ Rx^n.

3 > 🔥 of Carboxylic Acid :-

(a) α-hydroxy COOH :-

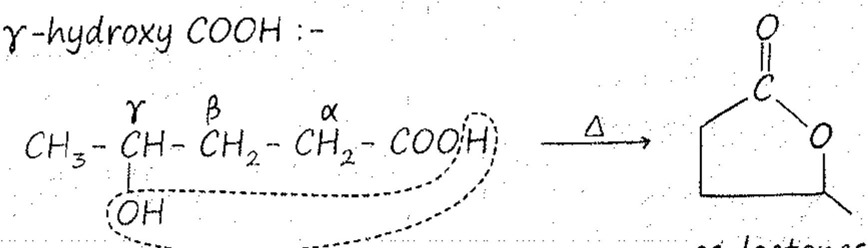


(Cyclic diester)

(b) β-hydroxy COOH :-

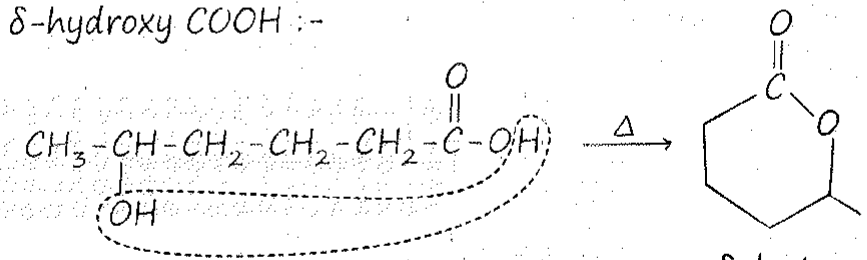
$$CH_3-\underset{OH}{\underset{|}{\overset{\beta}{C}H}}-\overset{\alpha}{C}H_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-OH$$

(c) γ-hydroxy COOH :-



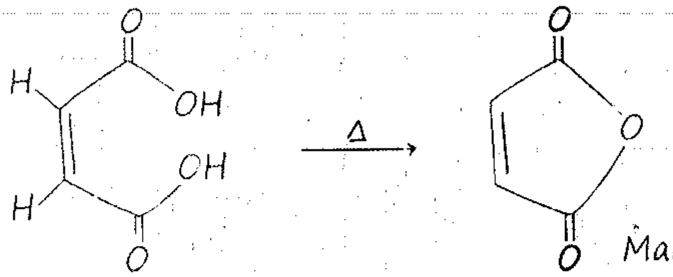
γ-lactones

(d) δ-hydroxy COOH :-



δ-lactones

Note:-



Maleic anhydride.

Maleic Acid.

6 Nitrogen Compounds (Amines)

1> Hoffmann Exhaustive Ammonolysis :-

$$\ddot{N}H_3 + R-X \xrightarrow{S_N^2} R-NH_2 + HX$$

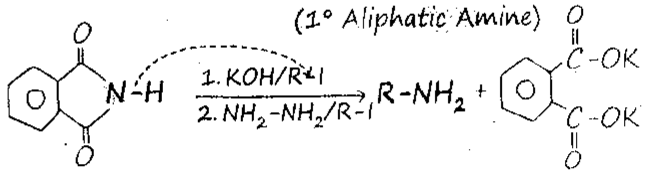
$$R-\ddot{N}H_2 + R-X \xrightarrow{S_N^2} R-\underset{H}{\ddot{N}}-R + HX$$

$$R-\ddot{N}H-R + R-X \xrightarrow{S_N^2} R-\underset{R}{\ddot{N}}-R + HX$$

$$R-\underset{R}{\ddot{N}}-R + \underbrace{R-X}_{1°/2°} \xrightarrow{S_N^2} R-\overset{R}{\underset{R}{N^{\oplus}}}-R + X^{\ominus}$$

2> Gabriel - Pthalimide Synthesis :-

(1° Aliphatic Amine)



3> Hoffmann's Bromamide degradation :- '1' C less!

(1° Ali/Aromatic Amine)

$$R-\boxed{\overset{O}{\overset{\|}{C}}}-NH_2 + \boxed{4}\,NaOH + Br_2 \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(alkyl isocyanate → intermediate)

** If R = Chiral => Chirality is Retained.*

4> Schmidt Rx^n :-

$$R-\overset{O}{\overset{\|}{C}}-OH + N_3H \xrightarrow{dil.H_2SO_4}$$

5> Curtius Rx^n :-

$$R-\overset{O}{\overset{\|}{C}}-Cl + NaN_3 \xrightarrow{dil.H_2SO_4}$$

6> Lossen rxn :-

$$R-\overset{O}{\overset{\|}{C}}-NH-O-\overset{O}{\overset{\|}{C}}-Ar \xrightarrow[dil.H_2SO_4]{OH^-/}$$

(alkyl isocyanate) $\underline{R}$-N=C=O
Ar
(intermediate)

$$\xrightarrow{H_3O^+} R-NH_2 + CO_2$$

7> REDUCTION of N-Containing Compounds :-

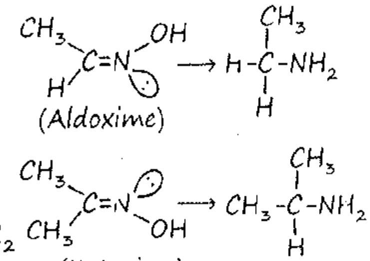
R.A.:-
- $H_2/Ni/Pt/Pd$.
- $(NH_4)SH$
- $LiAlH_4$
- Mendius Rx^n { • H_2/Na-EtOH (Hg) } CN → CH_2-NH_2
- Sn + HCl
- Zn + HCl
- Fe + HCl
- $NaBH_3CN$ } Borch Red^n

$NO_2 \longrightarrow -NH_2$

$CN \longrightarrow -CH_2-NH_2$

$NC \longrightarrow -NH-CH_3$

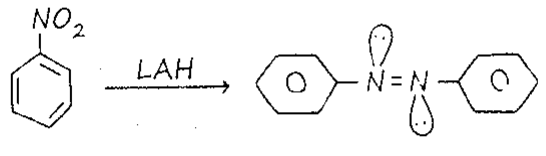
$-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow -CH_2-NH_2$



(Aldoxime)

(Ketoxime)

Note:-



Anti

8> Ritter Rx^n :-

H^+ Med^m, Jaha C^+ Stable banega waha NH_2 lagao.

$$CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}=\underset{-}{C}H_2 \xrightarrow[dil.\ H_2SO_4/\Delta]{H-C\equiv N} CH_3-\overset{CH_3}{\overset{|}{\underset{NH_2}{\underset{|}{C}}}}-CH_3$$

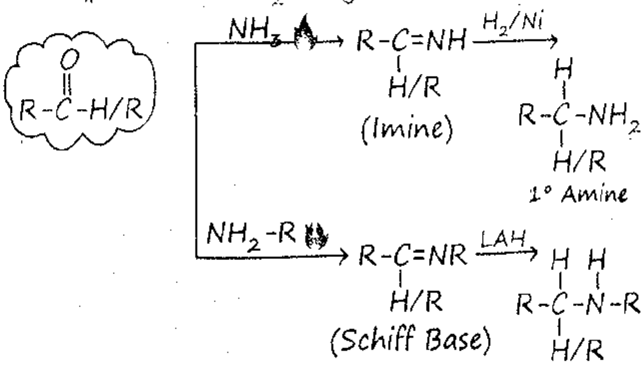
"1° amine connected to 3°C."

9> From Alcohols :- DM:- **OH- hatao NH_2-lagao.**

$$R-OH + \ddot{N}H_3 \xrightarrow[723K]{Al_2O_3 \text{ or } ThO_2} R-NH_2$$

10> From Carbonyl Compound :-

"$\overset{O}{\|}$" hatao "NH_2" lagao !



(Imine)

1° Amine

(Schiff Base)

2° Amine

11> 🔥 of α, β, γ & δ ..... amino acids:-

Just Remove COOH & Make it CO_2

"COOH" hatao "H" lagao.

$$NH_2-(CH_2)_n-COOH \xrightarrow[\text{🔥}]{NaOH + CaO} NH_2-(CH_2)_n-H$$

(Sodalime)

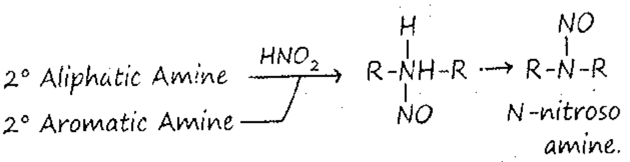
12> Rx^n with HNO_2 [$NaNO_2$ + HCl]

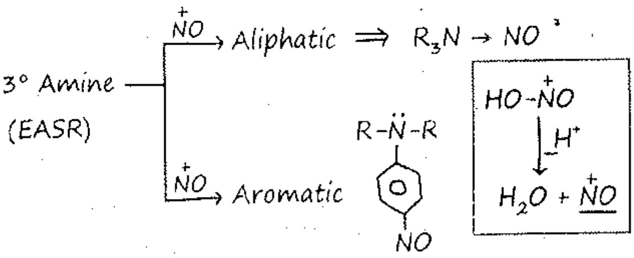
(Diazotisation)

$Temp^r = 0-5°C.$

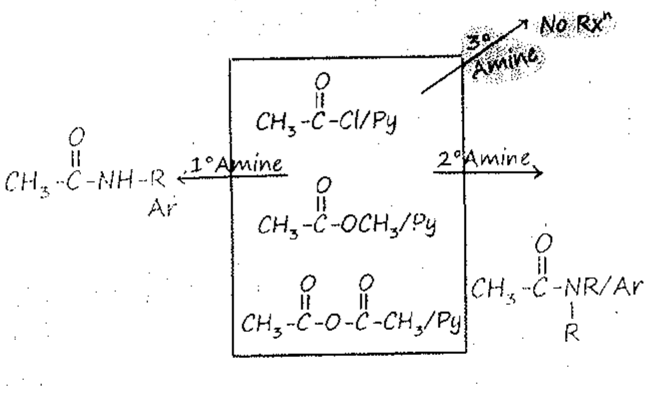
1° Aliphatic Amine $\xrightarrow{HNO_2}$ $R-OH + HCl + N_2$

1° Aromatic Amine $\xrightarrow{HNO_2}$ $Ph-N_2^+Cl^- + 2H_2O$





13> Rx^n with Acylating Agents :-



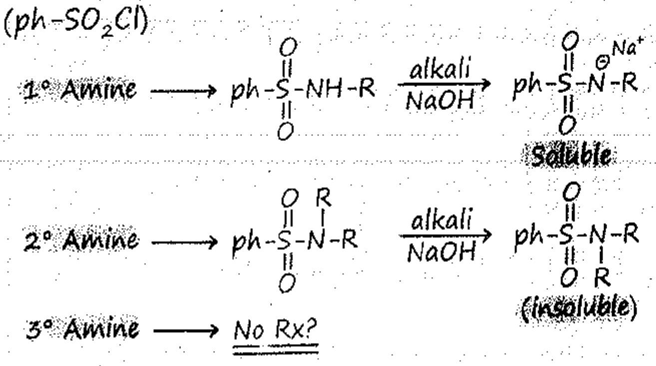
14> Schotten Baumann :-

(1°Amine with R-x)

$$CH_3CH_2-\ddot{N}H_2 + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_3$$

DISTINGUISH TEST :-

1. Hinsberg Test :- benzene sulphonyl chloride. (ph-SO_2Cl)



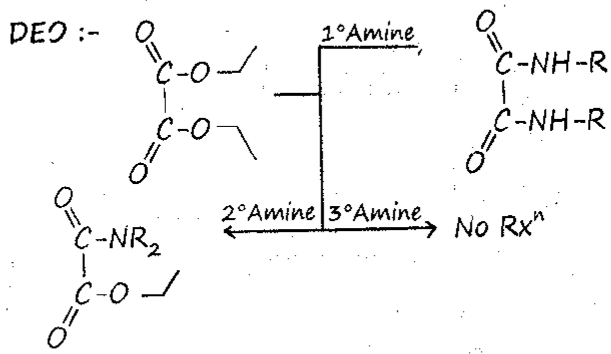
2. Hoffmann Musard Oil Test :-

(Only for 1° Amine)

$$R-\ddot{N}H_2 + CS_2 \xrightarrow[AgNO_3/\text{🔥}]{HgCl_2/\text{🔥} \text{ or}} R-NCS + HgS + 2HCl$$

intermediate :- N-alkyl isothiocyanate

3. Hoffmann Test :- (Diethyl oxalate).

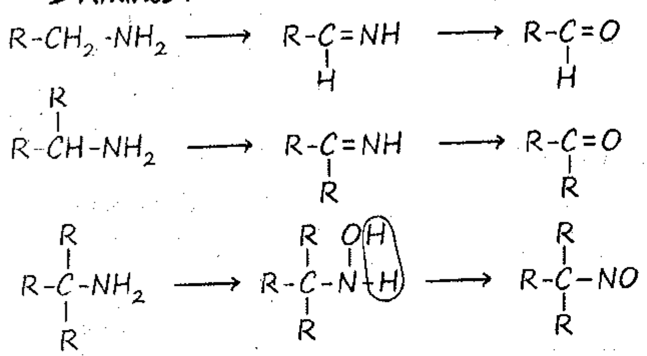


(oily liquid)

OXIDATION of AMINES :-

1. Aliphatic Amine with $KMnO_4$:-

1°Amines :-



2°Amines :-

$$R_2NH \xrightarrow{KMnO_4} R_2N-NR_2$$

3°Amines :-

$$R_3N \xrightarrow{KMnO_4} \text{No } Rx^n.$$

2. Oxidation with H_2SO_5 :-

$R\text{-}CH_2\text{-}NH_2 \longrightarrow R\text{-}CO\text{-}NHOH$ (n-hydroxy Amide)

$R\text{-}\underset{\substack{| \\ R}}{C}H\text{-}NH_2 \longrightarrow R\text{-}\underset{\substack{| \\ R}}{C}=N\text{-}OH$ (Ketoxime)

$R\text{-}\overset{\substack{R \\ |}}{\underset{\substack{| \\ R}}{C}}\text{-}NH_2 \longrightarrow R\text{-}\overset{\substack{R \\ |}}{\underset{\substack{| \\ R}}{C}}\text{-}NO$ (Nitroso alkane)

2° amine :- $R_2NH \xrightarrow{H_2SO_5} R\text{-}\overset{\substack{R \\ |}}{N}\text{-}OH$

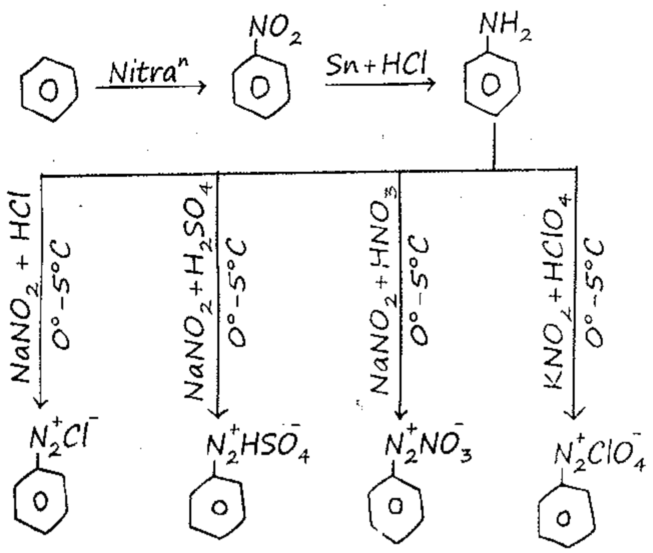
3° amine $R_3N \xrightarrow{H_2SO_5} R_3\overset{+}{N} \longrightarrow \overset{-}{O}$

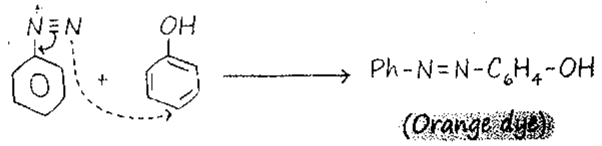
3. Carbylamine Test (Hoffmann isocyanide Test) :-

$\underset{Ar}{R}\text{-}NH_2 + CHCl_3 + KOH \longrightarrow \underset{Ar}{R}\text{-}NC + KCl + H_2O$

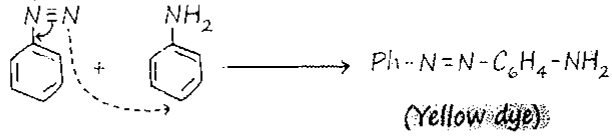
$(:CCl_2) = DCC.$ (Foul Odour)

BENZENE DIAZONIUM SALTS :-

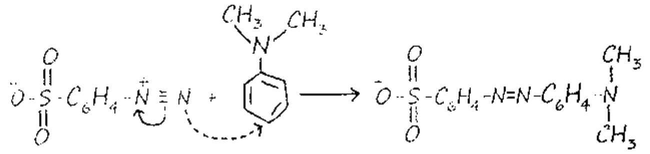




(Orange dye)



(Yellow dye)



(Methyl orange)

Indicator :- Acid Base Titration.

BIOMOLECULES

Carbohydrates

Classification of Carbohydrates:

A. Monosaccharides: *A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone.*

Examples: *Glucose, fructose, arabinose etc.*

B. Oligosaccharides: *These carbohydrates yield two to ten monosaccharide units on hydrolysis. They are further classified as disaccharides, trisaccharides etc, depending upon the no.of monosaccharides, they provide on hydrolysis.*

C. Polysaccharides: *They yield a large number of monosaccharide units on hydrolysis.*

Example *: Starch, Cellulose etc.*

Monosaccharides :

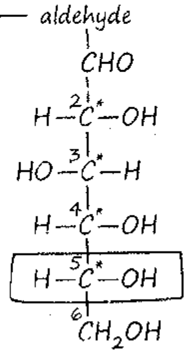
- *If a monosaccharide contains an **aldehyde group, it** is known as **an aldose** and if it contains a keto group, it is called ketose*

  *(a) **Glucose**: It is an aldohexose*

  aldehyde

  6C

  Structure of glucose $(C_6H_{12}O_6)$



open chain structure of glucose

D-Glucose

Reaction of Glucose :

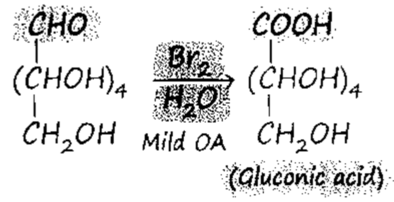
- ***On prolonged heating with HI,*** *it forms n-hexane, suggesting carbons are linked in straight chain.*

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HI, \Delta} \underset{(n\text{-hexane})}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

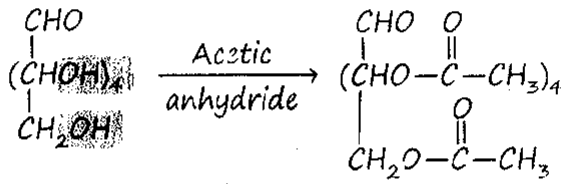
- *Presence of **carbonyl group** (—CHO) is confirmed by the following reactions.*

$$\underset{\text{Cyanohydride}}{\begin{array}{c} CH{<}^{CN}_{OH} \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}} \xleftarrow{HCN} \begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{NH_2OH} \underset{\text{Oxime of glucose}}{\begin{array}{c} CH=N-OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}}$$

- Carbonyl group present, is an aldehyde and it is confirmed by the given reaction

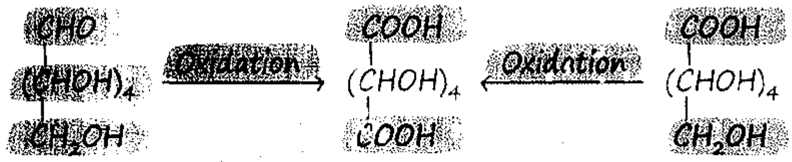


- Acetylation of glucose gives glucose pentaacetate which confirms presence of five OH groups



acid/acid derivatives + alcohol
↓
Ester

- Glucose and gluconic acid is oxidised to saccharic acid by nitric acid. This indicates presence of primary -OH group



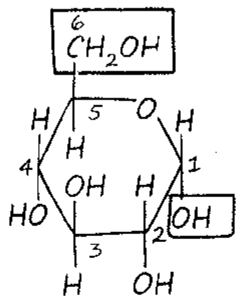
Saccharic acid　　Gluconic acid

Cyclic Structure of Glucose

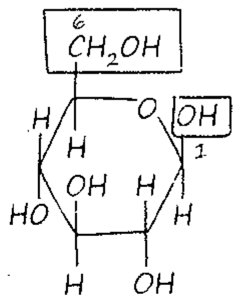
- The given observations could not explain chain structure of glucose
  (i) It does not react with $NaHSO_3$ or Schiff's reagent
    - It does not give 2, 4-DNP test and it does not react with Grignard Reagent.

  (ii) Pentaacetate of glucose does not react with NH_2OH.

  (iii) Glucose exist in two different crystalline forms, i.e. α and β forms.



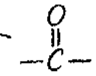
α-D-(+)-Glucopyranose

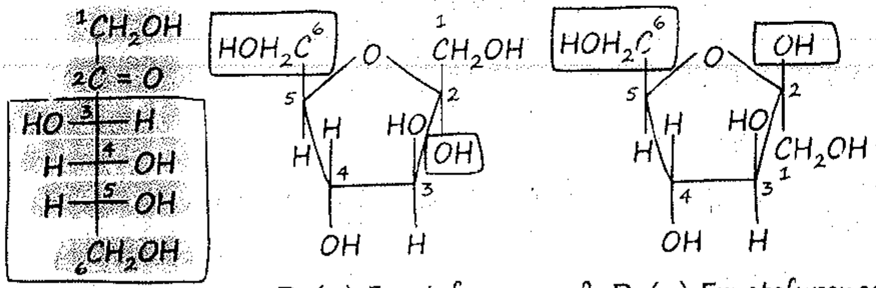


(Same side)

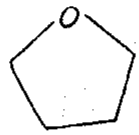
β-D-(+)-Glucopyranose

- α and β forms of glucose are called anomers as they only differ at C1 position. Six membered cyclic structure of glucose is called pyranose structure (*b*) **Fructose**

- Fructose is a ketohexose  6C
- Following structure have been assigned to this molecule ($C_6H_{12}O_6$)



D-(−) fructose α-D-(−) Fructofuranose β-D-(−) Fructofuranose



Furanose ring

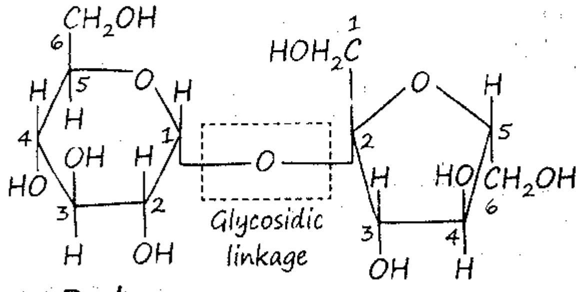
Fructose & glucose are functional isomers of each other

Tests of Glucose and Fructose

Both glucose and fructose reduce Tollen's reagent and Fehling's solution. They are also called reducing sugars.

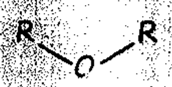
Disaccharides

(*i*) **Sucrose ⟹ α-D-Glucose + β-D-Fructose**



α-D-glucose β-D-fructose

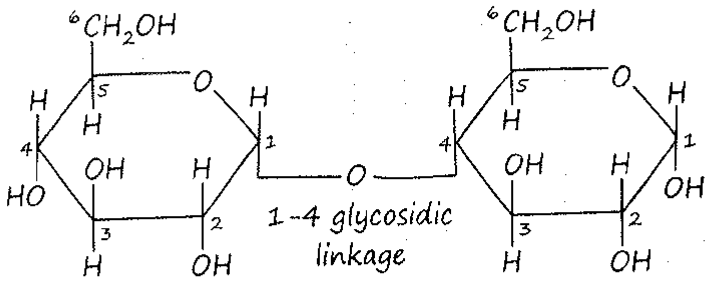
1-2 glycosidic linkage



ether linkage

- It is dextrorotatory
- It is non reducing sugar

(*ii*) **Maltose ⟹ α-D-Glucose + α-D-Glucose**

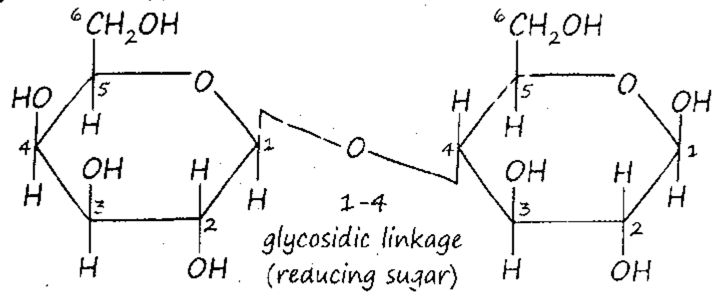


α-D-glucose α-D-glucose

Sucrose - α-D Glu + β-D Fru
Maltose - α-D Glu + α-D Glu
Lactose - β-D-Gal + β-D-Glu

- It is dextrorotatory
- It is reducing sugar
- It gives positive test with Tollen's reageent and Fehling's solution

(iii) Lactose ⟹ β-D galactose + β-D Glucose



β-D-Galactose β-D-glucose

Polysaccharides

(i) **Starch :** It is Polymer of α-D Glucose. It consists of two components. Amylose and Amylopectin.

Amylose (15-20% of starch)	Amylopectin (80-85% of starch)
• Water soluble component • Unbranched chain which is formed by C1-C4 glycosidic linkage of α-D Glucose unit	• Water insoluble component • Branched chains which is formed by C1-C4 glycosidic linkages whereas branching occurs by C1-C6 glycosidic linkages

(ii) **Cellulose**

- It is a straight chain polysaccharide
- It is composed of β-D-glucose units

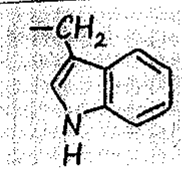
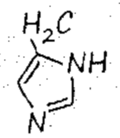
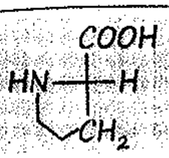
(iii) **Glycogen**

- It is called **animal starch**
- Its structure is **similar to amylopectin** and is rather more **highly branched.**

Proteins

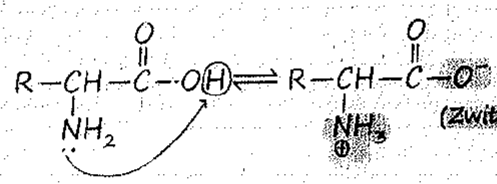
- All proteins are polymers of α-amino acid
- Structure of some commonly occurring amino acids along with their 3-letter and 1 letter symbols are given in the following table.
- The amino acids which **can be synthesised in the body**, are known as **non-essential amino acids.**

S.No.	Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1.	Glycine	H	Gly	G
2.	Alanine	$-CH_3$	Ala	A
3.	Valine*	$(H_3C)_2CH-$	Val	V
4.	Leucine*	$(H_3C)_2CH-CH_2-$	Leu	L
5.	Isoleucine*	$H_3C-CH(CH_3)-CH-$	Ile	I
6.	Arginine*	$HN=C(NH_2)-NH-(CH_2)_3-$	Arg	R

7.	Lysine*	$H_2N-(CH_2)_4-$	Lys	K
8.	Glutamic acid	$HOOC-(CH_2)_2-$	Glu	E
9.	Aspartic acid	$HOOC-CH_2-$	Asp	D
10.	Glutamine	$H_2N-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-$	Gln	Q
11.	Asparagine	$H_2N-\overset{O}{\overset{\|}{C}}-CH_2-$	Asn	N
12.	Threonine*	$H_3C-CHOH-$	Thr	T
13.	Serine	$HO-CH_2-$	Ser	S
14.	Cysteine	$HS-CH_2-$	Cys	C
15.	Methionine*	$H_3C-S-CH_2-CH_2-$	Met	M
16.	Phenylalanine*	$C_6H_5-CH_2-$	Phe	F
17.	Tyrosine	$(p)HO-C_6H_4-CH_2-$	Tyr	Y
18.	Tryptophan*		Trp	W
19.	Histidine*		His	H
20.	Proline		Pro	P

* essential amino acid

- The amino acids which cannot be synthesised in the body and must be obtained through diet are known as essential amino acids.
- In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion. This is neutral but contains both positive and negative charges.



Structure of Proteins

(a) **Fibrous proteins :**

- The polypeptide chains run parallel and held together by hydrogen and disulphide bonds shows fibre like structure
- They are insoluble in water e.g. keratin (present in hair, wool, silk), myosin (present in muscles) etc.

(b) Globular proteins :

- In this case polypeptide chains coil around to give a spherical shape
- They are usually soluble in water e.g. insulin, globulin

Vitamins

(i) Fat soluble vitamins : Vitamins are soluble in fat and oils. These are vitamins A, D, E and K.

(ii) Water soluble vitamins : B group vitamins and vitamin C are water soluble vitamins.

	Name of Vitamin	Deficiency Diseases
1.	Vitamin A	Xerophthalmia
2.	Vitamin B_1	(Thiamine) Beri beri
3.	Vitamin B_2	(Riboflavin) **Cheilosis**
4.	Vitamin B_{12}	Pernicious **anaemia**
5.	Vitamin C	(Ascorbic acid) **Scurvy**
6.	Vitamin D	**Rickets** (in children) osteomalacia (in adults)
7.	Vitamin K	**Increased blood clotting time**

8 Polymers

POLYMER

Classification of Polymers

- *Classification based on source*
  - (a) ***Natural polymers*** : These polymers are found in plants and animals. Examples are proteins, starch, rubber etc.
  - (b) ***Semi-synthetic polymers*** : Cellulose derivatives as cellulose acetate and cellulose nitrate are semi-synthetic polymers.
  - (c) ***Synthetic polymers*** : These are **man made polymers.** Examples are **Buna-S, nylon 6, 6 polythene etc.**

Type of Polymerisation Reaction

(A) Addition polymerisation or chain growth polymerisation

- The molecules of the same monomer or different monomers add together on a large scale to form a polymer.
- Monomers used are **unsaturated compounds**, e.g. **alkenes, alkadienes** and **their derivatives.**
- Chain growth can take place through the formation of either free radicals or ionic species.
- The addition polymers formed by the polymerization of a single monomeric species are known as homopolymers.

  Example : Polythene

$$\underset{\text{Ethene}}{nCH_2=CH_2} \longrightarrow \underset{\text{Polythene}}{-\!\!(CH_2-CH_2)_n\!\!-}$$

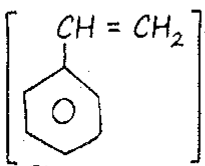
- The polymers made by addition polymerisation from two different monomers are termed as copolymers.

  Example : Buna-S

$$\underset{\text{1, 3-Butadiene}}{nCH_2=CH-CH=CH_2} + \underset{\text{Styrene}}{nC_6H_5CH=CH_2}$$

$$\downarrow$$

$$\underset{\text{Butadiene-styrene copolymer (Buna-S)}}{-\!(CH_2-CH=CH-CH_2-\overset{C_6H_5}{\overset{|}{C}H}-CH_2)_n}$$



Styrene

- ***Preparation and uses of important addition polymers***
  - (i) Polythene : There are two types of polythene

    Low density polythene :

  It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in presence of a **peroxide initiator.**

- It is obtained through free radical addition and H-atom abstration.
- It has highly branched structure.
- They are chemically inert, tough but flexible and poor conductor of electricity.

$\boxed{\text{High density polythene :}}$ HDPE - Low pressure 6-7 atm

$$nCH_2 = CH_2 \xrightarrow[(333\text{-}343)\ K(6\text{-}7)atm]{TiCl_4,\ (C_2H_5)_3Al} \underset{\text{High density polythene}}{-\!\!\left(CH_2-CH_2\right)\!\!-_n}$$

- Catalyst $TiCl_4$, $(C_2H_5)_3Al$ is called **Ziegler-Natta catalyst**
- The polymer obtained has high density due to close packing.
- These are also called linear polymers.
- It is also **chemically inert, more tough** and **hard.**

(ii) $\boxed{\text{Polytetrafluoroethene (Teflon)}}$

$$nCF_2 = CF_2 \xrightarrow[\text{high pressure}]{\text{Catalyst}} \underset{\text{Teflon}}{-\!\!\left[CF_2-CF_2\right]\!\!-_n}$$

Uses : It is used in **making oil seals, gaskets** and **non-stick surface coated utensils.**

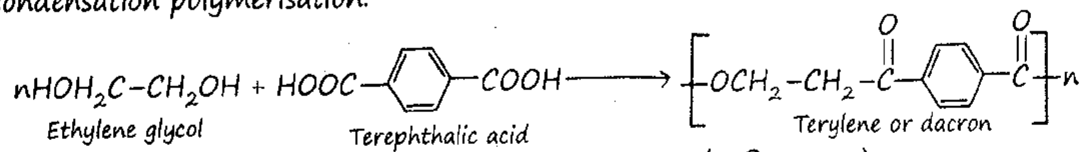
(iii) $\boxed{\text{Polyacrylonitrile :}}$

$$nCH_2 = CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerization}} -\!\!\left[-CH_2-\underset{\;}{\overset{\overset{\displaystyle CN}{|}}{C}}H-\right]\!\!-_n$$

Uses : It is used as a **substitute for wool** in making commercial fibers as orlon or acrilan.

(B) $\boxed{\textbf{Condensation polymerisation or step growth polymerisation}}$

- It generally involves a repetitive condensation reaction between two bi-functional or tri-functional monomeric units.
- This is also called step growth polymerisation. Preparation and uses of some polymers obtained by condensation polymerisation.



(i) $\boxed{\text{Polyamides :}}$ These polymers possess **amide linkages** $\left(\overset{O}{\overset{\|}{-C}}-NH-\right)$ and are called nylons.

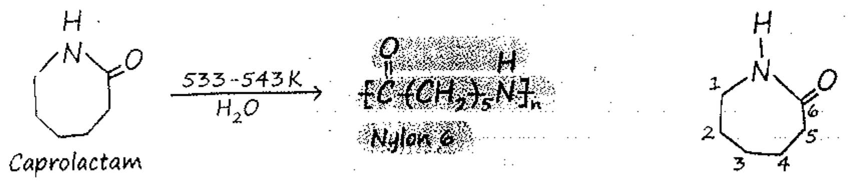
- $\boxed{\textbf{Nylon 6,6 :}}$

$$\underset{\text{adipic acid}}{nCOOH(CH_2)_4COOH} + \underset{\text{hexamethylene diamine}}{nNH_2(CH_2)_6NH_2}$$

$$\xrightarrow{553\ K\ \text{High pressure}} -\!\!\left[NH-(CH_2)_6NH-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]\!\!-_n + nH_2O$$

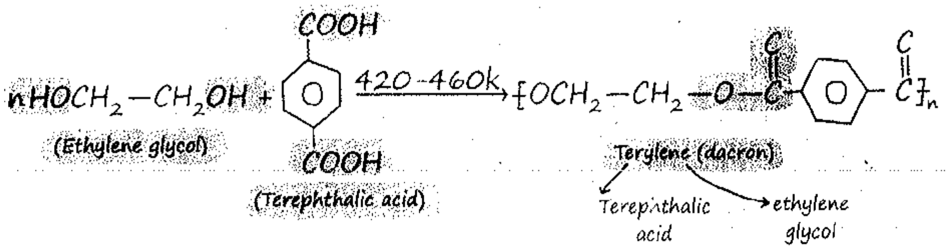
Uses : It is used in making sheets, bristles for brushes and in textile industry.

➲ Nylon 6 :



Uses : It is used in manufacture of tyre cords, fabrics and ropes.

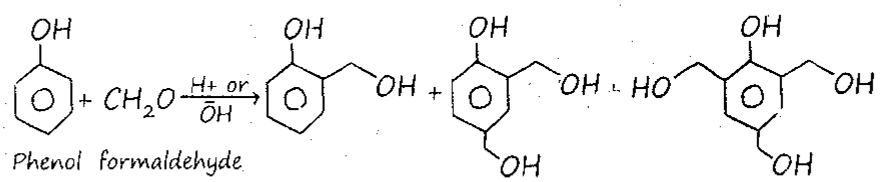
(ii) Polyesters : These are condensation products of dicarboxylic acids and diols.

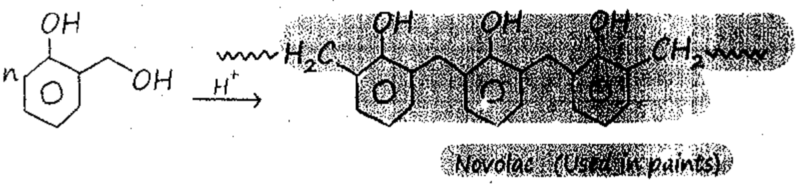


[Ester linkages → acid + alcohol]

Uses : It is used in blending with cotton and wool fibres.

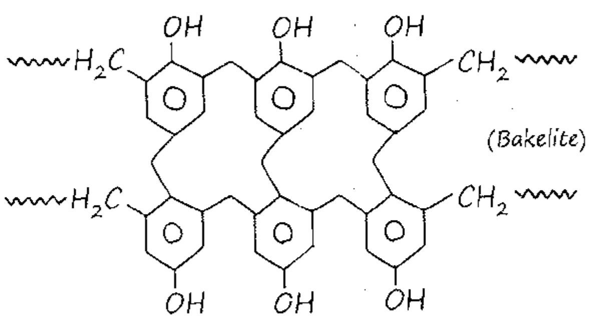
(iii) Phenol formaldehyde polymer (Bakelite)





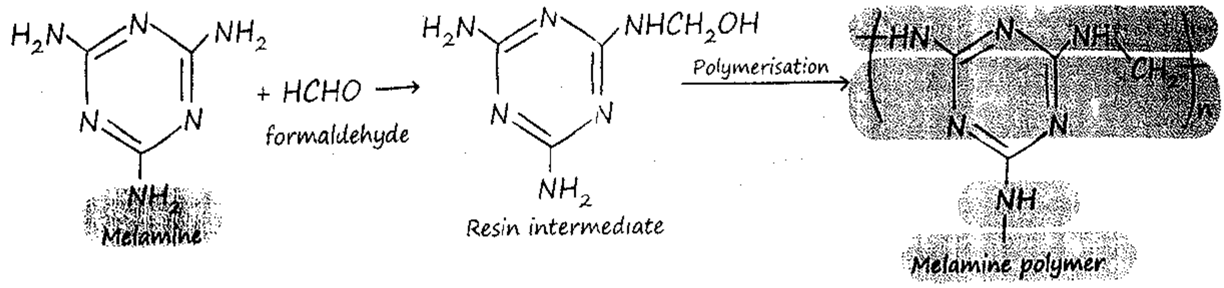
➲ Novolac on heating with formaldehyde undergoes cross linking to form bakelite

➲ Bakelite is thermosetting polymer which can not be reused or remoulded



Uses : It is used for making combs, electrical switches and handles of various utensils.

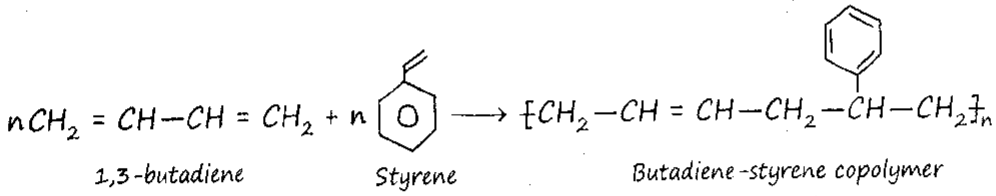
(iv) Melamine-formaldehyde polymer



Uses : It is used in the manufacture of unbreakable crockery.

Copolymerisation

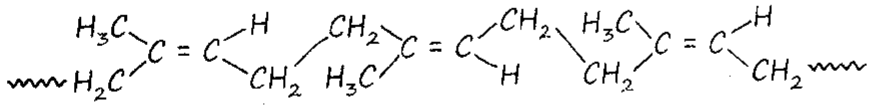
- Here a mixture of more than one monomeric species are allowed to polymerise and form a copolymer
- The copolymer can be made both by chain growth (addition) and by step growth (Condensation) polymerisation.



Uses : It is used in manufacture of autotyres, floortiles, cable insulation etc.

Rubber (Elastomer)

(i) Natural rubber: It is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as **cis-1, 4-polyisoprene**



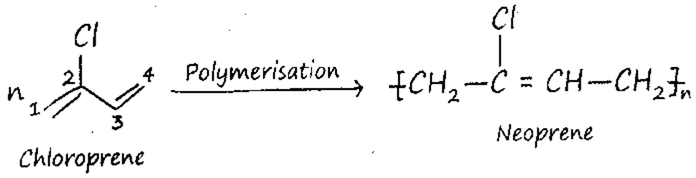
Vulcanisation of rubber : This process consists of heating a mixture of raw rubber with sulphur and appropriate at additive 273 K to 415 K.

- Sulphur forms cross links at the reactive sites of double bond.
- Due to vulcanisatison rubber gets stiffened.

5% sulphurised rubber is used in tyre manufacturing.

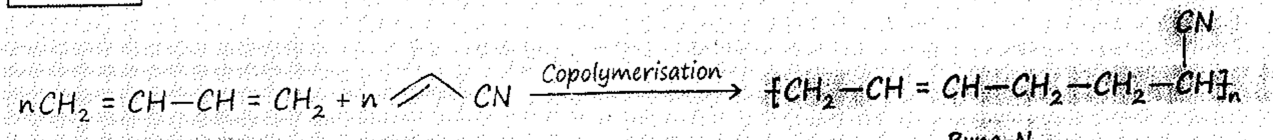
(ii) Synthetic rubbers :

(a) Neoprene



Uses : It is used for the manufacture of conveyor belts, gaskets and hoses.

(b) Buna-N



Uses : It is used in making oil seals, tank lining etc.

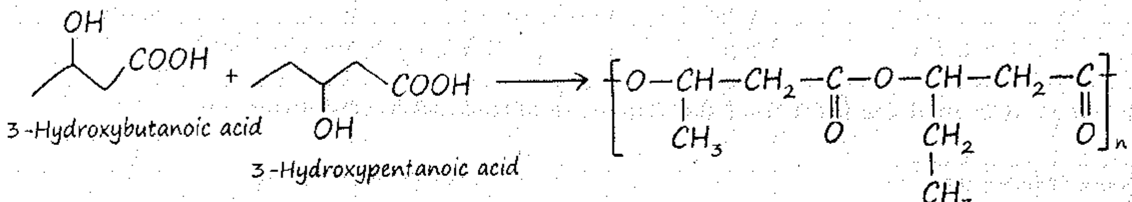
BIODEGRADABLE POLYMERS

Classification of Polymers

$$HO-\underset{\underset{CH_3}{|}}{\overset{\beta}{HC}}-H_2\overset{\alpha}{C}-COOH \qquad HO--\underset{\underset{\underset{CH_3}{|}}{CH_2}}{\overset{\beta}{HC}}-\overset{\alpha}{CH_2}-COOH$$

(β-hydroxybutanoic acid) (β-hydroxypentanoic acid)

- Poly β-hydroxybutyrate -co- β-hydroxy valerate (PHBV)



Uses : It is used in orthopaedic devices and in controlled release of drugs.

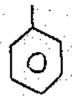
- Nylon 2-nylon 6

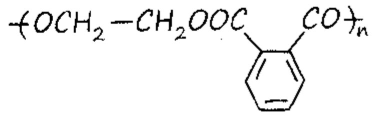
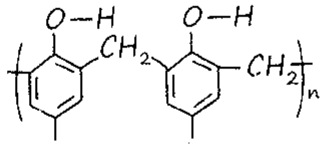
$$n\,H_2N-CH_2-COOH + n\,H_2N(CH_2)_5COOH \longrightarrow \left[NH-CH_2-\overset{\overset{O}{\|}}{C}-NH(CH_2)_5-\overset{\overset{O}{\|}}{C}\right]_n$$

Glycine Caproic acid nylon 2-nylon 6

POLYMERS OF COMMERCIAL IMPORTANCE

Some commercially important polymers along with their structures and uses are given below in table.

Name of polymer	Monomer	Structure	Uses
Polypropene	**Propene** $CH_3-CH=CH_2$	$-\!\!(CH_2-\underset{}{\overset{\overset{CH_3}{|}}{CH}})\!\!-_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene $CH=CH_2$ 	$-\!\!(CH_2-\overset{\overset{C_6H_5}{|}}{CH})\!\!-_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.

Polyvinyl chloride (PVC)	Vinyl chloride $CH_2=CH(Cl)$	$\text{+}CH_2-CH(Cl)\text{+}_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\text{+}NH-CO-NH-CH_2\text{+}_n$	For making unbreakable cups and laminated sheets.
Glyptal glycol	(a) Ethylene glycol (b) Phthalic acid		Manufacture of paints and lacqures.
Bakelite	(a) Phenol (b) Formaldehyde		For making combs, electrical switches, handles of utensils and computer discs.

9 Chemistry in Everyday Life

(1) Some Important Terms

- **Drugs : Drugs** are **chemical of low molecular masses** (~100-500u). These interact with **macromolecular targets** and produce **a biological response**. When the **biological response is therapeutic** and useful, these are **called medicines**.
- Enzyme : Proteins which perform the role of biological catalysts in the body are called enzymes.
- **Receptors** : Proteins which are crucial to communication system in the body are called receptors.
- **Enzyme inhibitors :** Drugs can block the **binding site of the enzyme** and **prevent the binding of substrate**, or can inhibit the **catalytic activity of enzyme**. Such drugs are **called enzyme inhibitors**.
- **Competitive inhibitors : Drugs compete with natural substrate for their attachment on the active site of enzymes.** Such drugs are called **competitive inhibitors**.
- Allosteric site : Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site.
- **Chemical messengers** : In **human body, message between two neurons** and **that between neurons to muscles** is **communicated through certain chemicals.** These are called **chemical messengers**.
- Antagonists : **Drugs that bind to the receptor site and inhibit its natural function are called antagonists.**
- **Agonists : Drugs that mimic the natural messenger by** switching on the receptor are called agonists.

(2) Therapeutic Action of Different Classes of Drugs

Examples

(I) Antacids :

- Over production of acid in the stomach causes irritation and pain
- Histamine stimulates the secretion of pepsin and HCl in the stomach
- Antacids prevent the interaction of histamine with receptors present in the stomach wall. This results in the release of lesser amount of acid.

Examples of Antacids

Cimetidine (Tegamet), ranitidine (Zantac)

(II) Antihistamines :

- *Histamine is a potent vasodilator*
- ***Histamine is also responsible for the nasal congestion** associated **with common cold and allergic response to pollen.***
- ***Synthetic drugs,** bromphenirамine (**Dimetapp**) and terfenadine (**Seldane**), act as antihistamines*

(III) Neurologically active drugs :

- ***Tranquilizers** and **analgesics are** neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.*

(a) **Tranquilizers** :

- *These drugs are used for the **treatment of stress, and mild or even severe mental diseases.***
- *These **relieve anxiety, stress, irritability or excitement by inducing a sense of well being.***
- *They form **an essential component of sleeping pills.***

Examples are : *Iproniazid, phenelzine (Nardil), Meprobamate, Chlordiazepoxide, Equanil*

- *Derivatives of barbituric acids also constitute important class of tranquilizers.*

Examples: *Veronal, amytal, nembutal, luminal and seconal*

(b) **Analgesics** : *These drugs* **reduce** *or* **abolish pain.** *These are of two types :*

(i) **Non-narcotic analgesics** : *These drugs inhibit synthesis of prostaglandins which stimulate inflammation in the tissue and cause pain.*

Examples: *Aspirin and paracetamol*

(ii) **Narcotic analgesics** : *Morphine when administered in medicinal dose, relieve pain and produce sleep.*

(IV) Antimicrobials :

- *An antimicrobial destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria, fungi, virus, parasites selectively*
- *Antibiotics, antiseptics and disinfectants are antimicrobial drugs*

(A) **Antibiotics** : **Antibiotics are used as drugs to treat infections** *because of* **their low toxicity for humans and animals.**

- *Arsphenamine also known as salvarsan was used to treat syphilis caused by bacteria spirochete.*

- Antibiotics are of two types :

(a) **Bactericidal:** These antibiotics have killing effect on microbes

Examples: Penicillin, Aminoglycosides, Ofloxacin

(b) **Bacteriostatic:** These antibiotics have inhibitory effect on microbes.

Examples: Erythromycin, Tetracycline, chloramphenicol

Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad spectrum antibiotics.

Examples: Ampicillin, Amoxycillin, Chloramphenicol, vancomycin, ofloxacin.

Antibiotics effective mainly against Gram-positive or Gram-negative bacteria are narrow spectrum antibiotics.

Example: Penicillin G

(B) Antiseptics and disinfectants:

(a) **Antiseptics:** These are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces.

Examples: Furacine, soframicine

- Dettol is a mixture of chloroxylenol and terpineol.
- Bithional is added to soaps to impart antiseptic properties.
- 2-3 per cent solution in alcohol-water mixture is known tincture of iodine. It is applied on wounds.
- Boric acid in dilute aqueous solution is weak antiseptic for eyes.
- 0.2 per cent solution of phenol is an antiseptic.

(b) **Disinfectants :**

- These are applied to inanimate objects such as floors, drainage system, instruments etc.
- 1% solution of phenol is used as disinfectant
- Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and SO_2 in very low concentrations, are disinfectants.

(V) Antifertility drugs :

- Antifertility drugs are used to control birth in human beings.
- Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives.
- Norethindrone and novestrol are used as antifertility drugs.

(3) Chemicals in Food

(I) Artificial Sweetening Agents :

Natural sweeteners, e.g., sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners.

Artificial sweetener	Sweetness value in comparison to cane sugar
(a) Aspartame	100
(b) Saccharin	550
(c) Sucralose	600
(d) Alitame	2000

As Sachin Scores all time

PYQ

Aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.

Funnel-shaped opening provided with many finger-like Fimbriae. It helps to collect the ovum.

Sucralose is trichloro derivative of sucrose. It is stable at cooking temperature.

(II) Food Preservatives :

- *Food preservatives prevent spoilage of food due to microbial growth.*

Examples : $\underbrace{\text{Table salt, sugar, vegetable oils,}}_{\text{Class - 1 preservatives}}$ $\underbrace{C_6H_5COONa \text{ etc.}}_{\text{Class - 2 preservatives}}$

(III) Antioxidants in Food :

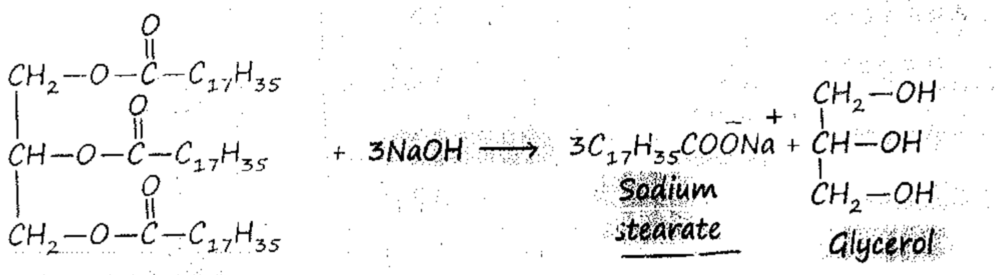
- ***These help in food preservation by retarding the action of oxygen on food.***
- ***These are more reactive towards oxygen than food materials which they are protecting.***
- *Butylated hydroxytoluene (BHT) and butylated hydroxy anisole (BHA) are most familiar antioxidants.*
- *SO_2 and sulphite are useful antioxidants for wine and beer, sugar syrups and cut, peeled or dried fruits and vegetables.*

(4) Cleansing Agents

Two types of detergents are used as cleansing agents.

(i) **Soaps :**

- Soaps are sodium or potassium salts of long chain fatty acids.
- Soaps containing sodium salts are formed by heating fat with aqueous NaOH. This reaction is called saponification



Glyceryl ester of stearic acid (Fat)

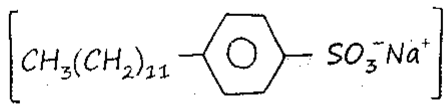
By - product

(ii) Synthetic Detergents : These are cleansing agents which have all the properties of soaps, but can be used both in soft and hard water.

These are of Three Types

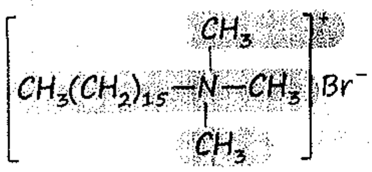
(a) **Anionic detergents** : Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons.

Examples : Sodium laurylsulphate ($CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$),

Sodium dodecylbenzene sulphonate 

(b) **Cationic detergents** : Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions.

Examples : **Cetyltrimethyl ammonium bromide**



(c) **Non-ionic detergents** : Non-ionic detergents do not contain any ion in their constitution.

Examples : Detergent formed when stearic acid reacts with polyethylene glycol.

$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethylene glycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH}$$

$$\Big\downarrow -H_2O$$

$$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

- Liquid dishwashing detergents are non-ionic type
- Detergents and soap remove grease and oil by micelle formation