# STOICHIOMETRY

## Mole concept

1) $$n_A = \frac{W_A}{M_A} = \frac{\#\,\text{particles}}{6.02\times10^{23}} = \frac{\text{Vol}(A)}{22.4\ \text{L/mol}}$$

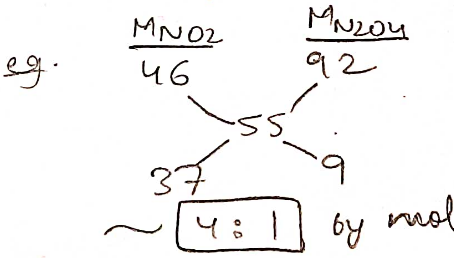
2) Avg. molecular wt. = $\boxed{\frac{W_{Total}}{n_{Total}}}$

3) Vapor Density = $\left(\frac{M_A}{2}\right)$

4) $\%\ \text{mass} = \frac{\text{wt. (element)}}{W_{Total}} \times 100\%$

5) $\%\ \text{mol} = \frac{n_{element}}{n_{Total}} \times 100\%$

☆ In questions, prefer to use mixture & Alligation Trick



6) $(M.F.) = (E.F)n$

7) $n = \left(\frac{\text{M.F. mass}}{\text{E.F. mass}}\right)$

☆ In questions about finding EF, if %s of given elements don't add up to 100% ⇒ Rest of the element is Oxygen (O)

## Stoichiometry

1) $aA + bB \longrightarrow cC + dD$

Balanced Chem. Rxn,

$$\boxed{\frac{n_A}{a} = \frac{n_B}{b} = \frac{n_C}{c} = \frac{n_D}{d}}$$

2) POAC

$A_2B_3 + B_4C_3 \longrightarrow C_5A_2 + A_2B_5$

Ⓑ $\boxed{3n_{A_2B_3} + 4n_{B_4C_3} = 5n_{A_2B_5}}$

3) $\% \text{ yield} = \frac{W_{actual}}{W_{expected}} \times 100\%$

4) $\% \text{ purity} = \frac{W_{pure}}{W_{impure\ sample}} \times 100\%$

5) Limiting Reagent

Compare $\left(\frac{n_A}{a}\right)$.

Reactant with lower $\left(\frac{n_A}{a}\right)$ is the LR.

## Concentration Terms

A → Solvent
B → Solute
S → Soln

1) $\% \, v/v = \frac{V_B}{V_S} \times 100\%$

2) $\% \, w/v = \frac{w_B}{V_S \, (100 \, ml)} \times 100\%$

3) $M = \frac{n_B}{V_S \, (\text{in L})}$

4) $x_B = \left(\frac{n_B}{n_A + n_B}\right)$

☆ $\boxed{\Sigma x_i = 1}$

5) $m = \frac{n_B}{W_A \, (\text{in kg})}$

6) $ppm = \frac{W_B}{W_S} \times 10^6$

$\sim \frac{W_B}{W_A} \times 10^6$

7) $N = \frac{eq(B)}{V_S \, (\text{in L})}$

### Relations b/w Conc. Terms

- $N = M \times n_f$
- $eq. = mol \times n_f$
- $\% \, w/v = \% \, w/w \times d_s$
- $\boxed{M = \frac{\% \, w/v \times 10}{M_B}}$
- $M = \frac{(\% \, w/w)(d_s) \times 10}{M_B}$
- $\boxed{m = \frac{1000 M}{1000 d_s - M M_B}}$
- $\boxed{m = \frac{1000 \, x_B}{M_A \, x_A}}$
- $M = \frac{1000 \, d_s \, x_B}{M_A x_A + M_B x_B}$

## Dilution & Mixing

1) $M_1V_1 = M_2V_2$

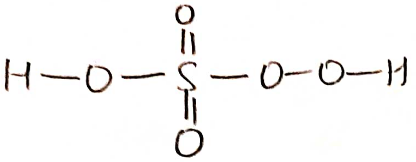
2) $M_1V_1 + M_2V_2 = M_f V_f$

☆ $\boxed{V_f = V_1 + V_2}$ iff $\rho_A = \rho_B$

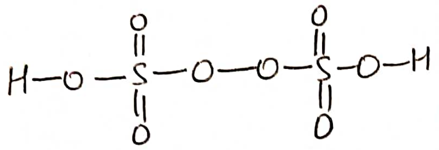
In general $\boxed{\rho_1 V_1 + \rho_2 V_2 = \rho_f V_f}$

# Redox Reactions

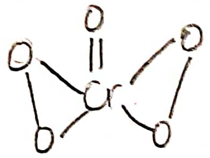
$H_2SO_5$
(Caro's Acid)



$H_2S_2O_8$
(Marshell's Acid)



$CrO_5$



$C_3O_2$
(Carbon suboxide)

$O=C=C=C=O$

## Balancing Redox Rxns

① Ion-$e^-$ :
O by $H_2O$
H by $H^+$
$e^-$ for conserving charge

② Oxi^n no. : Cross Multiply #$e^-$ exchanged in Oxi^n & Red sides

③ Algebraic Eqn. Method :

- Add coeffs a, b, c . . . to skeletal rxn chems-
- Use POAC & conserve charge (on all elems)
- Assume any one of the coeffs to be 1.

# Equivalent Concept

**n-factor** – Charge transferred per mol of specie

① Ions : Charge on Ion

② Salts : Total +ve charge on Cation

Mohr's Salt – $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

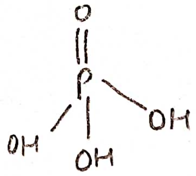
Potash Alum – $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

③ Acid – Basicity (in rxn)

④ Bases – Acidity (in rxn)

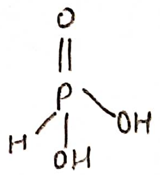
Exceptions

$\boxed{H_3PO_4}$
(Best Oxi^n Ag)



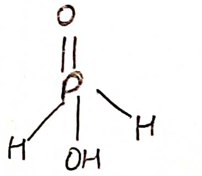
$n_f = 3$

$\boxed{H_3PO_3}$



$n_f = 2$

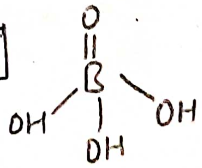
$\boxed{H_3PO_2}$



(But Red. Ag)
(Strongest Acid)

$n_f = 1$

$\boxed{H_3PO_4}$



$n_f = 1$

⑤ Oxi & Red Ag. – (Intermolecular)

S.1

$$KMnO_4 \begin{cases} \xrightarrow{\text{Acidic}} Mn^{2+} & \underline{n_f=5} \\ \xrightarrow{\text{Neutral}} MnO_2 & \underline{n_f=3} \\ \xrightarrow{\text{Basic}} MnO_4^- & \underline{n_f=1} \end{cases}$$

S.2 $Cr_2O_7^{2-} \xrightarrow[\text{Acidic}]{} Cr^{3+}$

$\underline{n_f = 6}$ $\underline{n_f = 3}$

S.3 Oxi Ag

$H_2O_2 \rightarrow H_2O$

$\underline{n_f = 2}$ $\underline{n_f = 1}$

Red Ag

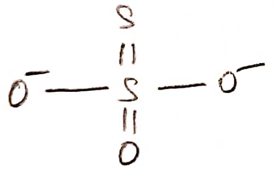
$H_2O_2 \rightarrow O_2$

$\underline{n_f = 2}$ $\underline{n_f = 2}$

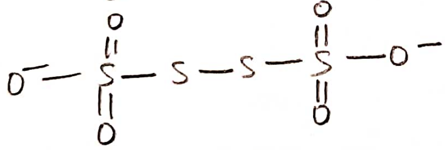
S.4 $S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

$\underline{n_f = 1}$ $\underline{n_f = 2}$

$\boxed{S_2O_3^{2-}}$



$\boxed{S_4O_6^{2-}}$



Special Case : More than one atom undergoing oxidation / reduction

eg $\overset{+2\,+3}{Fe\,C_2O_4} \longrightarrow Fe^{3+} + \overset{+4}{CO_2}$

$n_f(FeC_2O_4) = n_f(Fe) + 2n_f(C) = (1\times1)+(2\times1)$
$= ③$

$n_1 \longrightarrow$ # $e^-$ transferred in oxi

$n_2 \longrightarrow$ # $e^-$ transferred in Red

⑥ Oxi & Red Ag.- (Intramolecular)

Case I — $n_1 = n_2$

$$\boxed{n_f = n_1}$$

Case - II — $n_1 \neq n_2$

$$\rightarrow \boxed{n_f = |n_1 - n_2|}$$

NOTE: All elems. which are undergoing Red/ox must be Balanced to calculate $n_1$ & $n_2$

⑦ Oxi & Red Ag — (Disproportionation)

$$\boxed{n_f = \frac{n_1 \times n_2}{n_1 + n_2}}$$

⑧ General Method

- Balance rxn using ion-$e^-$ method

★— $\boxed{n_f(A) = \dfrac{\#e^- \text{ involved}}{\text{Coeff.}(A)}}$

★★ Special Case : When an element is not wholly transferred in 1 product.

eg. $2KMnO_4 + 16H\overset{-1}{Cl} \longrightarrow 2K\overset{-1}{Cl} + 2Mn\overset{-1}{Cl_2} + 5\overset{0}{Cl_2}$

$16\,HCl \rightarrow 10e^-$

$\rightarrow n_f(HCl) = \frac{10}{16} = \textcircled{\tfrac{5}{8}}$

⑨ Law of Equivalence

(i) $aA + bB \longrightarrow cC + dD$

$$\boxed{eq(A) = eq(B) = eq(C) = eq(D)}$$

(ii) in a compound $M_mN_n$

$$\boxed{eq(M_mN_n) = eq(M) = eq(N)}$$

## ⑩ Formulae

- $eq. = \frac{\text{Given wt.}}{E \ (\text{Eq. wt})}$
- $eq. = n_f \times n$ (Moles)
- $N = M \times n_f$
- $eq. = N \times V$ (in L)

## Titration

Iodiometric & Iodometric

$$\underbrace{Na_2S_2O_3}_{n_f=1} + I_2 \longrightarrow I^- + \underbrace{Na_2S_4O_6}_{n_f=2}$$

$$\boxed{eq.(Na_2S_2O_3) = eq(I_2)}$$

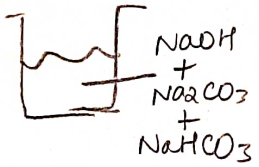
$$(\text{Ox. Agent}) + I^- \longrightarrow I_2 + \sim\sim$$

$$I_2 + Na_2S_2O_3 \longrightarrow I^- + Na_2S_4O_6$$

$$\boxed{eq(\text{Ox. Ag}) = eq(I_2) = eq(Na_2S_2O_3)}$$

$\boxed{Na_2S_2O_3} \Rightarrow$ Hyposolution

## Double Titration



① HPh

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

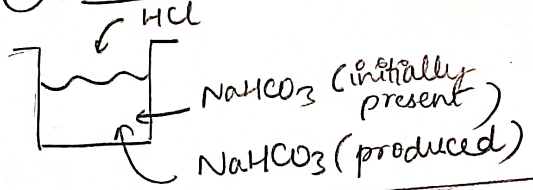
$$HCl + \underbrace{Na_2CO_3}_{\boxed{n_f=1}} \longrightarrow NaHCO_3 + NaCl$$

$\boxed{n_f=1}$

$$\boxed{eq(HCl) = eq(NaOH) + eq(Na_2CO_3)}$$

At first eq. pt.

② MeOH



$$\boxed{eq(HCl) = \underset{\text{initial}}{eq(NaHCO_3)} + \underset{\text{produced}}{eq(NaHCO_3)}}$$

At 2nd eq. pt.

NOTE: Only $Na_2CO_3$ displays the property of having $n_f = 1$ with HPh. No other base shows variation in neutralisation.

## Volume strength of $H_2O_2$

Vol. of $O_2$ produced by 1L $H_2O_2$ at STP.

$$\boxed{M_{H_2O_2} = \frac{V}{11.2}} \qquad \boxed{N_{H_2O_2} = \frac{V}{5.6}}$$

$\because n_f(H_2O_2) = 2$

## % Oleum strength

Oleum : (100g) $\underbrace{H_2SO_4}_{(100-x)}$ $\underbrace{SO_3}_{x}$

| | | | | |
|---|---|---|---|---|
| eg. | $SO_3$ + | $H_2O$ | $\longrightarrow$ | $H_2SO_4$ |
| wt. | 40g | 9g | | 49g |

$$\left(\%\ \text{Oleum strength}\right) = \underset{\text{initial}}{wt.(H_2SO_4)} + \underset{\text{produced by free } SO_3}{wt.(H_2SO_4)}$$

$$= (100-40)+49 = \boxed{109\%}$$

In General,

$$\boxed{\frac{wt(SO_3)}{80} = \frac{(\%\ Ol.\ Str. - 100)}{18}}$$

wt. of $SO_3$ in 100g of oleum

**NOTE:** $\boxed{(\%\ \text{Oleum Str.} - 100)}$

↳ wt. of $H_2O$ added to convert $SO_3 \rightarrow H_2SO_4$ per 100g oleum.

## Hardness of water

- → Temporary — Bicarbonates of $Ca^{2+}$ & $Mg^{2+}$
- → Permanent — $Cl^-$ & $SO_4^{2-}$ of $Ca^{2+}$ & $Mg^{2+}$

Ways to Remove

Temporary
- → Heating
- → Clark's Process (adding $Ca(OH)_2$)
- → Add^n of $Na_2CO_3$

Pemanent
- → Permutit Process ($\underbrace{Na_2Z}_{\text{zeolite}} = \underbrace{Na_2Al_2Si_2O_8}_{\text{Sodium Alumino orthosilicate}} \cdot xH_2O$)
- → Calgon's Process ($Na_2[Na_4(PO_3)_6]$ Sodium Hexa-meta Phosphate)
- → $Na_2CO_3$ & $Na_3PO_4$
- → Ion-Exchange-Resin Process (Demineralised Water)

**NOTE:** Hardness of any substance is calculated w.r.t $CaCO_3$

$$eq.(M) = eq.(CaCO_3)$$

$$\boxed{\left(\text{Degree of Hardness}\right) = \frac{wt.(CaCO_3)}{wt.(soln)} \times 10^6\ ppm}$$

## Available Chlorine

$$\boxed{\left(\%\ \text{available } Cl_2\right) = \frac{wt.(Cl\ \text{released})}{wt.\ \text{sample}} \times 100\%}$$

# ATOMIC STRUCTURE

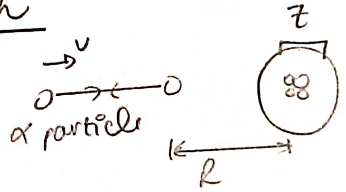
## Rutherford & Before

Cathode Rays — $C \rightarrow A$
e/m ratio const.
called $e^-$.

Anode Rays (Canal) — $A \rightarrow C$
e/m ratio varies

| | e | p | n |
|---|---|---|---|
| Mass | $9.1\times10^{-31}$ | $1.67\times10^{-27}$ | $1.67\times10^{-27}$ |
| Charge | $-1.6\times10^{-19}$ | $+1.6\times10^{-19}$ | 0 |

## Closest Approach



At closest dist,

$$\boxed{KE_{\text{initial}} = P.E} \Rightarrow \frac{1}{2}mv^2 = \frac{k(2e^-)(Ze^-)}{R}$$

## Bohr's Model

— $\boxed{mvr = n\hbar}$

— $\boxed{\underset{(\text{in eV})}{E} = \frac{12400}{\lambda} \rightarrow (\text{in Å})}$ ($E = h\nu$ in general)

for one photon

$1\text{eV} = 1.6\times10^{-19}\text{ J}$

— $\boxed{\underset{(\text{photo-}e^-)}{K.E} = h\nu - \underbrace{h\nu_0}_{\text{work fxn}}}$

— $\boxed{\underbrace{V}_{\text{Stopping Potential}} = \frac{h\nu}{e} - \frac{h\nu_0}{e}}$

— $\boxed{v = \left(\frac{ke^2}{\hbar}\right)\left(\frac{Z}{n}\right)}$

$v = 2.18\times10^{6}\left(\frac{Z}{n}\right)$ m/s

— $\boxed{r = \left(\frac{\hbar^2}{2mke^2}\right)\left(\frac{n^2}{Z}\right)}$

$r = 0.529\left(\frac{Z}{n}\right)$ Å

— $\boxed{K.E = \frac{1}{2}m\left(\frac{ke^2}{\hbar}\right)^2\left(\frac{Z^2}{n^2}\right)}$

$K.E = -13.6\left(\frac{Z^2}{n^2}\right)$ eV/atom

$= -2.18\times10^{-18}\left(\frac{Z^2}{n^2}\right)$ J/a

$= -1312\left(\frac{Z^2}{n^2}\right)$ kJ/mol

— $\boxed{T \propto \frac{n^3}{Z^2}}$

— for H atom,

$K.E_1 = -13.6$ eV
$K.E_2 = -3.4$ eV
$K.E_3 = -1.5$ eV
$K.E_4 = -0.85$ eV

## Spectral lines

Limiting line — $\infty \rightarrow n$

α (or 1st line) — $(n+1) \rightarrow n$

Lymann — UV
Balmer — Visible
Paschen } Infrared
⋮

$n_2 \rightarrow n_1$

$$\boxed{\Delta E = -13.6\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right](Z)^2}$$

$$\boxed{\frac{1}{\lambda} = -R_H\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right](Z)^2}$$

$$\underline{R_H = 1.1 \times 10^7\, m^{-1}}$$
$$\left(\frac{2\pi^2 e^4 \pi m}{h^3 c}\right)$$

**NOTE:** $\underline{\lambda \propto \frac{1}{\Delta E}} \rightarrow \boxed{\begin{array}{l}\lambda_{min} : \infty \rightarrow n \\ \lambda_{max} : (n+1) \rightarrow n\end{array}}$

$$- \boxed{\begin{pmatrix}\text{Max no.} \\ \text{of spectral} \\ \text{lines}\end{pmatrix} = {}^{(n_2-n_1)}C_2}$$

Zeeman eff. → B
Strark eff. → E
(splitting of spectral lines in these fields)

## De-Broglie

$$- \boxed{\lambda_d = \frac{h}{p}} = \frac{h}{mv}$$

$h = 6.626 \times 10^{-34}$ Js

$$- \boxed{\lambda_d = \frac{h}{\sqrt{2mKE}}}$$

$$- \boxed{\lambda_d = \frac{h}{\sqrt{2mqV}}}$$

for $e^-$, $\underline{\lambda_d = \sqrt{\frac{150}{V}}}$
(in Å)

**NOTE:** $e^-$ in nth shell makes n waves per circumference

## Heisenberg's Uncertainty Principle

$$- \boxed{\Delta x \Delta p \geq \frac{h}{4\pi}}$$

$- \Delta x \Delta v \geq \dfrac{h}{4\pi m}$

$- \Delta x \Delta \lambda \geq \dfrac{\lambda^2}{4\pi}$

$- \Delta E \Delta t \geq \dfrac{h}{4\pi}$

$- \Delta(KE)\, \Delta x \geq \dfrac{h\nu}{4\pi}$

## Schrodinger wave Eqn

$$- \quad \nabla^2\psi + \frac{2m(E-V)^2}{\hbar}\psi = 0$$

$$\nabla = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

$$- \quad \underline{E\psi = \hat{H}\psi}$$

**NOTE:** Only $\underline{n, l, m}$ come from SWE

## Quantum NOs

$- \begin{pmatrix}\text{Orbital} \\ \text{angular} \\ \text{momentum}\end{pmatrix} = \underline{\sqrt{l(l+1)}\,\hbar}$

$- (\text{Spin multiplicity}) = \underline{2|s|+1}$

where $s = \frac{n}{2} \rightarrow$ # unpaired $e^-$s

$- \begin{pmatrix}\text{Spin only} \\ \text{magnetic} \\ \text{moment}\end{pmatrix} = \underline{\sqrt{n(n+2)}\ \text{B.M}}$

where $B.M = \frac{e\hbar}{2m} = 9.27 \times 10^{-24}$

**NOTE:** $l = 1$ $\begin{cases} m = -1\ (P_x \text{ OR } P_y) \\ m = 0\ (P_z) \\ m = 1\ (P_y \text{ OR } P_x) \end{cases}$

$l = 2$ $\begin{cases} m = -2\ (d_{x^2-y^2} \text{ OR } d_{xy}) \\ m = -1\ (d_{yz} \text{ OR } d_{xz}) \\ m = 0\ (d_{z^2}) \end{cases}$

③

for one $e^-$ system,

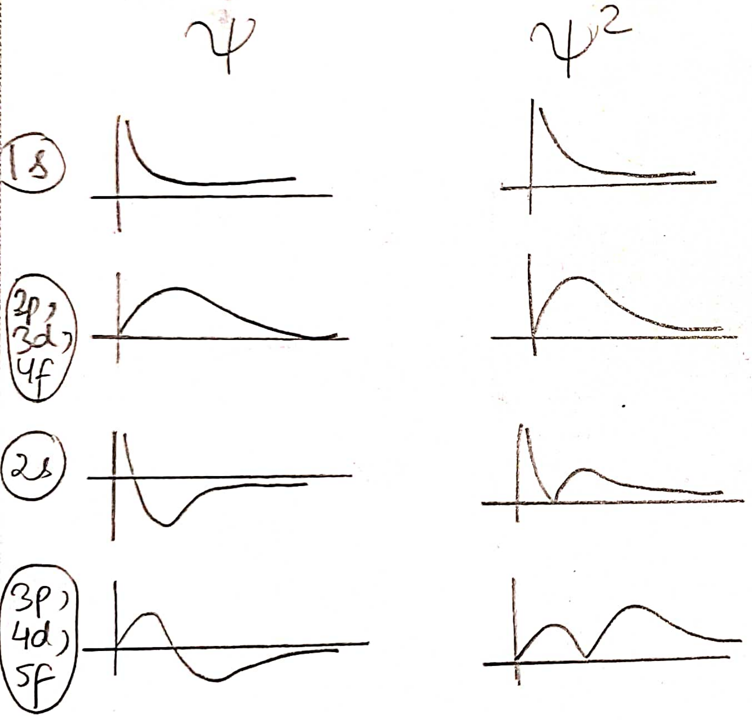
$\boxed{\text{Energy} \propto n}$

for multi $e^-$ system,

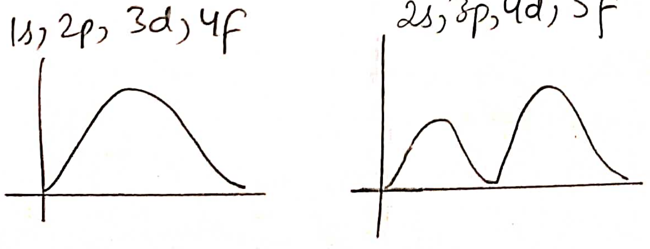
$\boxed{\text{Energy} \propto (n+l)}$

Priority if $(n+l)$ is same

## Graphs



$P = (\psi^2)(4\pi r^2 dr)$

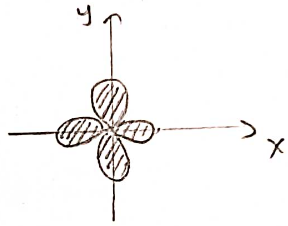


$\#\left(\begin{matrix}\text{Spherical/Radial} \\ \text{nodes}\end{matrix}\right) = \underline{n-l-1}$

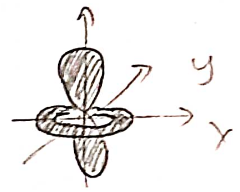
$\#(\text{Angular nodes}) = \underline{l}$

Total nodes $= \underline{(n-1)}$

$d_{x^2-y^2}$



$d_{z^2}$



## Finding orbital represented by ψ

① To find position of Radial Node, find at which all pts,
$\psi^2 = 0 \Rightarrow \underline{\psi = 0}$

② Take highest common power of σ out of bracket. Its exponent is $\boxed{l}$

③ Highest power of σ inside bracket is $\boxed{n-l-1}$

④ if no θ or φ ⇒ s-orbital
if only θ ⇒ orbital along z-axis
if both θ & φ ⇒ orbital inclined to z-axis

# PERIODIC PROPERTIES

| Period | # elements |
|---|---|
| 1 | 2 |
| 2 | 8 |
| 3 | 8 |
| 4 | 16 |
| 5 | 16 |
| 6 | 32 |

## Atomic Size

- $r_{AB} = r_A + r_B - 0.09\underbrace{|\Delta EN|}_{\text{Pauling's Scale}}$

### d-block

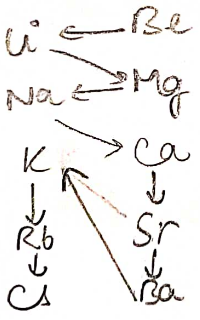
- $Sc < Y < La$

  BUT for the Rest $Zn < Cd \sim Hg \sim Uub$

### p-block

- $B < \underbrace{Ga < Al} < In \sim Tl$

### s-block



- $F^- < Cl^- < Br^- < H^- < I^-$

## Ionisation Enthalpy

- $I.E_1 < IE_2$ (Successive I.E)

### p-block

- $B > Tl > Ga > Al > In$
- $C > Si > Ge > \underbrace{Pb > Sn}$

### d-block

G 7,8,9,11,12 — $5d > 3d > 4d$
G 4,5,6,10 — $5d > 4d > 3d$
G 3 — $3d > 4d > 5d$

- $Li < \underbrace{B < Be} < C < \underbrace{O < N} < F \ll N$

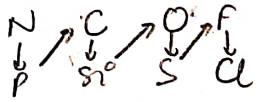
## Electron-Affinity

($EA_2$ always $< 0$)

### p-block

- $\underbrace{Cl > F} > Br > I$
- $S > Se > Te > \underline{O}$

  $P > As > Sb > \underline{N}$ ($\frac{E.A < 0}{\text{for N-family}}$)



### 2nd period

$\underbrace{Ne < Be < N} < \underbrace{B < Li} < C < O < F$

- Bi > Pb
- I > S (Highest of G16 < lowest of G17)

## Electronegativity

- F > O > N > Cl > Br > I~S~C > P~H
- Ga > Al
- Tl > In
- Pb > Sn

① Pauling's Scale

$$\boxed{\Delta EN = 0.208\sqrt{\underbrace{\Delta_{A-B}}_{\text{Resonance energy}}}}$$

$$\Delta_{A-B} = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

② Mulliken Scale

$$\chi_M = \frac{EA + IE}{2} \text{ (eV/atom)}$$

$$\boxed{\underset{\text{(Pauling)}}{\chi_p} = \frac{\chi_M}{2.8}}$$

③ Allred–Rochow

$$\boxed{\chi_{AR} = 0.357\,\frac{Z_{eff}}{r^2} + 0.744}$$

- $$\boxed{(\%\text{ ionic character}) = 16(\Delta EN) + 3.5(\Delta EN)^2}$$

## Nature of Ox, HOx., Oxy....

$$(\text{Acidic strength}) \propto \underbrace{(O.S)}_{\text{Priority}} \propto \underline{(E.N)}$$

$$(\text{Basic strength}) \propto \underbrace{\frac{1}{(O.S)}}_{\text{Priority}} \propto \frac{1}{(E.N)}$$

- Exception

$$\overset{+3}{H_3\underline{P}O_2} \qquad \overset{+4}{H_3\underline{P}O_3} \qquad \overset{+5}{H_3\underline{P}O_4}$$

↑

Most Acidic
(Best Red. Ag.)

Amphoteric Oxides
- SnO, SnO$_2$, ZnO, BeO, Al$_2$O$_3$, V$_2$O$_3$, Sb$_2$O$_3$, PbO$_2$, PbO, MnO, Ga$_2$O$_3$, As$_2$O$_3$, Cr$_2$O$_3$

Amphoteric Metals – Be, Sn, Ga, Al, Zn, Pb

Neutral Oxides – H$_2$O, CO, NO, N$_2$O

## Inert Pair Effect

| | G13 | 14 | 15 |
|---|---|---|---|
| PE | $Tl^{+3}$ × | $Pb^{+4}$ × | $Bi^{+5}$ × |
| | $Tl^{+1}$ | $Pb^{+2}$ | $Bi^{+3}$ |

More Stable

P: 2, 3 ] +(n+2) more stable
4
5, 6 ] +n more stable

## Diagonal Reln

(Metallic Radius): $r_{Mg} > r_{Li} > r_{Al}$

(Ionic radius): $r_{Li^+} > r_{Mg^{2+}} > r_{Al^{3+}}$

Liq. Elems – Ga, Br, Fr, Cs, Hg

Metalloids – At, Te, Sb, Ge, Po, As, Si

## Hydration & Lattice Energy

$$\propto \left(\frac{\text{Charge}}{\text{Size}}\right) \rightarrow \text{Dominant Factor}$$

$$\boxed{H.E \propto \left(\text{Hydrated Radii}\right) \propto \frac{1}{(\text{Mobility})}}$$

if H.E > L.E → salt is soluble, else insoluble

# CHEMICAL BONDING

## InterMolecular Bonds

- I–D $E \propto \frac{1}{r^2}$
- I–iD $E \propto \frac{1}{r^4}$
- D–D (Kossum forces) $E \propto \frac{1}{r^3}$
- D–iD (Debye forces) $E \propto \frac{1}{r^6}$
- iD–iD (London & Dispersion forces) $E \propto \frac{1}{r^6}$

Van-Der Walls forces

- H-bond (Strong-D–D) – F, O, N, Cl (Chelation), C (Sp hybridised)

- **Meting & Boiling Pt.**
  - $\propto$ Molecular force of Att^n.
  - if same, $\propto$ (Mol. wt. of Molecule)
  - if same also, $\propto$(Surface Area)

- **Molecular F.P/B.P**

$PH_3 < AsH_3 < \underbrace{NH_3} < SbH_3 < BiH_3$

(even though H-bond, wt. of Sb & Bi so ↑, ⇒ $SbH_3$ & $BiH_3 > NH_3$)

## Ionic Bond

- **I.E & E.A** are calculated using **Born–Haber cycle**
- $\Delta E.N \geq 1.7 \rightarrow$ Ionic Bond

## Fajan's Rule

**Polarisation** (Priority-wise factors)

- e-config of cation: $\underbrace{PNGC}_{Zn^{2+}, Cd^{2+}, Ag^+, Au^+, Hg^{4+}} > \underbrace{(18+2)}_{Tl^+, Pb^{2+}} > \underbrace{\text{Noble ga}}_{Na^+, Mg^+, Al^{3+}}$
- Charge of cation/Anion $\boxed{\text{Polarisation} \propto \text{Charge}}$
- $\boxed{(\text{Polarisation}) \propto \frac{1}{\text{Size(Cation)}} \propto \text{Size(Anion)}}$

## Applications

- Polarisation $\propto$ (Covalent Char) $\propto \left(\frac{1}{\text{Ionic Char}}\right)$
- (Solubility in $H_2O$) $\propto$ (Ionic)
- (Colour intensity) $\propto$ (Covalent)

**NOTE:**
$BeF_2 \rightarrow$ Predominantly covalent
$AlF_3 \rightarrow$ Predominantly Ionic

## – Thermal Stability

- Mono-anion ($F^-, N^{3-}, H^-, O^{-}$, etc)

$$\boxed{\begin{pmatrix}\text{Thermal}\\ \text{stability}\end{pmatrix} \propto \text{L.E} \propto \left(\frac{\text{Charge}}{\text{size}}\right)}$$

- Poly-anion ($CO_3^{2-}, SO_4^{2-}, O_2^-, O_2^{2-}$, etc)

$$\boxed{\begin{pmatrix}\text{Thermal}\\ \text{Stability}\end{pmatrix} \propto \begin{pmatrix}\text{Ionic}\\ \text{Char}\end{pmatrix}}$$

## – Solubility in Water
### (S-block Elements)

- Solubility of salts decreases down the group.
- Alkali Metals – $F^-, OH^-, HCO_3^-, CO_3^{2-}$ increases down the grp.
- Alkali Earth Metals – $F^-, OH^-, HCO_3^-$ increases down the grp.
  - solubility of $BeF_2$ is exceptionally high.

**EXCEPTIONS**

- $MgF_2 < CaF_2 < SrF_2 < BaF_2 < \underline{BeF_2}$
- $\underline{NaI > LiI} > KI > RbI > CsI$
- $LiCl > CsCl > RbCl > NaCl > KCl$

## Covalent Bond

$$(\text{Covalency}) = \begin{pmatrix}\#\text{Covalent}\\ \text{Bonds}\end{pmatrix} + \begin{pmatrix}\#\text{coordinate}\\ \text{Bonds}\end{pmatrix}$$

* Max covalency of 2nd period elements is 4.

## Lewis Octet Theory

## Conversion of Coordinate Bond into Simple Covalent

if $A \in$ 2nd period

$$A(:) \xrightarrow{} \square B$$
$$\equiv$$
$$A \longrightarrow B$$
$$\equiv$$
$$\boxed{A^+ - B^-}$$

if $A \in$ 3rd, 4th

$$A(:) \xrightarrow{} \square B$$
$$\equiv$$
$$A \longrightarrow B$$
$$\equiv$$
$$A^+ - B^- \equiv \boxed{A = B}$$

## Resonance

Delocalisation of $\pi$-$e^-$s.

Happens in conjugated systems, i.e existence of (=/=), (=/+), (=/-) Backbond in alternate position

$$\text{Bond order} = \frac{\begin{pmatrix}\#\text{Bond b/w two}\\ \text{atoms in all}\\ \text{resonating structures}\end{pmatrix}}{\begin{pmatrix}\#\text{Resonating}\\ \text{structures}\end{pmatrix}}$$

* $\boxed{B.O = \frac{\sigma + \pi}{\sigma}}$ b/w two atoms

$$B.O \propto \begin{pmatrix}\text{Bond}\\ \text{strength}\end{pmatrix} \propto \begin{pmatrix}\text{Bond}\\ \text{Energy}\end{pmatrix} \propto \left(\frac{1}{\text{Bond length}}\right)$$

## Valence Bond Theory (VBT)

Order of Bond Strength
(b/w orbitals)

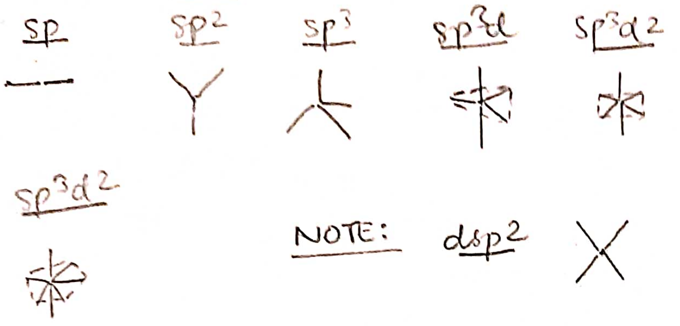
- $\boxed{(np-mp) > (np-ms) > (ns-ms)}$

  n → Shell of 1st orb.
  m → Shell of 2nd orb.

NOTE: Shell is dominant factor, so even $(ns - ns) > (n+1)p - (n+1)p)$

- $\boxed{(d\pi - d\pi) > (d\pi - p\pi) > (p\pi - p\pi)}$

## Hybridisation



## VSEPR

### Order of Repulsion

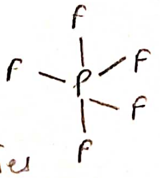
- $(lp-lp) > (lp-bp) > (bp-bp)$
- (Multiple bond − Mb) > (Mb − Sb) > (Single Bond − Sb)

### Bent's Rule

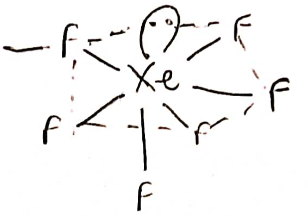
- sp³d : More E.N atom → Axial position
  l.p → Eq. position
- sp³d³ : More E.N atom → Eq. post.
  l.p → Ax. post.

NOTE: $\theta$ (∠ b/w bonds) ∝ (%. S-char) ∝ (E.N of central atom) ∝ $\frac{1}{\text{(Bond length)}}$

NOTE:
- In $PF_5$, due to berry pseudorotation all bond lengths/energies are equal.
- $SF_6$ is inert



- $SCl_6$, $SBr_6$, $SI_6$ → Do not exist
- XX' do not exist (where X' > X)
  XX' : Interhalogen comp.



} Distorted/Capped octahedral shape ($XeF_6$)

## Hybⁿ in odd e⁻-species

- If side atom of High E.N (F, O, N, Cl), then unpaired e⁻ included in hybⁿ.
- If l.p. & unpaired e⁻ both present, unp. e⁻ NOT included.

## Hybⁿ in solid Compounds

$N_2O_{4(s)} \rightarrow NO^+ + NO_3^-$
$I_2Cl_6(s) \rightarrow ICl_2^+ + ICl_4^-$
$N_2O_5(s) \rightarrow NO_2^+ + NO_3^-$
$I_2O_4(s) \rightarrow IO^+ + IO_3^-$
$PCl_5(s) \rightarrow PCl_4^+ + PCl_6^-$

NOTE: $PBr_5(s) \rightarrow PBr_4^+ + Br^-$
$XeF_6(s) \rightarrow XeF_5^+ + F^-$

## Drago's Rule

No hybⁿ when
- steric no. = 4 & central atom has 1 l.p.
- Central atom ∈ 3rd or Higher Period
- (E.N of side atom) < 2.5

$PH_3$ $H_2S$ $HCl$
$AsH_3$ $H_2Se$ $HBr$
$SbH_3$ $H_2Te$ $HI$

## Bond Angle

Priority-wise:

- Hyb$^n$ of Central Atom (Direct prop.)
- # l.p (Indirect prop.)
- E.N of
  - Central Atom (Direct)
  - Side Atom (Indirect)

NOTE: if Bulky side atom/group, E.N does NOT matter. (eg - Cl$^-$, CH$_3^-$, ...)

[Bond order, Bond Energy & Bond length have been covered under Resonance]

## Bonding in e$^-$-Deficient Species

### Back Bonding

Cond$^n$s :-

- one atom must have l.p & other a vacant orbital

- One of the bonded atoms (A or B) should be of 2nd period. Other one can be of 2nd or 3rd period.

NOTE: Hyb$^n$ of central atom changes when it donates a l.p to form a back bond.

SUB NOTE: if side atom is Cl, Br, I, then hyb$^n$ does NOT change.

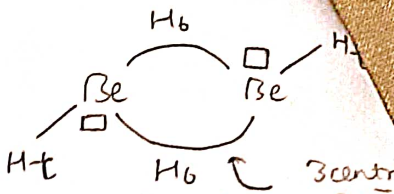
NOTE: Max. 1 back-bond is formed by any atom with another atom.

## Bridge Bonding

### Be

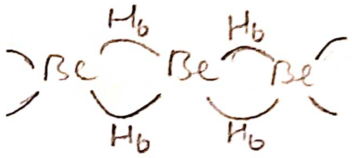
- BeF$_2$ X No dimer (St Back

- BeH$_2$
  - gas



3centr -2e bond (BANANA BOND

  - Solid

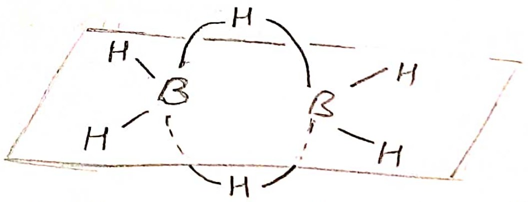


NOTE: Bond length (Be$-$H$_b$) > Bond length (Be$-$H$_t$)

### B

- BF$_3$ X No dimer (Strong Back Bond
- BCl$_3$, BBr$_3$, BI$_3$ X No dimer (High stearic Crowding
- BH$_3$ Dimer
  Polymer X (only 1 vacant o

NOTE:



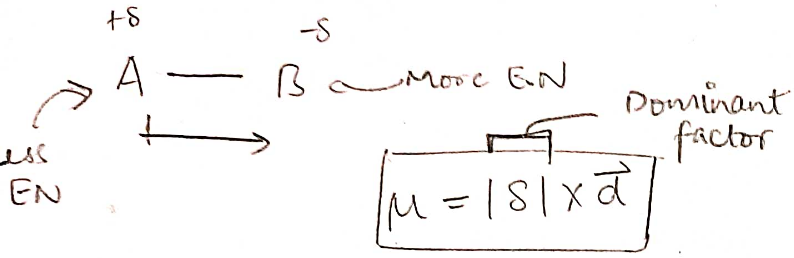
Bridge bond is above & below the plane

### Al

- AlF$_3$ X No dimer (Predominant ionic
- AlCl$_3$, AlH$_3$, Al(CH$_3$)$_3$
  - Dimer in vapour
  - Polymer in solid
- AlBr$_3$, AlI$_3$ Dimer
  Polymer X (stearic Crowding

## Dipole Moment (μ)

(Ionic char in Cov. compound)



$$\boxed{\mu = |\delta| \times \vec{d}}$$

$1D = 10^{-18}$ esu cm

$1D = 3.3 \times 10^{-30}$ Cm

$e^-$ — $4.8 \times 10^{-10}$ esu
$e^-$ — $1.6 \times 10^{-19}$ C

- $NH_3 > NF_3$
- $\underbrace{CH_3Cl > CH_3F}\ > CH_3Br > CH_3I$
- $CH_2F_2 > CH_3F > CHF_3 > CH_4/CF_4$

  F: $\boxed{2 > 1 > 3}$
- $CH_3X > CH_2X_2 > CHX_3 > CH_4/CX_4$

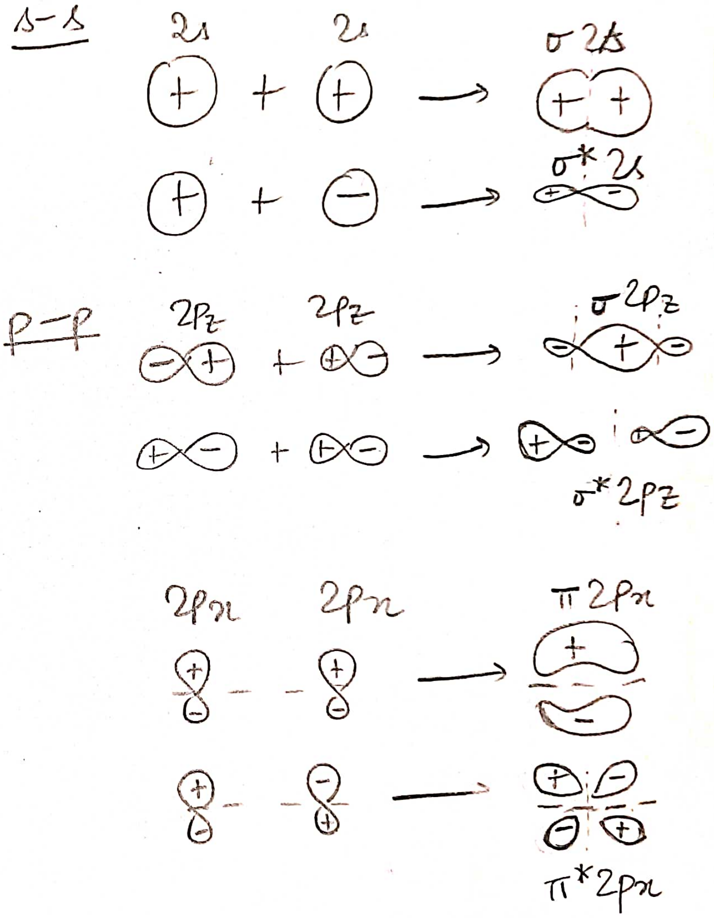
  X: $\boxed{1 > 2 > 3}$

  {X = Cl, Br, I}

$$\boxed{\begin{pmatrix}\%\text{ ionic}\\ \text{char}\end{pmatrix} = \frac{|\delta|}{|e|} \times 100\%}$$

## Molecular Orbital Theory

(Gerade orbitals) — orbitals which remain same after rotating 180° abt 2 axis subsequently



NOTE: Gerade — σ, π*
ungerade — σ*, π

## $e^-$ – Config

Upto 14e

$(\sigma 1s)(\sigma^* 1s)(\sigma 2s)(\sigma^* 2s)\underbrace{(\pi 2p_x = \pi 2p_y)(\sigma 2p_z)}(\pi^* 2p_x = \pi^* 2p_y)(\sigma^* 2p_z)$

15$e^-$ to 20$e^-$

$(\sigma 1s)(\sigma^* 1s)(\sigma 2s)(\sigma^* 2s)(\sigma 2p_z)(\pi 2p_x = \pi 2p_y)(\pi^* 2p_x = \pi^* 2p_y)(\sigma^* 2p_z)$

B.O

| $e^-$ | B.O |
|---|---|
| ⋮ | ⋮ |
| 12 | 2 |
| 13 | 2.5 |
| 14 | 3 |
| 15 | 2.5 |
| 16 | 2 |
| ⋮ | ⋮ |

$$\boxed{B.O = \frac{1}{2}[N_b - N_a]}$$

# $e^-$ in ABMO

# $e^-$ in BMO

if unpaired $e^-$ – Paramagnetic

EXCEPTIONS

- CO : $(\sigma 1s^2)(\sigma 2p_z^2)(\pi 2p_x^2 = \pi 2p_y^2)(\sigma^* 2s^2)$

  B.O (CO) = 3

  B.O ($CO^+$) = 3.5

- Halogens show color despite being diamagnetic

  $F_2$ → Pale yellow

  $Cl_2$ → light green

  $Br_2$ → Brown

  $I_2$ → Violet

Reason: Diff. b/w HOMO & LUMO is NOT too great.

HOMO – Highest occupied MO

LUMO – Lowest unoccupied MO

# GASEOUS STATE

## Unit Conversions

Temperature -

$$\boxed{\frac{C-0}{100-0} = \frac{K-273}{373-273} = \frac{F-32}{212-32}}$$

Volume -

$1 m^3 = 1000 L$

$1 dm^3 = 1 L$

$1 cm^3 = 1 mL$

Pressure -

1 atm = 760 mm Hg = 76 cm Hg
= 760 torr

1 atm = 1.01 bar = $1.013 \times 10^5$ Pa

## Gas laws

Boyle's law - $\boxed{PV = \text{const.}}$
given T const.

Charles' law - $\boxed{\frac{V}{T} = \text{const}}$
given P const.

$$\begin{pmatrix}\text{Vol. at}\\ t^\circ C\end{pmatrix} = V_0 + \frac{t}{273} V_0$$

$V_0$ → Vol. at 0°C

Gay Lussac's Law - $\boxed{\frac{P}{T} = \text{const.}}$

$$\begin{pmatrix}\text{Pressure}\\ \text{at } t^\circ C\end{pmatrix} = P_0 + \frac{t}{273} P_0$$

$P_0$ → Pressure at 0°C

Avogardo's law - $\boxed{\frac{V}{n} = \text{const.}}$
given P, T const

## Ideal gas Eqn

$$\boxed{PV = nRT}$$

$R = 0.0821 \frac{atm\,L}{mol\,K}$ (use $\frac{25}{300}$)

$= 8.314 \frac{J}{mol\,K}$ (use $\frac{25}{3}$)

$= 2 \frac{cal}{mol\,K}$

## Dalton's law of Partial Pressures

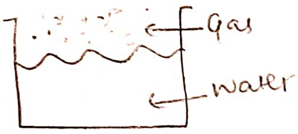
(only applicable for non-reacting gases)

$$\boxed{P_{gas} = X_{gas} \cdot P_{Total}}$$

∵ Each gas is assumed to occupy the whole volume.

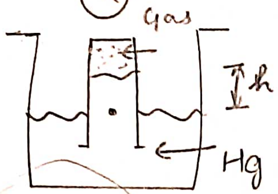
## Configurations (FBD of liq. column)

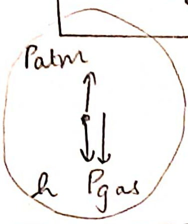
①



$$\boxed{P_{\text{wet gas}} = P_{gas} + \left(\text{Vapour Pressure}\right)}$$

②

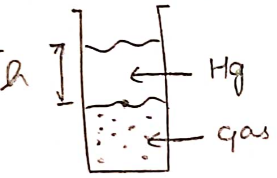


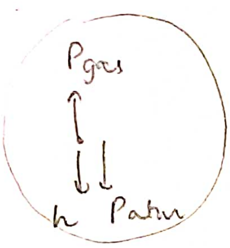


$$\boxed{P_{atm} = P_{gas} + h \text{ mm Hg}}$$

③

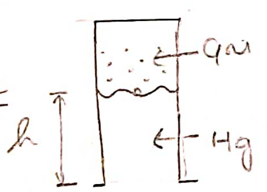
3.1

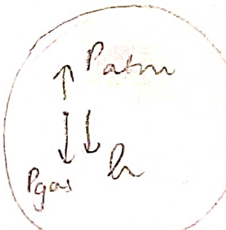




$$\boxed{P_{gas} = (\underbrace{P_{atm}}_{760} + h) \text{ mm Hg}}$$

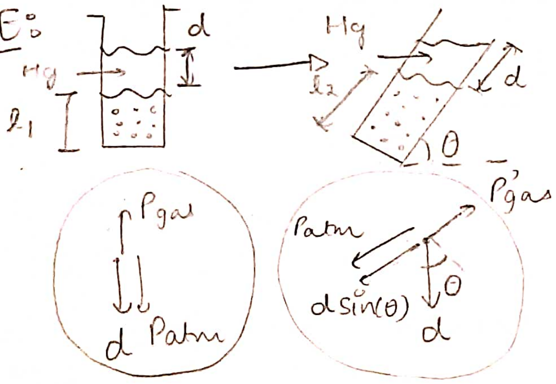
3.2





$$\boxed{\underbrace{P_{atm}}_{76 \text{ mm Hg}} = P_{gas} + h}$$

NOTE:

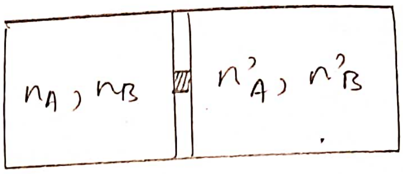


$$P_g V = P_g' V'$$

$$\Rightarrow (P_{atm} + \rho g d)\cancel{A} l_1 = (P_{atm} + \rho g d \sin\theta)\cancel{A} l_2$$

$$\Rightarrow \boxed{(P_{atm} + \rho g d) l_1 = (P_{atm} + \rho g d \sin(\theta)) l_2}$$

## Graham's law of Diffusion



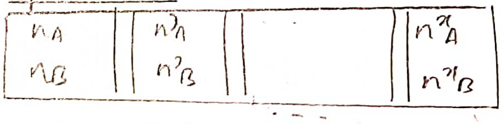
$$\boxed{\frac{r_A}{r_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}}}$$

NOTE: $\frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{x_A}{x_B} = \frac{w_A \cdot M_B}{w_B \cdot M_A}$

$$\frac{n'_A/t_A}{n'_B/t_B} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}}$$

if $t_A = t_B$, $\boxed{\frac{n'_A}{n'_B} = \frac{n_A}{n_B}\sqrt{\frac{M_B}{M_A}}}$

- Enrichment/ separation factor



n → # steps

$$\boxed{\frac{n^n_A}{n^n_B} = \frac{n_A}{n_B}\left(\frac{M_B}{M_A}\right)^{n/2}}$$

Enrichment/ Separation Factor

- Rate of effusion $\boxed{r \propto \frac{PA}{\sqrt{2\pi MRT}}}$

A → cross-sectional area of orifice

# Kinetic Theory of Gases

- Kinetic Eqn of Gas

$$\boxed{PV = \frac{1}{3} m N v_{rms}^2}$$

m → wt. of one molecule
N → # Molecules
$v_{rms}$ → Rt. mean sq. velocity

- Kinetic energy

– n mol : $\frac{3}{2}nRT$
– 1 molecule : $\frac{3}{2}k_bT$

(Boltzman const.) $k_b = \frac{R}{N_A} = 1.38\times10^{-23}\,\frac{J}{K}$

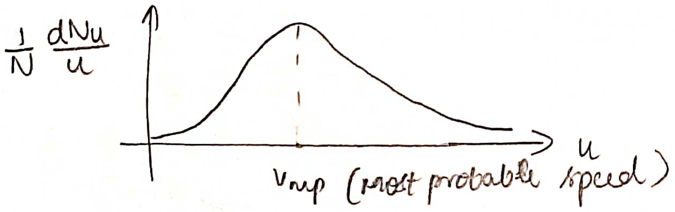
- Density of Gas

$$\boxed{d = \frac{PM}{RT}}$$

## Maxwell Dist. of Molecular speeds

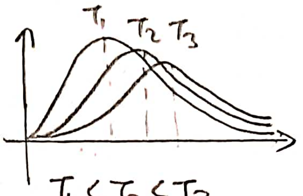
$$dN_u = 4\pi N\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mu^2}{2RT}} u^2\, du$$

N → # gas molecules
$N_u$ → # molecules having velocity in range u to (u+du)



NOTE: – Area under curve $\left(\frac{1}{N}\frac{dN_u}{du} \text{ v/s } u\right)$ is 1.

– if T↑,
– $v_{mp}$↑
– (fraction of molecules with very low speed) ↓
– ... very high speed ↑
– ... $v_{mp}$ ↓



$T_1 < T_2 < T_3$

– Graphs same when $v_{mp}$ same

## Molecular Speeds

- Most probable : $\sqrt{\frac{2RT}{M}}$
- Average : $\sqrt{\frac{8RT}{\pi M}}$
- Rt. mean sq. : $\sqrt{\frac{3RT}{M}}$

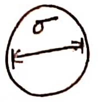
NOTE: $v_{mp} < v_{avg} < v_{rms}$

## Maxwell Distribution of Kinetic Energy

$$dN_E = 2\pi N\left(\frac{1}{\pi RT}\right)^{3/2} e^{-E/RT} \sqrt{E}\, dE$$

- Most probable Kinetic Energy ($E_{mp}$) – $\boxed{\frac{1}{2}RT}$

## Collision freq. ($Z_{11}$)



$N^* = \frac{N}{V}$

- $\boxed{Z_1 = (\pi\sigma^2)(\sqrt{2}\,V_{avg})(N^*)}$

(Collisions b/w a molecule with other molecules per unit time)

- $Z_{11} = Z_1\left(\frac{N^*}{2}\right)$

(Total #collisions b/w the similar molecules per unit time per unit time) $= \boxed{\frac{1}{\sqrt{2}}\pi\sigma^2 V_{avg}(N^*)^2}$

- $\boxed{N^* \propto \frac{P}{T}}$

- $\boxed{Z_{11} \propto \frac{P^2}{T^{3/2}}}$

  - At P = const.
    $Z_{11} \propto \frac{1}{T^{3/2}}$
  - At T = const.
    $Z_{11} \propto P^2$
  - At V = const. (rigid container)
    $\frac{P}{T} = \text{const.}$
    $\Rightarrow \boxed{Z_{11} \propto \sqrt{T}}$

## Mean Free Path ($\lambda$)

- Avg. dist. travelled by a gas molecule b/w two successive collisions

- $\boxed{\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}}$

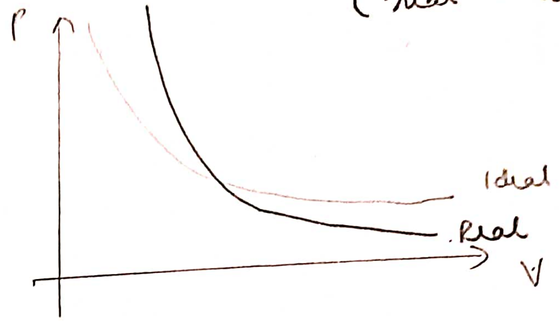
- $\boxed{\lambda \propto \frac{T}{P}}$

  - At P = const. $\lambda \propto T$
  - At T = const. $\lambda \propto \frac{1}{P}$
  - At V = const. (rigid container) $\boxed{\lambda = \text{Const}}$ $[\because P/T = \text{const.}]$

## Real Gas

High P → significant devi
(Vreal > Videal)

Low P & High T → Behaviour closer to ideal gas
(Vreal < Videal)



- Volume Correction

$V_{ideal} = V_{real} - \underset{\text{Correction}}{\text{ⓥ}}$
$= V_{real} - nb$

b → excluded vol. for 1 mol gas molecules
(extended vol. or co-volume)

$\boxed{b = 4 \times (\text{Vol. of 1 mol gas molecules})}$

- Pressure Correction
  - Depends on force & freq. of collision

$P_{real} = P_{ideal} - \underset{\text{Correction}}{\text{Ⓟ}}$
$= P_{ideal} - \frac{an^2}{V^2}$

- $\boxed{(\text{Excluded Volume for one gas molecule}) = 4 \times \left(\frac{4}{3}\pi r^3\right)}$

- Vander Wall's Eqn

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

NOTE: Not applicable to $H_2$ & He as only repulsive forces exist b/w molecules of these gase; which are not considered while calculating corrections.

## Compressibility Factor

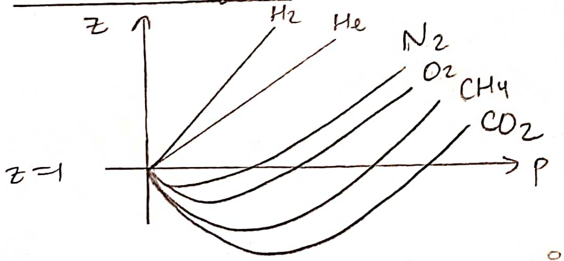
$Z = \frac{V_{real}}{V_{ideal}}$ $\left(V_m = \frac{V}{n}\right)$

$\Rightarrow \boxed{Z = \frac{P_{ideal} V_{real}}{nRT}} = \frac{PV_m}{RT}$

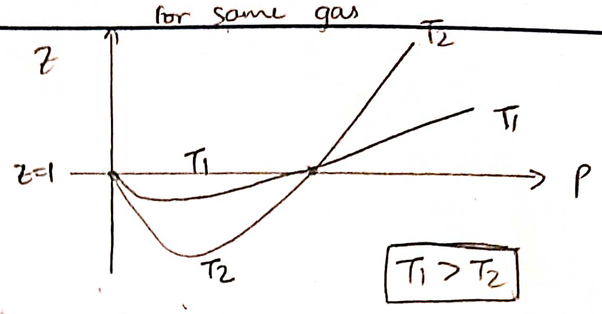
NOTE: - if Z=1, Gas is ideal

- if $Z<1 \Rightarrow V_R < V_i$
  - → −ve deviation
  - → attractive forces dominant
  - → low Pressure
  - → can be compressed (liquified)
- if $Z>1 \Rightarrow V_R > V_i$
  - → +ve deviation
  - → repulsive forces dominant
  - → High P
  - → Difficult to compress

- Variation of Z



NOTE: Lower the dip, easier it is to liquify gas.



## Z under diff. condⁿs

① Low P $(V-nb) \sim V$

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

$\Rightarrow \boxed{Z = 1 - \frac{a}{V_m RT}}$

② Low P & High T $\left(P + \frac{an^2}{V^2}\right) \sim P$

$(V-nb) \sim V$

$PV_m = RT$

$\Rightarrow \boxed{Z = 1}$

③ High P $\left(P + \frac{an^2}{V^2}\right) \sim P$

$P(V_m - b) = RT$

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

## Misc. Pts.

① Second Virial coeff − $\left(b - \frac{a}{RT}\right)$

Third virial coeff. − $b^2$

② Critical Constants

P.T.O−

- ($P_c$) – Min. P req. to cause liq. at $T_c$.

$$\boxed{P_c = \frac{a}{27b^2}}$$

- ($V_c$) – volume occupied by one mol. gas at $P_c$ & $T_c$

$$\boxed{V_c = 3b}$$

- ($T_c$) – Max T at which a gas can be liquified.

$$\boxed{T_c = \frac{8a}{27Rb}} = \frac{8T_b}{27}$$

③ Boyle Temp. ($T_b$):

T at which gas behaves as ideal gas for a defined range of low pressure

$$\boxed{T_b = \frac{a}{Rb}}$$

④ Inversion Temp. ($T_i$):

T at which gas shows no Joule–Thompson effect

$$\boxed{T_i = \frac{2a}{Rb}} = 2T_b$$

OTE:

(Joule – Thompson effect)
- all gases except $H_2$ & He – cooling effect
- $H_2$ & He – heating effect

## Eudiometry

| Absorbant | Gas Absorbed |
|---|---|
| – NaOH/KOH solⁿ | $CO_2$, $SO_2$, $NO_2$, Halogens |
| – Ammonical $Cu_2Cl_2$ | CO, $C_2H_2$ |
| – Turpentine Oil | $O_3$ |
| – Alkaline Pyrogallol | $O_2$ |
| – Conc. $H_2SO_4$ | Moisture, $NH_3$ |
| – $FeSO_4$ solⁿ | NO |
| – Heated Mg | $N_2$ |

# CHEMICAL EQUILIBRIUM

## Active Mass

- for liq. (Active Mass) = (Molar conc.)
- for gases [density ≠ const] (Active Mass) → (Molar conc.)
  → (Partial P)
- for solids & liq. medium in which the rxn is taking place [∵ density = const.] (Active Mass) = const. [assumed to be 1]
- $(\text{Active mass}) = \frac{\text{mol.}}{\text{vol.}} = \frac{w}{M \times V} = \boxed{\frac{\text{density}}{\text{Molar Mass}}}$

## Law of Mass Action

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$R_f \propto [A]^a[B]^b \Rightarrow R_f = \underbrace{K_f}_{\text{Rate const. of fwd rxn}}[A]^a[B]^b$$

$$R_b \propto [C]^c[D]^d \Rightarrow R_b = \underbrace{k_b}_{\text{Rate const of bwd rean}}[C]^c[D]^d$$

NOTE: Rate const. (k) depends only on Temperature & Catalyst.

## Law of Chemical Eq.

At eq. $\boxed{R_f = R_b}$ (condn for eq)

$$\Rightarrow k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

$$\Rightarrow \frac{K_f}{K_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\Rightarrow \boxed{K_{eq} \quad \frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

Units:

Keq →

$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ $\left(\frac{mol}{L}\right)^{\Delta n_g}$

$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$ $(atm)^{\Delta n_g}$

$K_x = \frac{(\chi_C)^c(\chi_D)^d}{(\chi_A)^a(\chi_B)^b}$ unitless

NOTE: — Defn & value of Keq only holds at eq.

— Keq is fixed for a given T i.e it is T dependent

— Keq is independent of conc., pressure, volume, catalyst, etc.

☆ When aq. species (solute/ions) & gaseous substance are present together,

eg:- $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_{pc} = \frac{[NH_4^+][OH^-]}{P_{NH_3}}$$

(Partial P of gas) → p

(Conc. of aq. species) ↑ c

## Reln b/w (Kp & Kc) & (Kp & Kx)

- $K_p = K_c (RT)^{\Delta n_g}$
- $K_p = K_x (P_{Total})^{\Delta n_g}$

**NOTE:** $K_p = K_c$ ∀ $\Delta n_g$, when

$$\boxed{T = \frac{1}{R} \sim 12K}$$

## Factors Affecting Keq

① Mode of Repn & Stoichiometry of Rean

If Keq of rean
$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$
is K, then

- $cC(g) + dD(g) \rightleftharpoons aA(g) + bB(g)$ ; ($\frac{1}{K}$)
- $2aA(g) + 2bB(g) \rightleftharpoons 2cC(g) + 2dD(g)$, ($K^2$)
- $\frac{a}{2}A(g) + \frac{b}{2}B(g) \rightleftharpoons \frac{c}{2}C(g) + \frac{d}{2}D(g)$, ($\sqrt{K}$)
- If reans with Keq = $K_1$ & $K_2$ respectively are added (or subtracted), the Keq of resulting rean will be ($K_1K_2$) (or ($K_1/K_2$))

) Effect of Temp.

- $$\boxed{\log(K_{eq}) = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}}$$

ΔS → Entropy change
ΔH → Enthalpy change

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

OTE: When T↑, rean moves in Endothermic dirxn. ($\Delta H > 0$)

imilarly, when T↓ ⇒ Exothermic dirxn ($\Delta H < 0$)

## Rean Quotient

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$ at ANY ins

At eq, $\boxed{Q = K_{eq}}$

if $Q > K_{eq}$ ⇒ Rean moves Bwd
if $Q < K_{eq}$ ⇒ Rean moves Fwd

## Le Chatelier's Principle

Rean shifts in a dirxn so as to nullify effect of change

- Conc.: $A(g) \rightleftharpoons B(g)$

  if [A]↓ ⇒ Rean moves bwd
  if [A]↑ ⇒ Rean moves fwd

- Pressure: if P↑ ⇒ Rean will move in dirxn where less # gaseous moles formed

  NOTE: if $\boxed{\Delta n_g = 0}$, no change takes place

- Volume: if V↑ ⇒ Rean will move in dirxn where more # gaseous moles formed

- Addn of Inert Gas

  ① At V = const., No change
  ② At P = const, towards more # gaseous moles
  ⇓
  ( Inert gas ⇒ V↑ ) ⇒

**NOTE:** Addn or removal of solid results in no change.
(Regardless of wether it is inert or a reactant/ product)

## Degree of Dissociation & Vapour Density

$\alpha \rightarrow$ # mol. dissociated per mole of a particular specie.

$$A(g) \rightleftharpoons nB(g)$$

$n_i$: $a$ $\quad$ $0$

$n_f$: $a(1-\alpha)$ $\quad$ $na\alpha$

$D \rightarrow$ Theoretical V.D.
$d \rightarrow$ observed V.D

By Conseration of Mass,

$$w_i = w_f$$

$$\Rightarrow M_i n_i = M_f n_f$$

$$\Rightarrow \frac{M_i}{M_f} = \frac{D}{d} = \frac{n_f}{n_i} = \frac{a(1-\alpha)+na\alpha}{a}$$

$$\Rightarrow \boxed{\frac{M_i}{M_f} = \frac{D}{d} = \underline{1+(n-1)\alpha}}$$

$$\boxed{\alpha = \frac{D-d}{(n-1)d}}$$

(Remember the process, not the formula!)

## Physical Eq.

① $H_2O(l) \rightleftharpoons H_2O(g)$ ; $\Delta H > 0$

T↑ ⇒ Fwd reaⁿ
P↑ ⇒ Bwd reaⁿ

② $H_2O(s) \rightleftharpoons H_2O(l)$ ; $\Delta H > 0$

T↑ ⇒ Fwd reaⁿ

☆ Vol. of $H_2O(s)$ > vol. of $H_2O(l)$

P↑ ⇒ Reaⁿ moves to V↓
⇓
Fwd (liq. side)

NOTE: This is true for most solids, i.e. their vol. is greater than their liq. form.

③ Graphite(s) $\rightleftharpoons$ Diamond(s)

- $\boxed{\Delta H > 0}$
- Graphite → More Volume, → Less Energy
- Diamond → Less Volume, → More Energy

So T↑ ⇒ Fwd Reaⁿ
P↑ ⇒ V↓ ⇒ Fwd Reaⁿ

# IONIC EQUILIBRIUM

## Factors affecting Degree of Dissoc.

1) Nature of Electrolyte — $\alpha \sim 1 \Rightarrow$ strong; $\alpha << 1 \Rightarrow$ weak

2) Temp — $\boxed{\alpha \propto \text{Temp.}}$

as $\Delta H > 0$ for dissoc. rea^n^s.

3) Dilution — $\boxed{\text{Dil} \uparrow \Rightarrow \alpha \uparrow}$

as $K_{eq} = C\alpha^2$ & $C \propto \frac{1}{V}$ and Dil $\Rightarrow V \uparrow$

## Common Ion Effect

Suppression of DoD of weak electrolyte in presence of strong electrolyte having common ion.

eg: (I) $CH_3COOH \rightleftharpoons \boxed{CH_3COO^-} + H^+$

$CH_3COONa \longrightarrow \boxed{CH_3COO^-} + Na^+$

Common Ion

$\Rightarrow$ DoD of rea^n (I) $\downarrow$

## Acid–Base Theories

| | Acid | Base |
|---|---|---|
| 1) Arrhenius – | give $H^+$ in aq. soln | give $OH^-$ in aq. soln |
| 2) Bronsted Lowry – | give $H^+$ | take $H^+$ |
| 3) Lewis – | take l.p. (Electrophiles) | give l.p (Nucleophiles) |

NOTE:

| Electrolyte | Conj. base/acid |
|---|---|
| Strong | weak |
| Weak | strong |

## Weak Monoacidic Bases & Monobasic Acids

1) Acids

$$\alpha = \sqrt{\frac{K_a}{C}} \qquad [H^+] = C\alpha = \sqrt{K_a C}$$

$$\boxed{pH = \frac{1}{2}(pK_a - \log(C))}$$

2) Bases

$$\alpha = \sqrt{\frac{K_b}{C}} \qquad [OH^-] = C\alpha = \sqrt{K_b C}$$

$$\boxed{pOH = \frac{1}{2}(pK_b - \log(C))}$$

NOTE: These formulae only work if $\alpha < 0.02$ M.

Else, $K = \frac{C\alpha^2}{(1-\alpha)}$ & $[H^+] = C\alpha$ (or $[OH^-] = C\alpha$)

## Mixing of Weak Acids & Weak Bases

Let us take $V_1$ of $M_1$ mol/L $HA_1$ (or $B_1OH$) & $V_2$ of $M_2$ mol/L $HA_2$ (or $B_2OH$).

$$\boxed{M_{net} = \sqrt{K_1 C_1 + K_2 C_2}}$$

$$C_1 = \frac{M_1V_1}{M_1V_1 + M_2V_2}$$

$$C_2 = \frac{M_2V_2}{M_1V_1 + M_2V_2}$$

| | Acids | Bases |
|---|---|---|
| $K_1 =$ | $K_{a_1}$ | $K_{b_1}$ |
| $K_2 =$ | $K_{a_2}$ | $K_{b_2}$ |

## Self-dissoc. of Water

1) For pure water $\boxed{[H_2O] = 55.5\ mol/L.}$

$$M_{H_2O} = \frac{W_{solute}}{V_{solvent}} = \frac{n_{H_2O}}{V_{H_2O}} = \frac{1000g}{18g/mol} \times \frac{1}{1L}$$

(H2O is both solute & solvent here)

$$= \underline{55.5\ mol/L}$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

$$K_{eq.} = \frac{[H^+][OH^-]}{[H_2O]} = \frac{[H^+][OH^-]}{55.5}$$

$$\Rightarrow \boxed{[H^+][OH^-] = K_w} \ \& \ \boxed{K_w = 55.5 K_{eq.}}$$

Ionic product of water.

@ T = 25°C, $\boxed{K_w = 10^{-14}}$

NOTE: (i) For pure water at any T, $\boxed{[H^+] = [OH^-] = \sqrt{K_w}} = 10^{-7}$ @ 25°C

(ii) $\boxed{pH + pOH = pK_w} = 14$ @ 25°C

*(iii) $\boxed{T\uparrow \Rightarrow K_w\uparrow \Rightarrow pH\downarrow}$

2) $\boxed{K_a K_b = K_w}$

electrolyte   conjugate

NOTE: While calculating pHs of extremely dil. solns of strong electrolytes, we also take into account the [H+] & [OH−] furnished by [H2O] itself.

eg. $10^{-8}$ M HCl

$$[H^+] = 10^{-8} + \underbrace{10^{-7}}_{\text{by water}}$$

$$= 11 \times 10^{-8}$$

$$pH = 8 - \log(11) = \boxed{6.9}$$

## Salt Hydrolysis

1) SA+SB salt – Salt does NOT hydrolyse

2) SA+WB salt –

$$K_h = \frac{K_w}{K_b} \qquad h = \sqrt{\frac{K_w}{K_b C}}$$

$$\boxed{pH = 7 - \frac{1}{2}[pK_b + \log(C)]}$$

3) WA+SB salt –

$$K_h = \frac{K_w}{K_a} \qquad h = \sqrt{\frac{K_w}{K_a C}}$$

$$\boxed{pH = 7 + \frac{1}{2}[pK_a + \log(C)]}$$

4) WA+WB Salt –

$$K_h = \frac{K_w}{K_a K_b} \qquad h = \sqrt{\frac{K_w}{K_a K_b}}$$

$$\boxed{pH = 7 + \frac{1}{2}[pK_a - pK_b]}$$

5) Amphiprotic/Amphoteric Salts—

For $M_k H_{(n-k)} A$ salt of $H_nA$ acid, $\boxed{pH = \frac{1}{2}\left[pK_{a_k} + pK_{a_{(k+1)}}\right]}$

## Buffer Soln

1) Mix Buffer

1.1) Acidic Buffer –

1.1.1) Weak Acid + (its strong basic salt)

1.1.2) Weak Acid + (its conj base)

1.2) Basic Buffer –

1.2.1) Weak Base + (its strong acidic salt)

1.2.2) Weak Base + (its conj. acid)

2) Simple Buffer

2.1) Salt of weak Acid & weak Base

ACIDIC BUFFER

$$\boxed{pH = pKa + \log\left(\frac{[\text{Conj. Base}]}{[\text{Acid}]}\right)}$$

Buffer Action :

i) Add$^n$ of $H^+$ –

$$CH_3COOH^- + H^+ \longrightarrow CH_3COOH$$

$[\,]_i$ : $S$ $\quad x \quad$ $a$

$[\,]_f$ : $S-x$ $\quad 0 \quad$ $a+x$

$$\boxed{pH = pKa + \log\left(\frac{S-x}{a+x}\right)}$$

ii) Add$^n$ of $OH^-$ –

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

$[\,]_i$ : $a$ $\quad x \quad$ $S$

$[\,]_f$ : $a-x$ $\quad 0 \quad$ $S+x$

$$\boxed{pH = pKa + \log\left(\frac{S+x}{a-x}\right)}$$

BASIC BUFFER

$$\boxed{pOH = pK_b + \log\left(\frac{[\text{Conj. Acid}]}{[\text{Base}]}\right)}$$

NOTE: 1) For effective buffer

Acidic

$0.1 \leq S/a \leq 10$

$\Rightarrow \boxed{pH = pKa \pm 1}$

Basic

$0.1 \leq S/b \leq 10$

$\boxed{pOH = pK_b \pm 1}$

2) $$\boxed{\text{Buffer capacity} = \frac{\left(\begin{array}{c}\text{Change in mols of}\\ H^+/OH^- \text{ per L}\end{array}\right)}{\Delta pH}}$$

3) 'Boric Acid + Borax' is a buffer.

$$\underset{\text{(Borax)}}{Na_2B_4O_7} \xrightarrow[\text{of } H_2O]{\text{in presence}} \underset{\text{(conj base)}}{B(OH)_4^-} + \underset{\text{(Boric Acid)}}{B(OH)_3}$$

## Solubility & solubility product.

eg:- $Li_3Na_3(AlF_6)_2 \rightleftharpoons 3Li^+ + 3Na^+ + 2AlF_6^{-3}$

$[\,]_i$ : $C$ $\quad 0 \quad 0 \quad 0$

$[\,]_f$ : $C - CS$ $\quad 3s \quad 3s \quad 2s$

$$K_{sp} = [Li^+]^3[Na^+]^3[AlF_6^{-3}]^2$$
$$= (3s)^3(3s)^3(2s)^2$$
$$= 3^6 2^2 s^8$$

Q. At 25°C, Ksp for $PbBr_2$ is $8 \times 10^{-5}$. If salt is 80% dissociated, what is solubility of $PbBr_2$?

A) $S$ = Max. # mol. dissolved.

In this case $(0.8)s$ mol. of salt dissolves.

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

$[\,]_i$ : $\quad 0 \quad 0$

$[\,]_f$ : $\quad (0.8)s \quad (1.6)s$

$$K_{sp} = [0.8s][1.6s]^2 = 8 \times 10^{-5}$$

$$\Rightarrow \boxed{s = \sqrt[3]{\frac{10^{-4}}{2.56}}}$$

## Precipitate Formation

$$AB \rightleftharpoons A^+ + B^-$$

$\boxed{Q = [A^+][B^-]}$ at any pt. of time.

↑
Ionic prod.

$$\boxed{\begin{array}{l} Q < K_{sp} : \text{ppt NOT form} \\ Q = K_{sp} : \text{Eq. cond}^n \\ Q > K_{sp} : \text{ppt will form} \end{array}}$$

## Solubility of AgCN

$CN^-$ being conj base of HCN (weak acid) it hydrolyses

$$\begin{array}{lccc} & AgCN \rightleftharpoons & Ag^+ & + \; CN^- \\ [\;]_f : & & x & x \end{array}$$

$$\begin{array}{lccc} & CN^- + H_2O \rightleftharpoons & HCN & + \; OH^- \\ [\;]_f : (x-y) & & y & y \end{array}$$

At eq. $[CN^-] = (x-y)$
$[HCN] = y$

$K_{sp} = [Ag^+][CN^-]$
$= x(x-y)$

$K_h = \dfrac{y^2}{(x-y)}$

$\Rightarrow \boxed{K_{sp}K_h = xy^2}$

If :

$$\boxed{\begin{array}{lcl} \text{Basic Medium introduced} & \Rightarrow & \text{Solubility of AgCN} \downarrow \\ \text{Acidic Medium introduced} & \Rightarrow & \text{solubility of AgCN} \uparrow \end{array}}$$

f base radical weak (like $NH_4^+$) instead of acid radical (like $CN^-$)

$$\boxed{\begin{array}{lcl} \text{Basic Medium introduced} & \Rightarrow & \text{Solubility} \uparrow \\ \text{Acidic Medium introduced} & \Rightarrow & \text{Solubility} \downarrow \end{array}}$$

## Solubility of AgCl in aq. $NH_3$

Let initial conc. of $NH_3 = z$

$$\begin{array}{lccc} & AgCl \rightleftharpoons & Ag^+ & + \; Cl^- \\ [\;]_f : & & x & x \end{array}$$

★ $Ag^+$ reacts with $NH_3$ to form Tollen's Reagent. (very stable)

$$\begin{array}{lccc} & Ag^+ \;+ & 2NH_3 \rightleftharpoons & [Ag(NH_3)]^+ \\ [\;]_f : & (x-y) & (z-2y) & y \end{array}$$

Since product very stable $\boxed{(z-2y) \sim (z-2x)}$

At eq, $[Ag^+] = (x-y)$
$[NH_3] = (z-2x)$
$[Ag(NH_3)^+] = y$
$[Cl^-] = x$

$K_{sp} = x(x-y)$ $\quad K_f = \dfrac{x}{(x-y)(z-2x)^2}$

$$\boxed{K_{sp}K_f = \frac{x^2}{(z-2x)^2}}$$

## Acid-Base Titn

Read graphs from notes

1) Acidic Indicator (HIn)
eg:- Phenolphthalein (HPh)

$$HIn \rightleftharpoons H^+ + In^-$$

$K_{In} = \dfrac{[H^+][In^-]}{[HIn]} \Rightarrow \boxed{pH = pK_{In} + \log\left(\dfrac{[In^-]}{[HIn]}\right)}$

2) Basic Indicator (InOH)
eg:- Methyl orange (MeOH)

$$\boxed{pOH = pK_{In} + \log\left(\frac{[In^-]}{[InOH]}\right)}$$

## Working Range

Acidic In : $pK_{In} - 1 \leq pH \leq pK_{In} + 1$

Basic In : $pK_{In} - 1 \leq pOH \leq pK_{In} + 1$

# CHEMICAL KINETICS

$aA + bB \rightarrow cC$

$$ROR = \left(\frac{1}{a}\right)\left(\frac{-dA}{dt}\right) = \left(\frac{1}{b}\right)\left(\frac{-dB}{dt}\right) = \left(\frac{1}{c}\right)\left(\frac{dC}{dt}\right)$$

Rate of disappearance of A $= \frac{dA}{dt}$

Rate of appearance of C $= \frac{dC}{dt}$

## Factors affecting ROR

1) Nature of Reactant
2) Conc. of Reactant
3) Temp. $\boxed{ROR \propto T\uparrow}$
4) catalyst
5) Surface Area $\boxed{RoR \propto S.A}$
6) Presence of light (if req.) $\boxed{RoR \propto (\text{Intensity of light})}$

## ate Law & order

$aA + bB \longrightarrow cC$

$\boxed{RoR = k[A]^p[B]^q}$ k → Rate const. of

p → order of Rea$^n$ wrt A

q → order of Rea$^n$ wrt B

$\boxed{\text{order of Rea}^n = (p+q)}$

TE (i) <u>Elementary</u> rea$^n$s (single step)

$\boxed{p=a}$ & $\boxed{q=b}$

(Law of Mass Action)

i) <u>Molecularity</u> — # molecular species participating in elementary rea$^n$. It is <u>not</u> defined for complex rea$^n$s.

or elem. rea$^n$s. $\boxed{\text{Order} = \text{Molecularity}}$

Orders can be fractional but Molecularity can <u>NOT</u> fractional

(iii) Order of complex rea$^n$ is determined by the <u>slowest step</u>-(rate determining step)

{i.e treating the step as the elem. rea$^n$ used to write Rate Law Exp.}

## First order Kinetics

$\left\{ -\frac{dA}{dt} = k[A] \right\}$

1) $kt = \ln(A_0) - \ln(A)$

2) $t_{1/2} = \frac{\ln(2)}{k}$

<u>NOTE:</u>

$t_{90\%} = t_{1/2} \times \left(\frac{10}{3}\right)$

$t_{99\%} = t_{1/2} \times \left(\frac{10}{3}\right)^2$

$t_{99.9\%} = t_{1/2} \times \left(\frac{10}{3}\right)^3$

3) $t_{av} = \frac{1}{k}$

## Second order Kinetics

(if conc. of reactants is diff.)

$A + B \rightarrow C$

i: a b

$$\boxed{kt = \left(\frac{1}{a-b}\right) \ln\left(\left(\frac{a-x}{b-x}\right)\left(\frac{b}{a}\right)\right)}$$

## Coeff of ROR & ROA(A)

$2A \longrightarrow P$ : $-\frac{dA}{dt} = k_A[A]$ $RDR = k_R[A]$

$ROR = \frac{1}{2}\left(\frac{-dA}{dt}\right) \rightarrow \boxed{k_R = 2k_A}$

unless specified, report $k_A$!

## Calc. of Ist Order Rea^n using diff. parameters

$$\boxed{kt = \ln\left(\frac{X_\infty - X_0}{X_\infty - X_t}\right)}$$

$X_\infty$ – Val. of parameter @ $t=\infty$
$X_t$ – Val. of parameter @ $t=t$
$X_0$ – Val. of parameter @ $t=0$

① **Decomp. of $H_2O_2$ in terms of $KMnO_4$ used**

$X$ = Vol. of $KMnO_4$ used.

Since no $H_2O_2$ left at $t=\infty$,
$\Rightarrow$ $X_\infty = 0$ $\Rightarrow$ $\boxed{kt = \ln\left(\frac{X_0}{X_t}\right)}$

② **Decomp. of $H_2O_2$ in terms of $O_2$ produced**

$X$ = Vol. of $O_2$ produced

Since no $O_2$ at $t=0 \Rightarrow X_0 = 0$.
$\Rightarrow$ $\boxed{kt = \ln\left(\frac{V_\infty}{V_\infty - V_t}\right)}$

③ **Hydrolysis of Ethyl Acetate in terms of NaOH used**

$X$ = Vol. of NaOH used.

④ **Hydrolysis of Sucrose**

$X$ = Observed rotation $(\theta)$

NOTE: (i) $\boxed{\theta = \alpha l C}$ — $C$: Conc. of sample (in g/ml); $l$: length of tube (in decimeter); $\alpha$: specific rotation

(ii) $\underset{\text{(Leavo)}}{\text{Sucrose}} + H_2O \longrightarrow \underset{\text{(Dextro)}}{\text{Glucose}} + \underset{\text{(Leavo)}}{\text{Fructose}}$

## Parallel & Series Rea^n (Ist order kinetics)

① **Parallel**

(i)
$$\begin{tikzcd} & bB \\ aA \arrow[ur] \arrow[dr] & \\ & cC \end{tikzcd}$$

$$\boxed{A_0 = A_t + \left(\frac{a}{b}\right)B_t + \left(\frac{a}{c}\right)C_t}$$

(ii)
$$\begin{tikzcd} & bB \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & cC \end{tikzcd}$$

$$\boxed{K_{net} = k_1 + k_2} \Rightarrow \boxed{\frac{1}{(t_{1/2})_{net}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}}$$

$$A = A_0 e^{-(k_1+k_2)t}$$

$$B = \frac{bk_1}{(k_1+k_2)} A_0\left[1 - e^{-(k_1+k_2)t}\right]$$

$$C = \frac{ck_2}{(k_1+k_2)} A_0\left[1 - e^{-(k_1+k_2)t}\right]$$

NOTE: $\boxed{\frac{B}{C} = \left(\frac{b}{c}\right)\left(\frac{k_1}{k_2}\right)}$

② **Series**

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\boxed{t_{max} = \frac{1}{(k_2-k_1)} \ln\left(\frac{k_1}{k_2}\right)}$$

$$\boxed{B_{max} = A_0\left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2-k_1}\right)}}$$

## Equilibrium (Ist order kinetics)

$ROR = R_f - R_b$
$k = k_f + k_b$

| Rea^n: | $A$ | $\underset{k_b}{\overset{k_f}{\rightleftharpoons}}$ | $B$ |
|---|---|---|---|
| $t=0$: | $a$ | | $0$ |
| $t=t$: | $(a-x)$ | | $x$ |
| $t=t_{eq}$: | $(a-x_e)$ | | $x_e$ |

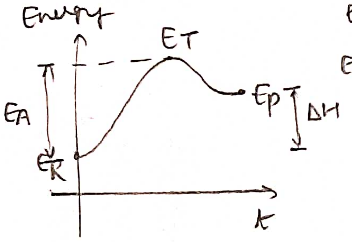
$$\boxed{(k_f + k_b)t = \ln\left(\frac{x_e}{x_e - x}\right)}$$

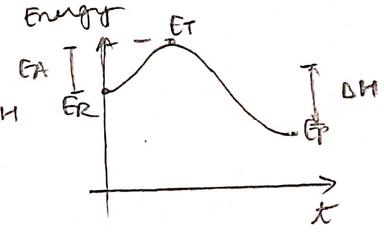
## Effect of T on RoR

$$R(T+\Delta T) = R(T)\,\alpha^{\Delta T/10}$$

α — temp. coeff ∈ [2, 3]

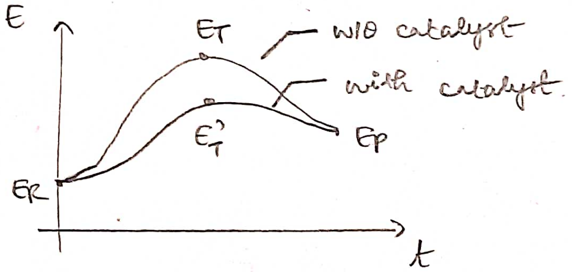
## Activation Energy & Effect of Catalyst





$E_R$ — Energy of Reactant
$E_P$ — Energy of Product
$E_T$ — Threshold Energy
$E_A$ — Activation Energy

NOTE: $E_A$ (fwd rxn) = $E_A$
$E_A$ (bwd rxn) = $E_A - \Delta H$



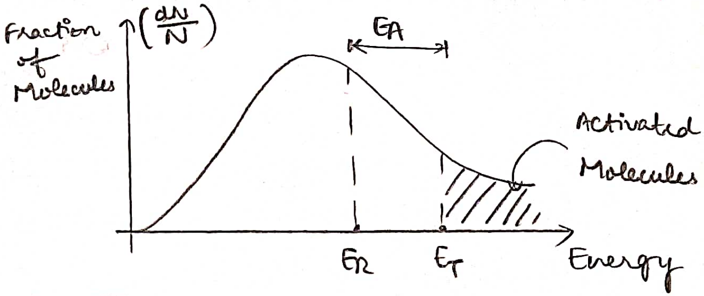
NOTE: ① Catalyst doesn't change energy of reactant & product

② Catalyst does not change ΔH & ΔG (Thus, also the spontaneity of rxn)

③ Catalyst does not change Keq. It brings eq. faster.

## Activated / Effective Molecules

Molecules whose energy ≥ $E_T$



$$\boxed{(\text{Fraction of Effective molecules}) = e^{-E_A/RT}}$$

### Arrhenius Eqn

$$\boxed{k = A\,e^{-E_A/RT}}$$

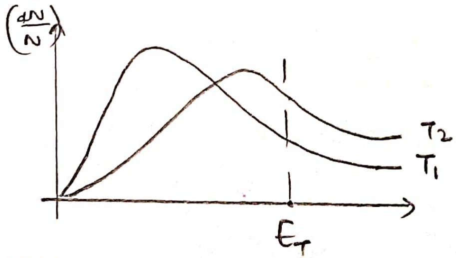
k — rate const.
A — Arrhenius const. / collision factor / pre-exponential factor

$$\Rightarrow \log(k) = \log(A) - \frac{E_A}{2.303RT}$$

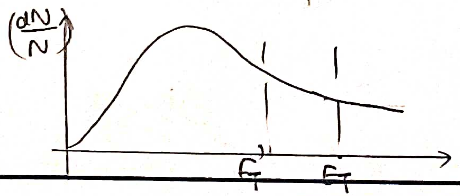
$$\Rightarrow \boxed{\log\left(\frac{k_2}{k_1}\right) = \frac{E_A}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

$k_i$ — Rate const at temp. $T_i$

① Temp. ($T_2 > T_1$)



② Catalyst



# Radioactivity

(Study from package)

#nuclei/atom at time 't'

$$\boxed{A = -\frac{dN}{dt} = \lambda N}$$

Activity

decay const.
(independent of temp.)

<u>NOTE:</u> No <u>significance</u> of <u>Arrhenius eqn</u> in radioactivity.

Units : $1\ Ci = 3.7 \times 10^{10}$ dps (disintegrations per sec.)

curie

$1\ Bq = 1$ dps (SI)

Becquerel

- <u>Specific Activity</u> - Activity of 1 g radioactive sample.

$$\boxed{\lambda t = \ln\left(\frac{N_0}{N_t}\right)}$$

$$N_0 = \left(\frac{W_0}{M}\right)(N_A) = n_0 N_A$$

$$\Rightarrow \boxed{\frac{A_0}{A} = \frac{N_0}{N} = \frac{n_0}{n} = \frac{w_0}{w}}$$

- <u>Half-life</u> - $\boxed{t_{1/2} = \frac{0.693}{\lambda}}$
- <u>Avg. life</u> - $\boxed{t_{av} = \frac{1}{\lambda} = 1.44\, t_{1/2}}$

# THERMODYNAMICS
# &
# THERMOCHEMISTRY

## Internal Energy

$\boxed{\Delta U = nC_v \Delta T}$ ($C_v$ - molar specific heat capacity)

NOTE (i) This formula is only valid when n = const.

(ii) For solids & liq,

$\boxed{\Delta U = ms\Delta T}$ (s → specific heat capacity)

## Work

{ W by sys = -ve
On sys = +ve }

$$\boxed{dW = -P_{ext}\, dV}$$

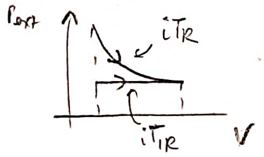
$iT_R$ : $W = -nRT\ln\left(\frac{V_2}{V_1}\right) = -nRT\ln\left(\frac{P_1}{P_2}\right)$

$iP_R$ : $W = -P_{ext}\,\Delta V$

$iV_R$ : $W = 0$ $(\Delta V = 0)$

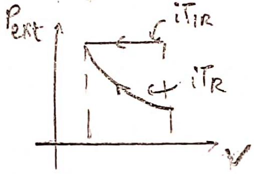
IR : $W = -P_{ext}\,\Delta V$

NOTE: (i) During expansion



$\boxed{W_{iT(R)} > W_{iT(IR)}}$

During contraction



$\boxed{W_{iT(R)} < W_{iT(IR)}}$

(ii) W = 0 when gas expands in vacuum (free expansion)

## First Law

$$\boxed{\Delta U = q + W}$$

{ Heat given to sys: q = +ve
Heat released from sys: q = -ve }

### Enthalpy (H)

$$H = U + P_{ext}V$$

$$\Rightarrow \boxed{\Delta H = \Delta U + \Delta(P_{ext}V)}$$

for a reversibly occuring reaⁿ (NOT necessarily a reversible reaⁿ)

$$\boxed{\Delta H = \Delta U + \Delta n_g RT}$$

{ $\Delta H = nC_p\Delta T \Rightarrow \Delta H = q_p$
$\Delta U = nC_v\Delta T \Rightarrow \Delta U = q_v$ }

Relⁿ b/w $C_p$ & $C_v$

$\boxed{C_p - C_v = R}$ $\boxed{\gamma = C_p/C_v}$

## Degrees of Freedom (f)

$$\boxed{\gamma = 1 + \left(\frac{2}{f}\right)}$$

$C_p = \frac{\gamma R}{(R-1)}$ $C_v = \frac{R}{(\gamma-1)}$

| Atomicity | Mono | Di | Tri (linear) | Tri (Non-linear |
|---|---|---|---|---|
| f : | 3 | 5 | 5 | 6 |
| (+2) $F_{vibrational}$ | 5 | 7 | 7 | 8 |

**NOTE:** for a mix. of gases $G_1, G_2, \ldots, G_m$.

$$\boxed{(C_p)_{mix} = \left(\frac{\Sigma n_i C_{p_i}}{\Sigma n_i}\right)} \qquad \boxed{(C_v)_{mix} = \left(\frac{\Sigma n_i C_{v_i}}{\Sigma n_i}\right)}$$

$$\gamma_{mix} = (C_p)_{mix} / (C_v)_{mix} = \left(\frac{\Sigma n_i C_{p_i}}{\Sigma n_i C_{v_i}}\right)$$

---

## Polytropic Process

$$PV^n = \text{const.}$$

if $n = \gamma$, process is known as Adiabatic Process

$$\boxed{W = \frac{P_2V_2 - P_1V_1}{(n-1)}}$$

**NOTE:** (i) for reversible AdB.

$$\boxed{\begin{aligned} PV^{\gamma} &= \text{const.} \\ TV^{(\gamma-1)} &= \text{const.} \\ PT^{\left(\frac{\gamma}{1-\gamma}\right)} &= \text{const.} \end{aligned}}$$

but $\boxed{q = 0}$ for any AdB process whether occuring reversibly or irreversibly.

(ii) $$\boxed{C = C_v + \frac{R}{1-n}}$$

molar specific heat capacity

---

## Second law

$$\boxed{\Delta S_{sys} + \Delta S_{surr} > 0}$$

for irreversible process.

$\Delta S_{sys} + \Delta S_{surr} = 0$ for reversible process

**NOTE:** $\left(\Delta S_{universe/\text{isolated system}}\right) \Leftrightarrow$ (Process is spontaneous)

Entropy – $\boxed{\Delta S = \int \frac{dq_{rev}}{T}}$

**NOTE:** (i) S: gas > liq. > solid

(ii) S ∝ (Mass & size)

(iii) S ∝ Mol. wt.

(iv) S ∝ Atomicity

## Entropy during Phase Change

$$\boxed{\Delta S = \frac{\Delta H_{sys\,(process)}}{T_{process\ pt.}}}$$

Process – Melting, Boiling, Sublimation

## Entropy during ThD Process

$$\boxed{\begin{aligned} \Delta S_{sys} &= nC_v \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right) \\ &= nC_p \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right) \end{aligned}}$$

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = -\frac{q_{sys}}{T_{surr}}$$

For Rev. process, $\Delta S_{surr} = -(\Delta S)_{sys}$.

IR: iT : $\Delta S_{surr} = \frac{W}{T_{surr}} = \boxed{\frac{-P_{ext}(V_2 - V_1)}{T_{surr}}}$

iP : $\Delta S_{surr} = \frac{-\Delta H_{sys}}{T_{surr}} = \boxed{\frac{-nC_p(T_2 - T_1)}{T_2}}$

iV : $\Delta S_{surr} = \frac{-\Delta U_{sys}}{T_{surr}} = \boxed{\frac{-nC_v(T_2 - T_1)}{T_2}}$

| NOTE: | $\Delta S_{sys}$ | $\Delta S_{surr}$ |
|---|---|---|
| $AdB_R$ | 0 | 0 |
| $AdB_{IR}$ | $\left(nC_v\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)\right)$ | 0 |

---

## Gibbs Free Energy

$$\boxed{dG = V\,dP - S\,dT}$$

For T = const.

$$\boxed{\Delta G = nRT\ln\left(\frac{P_2}{P_1}\right)}$$

$$\Delta G = \Delta G^{\circ} + RT\ln(Q)$$

@ eq. $\boxed{\Delta G = 0}$

$$\Downarrow$$

$$\boxed{\Delta G^{\circ} = -RT\ln(K)}$$

NOTE (i) $\boxed{(\Delta G)_{P,T} = \Delta H - T\Delta S}$

(ii) $(\Delta G)_{P,T} < 0 \Leftrightarrow$ Rxn is spontaneous

## Thermochemistry

1) $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

$= \sum BE(\text{Reactants}) - \sum BE(\text{Products})$

2) $(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = \Delta C_p (T_2 - T_1)$

3) $\Delta S_{T_2} - \Delta S_{T_1} = \Delta C_p \ln\left(\frac{T_2}{T_1}\right)$

$$dS = \frac{dq_{rev}}{T} = \frac{\Delta C_p \, dT}{T}$$

4) $\Delta H^o_{neu} = \Delta H^o_{ionisation} + \underbrace{\Delta H^o_{reac^n}}$

$-57.1$ kJ/mol

OR $-13.7$ kcal/mol

$[H^+ + OH^- \rightleftharpoons H_2O(l)]$

5) $$\boxed{\begin{pmatrix}\text{Resonance} \\ \text{Energy}\end{pmatrix} = \underbrace{\Delta H_f(\text{observed})}_{\text{(Comp. with Resonance)}} - \underbrace{\Delta H_f(\text{Theoretical})}_{\text{(Comp. w/o Resonance)}}}$$

eg –

$$\begin{tikzcd}
CuSO_4(s) \arrow[rd, "\Delta H_{soln}(CuSO_4)"] \arrow[dd, "\Delta H_{Hyd}"'] & \\
& CuSO_4(aq.) \\
CuSO_4 \cdot 5H_2O(s) \arrow[ru, "\Delta H_{soln}(\text{hyd } CuSO_4)"'] &
\end{tikzcd}$$