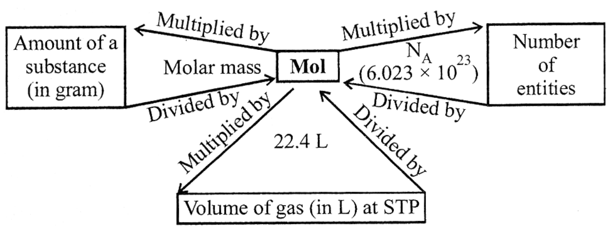
AAJ KA TOPPER

LAST MINUTE REVISION

Mission Physical Chemistry

PHYSICAL CHEMISTRY

1. Some Basic Concepts of Chemistry

- 

- Molecular Mass $= \dfrac{\text{Average relative mass of one molecule}}{\frac{1}{12} \times \text{mass of C} - 12 \text{ atom}}$

- Molecular mass $= 2 \times \text{VD}$

- Eq. wt. of metal $= \dfrac{\text{wt. of metal}}{\text{wt. of } H_2 \text{displaced}} \times 1.008$

- Eq. wt. of metal $= \dfrac{\text{wt. of metal}}{\text{wt. of oxygen combined}} \times 8$

  $= \dfrac{\text{wt. of metal}}{\text{wt. of chlorine combined}} \times 35.5$

- Molecular formula $= (\text{Empirical formula})_n$

- 1 amu $= 1.66 \times 10^{-24}$ g (amu - atomic mass unit)

- $n = \dfrac{w}{M}$

  where w is weight of substance and M is molar mass of substance, n is number of moles

- $n = \dfrac{\text{given particles}}{6.022 \times 10^{23}}$ where n is number of moles

- $n = \dfrac{\text{Given volume}}{22.4 \text{ lit at STP}}$ where n is number of moles

- Average atomic mass

  $= \dfrac{(\text{RA} \times \text{At.mass})_1 + (\text{RA} \times \text{At.mass})_2}{\text{RA}(1) + \text{RA}(2)}$

  where RA is relative abundance.

- 1 gram atom $= N_A$ atoms $= 6.023 \times 10^{23}$ atoms

  = Gram atomic mass

- 1 gram molecule $= N_A$ molecules

  $= 6.023 \times 10^{23}$ molecules = Gram molecular mass

- Mass % of an element

  $= \dfrac{\text{Mass of that element in the compound} \times 100}{\text{Molar mass of the compound}}$

- The value of n can be obtained by the following relationship

  $n = \dfrac{\text{Molecular mass}}{\text{Empirical formula mass}}$

- Normality (N)

  $= \dfrac{\text{Gram equivalent of the solute}}{\text{Volume of the solution in litre}} = \dfrac{W \times 1000}{\text{GEM} \times V \text{ in mL}}$,

  where GEM is gram equivalent mass of solute.

- Equivalent mass of an element $= \dfrac{\text{Atomic mass}}{\text{Valency}}$

- Equivalent mass of an acid $= \dfrac{\text{Molecular mass}}{\text{Basicity}}$

- Equivalent mass of a base $= \dfrac{\text{Molecular mass}}{\text{Acidity}}$

- Equivalent mass of a salt

  $= \dfrac{\text{Formula mass}}{\text{Total +ve or } -\text{ve charge}}$

- Equivalent mass of an oxidising agent

  $= \dfrac{\text{Molecular mass}}{\text{Total change in oxidation number}}$

- Molarity × GMM (solute) = Normality × GEM (solute), where GMM is gram molecular mass.
- Normality and molarity equations :

$N_1V_1 = N_2V_2$

$M_1V_1 = M_2V_2$ (For dilution)

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

(For reaction where n_1 and n_2 are no. of moles of the two reactants in a balanced chemical equation)

$M_3(V_1 + V_2) = M_1V_1 + M_2V_2$

(Final molarity on mixing two non-reacting solutions)

- Number of millimoles = Molarity × V in mL
- Number of equivalents = Normality × V in L
- Number of milliequivalents

= Normality × V in mL

- Number of gram atoms or mole of atoms

$$= \frac{\text{Mass of element in gram}}{\text{Gram atomic mass}}$$

- 1 mole = mass of 6.023×10^{23} particles (atoms/molecules)
- 1 mole atoms = Gram atomic mass (or 1 g atom) = 6.023×10^{23} atoms
- 1 mole molecules = Gram molecular mass (or 1 g molecule) = 6.023×10^{23} molecules

= 22.4 L at STP

- 1 mole ionic compound = Gram formula mass = 6.023×10^{23} formula units
- No. of gram equivalents

$$= \frac{\text{Weight of the solute(in g)}}{\text{Equivalent weight of the solute}}$$

- No. of milliequivalents

$$= \frac{\text{Weight of the solute(in g)}}{\text{Equivalent weight of solute}} \times 1000$$

- Strength of a solution

$$= \frac{\text{Wt. of the solute (in g)}}{\text{Vol. of solution (in litres)}}$$

- Parts per million (ppm) of substance A (ppm)

$$= \frac{\text{Mass of A}}{\text{Mass of solution}} \times 10^6 \quad \text{or}$$

$$= \frac{\text{Vol. of A}}{\text{Vol. of solution}} \times 10^6$$

- Molality (m) = $\dfrac{M}{\rho - \dfrac{MM_2}{1000}}$ or

Molarity (M) = $\dfrac{m\rho}{\left(1 + \dfrac{mM_2}{1000}\right)}$

where M_2 = molecular mass of solute,

ρ = density

- $M = \dfrac{n_1}{(n_1M_1 + n_2M_2)/\rho}$

Here, n_1M_1 = mass of solute,

n_2M_2 = mass of solvent

i.e., $n_1M_1 + n_2M_2$ = mass of solution.

2. Atomic Structure

1. No. of **subshells** in main shell = **n**
2. Total no.of **orbitals** in main shell = **(n)^2**
3. Total no. of **orbitals** in **subshell - 2l + 1**
4. Total no. of **electrons** in **main shell - 2n^2**
5. Total no. of **electrons** in **sub shell = 2(2l + 1)**
6. No. of **radial** or **spherical** nodes = **n – l – 1**

7. Nodal plane :

It is a plane passing through nucleus where probability of finding of electrons is zero.

No. of nodel plane = l

8. **Angular momentum of electron, mvr =** $\frac{nh}{2\pi}$
9. **Orbital angular momentum of electron.**

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

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

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

Where n = no. of unpaired electrons.

11. **Spin angular momentum =** $\sqrt{S(S+1)}\frac{\mathbf{h}}{\mathbf{2\pi}}$
12. **Maximum no. of lines produced when electron falls to ground level,** $= \frac{\mathbf{n(n-1)}}{\mathbf{2}}$
13. When electron returns from n_2 **to n_1 state, maximum no. of lines produced**

$$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

- $\bar{v} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$,

[R = 1.0968 × 10^7 m^{-1}];

$E = hv = \frac{hc}{\lambda}, \lambda = \frac{h}{\sqrt{2m \times K.E.}}$

- No. of spectral lines produced when an electron drops from nth level to ground level

$$= \frac{n(n-1)}{2}$$

- Heisenberg's Uncertainty Principle = (Δx) (Δp) $\geq$ h/4π

- Nodes (n–1) = total nodes, l = angular nodes, (n – l –1) = Radial nodes
- **Orbital angular momentum :**

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

14. Bohr's model formulae

- **Radius of nth shell**

$$r_n = 0.529 \times \frac{n^2}{Z} \text{Å} \quad \Rightarrow r \propto \frac{n^2}{Z}$$

- **Velocity of nth shell**

$$v_n = \frac{Z}{n} \times 2.185 \times 10^8 \text{ cm/s} \Rightarrow V \propto \frac{Z}{n}$$

- **No of revolutions made by nth shell** $v = \frac{Z^2}{n^3}s^{-1}$

$$\Rightarrow V \propto \frac{n^2}{n^3}$$

- **No. of wave made by e$^-$ in nth shell**

$$T_n = 1.5 \times 10^{-16} \times \frac{n^3}{Z^2}s \Rightarrow v \propto \frac{n^3}{Z^2}$$

- $IE = E_\infty - E_1$

IE = –E$_1$

IE = 0 – E$_1$ = –E$_1$

- **IE$_{\text{H-like atom}}$ × Z^2 = I.E$_{\text{H atom}}$ × Z^2**
- **KE =** $13.6 \times \frac{Z^2}{n^2}$ eV / atom
- **P.E. =** $-27.2 \times \frac{Z^2}{n^2}$ **eV/atom**
- **IE and TE = – 13.6 ×** $\frac{Z^2}{n^2}$ **eV/atom**
- **KE and TE =** $\frac{KE}{TE} = \frac{Ze^2}{2r} \times -\frac{2r}{Ze^2} = -1$
- **Angular momentum in orbit mvr =** $\frac{nh}{2\pi}$

3. Chemical Bonding

- (i) % ionic character

$$= \frac{\textbf{Actual dipole moment}}{\textbf{Calculated dipole moment}} \times 100$$

(ii) Dipole moment is helpful in predicting geometry and polarity of molecule.

Fajan's Rule:

Following factors are helpful in increasing covalent character in ionic compounds

i. Small cation

ii. Big anion

iii. High charge on cation/anion

iv. Cation having pseudo inert gas configuration ($ns^2p^6d^{10}$)

e.g. **Cu^+, Ag^+, Zn^{+2}, Cd^{+2}**

M.O. Theory:

i. Bond order = 1/2 (N_b–N_a)

ii. Higher the bond order, higher is the bond dissociation energy, greater is the stability, shorter is the bond length. on an atom in a Lewis

= [total number of valence electrons in the free atoms] – [total number of non-binding (lone pair) electrons] – $\frac{1}{2}$[total number bonding (shared) electrons]

Relative bond strength :

sp^3d^2 > dsp^2 > sp^3 > sp^2 > sp > p-p (Co-axial) > s-p > s-s > p-p (Co-lateral)

VSEPR theory

i. (LP-LP) repulsion > (LP-BP) > (BP-BP)

ii. NH_3 → Bond angle 106°45' because

(LP-BP) repulsion > (BP-BP) H_2O → 104°27' because (LP-LP) repulsion > (LP-LB) > (BP-BP)

- **Hybridisation :** $H = \frac{V+M-C+A}{2}$

MO Configuration

Case I :

2s–2p mixing occurs (total $e^- \le 14$)

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

Case II :

2s–2p mixing do not occurs (total e^- > 14 to 20)

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

Application of H-bonding

Physical State (densile nature)	∝	H-bond
Melting point (mp)	∝	H-bond
Boiling point (bp)	∝	H-bond
Viscosity	∝	H-bond
Surface Tension	∝	H-bond
Volatilty	∝	1/H-bond
Vapour Pressure	∝	1/H-bond

4. States of Matter

Boyle's Law at constant temperature and amount

$P_1V_1 = P_2V_2 = \text{Constant}$

Charle's Law

V = kT at constant pressure

k is the proportionality constant depends upon (i) Amount of Gas (ii) Temperature

Gay Lussac's Law :

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$ at constant volume

Avogadro's Law

$V \propto n$ (T and P constant)

$V = K_4 n$

$V_1/n_1 = V_2/n_2$ (Constant T and P)

Ideal Gas Equation

PV = nRT

Where R is Proportionality constant is also known as Gas constant it is same for all Gases

Value of R in different units

Magnitude	Unit
0.0821	Litre-atm K^{-1} mol^{-1}
82.1	ML-atm K^{-1} mol^{-1}
62.1	Litre-mm-Hg K^{-1} mol^{-1}
0.083	Litre bar K^{-1} mol^{-1}
8.314	Pascal m^3 K^{-1} mol^{-1}
8.314×10^7	erg K^{-1} mol^{-1}
8.314	Joule K^{-1} mol^{-1}
1.987	Cal K^{-1} mol^{-1}

Density ; d = PM/RT

$(d \propto P)$; $(d \propto 1/T)$

Graham's Law of Diffusion / Effusion

- Rate of diffusion $R \propto \frac{1}{\sqrt{d}}$

  where d is density of gas at constant temperature and pressure

- $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

- $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

Dalton's of Partial Pressure :

Calculate the total pressure of mixture of non-reacting gas and based on the law of conservation of amount

$P_1 = P_T \times x_1$ (where P_1 is a partial pressure, P_T is a Total pressure, x_1 is mole fraction)

Total pressure of Gaseous mixture at constant temperature : $P_T = \frac{(P_1V_1 + P_2V_2)}{(V_1 + V_2)}$

Aqueous Tension : $P_{moist} = P_{dry\ gas} + P_{water\ vapours}$

$$RH = \frac{\text{Mass of water vapour present in certain volume of air}}{\text{Maximum Mass of water vapour present in same volume of air saturated by water vapour}}$$

Molecular Speed

Most probable speed $= \sqrt{\frac{2KT}{m}} = \sqrt{\frac{2RT}{M}}$

Average speed $= \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{m}}$

Root mean square $= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3KT}{m}}$

$V_{mp} : V_{av} : V_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$

Kinetic Energy

Average Kinetic Energy = $\frac{3}{2}$ KT

Total Kinetic Energy = $\frac{3}{2}$ nRT

Compressibility Factor (Z) $\left(Z = \frac{PV}{nRT} = \frac{PV_m}{RT}\right)$

Ideal gases
- zero volume
- zero attractive force
- PV = nRT
- Z = 1

Real gases
- corrected equation
  $(P + an^2/V^2)(V - nb) = nRT$
- non-zero volume
- some intermolecular force

(+)ve
- Z > 1
- Repulsive forces
- Difficult to compress
- Difficult to Liquify

(–)ve
- Z < 1
- Attractive forces
- Easy to compress
- Easy to Liquify

Energy-Distance for different ion-Covalent Interaction

Types of Interaction	Energy-distance Functions
Ionic bond	$1/r$
Ion-dipole	$1/r^2$
Dipole-dipole	Stationary molecules - $1/r^3$
	Rotating molecules - $1/r^6$
Ion-induced dipole	$1/r^4$
Dipole-induced dipole	$1/r^6$
London forces	$1/r^6$

Critical Constant of the Gases

T_c or critical temp : $T_c = 8a / 27Rb$

P_c or critical pressure : $P_C = a/ 27b^2$

V_C or critical volume : $V_C = 3b$

$$Z_C = \frac{P_C V_C}{RT_C} = \frac{3}{8}$$ (For all real gases)

Van der Waal's Equation Real Gas

$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ where a and b are Van der Waal's constant.

Boyle's Temperature : $T_b = \frac{a}{Rb}$

AAJ KA TOPPER

5. Chemical Equilibrium

- $K_C = \frac{[B]}{[A]}$ = mol L^{-1}
- $K_p = \frac{P_B}{P_A}$ = Partial Pressure
- $K_x = \frac{X_B}{X_A}$ = mole fraction
- $K_P = K_C(RT)^{\Delta ng}$ where $\Delta n_g = n_p - n_R$
- **Predicting the extent of reaction :**
  - $K_C > 10^3$ [Forward reaction is favoured.]
  - $K_C < 10^{-3}$ [Reverse reaction is favoured.]
  - $10^{-3} < K_C < 10^3$ [Both reactants and products are present in equilibrium]
- **Free Energy Charge (ΔG)**

  a) If $\Delta G = 0$ then reversible reaction would be in equilibrium, $K_C = 1$

  b) If ΔG = (+) ve then equilibrium will be displaced in backward direction; $K_C < 1$

  c) If ΔG = (–) ve then equalibrium will shift in forward direction;

  $K_C > 1$
- (a) K_C unit $\rightarrow$ $(\text{moles/lit})^{\Delta n}$

  (b) K_P unit $\rightarrow$ $(\text{atm})^{\Delta n}$
- Reaction Quotient and Equilibrium Constant

  Consider the following reversible reaction

  $A + B \rightleftharpoons C + D$
- $\therefore Q_C = \frac{[C][D]}{[A][B]}$

Case I : If $Q_C < K_C$ then :

[Reactants] > [Products] then the system is not at equilibrium

Case II : If $Q_C = K_C$ then :

The system is at equilibrium.

Case- III : If $Q_C > K_C$ then :

[Products] > [Reactants]

The system is not at equilibrium.

- ΔG or a reaction under any set of conditions is related to its value under standard conditions, i.e. $\Delta G°$ by the equation

  $$\boxed{\Delta G = \Delta G° + 2.303\ RT \log Q}$$
- Under equlibrium condtions, for same number of moles of reactants and products

  $Q = K_P = K_C = K$ and $\Delta G = 0$

$\therefore$ $\boxed{\Delta G° = -2.303\ RT \log K}$

- We have replaced K_P by K called thermodyanmic equilibrium constant

Significance of $\Delta G°$

Significance of $\Delta G°$ can be explained from the following points

(i) If $\Delta G° < 0$, $\log K > 0$, $\Rightarrow K > 1$

Hence, reaction is spontaneas in forward direction.

(ii) Hence $\Delta G° < 0$, $\log K > 0$, $\Rightarrow K < 1$

Hence, reaction is non-spontaneous or a reaction proceeds in the forward direction to such a small proceeds in the forward direction to such a small extent that a very small amount of the product is formed.

(iii) If $\Delta G° = 0$, $\log K = 0$, $\Rightarrow K = 1$

hence, it represents equilibrium.

(iv) If $\Delta G°$ is large negative number,

K > > 1, the forward reaction is nearly complete.

(v) If $\Delta G°$ is a very small positive number,

K < < 1, then reverse reaction is nearly complete.

- **Mole of Representation of Reversible reaction.**

i. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ K_{C_1}

$\boxed{K_{C_1} = \frac{1}{K_{C_2}}}$ $\boxed{K_{C_1} = \frac{1}{K_{C_3}^2}}$

ii. $2NH_3 \rightleftharpoons N_2 + 3H_2 \; K_{C_2}$

$\boxed{K_{C_1} = \frac{1}{K_{C_4}^2}}$ $\boxed{K_{C_1^2} = K_{C_5}}$

iii. $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3 \; K_{C_3}$

$\boxed{K_{C_2} = \frac{1}{K_{C_3}^2}}$ $\boxed{K_{C_3} = \frac{1}{K_{C_4}}}$

iv. $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2 \; K_{C_4}$

$\boxed{K_{C_4^4} = \frac{1}{K_{C_5}}}$ $\boxed{K_{C_2} = K_{C_4^2}}$

iv. $2N_2 + 6H_2 \rightleftharpoons 4NH_3 \; K_{C_5}$

➢ Le-Chatelier's principle

i. Increase of reactant conc. (Shift reaction forward)

ii. Decrease of reactant conc. (Shift reaction backward)

iii. Increase of pressure (from more moles to less moles)

iv. Decrease of pressure (from less moles to more moles)

v. For exothermic reaction decrease in temp. (Shift forward)

vi. For endothermic increase in temp. (Shift forward)

➢ Effect of Temperature on Equilibrium Constant

According to Von't Hoff Equation,

k = $Ae^{-\Delta H/RT}$

Where, K = rate constant, E_a = activation energy, R = gas constant, T = absolute temperature and e = exponential constant.

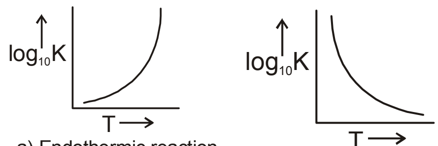
$$\log \frac{k_2}{k_1} = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where, $T_2 > T_1$

First case : When $\Delta H = 0$; $K_2 = K_1$.

Second case : When $\Delta H = +Ve$; $K_2 > K_1$

Thirds Case : When $\Delta H = -$ ve; $K_1 > K_2$



a) Endothermic reaction (Plots of logK versus T) b) Exothermic reaction

6. Ionic Equilibrium

i. **Lewis Acid (e^- pair acceptor) →**

CO_2, BF_3, $AlCl_3$, $ZnCl_2$, normal cation.

ii. **Lewis Base (e^- pair donor) →**

NH_3, ROH, ROR, H_2O, RNH_2 normal anions.

➢ Dissociation of Weak Acid and Weak Base

i. Weak Acid, $K_a = C_\alpha^2/(1-x)$ or $K_a = C_\alpha^2$; $\alpha << 1$

ii. **Weak Base,** $K_b = C_\alpha^2/(1-\alpha)$ or $K_b = C_\alpha^2$; $\alpha << 1$

d.o.d. $\propto \frac{1}{\text{dilution}}$ μ concentration

d.o.d. $\propto$ Temperature

d.o.d of strong electrolyte > weak electrolyte

d.o.d. $\propto$ dielectric constant of solvent.

➢ Buffer solution {Henderson equation} :

i. Acidic, **pH = pK_a** + log {Salt/Acid}

For maximum buffer action **pH = pK_a**

Range of buffer **pH = pK_a ± 1**

ii. Alkaline → **pOH = pK_b + log** {Salt/Base} for max. buffer action **pH = 14 – pK_b**

Range **pH = 14 – pK_b** ± 1

iii. Buffer Capacity = $\frac{\text{Moles/lit of Acid or Base mixed}}{\text{Change in pH}}$

- Relation between ionisation constant (K_i) and degree of ionisation (α):

$$K_i = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2 C}{(1-\alpha)} = \text{(Ostwald's dilution law)}$$

If is applicable to weak electrolystes for which $\alpha << 1$ then

$$\alpha = \sqrt{K_i V} = \sqrt{\frac{K_i}{C}} \text{ or } V\uparrow C\downarrow \alpha\uparrow$$

Common ion effect :

- By addition of X mole/L of a common ion, to a weak acid (or weak base) α becomes equal to

$$\frac{K_a}{X} = \left(\text{or } \frac{K_b}{X}\right) \text{[where } \alpha = \text{degree of dissociation]}$$

- i. If solubility product > ions product then the solution unsaturated and more of the substance can be dissolved in it.

  ii. If ionic product > solubility product the solution is super saturated (principle of precipitation).

- **Salt of weak acid and strong base :**

  $pH = 0.5\ (pK_w + pK_a + \log c)$

$$h = \sqrt{\frac{K_h}{c}}\ ;\ K_h = \frac{K_w}{K_a} \quad (h = \text{degree of hydrolysis})$$

Salt of weak base and strong acid:

$pH = 0.5\ (pK_w - pK_b - \log c)$

$$h = \sqrt{\frac{K_w}{K_b \times c}}$$

Salt of weak acid and weak base :

$pH = 0.5\ \ (pK_w - pK_a - pK_b)$

$$h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Solubility Product

Classification of salt on the basis of their solubility

i. Soluble, Solubility **> 0.1 M**

ii. Slightly Soluble, **0.01 M < Solubility < 0.1 M**

$$\mathbf{AgCl(s) \rightleftharpoons Ag^+ + Cl^-}$$

Applying the law of chemical equilibrium, we have

$$K_C = \frac{[Ag^+][Cl^-]}{[AgCl(s)]} \text{ or } \mathbf{K_C \times [AgCl(s)] = [Ag^+]\,[Cl^-]}$$

$$\mathbf{[Ag^+]\,[Cl^-] = K_C \times constant = K_{sp}}$$

$\mathbf{K_{sp}}$ = solubility product

$\mathbf{K_{sp}}$: product of molar concentrations of the ions (formed in the saturated solution at a given temperature) raised to the power equal to the number of times each ion occurs in the balanced equation for solubility equilibrium.

Application of Solubility Product

1. Relation Between Ksp and S

- **General form**

AxBy $\rightleftharpoons$	xA^{+y}	+	yB^{-x}
a	0		0
a – S	xS		yS

$K_{sp} = [A^{+y}]^x\,[B^{-x}]^y$

$= [xs]^x \times [ys]^y = x^x.s^x.\ y^y.s^y$

$$\boxed{K_{sp} = x^x\ y^y\ S^{(x+y)}}$$

2. Predicting precipitation in reactions :

(a) If $Q_{sp} < K_{sp}$, the solution is unsaturated.

(b) If $Q_{sp} > K_{sp}$, the solution is supersaturated and precipitation takes place.

(c) If $Q_{sp} = K_{sp}$, the solution is just saturated and no precipitation takes place.

7. Thermodynamics

- **First Law of Thermodynamcis :**

  $\Delta E = Q + W$

  Expression for pressure volume work

  $\mathbf{W = -P\Delta V}$

  Maximum work in a reversible expansion :

  $$W = -2.303\ n\ RT\ \log\frac{V_2}{V_1} = -2.303\ nRT\ \log\frac{P_1}{P_2}$$

  $W_{rev} \geq W_{irr}$

- $q_v = c_v\Delta T = \Delta U,\ q_p = c_p\Delta T = \Delta H$

Enthalpy changes during phase transformation

i. Enthalpy of Fusion

ii. Heat of Vapourisation

iii. Heat of Sublimation.

- **Enthalpy :** $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$
- **Kirchoff's equation** :

  $$\Delta E_{T_2} = \Delta E_{T_1} + \Delta C_V(T_2 - T_1)\ \text{[constant V]}$$

  $$\Delta H_{T_2} = \Delta E_{T_1} + \Delta C_P(T_2 - T_1)\ \text{[contant P]}$$

- **Entropy(s) :**

  Meassure of disorder or randomness

  $\Delta S = \Sigma S_P = -\Sigma S_R$

  $$\Delta S = \frac{q_{rev}}{T} = 2.03nR\ \log\frac{V_2}{V_1} = 2.303\ n\ R\ \log\frac{P_1}{P_2}$$

Entropy Changes in an Ideal Gas

$$\Delta S = 2.303nC_p\log\frac{T_2}{T_1} + 2.303nR\log\frac{P_1}{P_2}$$

$$\Delta S = 2.303nC_V\log\frac{T_2}{T_1} + 2.303nR\log\frac{V_2}{V_1}$$

1. **for isothermal process** :

   $$\Delta S = 2.303nR\log_{10}\frac{P_1}{P_2} \quad \text{or}$$

   $$\Delta S = 2.303nR\ \log_{10}\frac{V_2}{V_1}$$

2. **For isobaric process** :

   $$\Delta S = 2.303nC_P\log\left(\frac{T_2}{T_1}\right)$$

3. **For isochoric process** :

   $$\Delta S = 2.303nC_V\log\left(\frac{T_2}{T_1}\right)$$

4. **For adiabatic process**

- **$q = 0$ so $\Delta S = 0$**

  $\Delta S_{sys} = 0$

  $\Delta S_{surr.} = 0$

  $\Delta S_{Total} = 0$

- **Entropy and Spotaneity**

  $\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$

Case I : For a spontaneous process **$\Delta S_{Total} > 0$**

Case II : For non spontaneous process **$\Delta S_{Total} < 0$**

Case III : When process is at equilibrium **$\Delta S_{Total} = 0$**

In a reversible adiabatic process, as **$q = 0$**,

$\Delta S_{sys} = \Delta S_{surr} = \Delta S_{Total} = 0$

- **Free energy change :**

  $\Delta G = \Delta H - T\Delta S$, $\Delta G^\circ = nFE^\circ_{cell} - \Delta G =$ W(maximum) $- P\Delta V$, $\Delta G_{system} = -T\Delta S_{total}$

ΔH	ΔS	ΔG	Reaction characteristics
–	+	Alwasy negative	Reaction is spontaneous at all temperature
+	–	Alwasy positive	Reaction is nonspontaneos at all temperature
–	–	Negative at low temp.	Spontaneous at high temp. but positive at high temp.
+	+	Positive at low temp. but negative at high temp	Non spontaneous at low temp. & spontaneous at high temp.

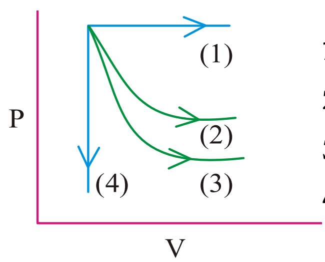
➤ Isothermal process

1. $\Delta T = 0$
2. $\Delta U = 0$
3. $q \neq 0$
4. $\Delta H = 0$

➤ Adiabatic process

1. $\Delta T \neq 0$
2. $\Delta U \neq 0$
3. $q = 0$
4. $\Delta H \neq 0$

➤ Graphical representation of **thermodynamic** processes



1) Isobaric process
2) Isothermal process
3) Adiabatic process
4) Isochoric process

for expansion:

$W_{Isobaric} > W_{Isothermal} > W_{Adiabatic} > W_{Isochoric}$

for compression :

$W_{Isobaric} > W_{Adiabatic} > W_{Isothermal} > W_{Isochoric}$

➤ Work for Osothermal Process

For expansion

1. $V_2 > V_1$
2. $W = -$ ve
3. $W = -P_{ext.}(V_2 - V_1)$
4. $W = -P_{ext.}\,\Delta V$
5. $W_{max.} \propto$ no. of moles

for compression

1. $V_1 > V_2$
2. $W = +$ve
3. $W = +P_{ext.}(V_1 - V_2)$
4. $W = +P_{ext.}\,\Delta V$

➤ Characteristics of Internal energy

Ideal gas	Real gas
$U = f(T)$ only	$U = f(T, P \text{ or } V)$
When T is constant	When T is constant
$\Delta U = 0,\ \Delta H = 0$	$\Delta U \neq 0,\ \Delta H \neq 0$
$\left(\frac{dU}{dV}\right)_T = 0$	$\left(\frac{dU}{dV}\right)_T \neq 0$

➤ Concept of Heat Capacity

Heat Capacity (s) $C = \frac{q}{\Delta T}$

Specific Heat Capacity (s) $s = \frac{q}{m\Delta T}$

Molar Heat Capacity (C_m) $C_m = \frac{q}{n\Delta T}$

➤ Work Done in Adiabatic Process

As $q = 0$

$\Delta U = W = nC_V\Delta T$

$W = nC_V(T_2 - T_1)$

$$W = \frac{nR}{\gamma - 1}(T_2 - T_1)$$

➤ Relation between C_P and C_V :

$C_P - C_V = R$

8. Solid State

Unit Cell	Corners	Body	Face	Total No. of atoms per unit cell
SCC	$1/8 \times 8 = 1$	----	----	1
BCC	$1/8 \times 8 = 1$	1	----	2
FCC/CCP	$1/8 \times 8 = 1$	----	$6 \times 1/2 = 3$	4
End Centred	$1/8 \times 8 = 1$	----	$2 \times 1/2 = 1$	2

Seven Primitive cells their Possible variations as centred unit cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles
Cubic	Primitive Body-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Orthorhombic	Primitive, Body- centred, Face-centred, End-centred	$a \neq a \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°,\ \gamma = 120°$
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°,\ \beta \neq 120°$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$

	S.C.	B.C.C.	F.C.C.	H.C.P.
No. of atom	**1**	**2**	**4**	**6**
P.E.	**52.4%**	**68%**	**74%**	**74%**
Void space	**47.6%**	**32%**	**26%**	**26%**
C.N.	**6**	**8**	**12**	**12**
No. of T.V.	**0**	**0**	**8**	**12**
No. of O.V.	**0**	**0**	**4**	**6**
Relationship between edge length and radius	$r = \frac{a}{2}$	$r = \frac{\sqrt{3}a}{4}$	$r = \frac{a}{2\sqrt{2}}$	$r = \frac{a}{2}$
Type of Packing	**AAA Type**		**ABCABC Type**	**ABAB AB type**

- $d = \dfrac{Z \times M}{N_A \times a^3}$

  d = density z = number of atom in a unit cell.

  N_A = 6.022 × 10^{23}

Square Close Packing

- The spheres in the adjacent row lie just one over & show a horizontal & vertical alignment
- **Co-ord^n 4**
- Packing fraction = 78.5%

Hexagonal Close Packing

- The spheres in every second row are seated in the depression.
- **Co-ordn 6**
- Packing fraction = 90.75% (91%)

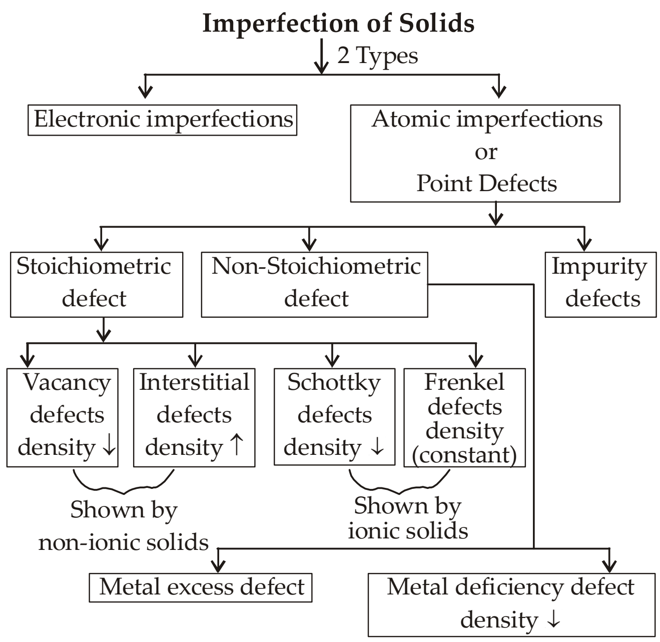
Tetrahedral Void

- **Co-ord^n = 4**
- **Radius Ratio=**$\dfrac{r_{void}}{r_{sphere}} = 0.225$
- **T.V's. Location at body diagonal**
- **Max No. of T.V. in one body diagonal = 2**
- **1st Nearest distn betn two T.V. = a/2**
- **2nd Nearest distn betn two T.V. =** $\dfrac{a}{\sqrt{2}}$
- **3nd Nearest distn betn two T.V. =** $\dfrac{\sqrt{3}a}{2}$
- **Distn betn Corner atom & T.V. =**$\dfrac{\sqrt{3}a}{4}$
- **Ratio betn T.V. & O.V. = 2 : 1**
- **Ratio betn T.V. & O.V. at 1 body digaonal=2:1**
- **Distance Between O.V. & T.V. =** $\dfrac{\sqrt{3}a}{4}$

Octahedral Void

- **Co-ordn = 6**
- **Radius Ratio=**$\dfrac{r_{void}}{r_{sphere}} = 0.414$
- **O.V's. Location at body center & as well as edge center**
- **Max No. of O.V. in one body diagonal = 1**
- **1st Nearest distn betn two O.V. =** $\dfrac{a}{\sqrt{2}}$
- **Distn betn edge center's O.V. & Body center's O.V. =** $\dfrac{a}{\sqrt{2}}$
- Diamond $= \dfrac{\pi\sqrt{3}}{6} = 0.34$

Defects in Crystal Structure :



➢ Radius ratio and co-ordination number (CN)

Limiting radius ratio	CN	Geometry
[0.155 – 0.225]	3	[Plane triangle]
[0.255 – 0.414]	4	[Tetrahedral]
[0.414 – 0.732]	6	[Octahedral]
[0.732 – 1]	8	[bcc]

➢ Relationship between radius of void (r) and the radius of the sphere (R): r (tetrahedral) **= 0.225 R; r (octahedral) = 0.414 R**

➢ Paramagnetic : Presence of unpaired electrons [attracted by magnetic field]

➢ **Ferromagnetic :**

Permanent magnetism [↑↑↑↑]

➢ **Antiferromagnetic :**

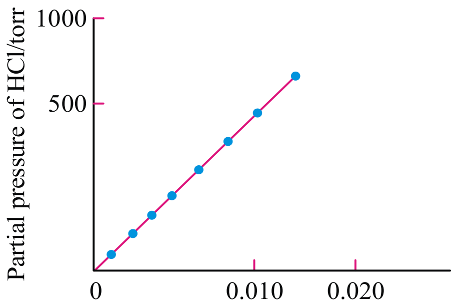
Net magnetic moment is zero [↑↓↑↓]

9. Solutions

Pressure of the Gas (or) Henry'a Law :

- The mass of a gas dissolved per unit volume of solvent is proportional to the pressure of the gas at constant temperature.
- **m α p or m = kp where k is Henry's constant**
- The partial pressure of the gas is proportional to the mole fraction of the gas (x) in the solution" and it is expressed as $p = K_H x$ Here K_H is the Henry' s law constant.

$\boxed{PP = K_H X_{gas}}$ $\boxed{PP = K_H \text{solubility}}$



Mole fraction of HCl in its Solution in cyclohexane

$\boxed{K_H \propto \frac{1}{\text{Solubility}}}$ $\boxed{\text{Solubility} \propto \frac{1}{\text{Temp}}}$

$\boxed{\text{Solubility} \propto p}$

$\boxed{\text{mass}_{Gas} \propto p}$

$\boxed{n_{Gas} \propto p}$

Positive Deviation	**Negative Deviation**
a) **Acetone + Ethanol**	a) **Acetone + Aniline**
b) **Acetone + CS_2**	b) **Acetone + $CHCl_3$**
c) **Acetone + C_6H_6**	c) **CH_3OH+CH_3COOH**
d) **$H_2O + CH_3OH$**	d) **$H_2O + HNO_3$**
e) **$H_2O + C_2H_5OH$**	e) **$CHCl_3$+$C_2H_5O–C_2H_5$**
f) **CCl_4 + toulene**	f) **H_2O + HCl**
g) **$CCl_4 + CHCl_3$**	g) **CH_3COOH+Pyridine**
h) **$CCl_4 + CH_3OH$** i)  **+ C_2H_5OH**	h) **$CHCl_3$ +** 

- Normality (N) = $\frac{\text{number of equivalents}}{\text{volume of the solution in litres}}$

- Molairty (M) = $\frac{\text{number of moles}}{\text{volume of the solution in litres}}$

- Raoult's law

  $P = p_A + p_B = p^\circ{}_A X_A + p^\circ{}_B X_B$

- Characteristics of an ideal solution :

  (i) $\Delta_{sol} V = 0$ (ii) $\Delta_{sol} H = 0$

- Relative lowering of vapour pressure

  $$= \frac{P_A^\circ - P_A}{P_A^\circ}; \quad \frac{P_A^\circ - P_A}{P_A^\circ} = X_B = \frac{n_B}{n_A + n_B}$$

- Colligative $\propto$ Number of particles ions/moles of solute properties

- Depression of freezing point, $\Delta T_f = K_f m$

- Elevation in boiling point with relative lowering of vapour pressure

  $$\Delta T_b = \frac{1000K_b}{M_1}\left(\frac{p^\circ - p}{p^\circ}\right) \text{ (}M_1 = \text{mol. wt. of solvent)}$$

- Osmotic pressure (P) with depression in freezing point $\Delta T_r P = \Delta T_r \times \frac{dRT}{1000K_f}$

- Relation between Osmotic pressure and other colligative properties :

i. $\pi = \frac{P_A^0 - P_A}{P_A^0} \times \frac{dRT}{M_B}$ Relative lowering of vapour pressure

ii. $\pi = \Delta T_b \times \frac{dRT}{1000K_b}$ Elevation in boiling point

iii. $\pi = \Delta T_f \times \frac{dRT}{1000K_f}$ Depression in freezing point

- $i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$

➢ Degree association a = $(1-i)\frac{n}{n-1}$ &

degree of dissociation (α) $=\frac{i-1}{n-1}$

Abnormal Molar mass

✪ **Electrolytes** undergo ionisation in aqueous solutions as a result number of particle in the solution increases hence magnitude of **colligative properties increases**.

van't Hoff's factor (i) =

a) $i = \frac{\text{observed colligative properties}}{\text{calculated colligative property}}$ (or)

b) $i = \frac{\text{Calculated molar mass of solute}}{\text{experimental molar mass of solute}}$ (or)

c) $i = \frac{\text{total number of moles of particles after dissociation or association}}{\text{number of moles of particles before dissociation or association}}$

d) $\boxed{i = \frac{\text{Normal / actual / Calculate / Original } M_{wt} \text{ of solute}}{\text{Abnormal / Observed / Theorical } M_{wt} \text{ of solute}}}$

Solute dissociation (or) Ionisation

If a **solute** is dissociated or ionised in solutions to give **'n' ions** and 'α' is the degree of ionisation,

	A_n	$\rightarrow$	nA
Initial moles	1		0

Number of moles after dissociation

$1-\alpha$ $\quad$ $n\alpha$

Degree of ionisation, $\boxed{\alpha = \frac{i-1}{n-1}}$

Solute association

If a solute is associated in solutions, n molecules associate and α is the degree of association,

	nA	A_n
Initial moles	**1**	**0**
Number of moles after dissociation	$1-\alpha$	α/n

Degree of ionisation, $\boxed{\alpha = \frac{1-i}{1-1/n}}$

Colligative properties with Van't Hoff factor :

Inclusion of **van't Hoff** factor modifies the equations for **colligative properties** as,

- Relative lowering of **vapour pressure** of solvent,

$$\frac{p^\circ - p}{p^\circ} = iX_{solute}$$

Depression of **freezing point**, $\Delta T_f = iK_f m$

Elevation of **boiling point**, $\Delta T_f = iK_b m$

Osmotic pressure of **solution**, $\pi = iCST$

AAJ KA TOPPER

10. Electrochemistry

Faraday's 1st Law

The mass of substance deposited at an electrode is directly proportional to charge pass through it.

Mass $\propto$ Charge (Q)

$W \propto Q$

$W = ZQ$ (Z = electrochemical equivalent)

(Q = Charge in Coulombs)

$W = Z\,I\,t$

I = current in Ampere

t = time in seconds

$W = Z\,Q$ (Q = 1C) **Remember**

then $W = Z$

1 F charge deposits

1 g eq of any substance

So $W = \frac{E\,I\,t}{F}$ sec of substance

= No. of faradays

Faraday's 2nd Law

If equal electricity is passed through two or more cells connected in series then the mass of substance deposited is directly proportional to equivalent mass

$W_1 \propto E_1$

$W_2 \propto E_2$

$$\frac{W_1}{E_1} = \frac{W_2}{E_2}$$

- Degree of dissociation : $\alpha = \frac{\lambda_{eq}}{\lambda^0_{eq}}$

- Kohlraush's law : $\Lambda^0_m = x\lambda^0_A + y\lambda^0_B$

- **Under standard conditions (E°)**

$E^o_{cell} = E^o_{RP}(\text{cathode}) - E^o_{RP}(\text{anode})$ (or)

$E^o_{cell} = E^o_{OP}(\text{anode}) - E^o_{OP}(\text{cathode})$ (or)

$E^o_{cell} = E^o_{OP}(\text{anode}) + E^o_{RP}(\text{cathode})$

- Nernst Equation

$$E = E^\circ - \frac{0.0591}{n}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]}$$

$$\& \; E^\circ_{Cell} = E^\circ_{right} + E^\circ_{left} \; \& \; K_{eq.} = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right]$$

$\Delta G = -nFE_{cell}$ &

$\Delta G^\circ = -nFE^\circ cell = -2.303\,RT\log K_c$

$$\& \; W_{max} = +nFE^\circ \; \& \; \Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

- **Application of Nernst Equation**

To find the $\mathbf{E_{cell}}$ of concentration cells

$$E_{cell} = \frac{0.059}{n}\log_{10}\left(\frac{C_2}{C_1}\right) \text{(for conc}^n\text{ cell } \mathbf{E^o_{cell} = 0})$$

To find the pH of concentration cell

For the measurement of Eq. constant (**K**)

$$\boxed{\mathbf{E^0_{cell} = \frac{0.059}{n}\log_{10}K_C}}$$

- Calculation of pH of an electrolyte by using a calomel electrode :

$$pH = \frac{E_{cell} - 0.2415}{0.0591}$$

- Thermodynamic efficiency of fuel cells :

$\eta = \frac{-\Delta G}{\Delta H} = \frac{-nFE^\circ_{cell}}{\Delta H}$ For $H_2 - O_2$ fuel cells it is 95%.

- $P = K_H.X$

Summing-up the Units of Different Quantities					
S.N.	Physical	Symbol	Expression	Commonly used Units	SI Units
1.	Resistance	Rq	$\mathbf{R = \frac{V}{I}}$	omh (Ω)	omh (Ω)
2.	Conductance	G	$\mathbf{R = \frac{1}{R}}$	omh^{-1} (Ω^{-1})	seimen(S)
3.	Specific resistance	ρ	$\rho = \frac{a}{1}$	ohm cm	ohm m
4.	Conductivity	k	$k = G\frac{l}{a} = \frac{1}{R}\frac{l}{a} = \frac{l}{p}$	ohm^{-1}cm^{-1} (Ω^{-1}cm^{-1})	S m^{-1}
5.	Equivalent conductivity	Λ_{eq}	$\Lambda_{eq} = \frac{k}{\text{normality}}$	ohm^{-1}cm^2 eq^{-1}(Ω^{-1}cm^{2}eq^{-1})	S m^2 eq^{-1}
6.	Molar conductivity	Λ_m	$\Lambda_m = \frac{k}{\text{molarity}}$	ohm^{-1}cm^2 eq^{-1}(Ω^{-1}cm^{2}eq^{-1}) S	m^2 mol^{-1}
7.	Cell constant	G*	$G^* = \frac{l}{a}$	cm^{-1}	m^{-1}

Effect of dilution on

Conductance → Increases

Λ_m & Λ_{eq} → Increases

Conductivity → Decreases

Debye–Huckel–Onsager equation :

$\Lambda_m = \Lambda^0_m - b\sqrt{C}$ (or) $\Lambda_{eq} = \Lambda^o_{eq} - b\sqrt{C}$

Λ_m = Molar conductance at given concentration

Λ^0_m = Molar conductance at infinite dilution

C = concentration in molarity.

b = Constant value depends on type of electrolyte, solvent & temp.

- With dilution the Degree of dissociation of weak electrolyte increases, so Λ_m increases.

11. Chemical Kinetics

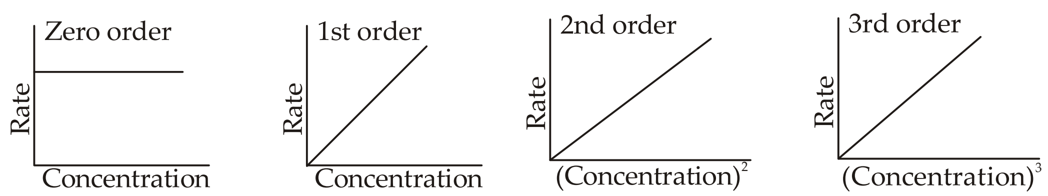
➢ **Rate of reaction =** Rate of disappearance of A

$$= \frac{\text{Decrease in concentration of A}}{\text{Time interval}} \quad \textbf{= Rate of appearance of B} = \frac{\text{Increase in concentration of B}}{\text{Time interval}}$$

Order	Integrated rate equation	Unitss of k obtained by plotting t vs	Straight line to	$t_{1/2}$ proportional
0	$k = \frac{1}{t}\{[A_0]-[A]\}$	mol L^{-1} s^{-1}	a – x	a
1	$k = \frac{2.303}{t}\log\frac{a}{a-x}$	s^{-1}	log (a – x)	independent of a
2	$k = \frac{x}{ta(a-x)}$ or	L mol^{-1} s^{-1}	$\frac{1}{(a-x)}$	$\frac{1}{a}$
	$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$	L mol^{-1} s^{-1}		$\frac{1}{a}$
n	$k = \frac{1}{t(n-1)}\left[\frac{1}{(a-x)^{n-1}}-\frac{1}{a^{n-1}}\right]$	L^{n-1} mol^{1-n} s^{-1}	$\frac{1}{(a-x)^{n-1}}$	$\frac{1}{a^{n-1}}$

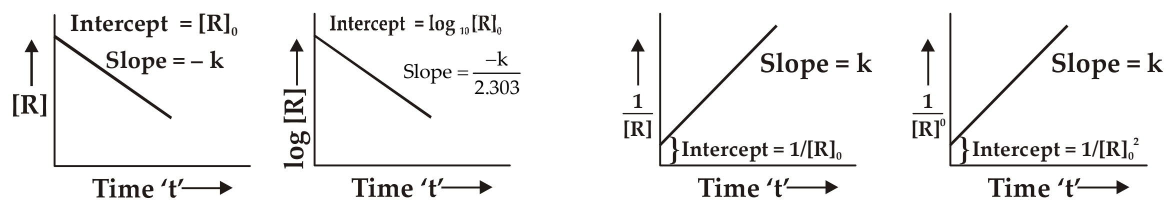
➢ **Some important graphs of diffrent order of reactions are given below :**

(a) Plots of rate vs concentrations

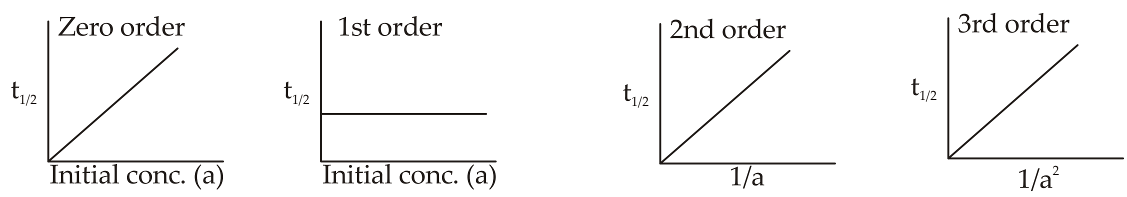


(b) Plots of integrated rate equations

Zero order **First Order** **Second Order** **Third Order**



(c) Plots of half-lives vs initial concentration



If reaction completion is given in percent, then take initial concentration (a) 100 and if reaction completion is given in fraction, then take initial concentration as 1.

Questions based on $t_{1/2}$ can be solved by another method also based on following diagram.

- **Order of reaction** It can be fraction, zero or any whole number.
- **Molecularity of reaction** is always a whole number. It is never more than three. It cannot be zero.
- **First Order Reaction :**

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)} \; \& \; t_{1/12} = \frac{0.693}{k} [A]_t = [A]_0 e^{-kt}$$

- **Zero Order Reaction :** $x = kt$ and $t_{1/2} = \frac{a}{2k}$

  The rate of reaction is independent of the concentration of the reacting substance.

- Time of n^{th} fraction of first order process,

$$t_{1/n} = \frac{2.303}{k}\log\left(\frac{1}{1-\frac{1}{n}}\right)$$

- Amount of substance left after 'n' half lives = $\frac{[A]_0}{2^n}$
- Arrhenius gave a mathematical expression to deduce the relationship between rate constant and temperature.

$$\boxed{k = Ae^{-E_a/RT}}$$

where, A is frequency factor and it is constant

E_a is activation energy

R is gas constant, T is temperature

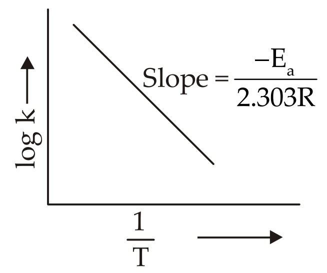
On taking log on both sides

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

Arrhenius equation : $\log k = -\frac{E_a}{2.303RT} + \log A$

This is an equation of straight line of the form y = mx + c.

If we draw a graph between log k and (1/T), we get a straight line with slope equal to $\frac{-E_a}{2.303R}$.



E_a can be calculated by measuring the slope of the lines. $E_a = -\text{slope} \times 2.303\ R$

If k_1 and k_2 are rate constants at temperatures T_1 and T_2 respectively then,

$$\boxed{\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$$

Factor $e^{-\frac{E_a}{RT}}$ in the Arrhenius equation is known as 'Boltzmann factor'.

Activation Energy

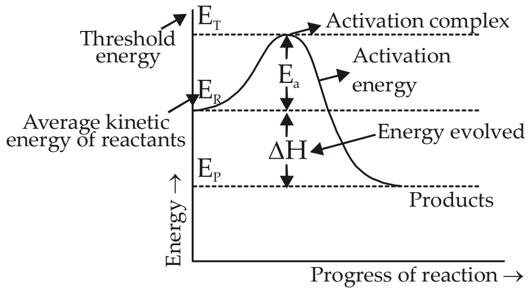
The minimum amount of energy absorbed by the reactant mole ules so that their energy becomes equal to threshold energy is called activation energy.

Or, we can say that it is the difference between threshold energy and the average kinetic energy possessed by reactant molecules.

Activation energy = Threshold energy – Average kinetic energy of reactant.

Arrhenius equation : $\log k = -\frac{E_a}{2.303RT} + \log A$

This is an equation of straight



➢Temperature coefficient (n) = $\frac{\text{Rate constant at (T+10°)}}{\text{Rate constantat T}}$

12. Surface Chemistry

- **Emulsion :** Colloidal soln. of two immiscible liquids [O/W emulsion, W/O emulsion]
- **Emulsifier :** Long chain hydrocarbons are added to stabilize emulsion.
- **Lyophilic colloid :** Starchy gum, gelatin have greater affinity for solvent.
- **Lyophobic colloid :** No affinity for solvent, special methods are used to prepare sol. [e.g. As_2S_3, $Fe(OH)_3$ sol]
- **Preparation of colloidal solution :**

  i. Disperision methods ii. Condensation method
- **Properties of colloidal solution :**

  i. Tyndal effect ii. Brownian movement

  iii. Coagulation iv. Filtrability
Positively charged colloid	Negatively charged colloid
Hydrated metallic oxide	Metal Cu, Ag, Au, Sol
$Al_2O_3.xH_2O$, $CrO_3.xH_2O$, $Fe_2O_3.xH_2O$	Metallic sulphides As_2S_3, Sb_2S_3, CdS sol
Basic dye stuffs methylene blue sol,	Acid dy stuff eosin, congo red
Haemoglobin (blood)	
Oxide TiO_2 Sol	Sols of starch, gum gelatin, clay
- **Hardy Schulze Rule**- This rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion.

• The higher the valency of the flocculating ion, the greater is its pricipitating power. Thus for the precipitation of As_2S_3sol (–ve) the precipitating power of Al^{3+}, Ba^{2+}, and Na^+ ions is in the order $Al^{3+} > Ba^{2+} > Na^+$.

• Similarly for precipitating $Fe(OH)_3$ sol (positive) the precipitating power of $[Fe(CN)_6]^{-3}$, SO_4^{2-} and Cl^- ions is in the order

$[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$

- The minimum concentration of an electrolyte in milli moles required to cause precipitation of 1 litre sol in 2 hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

Flocculation value $\alpha \dfrac{1}{\textbf{Flocculation power}}$

➢ **Gold Number**

- The number of a hydrophilic colloid that will jsut prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 10% NaCl solution is known as **Gold number** of that protector (Lyophilic colloid).
- The precipitation of the gold sol is indicated by a colour change from red to blue when the particle size just increases.
- The smaller the gold number of a protective Lyophilic colloid, **greater is its protection** power.
- **Note :** Gelatin and startch have the maximum & minimum protective powers.

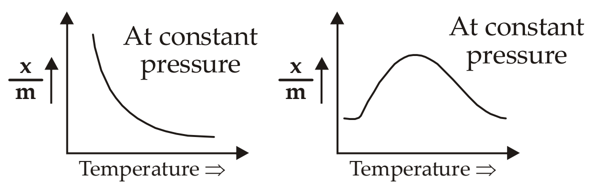
- **Protection Capacity** $\alpha \dfrac{1}{\textbf{Gold number}}$

➢ **Effect of temperature :**

⇒ **Extent of Adsorption** $\left(\dfrac{x}{m}\right)$

x ⇒ Mass of adsorbate

m ⇒ Mass of adsorbent



[A] Physisorption [B] Chemisorption

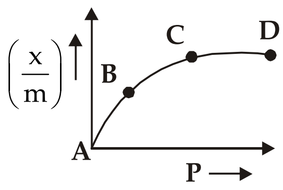
➢ **Effect of pressure :**

The variation in extent of adsorption with change in pressure at constant temperature can be explained with the help of some graphs called as adsorption isotherms.

i. Freundlish adsorption isotherm :

For physisorption, Freundlish explained the variation in adsorption due to the change in pressure graphically and mathematically as follows :

Here Adsorbate - Gas and Adsorbent - Solid



Case-I At low pressure (A → B)

$\dfrac{x}{m} \propto P$

Case-II At high pressure (C → D)

$\dfrac{x}{m} \propto P^0$

Case - III At intermediate pressure (B → C)

$\dfrac{x}{m} \propto P^{1/n}$ [Where n = 1 to ∞]

The resultant condition $\dfrac{x}{m} = KP^{1/n}$

At low pressure n = 1

At high pressure **n = ∞**

At intermediate pressure **1 < n < ∞**

∴ The value of (1/n) ranges from **0** to **1**.

Here,

x ⇒ Mass of adsorbate

m ⇒ Mass of adsorbent

p ⇒ pressure of adsorbate gas

K and **n** ⇒ Constants that depends on the nature of adsorbate and adsorbent.