CHEMICAL KINETICS & REDIOACTIVITY

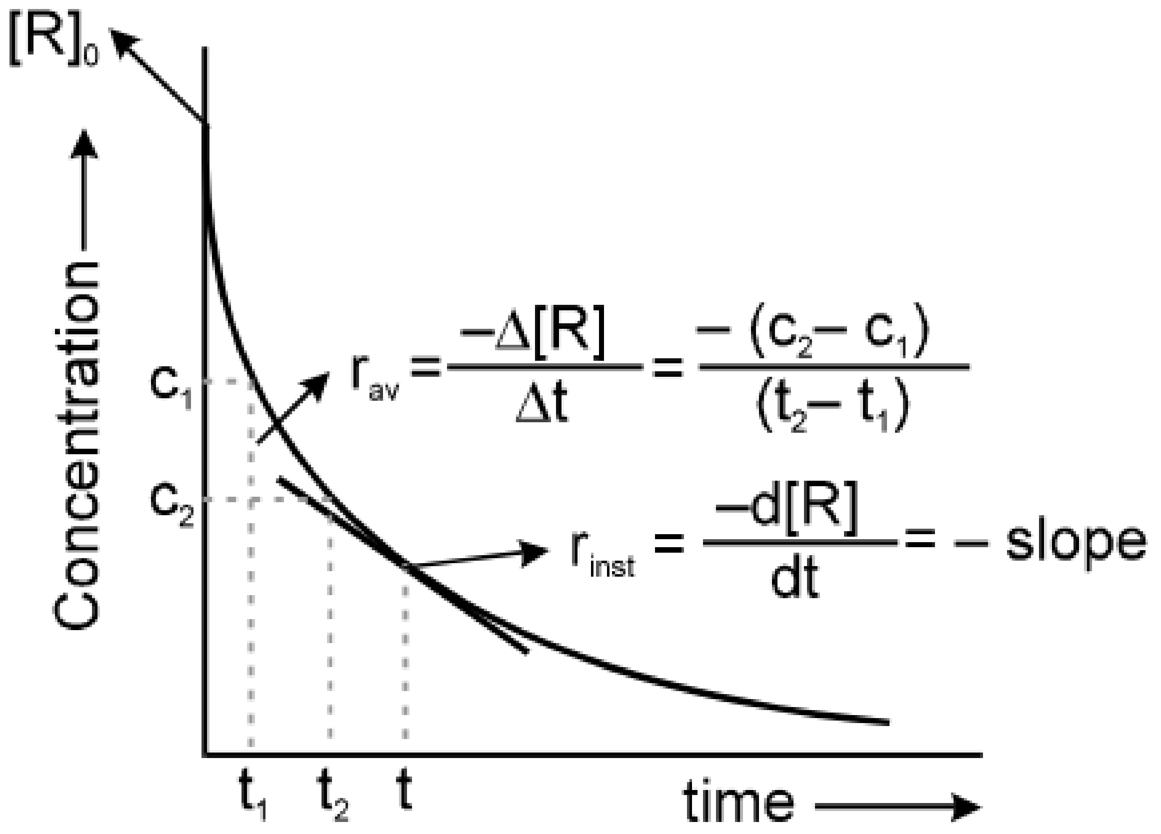
RATE/VELOCITY OF CHEMICAL REACTION :

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec}} = \text{mol lit}^{-1}\ \text{time}^{-1} = \text{mol dm}^{-3}\ \text{time}^{-1}$$

Types of Rates of chemical reaction :

For a reaction R $\longrightarrow$ P

$$\textbf{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$



$$R_{\text{instantaneous}} = \lim_{t \to 0} \left[\frac{\Delta c}{\Delta t}\right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :

Rate = K (conc.)^{order} – differential rate equation or rate expression

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = $(\text{conc})^{1-\text{order}}\ \text{time}^{-1}$

Order of reaction :

$m_1A + m_2B \longrightarrow$ products.

$R \propto [A]^p\ [B]^q$ Where p may or may not be equal to m_1 & similarly q may or may not be equal to m_2.

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is **overall order of the reaction.**

INTEGRATED RATE LAWS :

C_0 or 'a' is initial concentration and C_t or a – x is concentration at time 't'

(a) **zero order reactions :**

Rate = k [conc.]° = constant

$$\text{Rate} = k = \frac{C_0 - C_t}{'t'} \quad \text{or} \quad C_t = C_0 - kt$$

Unit of K = mol lit^{-1} sec^{-1}, Time for completion = $\frac{C_0}{k}$

$$\text{at } t_{1/2},\ C_t = \frac{C_0}{2},\ \text{so } kt_{1/2} = \frac{C_0}{2} \Rightarrow \quad \mathbf{t_{1/2} = \frac{C_0}{2k}} \qquad \therefore t_{1/2} \propto C_0$$

(b) **First Order Reactions :**

(i) Let a 1st order reaction is, $A \longrightarrow$ Products

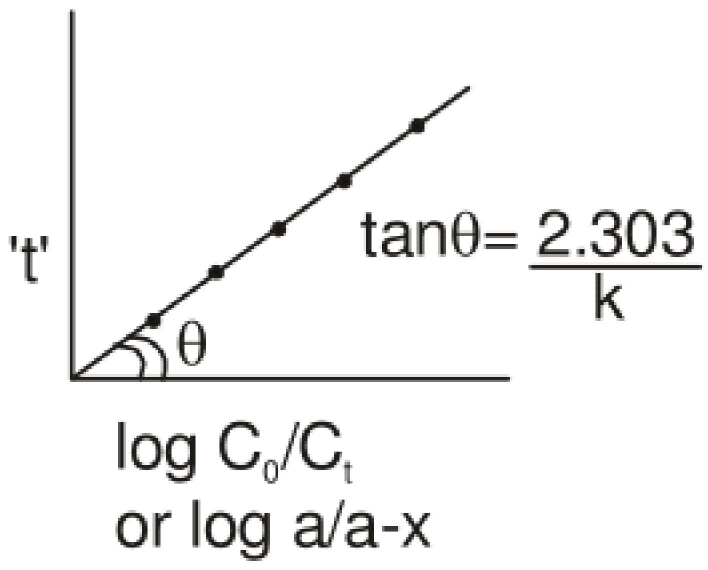
$$\mathbf{t = \frac{2.303}{k} \log \frac{a}{a-x}} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

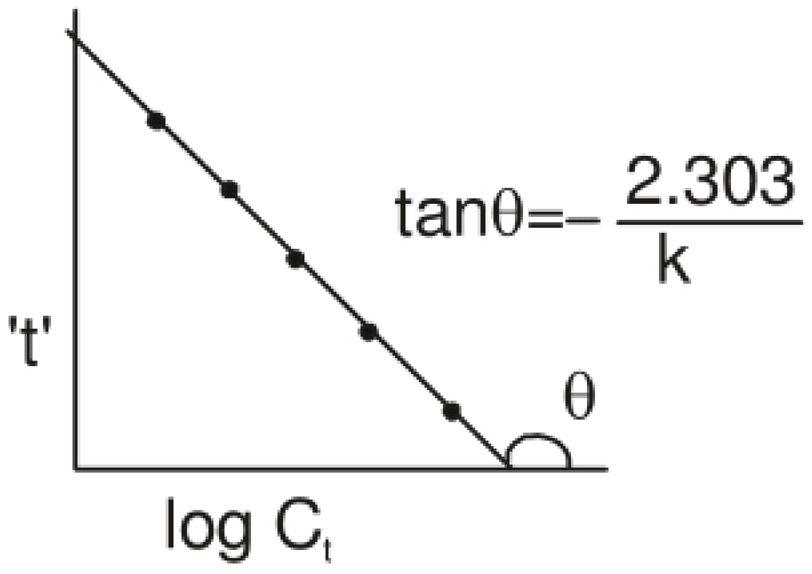
$$\Rightarrow \quad t_{1/2} = \frac{\ell n 2}{\mathbf{k}} \mathbf{=} \frac{0.693}{\mathbf{k}} = \text{Independent of initial concentration.}$$

$$t_{Avg.} = \frac{1}{k} = 1.44\ t_{1/2}.$$

Graphical Representation :

$$t = -\frac{2.303}{k} \log C_t + \frac{2.303}{k} \log C_0$$





(c) **Second order reaction :**

2nd order Reactions

Two types

$A \quad + \quad A \longrightarrow$ products	$A \quad + \quad B \longrightarrow$ products.
a a	a b 0
(a – x) (a –x)	a – x b – x
$\therefore \frac{dx}{dt} = k\,(a-x)^2$	$\frac{dx}{dt} = k\,(a-x)\,(b-x)$
$\Rightarrow \frac{1}{(a-x)} - \mathbf{\frac{1}{a} = kt}$	$\mathbf{k =} \frac{2.303}{t(a-b)} \mathbf{\log} \frac{b(a-x)}{a(b-x)}$

METHODS TO DETERMINE ORDER OF A REACTION

(a) Initial rate method :

$r = k\,[A]^a\,[B]^b\,[C]^c$ if $[B]$ = constant
$[C]$ = constant

then for two different initial concentrations of A we have

$r_{0_1} = k\,[A_0]_1^a$, $r_{0_2} = k\,[A_0]_2^a$

$$\Rightarrow \quad \frac{r_{0_1}}{r_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^a$$

(b) Using integrated rate law : It is method of trial and error.

(c) Method of half lives :

for nth order reaction $t_{1/2} \propto \dfrac{1}{[R_0]^{n-1}}$

(d) Ostwald Isolation Method :

rate $= k\,[A]^a\,[B]^b\,[C]^c = k_0\,[A]^a$

METHODS TO MONITOR THE PROGRESS OF THE REACTION :

(a) ***Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature or by measuring total volume of mixture under constant pressure and temperature.***

$$\therefore \quad \mathbf{k} = \frac{2.303}{t}\ \log\ \frac{P_0(n-1)}{nP_0 - P_t}$$

{Formula is not applicable when n = 1, the value of n can be fractional also.}

(b) ***By titration method :***

1. $\therefore\ a \propto V_0$ $\quad a - x \propto V_t \quad \Rightarrow \quad k = \dfrac{2.303}{t}\ \log\ \dfrac{V_0}{V_t}$

2. Study of acid hydrolysis of an easter.

$$k = \frac{2.303}{t}\ \log\ \frac{V_\infty - V_0}{V_\infty - V_t}$$

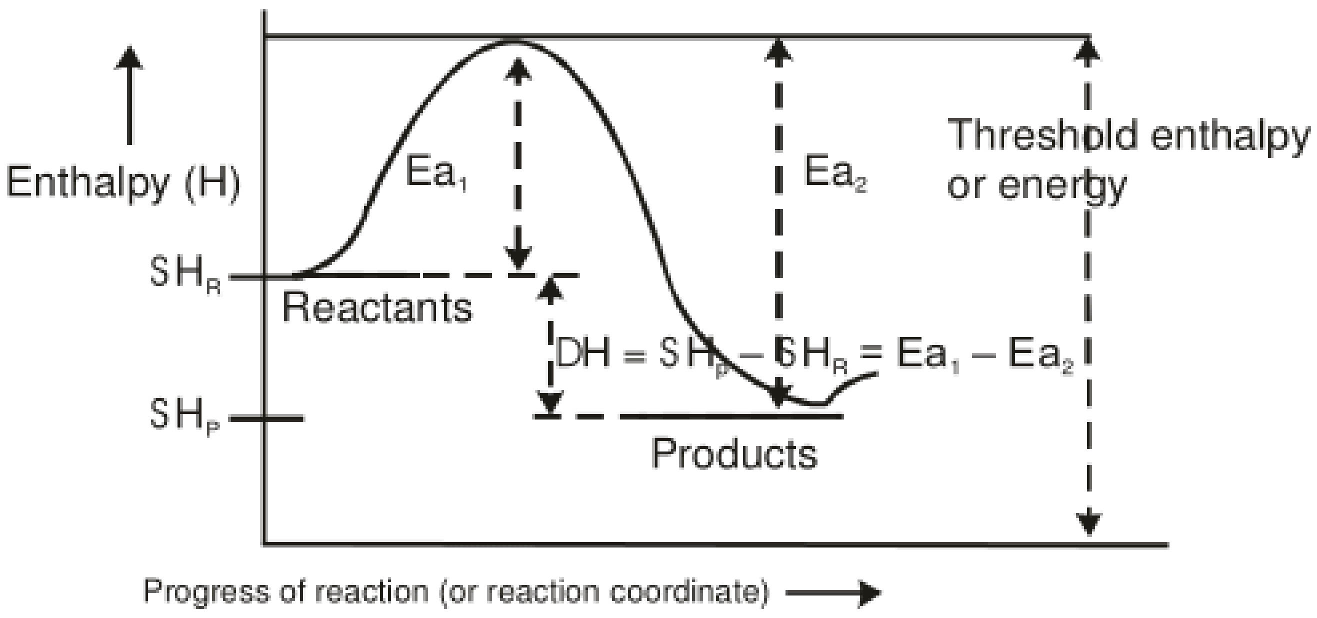
(c) ***By measuring optical rotation produced by the reaction mixture :***

$$k = \frac{2.303}{t}\ \log\left(\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}\right)$$

EFFECT OF TEMPERATURE ON RATE OF REACTION.

$$\text{T.C.} = \frac{K_{t+10}}{K_t} \approx 2 \text{ to } 3 \text{ (for most of the reactions)}$$

Arhenius theroy of reaction rate.



SH_R = Summation of enthalpies of reactants
SH_P = Summation of enthalpies of reactants
DH = Enthalpy change during the reaction
Ea_1 = Energy of activation of the forward reaction
Ea_2 = Energy of activation of the backward reaction

$$E_P > E_r \qquad \rightarrow \text{endothermic}$$
$$E_P < E_r \qquad \rightarrow \text{exothermic}$$

$$\Delta H = (E_P - E_r) = \text{enthalpy change}$$
$$\Delta H = E_{af} - E_{ab}$$
$$E_{threshold} = E_{af} + E_r = E_b + E_p$$

Arhenius equation

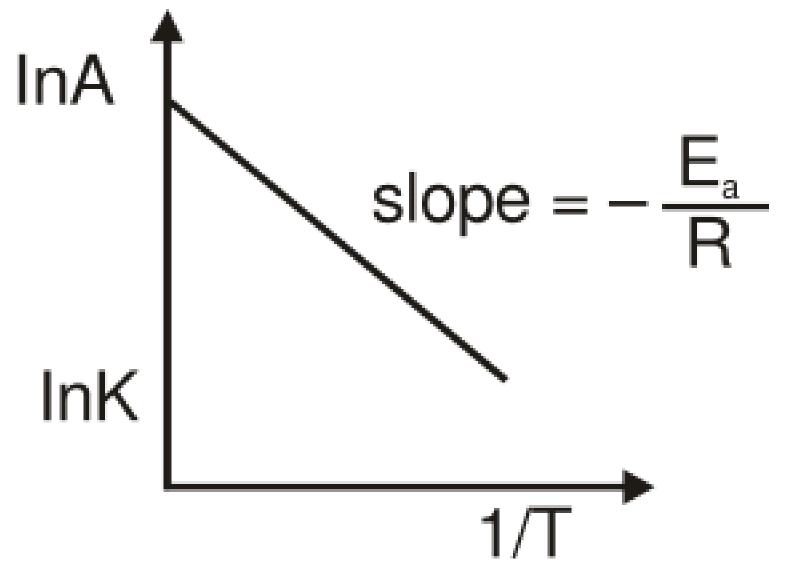
$$k = Ae^{-E_aRT} \qquad\qquad r = k\,[\text{conc.}]^{\text{order}}$$

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \qquad\qquad \log k = \left(-\frac{Ea}{2.303\ R}\right)\frac{1}{T} + \log A$$

If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}.\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

❖ $\ln k = \ln A - \dfrac{E_a}{RT}$



$E_a \geq O$

❖ $T \rightarrow \infty$, $K \rightarrow A$.

SOLID STATE

❍ Classification of Crystal into Seven System

Crystal System	Unit Cell Dimensions and Angles	Bravais Lattices	Example
Cubic	$a = b = c\ ;\ \alpha = \beta = \gamma = 90°$	SC, BCC, FCC	NaCl
Orthorhombic	$a \neq b \neq c\ ;\ \alpha = \beta = \gamma = 90°$	SC, BCC, end centred & FCC	S_R
Tetragonal	$a = b \neq c\ ;\ \alpha = \beta = \gamma = 90°$	SC, BCC	Sn, ZnO_2
Monoclinic	$a \neq b \neq c\ ;\ \alpha = \gamma = 90° \neq \beta$	SC, end centred	S_M
Rhombohedral	$a = b = c\ ;\ \alpha = \beta = \gamma \neq 90°$	SC	Quartz
Triclinic	$a \neq b \neq c\ ;\ \alpha \neq \beta \neq \gamma \neq 90°$	SC	H_3BO_3
Hexagonal	$a = b \neq c\ ;\ \alpha = \beta = 90°; \gamma = 120°$	SC	Graphite

❍ ANALYSIS OF CUBICAL SYSTEM

	Property	SC	BCC	FCC
(i)	atomic radius (r) a = edge length	$\frac{a}{2}$	$\frac{\sqrt{3}}{4}a$	$\frac{a}{2\sqrt{2}}$
(ii)	No. of atoms per unit cell (Z)	1	2	4
(iii)	C.No.	6	8	12
(iv)	Packing efficiency	52%	68%	74%
(v)	No. voids			
	(a) octahedral (Z)	__	__	4
	(b) Tetrahderal (2Z)	__	__	8

❍ NEIGHBOUR HOOD OF A PARTICLE :

(I) Simple Cubic (SC) Structure :

Type of neighbour	Distance	no.of neighbours
nearest	a	6 (shared by 4 cubes)
$(\text{next})^1$	$a\sqrt{2}$	12 (shared by 2 cubes)
$(\text{next})^2$	$a\sqrt{3}$	8 (unshared)

(II) Body Centered Cubic (BCC) Structure :

Type of neighbour	Distance	no.of neighbours
nearest	$2r = a\frac{\sqrt{3}}{2}$	8
$(\text{next})^1$	$= a$	6
$(\text{next})^2$	$= a\sqrt{2}$	12

(III) Face Centered Cubic (FCC) Structure :

Type of neighbour	Distance	no. of neighbours
nearest	$\frac{a}{\sqrt{2}}$	$12 = \left(\frac{3 \times 8}{2}\right)$
$(\text{next})^1$	a	$6 = \left(\frac{3 \times 8}{4}\right)$
$(\text{next})^2$	$a\sqrt{\frac{3}{2}}$	24

❍ DENSITY OF LATTICE MATTER (d) = $\frac{Z}{N_A}\left(\frac{M}{a^3}\right)$

where N_A = Avogadro's No. M = atomic mass or molecular mass.

❍ IONIC CRYSTALS

C.No.	Limiting radius ratio $\left(\frac{r_+}{r_-}\right)$
3	0.155 – 0.225 (Triangular)
4	0.225 – 0.414 (Tetrahedral)
6	0.414 – 0.732 (Octahedral)
8	0.732 – 0.999 (Cubic).

❍ EXAMPLES OF A IONIC CRYSTAL

(a) Rock Salt (NaCl) Coordination number (6 : 6)

(b) CsCl C.No. (8 : 8)

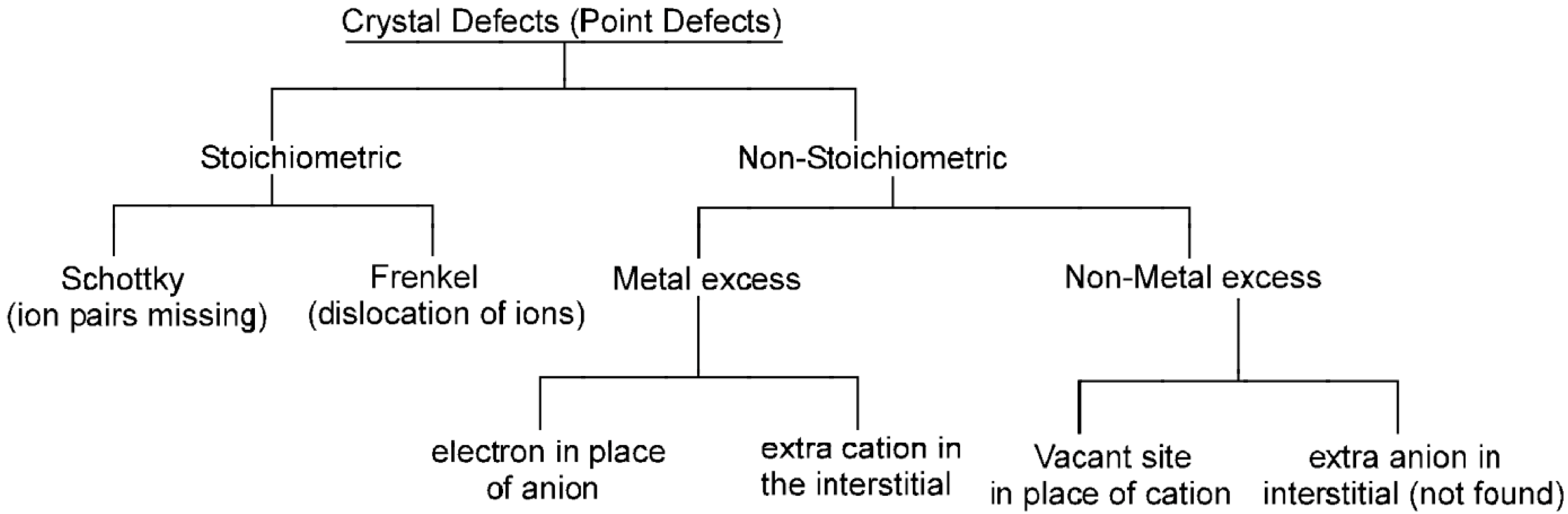
Edge length of unit cell :-

$$a_{sc} = \frac{2}{\sqrt{3}}(r_+ + r_-)$$

(c) Zinc Blende (ZnS) C.No. (4 : 4) $a_{fcc} = \frac{4}{\sqrt{3}}(r_{Zn^{2+}} + r_{s^{2-}})$

(d) Fluorite structure (CaF_2) C.No. (8 : 4) $a_{fcc} = \frac{4}{\sqrt{3}}(r_{Ca^{2+}} + r_{F^-})$

Crystal Defects (Imperfections)



SOLUTION & COLLIGATIVE PROPERTIES

OSMOTIC PRESSURE :

(i) $\pi = \rho gh$ Where, ρ = density of soln., h = equilibrium height.

(ii) **Vont – Hoff Formula** (For calculation of O.P.)

$$\pi = CST$$

$$\pi = CRT = \frac{n}{V} RT \text{ (just like ideal gas equation)}$$

$\therefore$ C = total conc. of all types of particles.

$$= C_1 + C_2 + C_3 + \ldots\ldots\ldots\ldots\ldots\ldots$$

$$= \frac{(n_1 + n_2 + n_3 + \ldots\ldots\ldots)}{V}$$

Note : If V_1 mL of C_1 conc. + V_2 mL of C_2 conc. are mixed.

$$\pi = \left(\frac{C_1V_1 + C_2V_2}{V_1 + V_2}\right)RT \quad ; \qquad \pi = \left(\frac{\pi_1V_1 + \pi_2V_2}{RT}\right)$$

Type of solutions :

(a) Isotonic solution – Two solutions having same O.P.

$\pi_1 = \pi_2$ (at same temp.)

(b) Hyper tonic– If $\pi_1 > \pi_2$. $\Rightarrow$ Ist solution is hypertonic solution w.r.t. 2nd solution.

(c) Hypotonic – IInd solution is hypotonic w.r.t. Ist solution.

Abnormal Colligative Properties : (In case of association or dissociation)

VANT HOFF CORRECTION FACTOR (i) :

$$i = \frac{\text{exp/observed/actual/abnormal value of colligative property}}{\text{Theoritical value of colligative property}}$$

$$= \frac{\text{exp./observed no. of particles / conc.}}{\text{Theoritical no. of particles}} = \frac{\text{observed molality}}{\text{Theoritical molality}}$$

$$= \frac{\text{theoretical molar mass (formula mass)}}{\text{experimental/observed molar mass (apparent molar mass)}}$$

- $i > 1 \Rightarrow$ dissociation.
  $i < 1 \Rightarrow$ association.

- $$i = \frac{\pi_{exp.}}{\pi_{theor}}$$

$\therefore \quad \pi = iCRT$

$$\pi = (i_1C_1 + i_2C_2 + i_3C_3\ldots\ldots)\,RT$$

Relation between i & α (degree of dissociation) :

$i = 1 + (n - 1)\alpha$ Where, $n = x + y$.

Relation b/w degree of association β & i.

$$i = 1 + \left(\frac{1}{n} - 1\right)\beta$$

RELATIVE LOWERING OF VAPOUR PRESSURE (RLVP) :

Vapour pressure : $P_{\text{Soln.}} < P$

Lowering in VP $= P - P_S = \Delta P$

Relative lowering in vapour pressure RLVP $= \dfrac{\Delta P}{P}$

Raoult's law : (For non – volatile solutes)

Experimentally relative lowering in V.P = mole fraction of the non volatile solute in solutions.

$$\text{RLVP} = \frac{P - P_s}{P} = X_{\text{Solute}} = \frac{n}{n+N}$$

$$\boxed{\frac{P - P_s}{P_s} = \frac{n}{N}}$$

$$\boxed{\frac{P - P_s}{P_s} = (\text{ molality }) \times \frac{M}{1000}}$$ (M = molar mass of solvent)

If solute gets associated or dissociated

$$\frac{P - P_s}{P_s} = \frac{i.n}{N}$$

$$\frac{P - P_s}{P_s} = i \times (\text{molality}) \times \frac{M}{1000}$$

- According to Raoult's law

  (i) $p_1 = p_1^0 X_1$. where X_1 is the mole fraction of the solvent (liquid).

  (ii) An alternate form → $\dfrac{p_1^0 - p_1}{p_1^0} = X_2$.

Elevation in Boiling Point :

$$\Delta T_b = i \times K_b m$$

$$K_b = \frac{RT_b^{\,2}}{1000 \times L_{vap}} \qquad \text{or} \qquad K_b = \frac{RT_b^{\,2} M}{1000 \times \Delta H_{vap}}$$

$$L_{vap} = \left(\frac{\Delta H_{vap}}{M}\right)$$

Depression in Freezing Point :

$$\therefore \Delta T_f = i \times K_f . m.$$

$$K_f = \text{molal depression constant} = \frac{RT_f^{\,2}}{1000 \times L_{fusion}} = \frac{RT_f^{\,2} M}{1000 \times \Delta H_{fusion}} .$$

Raoult's Law for Binary (Ideal) mixture of Volatile liquids :

$\mathbf{P_A = X_A P_A^o}$ $\therefore$ $\mathbf{P_B = X_B P_B^\circ}$

if $P_A^\circ > P_B^\circ$ $\therefore$ A is more volatile than B

$\therefore$ B.P. of A < B.P. of B

$\therefore$ According to Dalton's law

$$\mathbf{P_T = P_A + P_B = X_A P_A^0 + X_B P_B^0}$$

x_A' = mole fraction of A in vapour above the liquid / solution.

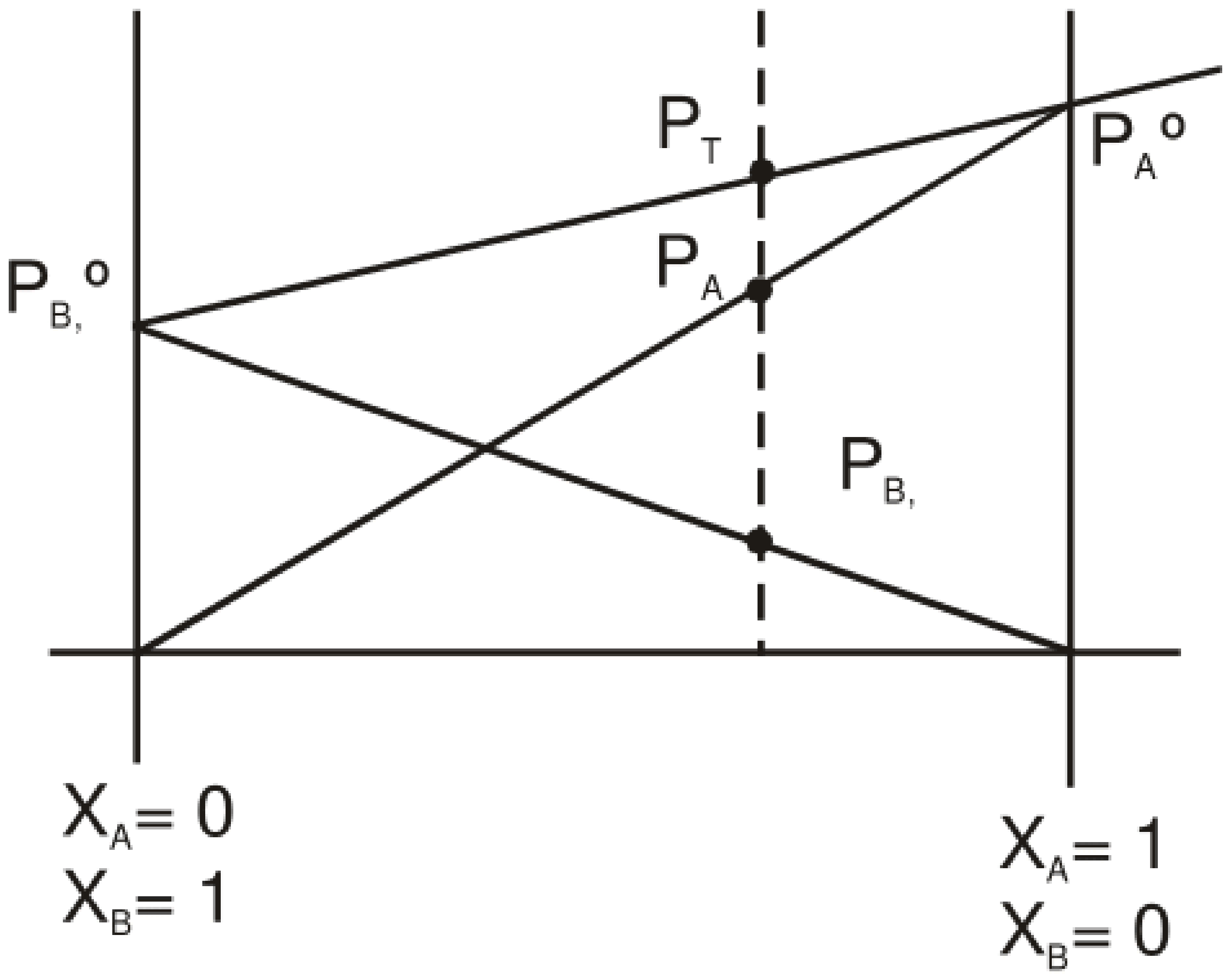
x_B' = mole fraction of B

$$\mathbf{P_A = X_A P_A^\circ = X_A' P_T}$$

$$\mathbf{P_B = X_B' P_T = X_B P_B^o}$$

$$\frac{1}{P_T} = \frac{x_A'}{P_A^o} + \frac{x_B'}{P_B^o} .$$

Graphical Representation :



A more volatile than B ($P_A^o > P_B^o$)

Ideal solutions (mixtures) :

Mixtures which follow Raoul'ts law at all temperature.

A ------ A $\Rightarrow$ A -------- B,
B ----- B

$\Delta H_{mix} = 0$: $\Delta V_{mix} = 0$:
$\Delta S_{mix} = +$ ve as for process to proceed : $\Delta G_{mix} = -$ ve

eg. **(1) Benzene + Toluene.**
(2) Hexane + heptane.
(3) $C_2H_5Br + C_2H_5I$.

Non-Ideal solutions : Which do not obey Raoult's law.

(a) Positive deviation : –

(i) $P_{T,exp} > (X_A P^o_A + X_B P_B{}^o)$

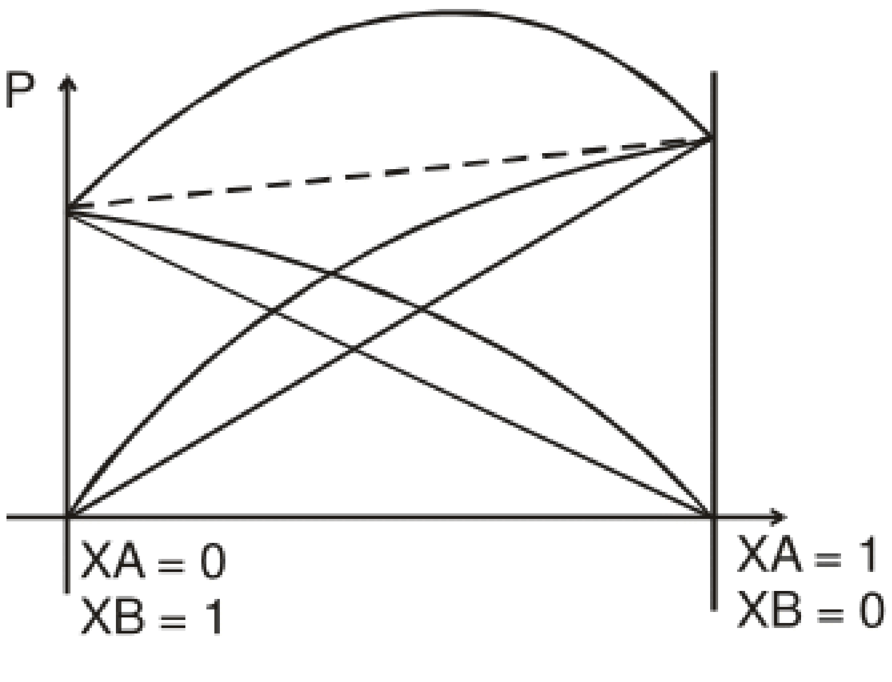
(ii) $\begin{matrix} A - - - - A \\ B - - - - B \end{matrix} > A ---- B$

$\downarrow$

Force of attraction

(iii) $\Delta H_{mix} = +ve$ energy absorbed
(iv) $\Delta V_{mix} = +ve$ (1L + 1L > 2L)
(v) $\Delta S_{mix} = +ve$
(vi) $\Delta G_{mix} = -ve$

eg. **$H_2O + CH_3OH$.**
$H_2O + C_2H_5OH$
C_2H_5OH + hexane
C_2H_5OH + cyclohexane.
$CHCl_3 + CCl_4 \rightarrow$ dipole dipole interaction becomes weak.



$P^0A > P^0B$

(b) Negative deviation

(i) $P_T \exp < X_A P_A{}^o + X_B P^o{}_B$

(ii) $\begin{matrix} A - - - - A \\ B - - - - B \end{matrix} < A ------ B.$

strength of force of altraction.

(iii) $\Delta H_{mix} = -ve$ (iv) $\Delta V_{mix} = -ve$ (1L + 1L < 2L)

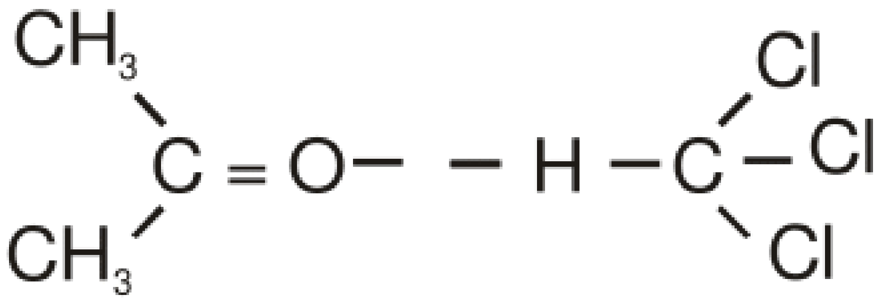
(v) $\Delta S_{mix} = +ve$ (vi) $\Delta G_{mix} = -ve$

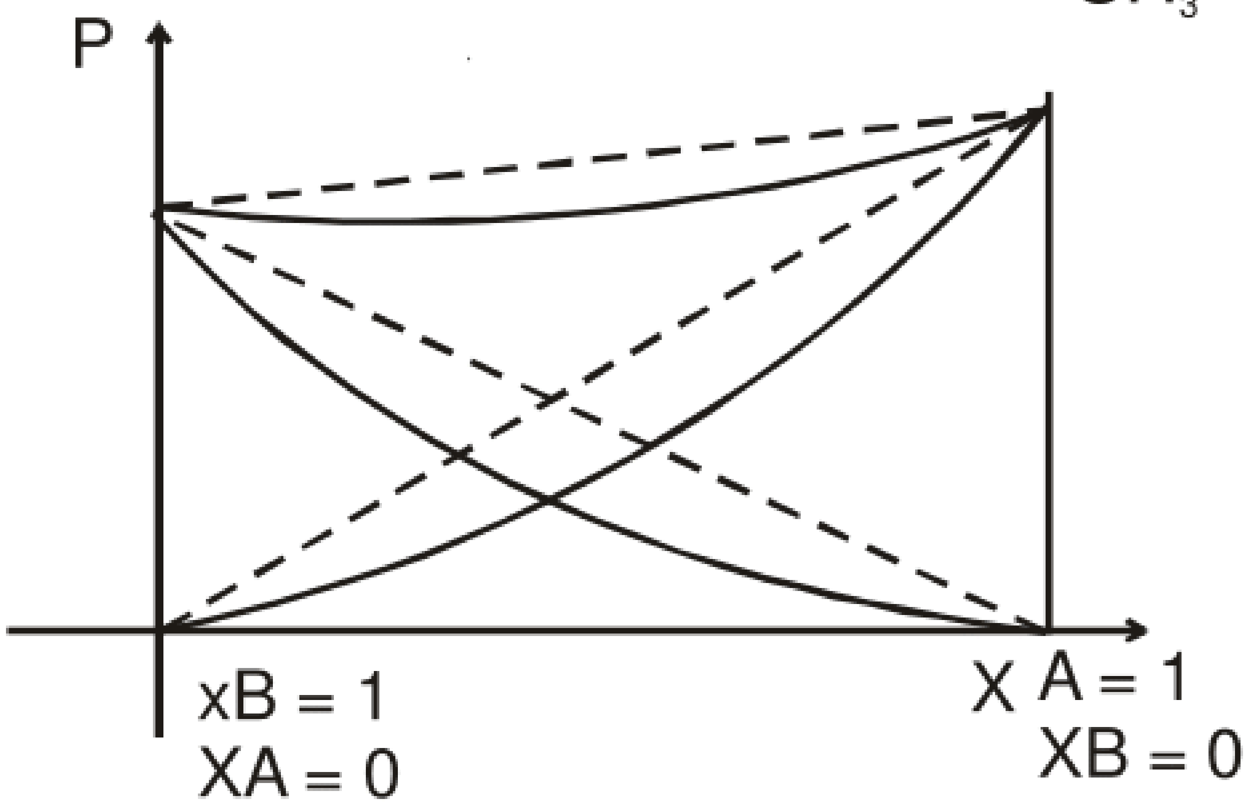
eg. **$H_2O + HCOOH$**

$H_2O + CH_3COOH$

$H_2O + HNO_3$

$CHCl_3 + CH_3OCH_3$ $\Rightarrow$





$P^0A > P^0B$

Immiscible Liquids :

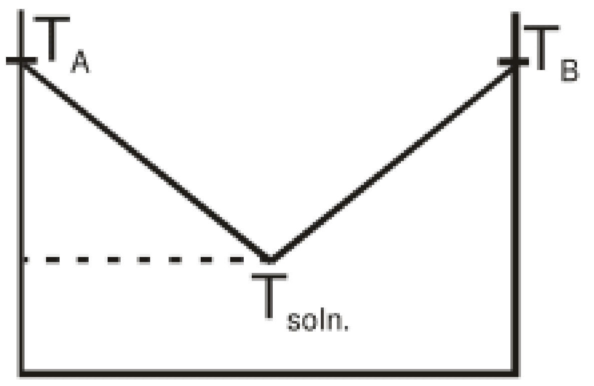
(i) $P_{total} = P_A + P_B$

(ii) $P_A = P_A^0 X_A = P_A^0$ [Since, $X_A = 1$].

(iii) $P_B = P_B^0 X_B = P_B^0$ [Since, $X_B = 1$].

(iv) $P_{total} = P_A^0 + P_B^0$ (v) $\frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$ (vi) $\frac{P_A^0}{P_B^0} = \frac{W_A M_B}{M_A W_B}$

$$P_A^0 = \frac{n_A RT}{V} \quad ; \quad P_B^0 = \frac{n_B RT}{V}$$



B.P. of solution is less than the individual B.P.'s of both the liquids.

Henry Law :

This law deals with dissolution of gas in liquid i.e. mass of any gas dissolved in any solvent per unit volume is proportional to pressure of gas in equilibrium with liquid.

$m \alpha p$

$m = kp$

$$m \rightarrow \frac{\text{weight of gas}}{\text{Volume of liquid}}$$

ELECTROCHEMISTRY

ELECTRODE POTENTIAL

For any electrode → oxidiation potential = – Reduction potential

E_{cell} = R.P of cathode – R.P of anode

E_{cell} = R.P. of cathode + O.P of anode

E_{cell} is always a +ve quantity & Anode will be electrode of low R.P

E^o_{Cell} = SRP of cathode – SRP of anode.

- **Greater the SRP value greater will be oxidising power.**

GIBBS FREE ENERGY CHANGE :

$\Delta G = - nFE_{cell}$

$\Delta G^o = - nFE^o_{cell}$

NERNST EQUATION : (Effect of concentration and temp on emf of cell)

$\Delta G = \Delta G^o + RT \ell nQ$ (where Q is raection quotient)

$\Delta G^o = - RT \ell n K_{eq}$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ell n\ Q$$

$$E_{cell} = E^o_{cell} - \frac{2.303\,RT}{nF} \log Q$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log Q \qquad [\text{At } 298\ K]$$

At chemical equilibrium

$\Delta G = 0$; $E_{cell} = 0$.

- $$\log K_{eq} = \frac{nE^o_{cell}}{0.0591}.$$

$$E^o_{cell} = \frac{0.0591}{n} \log K_{eq}$$

For an electrode M(s)/M^{n+}.

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}.$$

CONCENTRATION CELL :

A cell in which both the electrods are made up of same material.

For all concentration cell $E^o_{cell} = 0$.

(a) **Electrolyte Concentration Cell :**

eg. $Zn(s) / Zn^{2+} (c_1) || Zn^{2+}(c_2) / Zn(s)$

$$E = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

(b) **Electrode Concentration Cell :**

eg. $Pt, H_2(P_1 \text{ atm}) / H^+ (1M) \quad / H_2 (P_2 \text{ atm}) / Pt$

$$E = \frac{0.0591}{2} \log \left(\frac{P_1}{P_2}\right)$$

DIFFERENT TYPES OF ELECTRODES :

1. Metal-Metal ion Electrode $M(s)/M^{n+}$. $M^{n+} + ne^- \longrightarrow M(s)$

$$E = E^o + \frac{0.0591}{n} \log[M^{n+}]$$

2. Gas-ion Electrode $Pt /H_2(Patm) /H^+ (XM)$
as a reduction electrode

$$H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2 (Patm)$$

$$E = E^o - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]}$$

3. Oxidation-reduction Electrode $Pt / Fe^{2+}, Fe^{3+}$
as a reduction electrode $Fe^{3+} + e^- \longrightarrow Fe^{2+}$

$$E = E^o - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

4. Metal-Metal insoluble salt Electrode eg. $Ag/AgCl, Cl^-$
as a reduction electrode $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$

$$E_{Cl^- / AgCl / Ag} = E^0_{Cl^- / AgCl / Ag} - \mathbf{0.0591 \log [Cl^-]}.$$

ELECTROLYSIS :

(a) $K^+, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}$.

$$\xrightarrow[\text{Increasing order of deposition.}]{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

(b) Similarly the anion which is strogner reducing agent(low value of SRP) is liberated first at the anode.

$$\xrightarrow[\text{Increasing order of diposition}]{SO_4^{2-},\ NO_3^-,\ OH^-,\ Cl^-,\ Br^-,\ I^-}$$

FARADAY'S LAW OF ELECTROLYSIS :

First Law :

$w = zq$ $\qquad$ $w = Z\,it$ $\qquad$ Z = Electrochemical equivalent of substance

Second Law :

$$W \propto E \qquad \frac{W}{E} = \text{constant} \qquad \frac{W_1}{E_1} = \frac{W_2}{E_2} = \text{..........}$$

$$\frac{W}{E} = \frac{i \times t \times \text{current efficiency factor}}{96500}.$$

$$\textbf{Current efficiency} = \frac{\text{actual mass deposited/produced}}{\text{Theoritical mass deposited/produced}} \times 100$$

CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe AT CATHODE

$$E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{Cu^{2+}} = E^o_{Fe^{2+}/Fe} - \frac{0.0591}{2}\log\frac{1}{Fe^{2+}}$$

Condition for the simultaneous deposition of Cu & Fe on cathode.

CONDUCTANCE :

☞ $\text{Conductance} = \dfrac{1}{\text{Resistance}}$

☞ **Specific conductance or conductivity :**

(Reciprocal of specific resistance) $\qquad K = \dfrac{1}{\rho}$

K = specific conductance

☞ **Equivalent conductance :**

$$\lambda_E = \frac{K \times 1000}{\text{Normality}}$$

unit : -ohm^{-1} cm^2 eq^{-1}

☞ **Molar conductance :**

$$\lambda_m = \frac{K \times 1000}{\text{Molarity}}$$

unit : -ohm^{-1} cm^2 mole^{-1}

$$\text{specific conductance} = \text{conductance} \times \frac{\ell}{a}$$

KOHLRAUSCH'S LAW :

Variation of λ_{eq} / λ_M of a solution with concentration :

(i) Strong electrolyte

$$\lambda_M{}^c = \lambda_M^{\infty} - b\sqrt{c}$$

(ii) Weak electrolytes : $\lambda_{\infty} = n_+ \lambda^{\infty}{}_+ + n_- \lambda^{\infty}{}_-$

where λ is the molar conductivity

n_+ = No of cations obtained after dissociation per formula unit

n_- = No of anions obtained after dissociation per formula unit

APPLICATION OF KOHLRAUSCH LAW :

1. Calculation of $\lambda^0{}_M$ of weak electrolytes :

$\lambda^0{}_{M\,(CH3COOHl)} = \lambda^0{}_{M(CH3COONa)} + \lambda^0{}_{M(HCl)} - \lambda^0{}_{M(NaCl)}$

2. To calculate degree of diossociation of a week electrolyte

$$\alpha = \frac{\lambda_m^c}{\lambda_m^0} \quad ; \quad K_{eq} = \frac{c\alpha^2}{(1-\alpha)}$$

3. Solubility (S) of sparingly soluble salt & their K_{sp}

$$\lambda_M{}^c = \lambda_M{}^{\infty} = \kappa \times \frac{1000}{\text{solubility}}$$

$$K_{sp} = S^2.$$

Transport Number :

$$t_c = \left[\frac{\mu_c}{\mu_c + \mu_a}\right], \qquad t_a = \left[\frac{\mu_a}{\mu_a + \mu_c}\right].$$

Where t_c = Transport Number of cation & t_a = Transport Number of anion

IONIC EQUILIBRIUM

OSTWALD DILUTION LAW :

- Dissociation constant of weak acid (K_a),

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

If $\alpha << 1$, then $1 - \alpha \cong 1$ or $K_a = c\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times V}$

- Similarly for a weak base , $\alpha = \sqrt{\frac{K_b}{C}}$. Higher the value of K_a / K_b , strong is the acid / base.

Acidity and pH scale :

∴ pH = – log a_{H^+} (where a_{H^+} is the activity of H^+ ions = molar concentration for dilute solution).

[Note : pH can also be negative or > 14]

pH = – log [H^+] ; $[H^+] = 10^{-pH}$
pOH = – log [OH^-] ; $[OH^-] = 10^{-pOH}$
pKa = – log Ka ; $Ka = 10^{-pKa}$
pKb = – log Kb ; $Kb = 10^{-pKb}$

PROPERTIES OF WATER :

1. **In pure water [H^+] = [OH^-] so it is Neutral.**
2. **Molar concentration / Molarity of water = 55.56 M.**
3. **Ionic product of water (K_w) :**
   $K_w = [H^+][OH^-] = 10^{-14}$ at 25° (experimentally)
   pH = 7 = pOH ⇒ neutral
   pH < 7 or pOH > 7 ⇒ acidic
   pH > 7 or pOH < 7 ⇒ Basic
4. **Degree of dissociation of water :**

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18x10^{-10} \text{ or } 1.8x10^{-7}\%$$

5. **Absolute dissociation constant of water :**

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

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

$K_a \times K_b = [H^+] [OH^-] = K_w$

⇒ **Note: for a conjugate acid- base pairs**
$pK_a + pK_b = pK_w = 14$ at 25°C.
pK_a of H_3O^+ ions = –1.74
pK_b of OH^- ions = –1.74.

❍ pH Calculations of Different Types of Solutions:

(a) Strong acid solution :

(i) If concentration is greater than 10^{-6} M
In this case H^+ ions coming from water can be neglected,

(ii) If concentration is less than 10^{-6} M
In this case H^+ ions coming from water cannot be neglected

(b) Strong base solution :

Using similar method as in part (a) calculate first $[OH^-]$ and then use $[H^+] \times [OH^-] = 10^{-14}$

(c) pH of mixture of two strong acids :

Number of H^+ ions from I-solution = N_1V_1
Number of H^+ ions from II-solution = N_2V_2

$$[H^+] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

(d) pH of mixture of two strong bases :

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

(e) pH of mixture of a strong acid and a strong base :

If $N_1V_1 > N_2V_2$, then solution will be acidic in nature and

$$[H^+] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

If $N_2V_2 > N_1V_1$, then solution will be basic in nature and

$$[OH^-] = N = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

(f) pH of a weak acid(monoprotic) solution :

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

if $\alpha << 1 \Rightarrow (1 - \alpha) \approx 1$ ⇒ $K_a \approx C\alpha^2$

$\Rightarrow \quad \alpha = \sqrt{\frac{K_a}{C}}$ (is valid if $\alpha < 0.1$ or 10%)

On increasing the dilution

$\Rightarrow \quad C\downarrow \quad \Rightarrow \alpha \uparrow \qquad$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

RELATIVE STRENGTH OF TWO ACIDS :

$$\frac{[H^+] \text{ furnished by I acid}}{[H^+] \text{ furnished by II acid}} = \frac{c_1\alpha_1}{c_2\alpha_2} = \sqrt{\frac{k_{a_1}c_1}{k_{a_2}c_2}}$$

❍ SALT HYDROLYSIS :

	Salt of	Type of hydrolysis	k_h	h	pH
(a)	weak acid & strong base	anionic	$\frac{k_w}{k_a}$	$\sqrt{\frac{k_w}{k_a c}}$	$7+\frac{1}{2}pk_a+\frac{1}{2}\log c$
(b)	strong acid & weak base	cationic	$\frac{k_w}{k_b}$	$\sqrt{\frac{k_w}{k_b c}}$	$7-\frac{1}{2}pk_b-\frac{1}{2}\log c$
(c)	weak acid & weak base	both	$\frac{k_w}{k_a k_b}$	$\sqrt{\frac{k_w}{k_a k_b}}$	$7+\frac{1}{2}pk_a-\frac{1}{2}pk_b$
(d)	Strong acid & strong base	--------do not	hydrolysed-------		pH = 7

Hydrolysis of ployvalent anions or cations

For $[Na_3PO_4] = C$.

$\mathbf{K_{a1} \times K_{h3} = K_w}$

$\mathbf{K_{a1} \times K_{h2} = K_w}$

$\mathbf{K_{a3} \times K_{h1} = K_w}$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h1} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h1}}{c}} \qquad \Rightarrow [OH^-] = ch = \sqrt{K_{h1}\times c} \quad \Rightarrow [H^+] = \sqrt{\frac{\mathbf{K_W \times K_{a3}}}{\mathbf{C}}}$$

So $\mathbf{pH = \frac{1}{2}[pK_w + pK_{a3} + \log C]}$

BUFFER SOLUTION :

(a) Acidic Buffer : e.g. CH_3COOH and CH_3COONa. (weak acid and salt of its conjugate base).

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \qquad \text{[Henderson's equation]}$$

(b) Basic Buffer : e.g. $NH_4OH + NH_4Cl$. (weak base and salt of its conjugate acid).

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

SOLUBILITY PRODUCT :

$$K_{SP} = (xs)^x (ys)^y = x^x.y^y.(s)^{x+y}$$

CONDITION FOR PRECIPITATION :

If ionic product $K_{I.P} > K_{SP}$ precipitation occurs,

if $K_{I.P} = K_{SP}$ saturated solution (precipitation just begins or is just prevented).

CHEMICAL EQUILIBRIUM

At equilibrium :

(i) Rate of forward reaction = rate of backward reaction

(ii) Concentration (mole/litre) of reactant and product becomes constant.

(iii) $\Delta G = 0$.

(iv) $Q = K_{eq.}$

Equilibrium constant (K) :

$$K = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}} = \frac{K_f}{K_b}.$$

Equilibrium constant in terms of concentration (K_C) :

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

Equilibrium constant in terms of partial pressure (K_P) :

$$K_P = \frac{[P_C]^c\ [P_D]^d}{[P_A]^a\ [P_B]^b}$$

Equilibrium constant in terms of mole fraction (K_x) :

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b}$$

Relation between K_p & K_C :

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

Relation between K_p & K_X :

$K_P = K_x\ (P)^{\Delta n}$

* $$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$; ΔH = Enthalpy of reaction

Relation between equilibrium constant & standard free energy change :

$\Delta G^o = -\ 2.303\ RT \log K$

Reaction Quotient (Q) :

The values of expression $Q = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$

Degree of Dissociation (α) :

α = *no. of moles dissociated / initial no. of moles taken*

= fraction of moles dissociated out of 1 mole.

Note : % dissociation = α x 100

Observed molecular weight and Observed Vapour Density of the mixture :
Observed molecular weight of $A_n(g)$

$$= \frac{\text{molecular weight of equilibrium mixture}}{\text{total no. of moles}}$$

$$\alpha = \frac{D - d}{(n-1) \times d} = \frac{M_T - M_o}{(n-1)M_0}$$

External factor affecting equilibrium :

Le Chatelier's Principle:

If a system at equilibrium is subjected to a disturbance or stress that changes any of the factors that determine the state of equilibrium, the system will react in such a way as to minimize the effect of the disturbance.

Effect of concentration :

* If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .
* If the concentration of product is increased then equilibrium shifts in the backward direction

Effect of volume :

* If volume is increased pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
* If volume is increased then, for

$\Delta n > 0$ reaction will shift in the forward direction
$\Delta n < 0$ reaction will shift in the backward direction
$\Delta n = 0$ reaction will not shift.

Effect of pressure :

If pressure is increased at equilibrium then reaction will try to decrease the pressure, hence it will shift in the direction in which less no. of moles of gases are formed.

Effect of inert gas addition :

(i) Constant pressure :

If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

$\Delta n > 0$ reaction will shift in the forward direction
$\Delta n < 0$ reaction will shift in the backward direction
$\Delta n = 0$ reaction will not shift.

(ii) Constant volume :

Inert gas addition has no effect at constant volume.

Effect of Temperature :

Equilibrium constant is only dependent upon the temperature.

If plot of ℓnk vs $\frac{1}{T}$ is plotted then it is a straight line with slope = $-\frac{\Delta H^\circ}{R}$,

and intercept = $\frac{\Delta S^\circ}{R}$

- * For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature
- * For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature
- * For $\Delta H > 0$, reaction shiffts in the forward direction with increase in temperatutre
- * For $\Delta H < 0$, reaction shifts in the backward direction with increases in temperature.
- * If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .
- * If the concentration of product is increased then equilibrium shifts in the backward direction

Vapour Pressure of Liquid :

Relative Humidity = $\frac{\text{Partial pressure of } H_2O \text{ vapours}}{\text{Vapour pressure of } H_2O \text{ at that temp.}}$

Thermodynamics of Equilibrium :

$$\Delta G = \Delta G^0 + 2.303\ RT \log_{10} Q$$

Vant Hoff equation- $\log\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^0}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

THERMODYNAMICS

Thermodynamic processes :

1. **Isothermal process :** T = constant
   $dT = 0$
   $\Delta T = 0$
2. **Isochoric process :** V = constant
   $dV = 0$
   $\Delta V = 0$
3. **Isobaric process :** P = constant
   $dP = 0$
   $\Delta P = 0$
4. **Adiabatic process :** $q = 0$
   or heat exchange with the surrounding = 0(zero)

IUPAC Sign convention about Heat and Work :

Work done on the system = Positive
Work done by the system = Negative

1st Law of Thermodynamics

$$\Delta U = (U_2 - U_1) = q + w$$

Law of equipartion of energy :

$$U = \frac{f}{2} nRT \qquad \text{(only for ideal gas)}$$

$$\Delta E = \frac{f}{2} nR(\Delta T)$$

where f = degrees of freedom for that gas. (Translational + Rotational)
f = 3 for monoatomic
= 5 for diatomic or linear polyatmic
= 6 for non - linear polyatmic

Calculation of heat (q) :

Total heat capacity :

$$C_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} = J/^{o}C$$

Molar heat capacity :

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT} = J\ mole^{-1}\ K^{-1}$$

$$C_P = \frac{\gamma R}{\gamma - 1} \qquad C_V = \frac{R}{\gamma - 1}$$

Specific heat capacity (s) :

$$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT} = J\ gm^{-1}\ K^{-1}$$

WORK DONE (w) :

Isothermal Reversible expansion/compression of an ideal gas :

$$W = -\,nRT\ \ln (V_f/V_i)$$

Reversible and irreversible isochoric processes.

Since $dV = 0$

So $dW = -\,P_{ext}\,.\,dV = 0.$

Reversible isobaric process :

$$W = P\,(V_f - V_i)$$

Adiabatic reversible expansion :

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

Reversible Work :

$$W = \frac{P_2V_2 - P_1V_1}{\gamma-1} = \frac{nR\,(T_2 - T_1)}{\gamma-1}$$

Irreversible Work :

$$W = \frac{P_2V_2 - P_1V_1}{\gamma-1} = \frac{nR\,(T_2 - T_1)}{\gamma-1} = nC_v\,(T_2 - T_1) = -\,P_{ext}\,(V_2 - V_1)$$

and use $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

Free expansion–Always going to be irrerversible and since $P_{ext} = 0$

so $dW = -\,P_{ext}\,.\,dV = 0$

If no. heat is supplied $q = 0$

then $\Delta E = 0$ so $\Delta T = 0.$

Application of Ist Law :

$$\Delta U = \Delta Q + \Delta W \quad \Rightarrow \quad \Delta W = -P\,\Delta V$$

$$\therefore \quad \Delta U = \Delta Q - P\Delta V$$

Constant volume process

Heat given at constant volume = change in internal energy

$\therefore\ du = (dq)_v$

$du = nC_v dT$

$$C_v = \frac{1}{n}\cdot\frac{du}{dT} = \frac{f}{2}R$$

Constant pressure process :

$H \equiv$ Enthalpy (state function and extensive property)

$H = U + PV$

$\Rightarrow C_p - C_v = R$ (only for ideal gas)

Second Law Of Thermodynamics :

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$ for a spontaneous process.

Entropy (S) :

$$\Delta S_{system} = \int_A^B \frac{dq_{rev}}{T}$$

Entropy calculation for an ideal gas undergoing a process :

State A $\xrightarrow[\Delta S_{irr}]{irr}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

$$\Delta S_{system} = nc_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$ (only for an ideal gas)

Third Law Of Thermodynamics :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Gibb's free energy (G) : (State function and an extensive property)

$$G_{system} = H_{system} - TS_{system}$$

Criteria of spontaneity :

(i) If ΔG_{system} is (–ve) < 0 ⇒ process is spontaneous
(ii) If ΔG_{system} is > 0 ⇒ process is non spontaneous
(iii) If ΔG_{system} = 0 ⇒ system is at equilibrium.

Physical interpretation of ΔG :

→ The maximum amount of non-expansional (compression) work which can be performed.

$\Delta G = dw_{non\text{-}exp} = dH - TdS$.

Standard Free Energy Change (ΔG°) :

1. $\Delta G^o = -2.303\ RT \log_{10} K$
2. At equilibrium $\Delta G = 0$.
3. The decrease in free energy ($-\Delta G$) is given as :

$$-\Delta G = W_{net} = 2.303\ nRT \log_{10} \frac{V_2}{V_1}$$

4. ΔG_f^o for elemental state = 0
5. $\Delta G_f^o = G^o_{products} - G^o_{Reactants}$

Thermochemistry :

Change in standard enthalpy $\Delta H^\circ = H^0_{m,2} - H^0_{m,1}$

$= \text{heat added at constant pressure.}$

$= C_P \Delta T.$

If $H_{products} > H_{reactants}$

→ Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products

and if $H_{products} < H_{reactants}$

→ Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

Enthalpy change of a reaction :

$\Delta H_{reaction} = H_{products} - H_{reactants}$

$\Delta H^\circ_{reactions} = H^\circ_{products} - H^\circ_{reactants}$

$= \text{positive} - \text{endothermic}$

$= \text{negative} - \text{exothermic}$

Temperature Dependence Of ΔH : (Kirchoff's equation) :

For a constant pressure reaction

$\Delta H_2^\circ = \Delta H_1^\circ + \Delta C_P (T_2 - T_1)$

where $\Delta C_P = C_P \text{ (products)} - C_P \text{ (reactants)}$.

For a constant volume reaction

$$\Delta E_2^0 = \Delta E_1^0 + \int \Delta C_V . dT$$

Enthalpy of Reaction from Enthalpies of Formation :

The enthalpy of reaction can be calculated by

$\Delta H_r^\circ = \Sigma \nu_B \Delta H_f^\circ{}_{,products} - \Sigma \nu_B \Delta H_f^\circ{}_{,reactants}$

ν_B is the stoichiometric coefficient.

Estimation of Enthalpy of a reaction from bond Enthalpies :

$$\Delta H = \begin{pmatrix} \text{Enthalpy required to} \\ \text{break reactants into} \\ \text{gasesous atoms} \end{pmatrix} - \begin{pmatrix} \text{Enthalpy released to} \\ \text{form products from the} \\ \text{gasesous atoms} \end{pmatrix}$$

Resonance Energy :

$\Delta H^\circ_{resonance} = \Delta H^\circ_{f,\ experimental} - \Delta H^\circ_{f,\ calclulated}$

$= \Delta H^\circ_{c,\ calclulated} - \Delta H^\circ_{c,\ experimental}$

GASEOUS STATE

Temperature Scale :

$$\frac{C-O}{100-0}=\frac{K-273}{373-273}=\frac{F-32}{212-32} = \frac{R-R(O)}{R(100)-R(O)}$$

where R = Temp. on unknown scale.

Boyle's law and measurement of pressure :

At constant temperature, $V \propto \frac{1}{P}$

$$P_1V_1 = P_2V_2$$

Charles law :

At constant pressure, $V \propto T$ or $\frac{V_1}{T_1}=\frac{V_2}{T_2}$

Gay-lussac's law :

At constant volume, $P \propto T$ $\frac{P_1}{T_1}=\frac{P_2}{T_2}$ → temp on absolute scale

Ideal gas Equation :

$$PV = nRT$$

$$PV = \frac{w}{m}RT \text{ or } P = \frac{d}{m}RT \text{ or } Pm = dRT$$

Daltons law of partial pressure :

$$P_1=\frac{n_1RT}{v}, \quad P_2=\frac{n_2RT}{v}, \quad P_3=\frac{n_3RT}{v} \text{ and so on.}$$

Total pressure = $P_1 + P_2 + P_3 + \ldots\ldots\ldots\ldots$

Partial pressure = mole fraction X Total pressure.

Amagat's law of partial volume :

$$V = V_1 + V_2 + V_3 + \ldots\ldots$$

Average molecular mass of gaseous mixture :

$$M_{mix} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}} = \frac{n_1M_1+n_2M_2+n_3M_3}{n_1+n_2+n_3}$$

Graham's Law :

Rate of diffusion $r \propto \frac{1}{\sqrt{d}}$; d = density of gas

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \sqrt{\frac{V.D_2}{V.D_1}}$$

Kinetic Theory of Gases :

$PV = \frac{1}{3} mN \overline{U^2}$ Kinetic equation of gases

Average K.E. for one mole = $N_A \left(\frac{1}{2} m \overline{U^2}\right) = \frac{3}{2} K N_A T = \frac{3}{2} RT$

☞ Root mean suqare speed

$U_{rms} = \sqrt{\frac{3RT}{M}}$ molar mass must be in kg/mole.

☞ Average speed

$U_{av} = U_1 + U_2 + U_3 + \ldots\ldots\ldots\ldots U_N$

$U_{avg.} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{\pi m}}$ K is Boltzmman constant

☞ Most probable speed

$U_{MPS} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2KT}{m}}$

Van der Waal's equation :

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

☞ Critical constants :

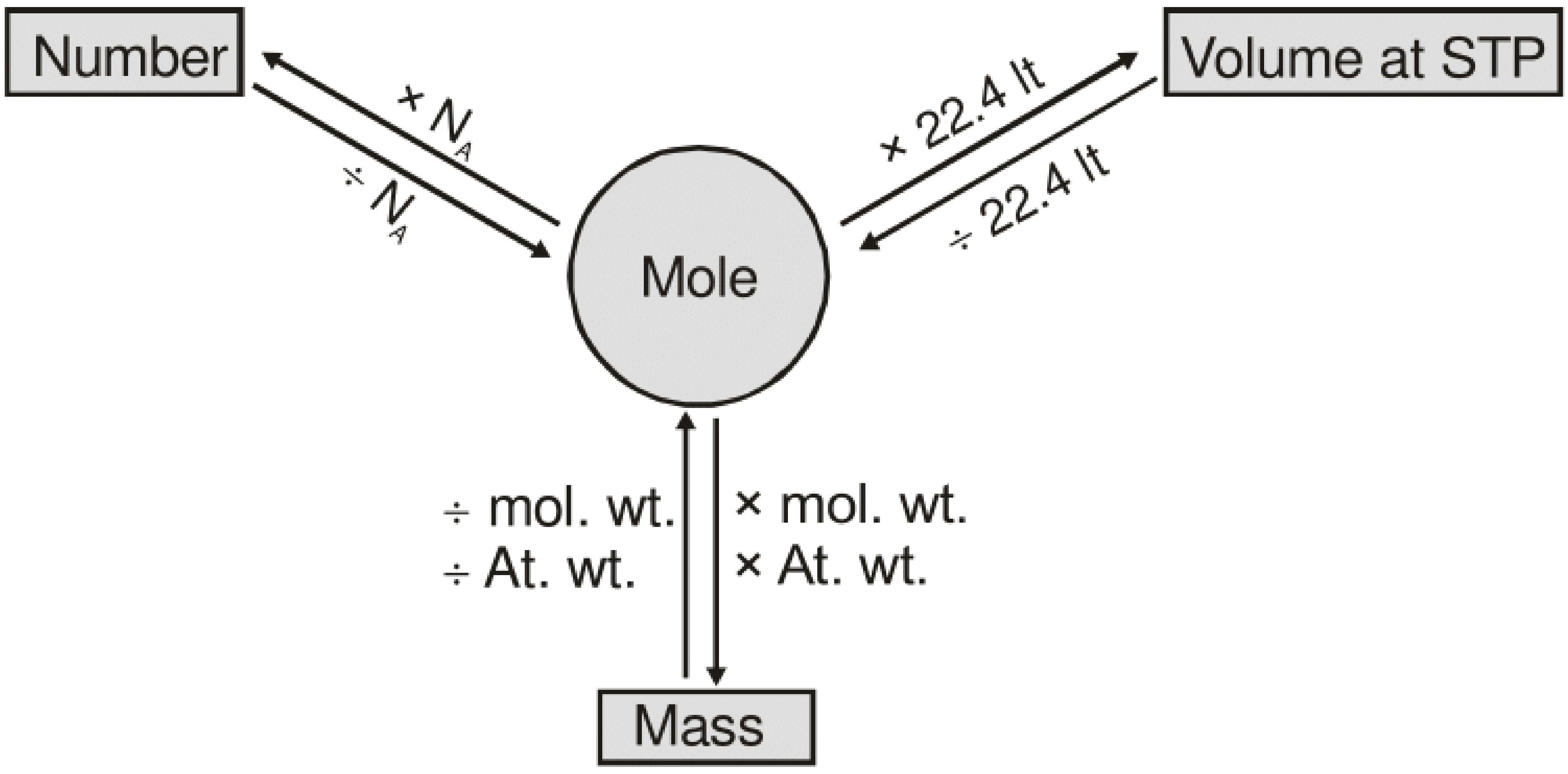
$V_c = 3b$, $P_C = \frac{a}{27b^2}$, $T_C = \frac{8a}{27Rb}$

STOICHIOMETRY

☞ Relative atomic mass (R.A.M) = $\dfrac{\text{Mass of one atom of an element}}{\frac{1}{12}\times\text{mass of one carbon atom}}$

= Total Number of nucleons

☞ **Y-map**



Density :

Specific gravity = $\dfrac{\text{density of the substance}}{\text{density of water at }4°C}$

For gases :

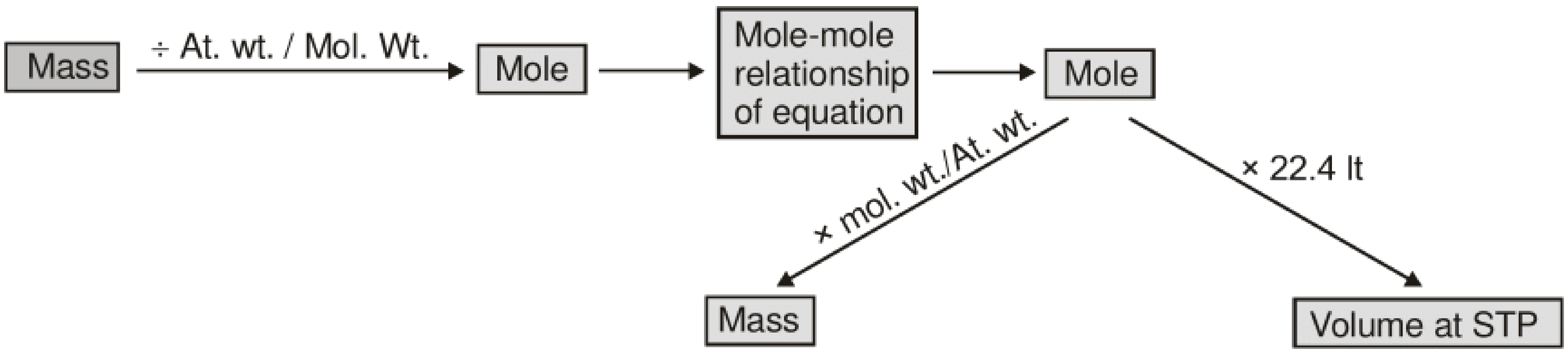
Absolute density (mass/volume) = $\dfrac{\text{Molar mass of the gas}}{\text{Molar volume of the gas}}$

$$\Rightarrow \quad \rho = \frac{PM}{RT}$$

Vapour density $\quad V.D. = \dfrac{d_{gas}}{d_{H_2}} = \dfrac{PM_{gas/RT}}{PM_{H_2/RT}} = \dfrac{M_{gas}}{M_{H_2}} = \dfrac{M_{gas}}{2}$

$M_{gas} = 2$ V.D.

Mole-mole analysis :



Concentration terms :

Molarity (M) :

$$\therefore \quad \text{Molarity (M)} = \frac{w \times 1000}{(\text{Mol. wt of solute}) \times V_{\text{inml}}}$$

Molality (m) :

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 1000 = 1000\ w_1 / M_1 w_2$$

Mole fraction (x) :

$$\therefore \quad \text{Mole fraction of solution } (x_1) = \frac{n}{n+N}$$

$$\therefore \quad \text{Mole fraction of solvent } (x_2) = \frac{N}{n+N}$$

$$x_1 + x_2 = 1$$

% Calculation :

(i) $$\% \text{ w/w} = \frac{\text{mass of solute in gm}}{\text{mass of solution in gm}} \times 100$$

(ii) $$\% \text{ w/v} = \frac{\text{mass of solute in gm}}{\text{Volume of solution in ml}} \times 100$$

(iii) $$\% \text{ v/v} = \frac{\text{Volume of solute in ml}}{\text{Volume of solution}} \times 100$$

Derive the following conversion :

1. Mole fraction of solute into molarity of solution $M = \dfrac{x_2 \rho \times 1000}{x_1 M_1 + M_2 x_2}$

2. Molarity into mole fraction $x_2 = \dfrac{M M_1 \times 1000}{\rho \times 1000 - M M_2}$

3. Mole fraction into molality $m = \dfrac{x_2 \times 1000}{x_1 M_1}$

4. Molality into mole fraction $x_2 = \dfrac{mM_1}{1000 + mM_1}$

5. Molality into molarity $M = \dfrac{m\rho \times 1000}{1000 + mM_2}$

6. Molarity into Molality $m = \dfrac{M \times 1000}{1000\,\rho - MM_2}$

M_1 and M_2 are molar masses of solvent and solute. ρ is density of solution (gm/mL)
M = Molarity (mole/lit.), m = Molality (mole/kg), x_1 = Mole fraction of solvent, x_2 = Mole fraction of solute

Average/Mean atomic mass :

$$A_x = \frac{a_1x_1 + a_2x_2 + \ldots.. + a_nx_n}{100}$$

Mean molar mass or molecular mass :

$$M_{avg.} = \frac{n_1M_1 + n_2M_2 + \ldots\ldots n_nM_n}{n_1 + n_2 + \ldots.n_n} \quad \text{or} \quad M_{avg.} = \frac{\sum_{j=1}^{j=n} n_jM_j}{\sum_{j=1}^{j=n} n_j}$$

Calculation of individual oxidation number :

Formula : Oxidation Number = number of electrons in the valence shell – number of electrons left after bonding

Concept of Equivalent weight/Mass :

For elements, equivalent weight (E) = $\dfrac{\text{Atomic weight}}{\text{Valency - factor}}$

For acid/base, $E = \dfrac{M}{\text{Basicity / Acidity}}$

Where M = Molar mass

For O.A/R.A, $E = \dfrac{M}{\text{no. of moles of } e^- \text{ gained / lost}}$

Equivalent weight (E) = $\frac{\text{Atomic or moleculear weight}}{\text{v.f.}}$

(v.f. = valency factor)

Concept of number of equivalents :

No. of equivalents of solute = $\frac{\text{Wt}}{\text{Eq. wt.}} = \frac{W}{E} = \frac{W}{M/n}$

No. of equivalents of solute = No. of moles of solute × v.f.

Normality (N) :

Normality (N) = $\frac{\text{Number of equivalents of solute}}{\text{Volume of solution (in litres)}}$

Normality = Molarity × v.f.

Calculation of valency Factor :

n-factor of acid = basicity = no. of H^+ ion(s) furnished per molecule of the acid.

n-factor of base = acidity = no. of OH^- ion(s) furnised by the base per molecule.

At equivalence point : $N_1V_1 = N_2V_2$

$n_1M_1V_1 = n_2M_2V_2$

Volume strength of H_2O_2 :

20V H_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20 lt. of O_2** gas at **S.T.P.**

Normality of H_2O_2 (N) = $\frac{\text{Volume, strength of } H_2O_2}{5.6}$

Molarity of H_2O_2 (M) = $\frac{\textbf{Volume strength of } \mathbf{H_2O_2}}{\mathbf{11.2}}$

Measurement of Hardness :

Hardness in ppm = $\frac{\text{mass of } CaCO_3}{\text{Total mass of water}} \times 10^6$

Calculation of available chlorine from a sample of bleaching powder :

% of Cl_2 = $\frac{3.55 \times x \times V\,(\text{mL})}{W(g)}$ where x = molarity of hypo solution

and v = mL. of hypo solution used in titration.

PHYSICAL CHEMISTRY

ATOMIC STRUCTURE

Planck's Quantum Theory :

$$\text{Energy of one photon} = h\nu = \frac{hc}{\lambda}$$

Photoelectric Effect :

$$h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

Bohr's Model for Hydrogen like atoms :

1. $$mvr = n\frac{h}{2\pi}$$ (Quantization of angular momentum)

2. $$E_n = -\frac{E_1}{n^2} z^2 = -2.178 \times 10^{-18} \frac{z^2}{n^2} \text{ J/atom} = -13.6 \frac{z^2}{n^2} \text{ eV}$$

$$E_1 = \frac{-2\pi^2 me^4}{n^2}$$

3. $$r_n = \frac{n^2}{Z} \times \frac{h^2}{4\pi^2 e^2 m} = \frac{0.529 \times n^2}{Z} \text{ Å}$$

4. $$v = \frac{2\pi ze^2}{nh} = \frac{2.18 \times 10^6 \times z}{n} \text{ m/s}$$

De–Broglie wavelength :

$$\lambda = \frac{h}{mc} = \frac{h}{p} \text{ (for photon)}$$

Wavelength of emitted photon :

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

No. of photons emitted by a sample of H atom :

$$\frac{\Delta n(\Delta n+1)}{2}$$

Heisenberg's uncertainty principle :

$$\Delta x.\Delta p > \frac{h}{4\pi} \quad \text{or} \quad m\,\Delta x.\Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x.\Delta v \geq \frac{h}{4\pi m}$$

Quantum Numbers :

* Principal quantum number (n) = 1, 2, 3, 4 .... to ∞.

* Orbital angular momentum of electron in any orbit $= \frac{nh}{2\pi}$.

* Azimuthal quantum number (ℓ) = 0, 1, ... to (n – 1).

* Number of orbitals in a subshell = $2\ell + 1$

* Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$

* Orbital angular momentum $L = \frac{h}{2\pi}\sqrt{\ell(\ell+1)} = \hbar\sqrt{\ell(\ell+1)}$

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