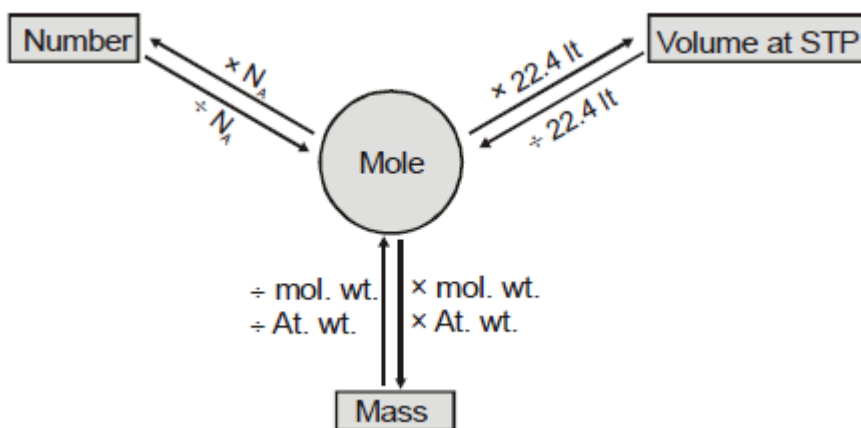


Basic Concept in Chemistry

STOICHIOMETRY

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

☞ **Y-map**



Density:

$$\text{Specific gravity} = \frac{\text{density of the substance}}{\text{density of water}}$$

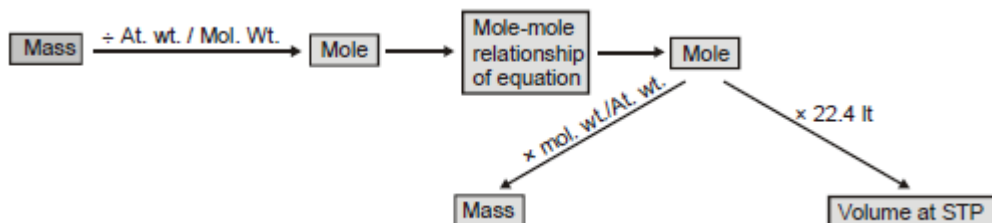
For gases:

$$\text{Absolute density mass / volume} = \frac{\text{Molar mass of the gas}}{\text{Molar volume of the gas}} \Rightarrow \rho = \frac{PM}{RT}$$

$$\text{Vapour density V.D} = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{PM_{\text{gas}/RT}}{PM_{\text{H}_2}/RT} = \frac{M_{\text{gas}}}{M_{\text{H}_2}} = \frac{M_{\text{gas}}}{2}$$

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

Mole-mole analysis:



Concentration terms:

Molarity (M):

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

Molality (m):

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 1000 = 1000w_1 / M_1w_2$$

Mole fraction (x):

$$\therefore \text{Mole fraction of solution}(X_1) = \frac{n}{n+N}$$

$$\therefore \text{Mole fraction of solvent}(X_2) = \frac{N}{n+N}$$

$$X_1 + X_2 = 1$$

% Calculation:

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

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

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

Average/Mean atomic mass:

$$A_x = \frac{a_1X_1 + a_2X_2 + \dots + a_nX_n}{100}$$

Mean molar mass or molecular mass:

$$M_{\text{avg}} = \frac{n_1M_1 + n_2M_2 + \dots + n_nM_n}{n_1 + n_2 + \dots + n_n} \quad \text{Or} \quad M_{\text{avg}} = \frac{\sum_{j=1}^{j=n} n_j M_j}{\sum_{j=1}^{j=n} n_j}$$

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) = $\frac{\text{Atomic Weight}}{\text{Valency - factor}}$

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

Where M = Molar mass

$$\text{For Oxidation \ Reduction, } E = \frac{M}{\text{no. of moles of } e^- \text{ gained / lost}}$$

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

(v. f. = valency factor)

Concept of number of equivalents:

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

No. of equivalents of solute = No. of moles of solute \times v.f

Normality (N):

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

Normality = Molarity \times 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) furnished 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.**

$$\text{Normality of } \text{H}_2\text{O}_2 \text{ (N)} = \frac{\text{Volume, strength of } \text{H}_2\text{O}_2}{5.6}$$

$$\text{Molarity of } \text{H}_2\text{O}_2 \text{ (M)} = \frac{\text{Volume strength of } \text{H}_2\text{O}_2}{11.2}$$

Measurement of Hardness:

$$\text{Hardness in ppm} = \frac{\text{mass of } \text{CaCO}_3}{\text{Total mass of water}} \times 10^6$$

Calculation of available chlorine from a sample of bleaching powder:

$\% \text{ of } \text{Cl}_2 = \frac{3.55 \times x \times V \text{ (mL)}}{W \text{ (g)}}$ Where x = molarity of hypo solution and v = mL. of hypo solution used in titration.

States of Matter

GASEOUS STATE

Temperature Scale:

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

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, $V \propto T$

$$\text{Or } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Gay-Lussac's law:

At constant volume, $P \propto T$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \text{Temp on absolute scale}$$

Ideal gas Equation:

$$PV = nRT$$

$$PV = \frac{wRT}{m} \quad \text{OR} \quad P = \frac{dRT}{m} \quad \text{OR} \quad Pm = dRT$$

Dalton's law of partial pressure:

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

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

Partial pressure = mole fraction \times Total Pressure.

Amagat's law of partial volume:

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

Average molecular mass of gaseous mixture:

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

Graham's Law:

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

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

Kinetic Theory of Gases

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

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

- Root mean square speed

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

- Average speed

$$U_{\text{avg}} = U_1 + U_2 + U_3 + \dots + U_N$$

$$U_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}} \text{ k is Boltzmann constant}$$

- Most Probable speed

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

van der Waal's equation

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

a and b are van der Waal's constants

Critical Constants:

Critical volume, $V_c = 3b$ at P_c and V_c

$$\text{Critical pressure, } P_c = \frac{a}{27b^2}$$

$$\text{Critical temperature, } T_c = \frac{8a}{27Rb}$$

Vander wall equation in virial form:

$$Z = \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots \right) - \frac{a}{V_m RT} = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT} \right) + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots$$

Reduced Equation of state:

$$\left(P_r + \frac{3}{V_r^2} \right) (3V_r - 1) = 8T_r$$

Atomic Structure

Estimation of closest distance of approach (derivation) of α -particles:

$$R = \frac{4KZe^2}{m_\alpha V_\alpha^2} \quad (k=9 \times 10^9 \text{ Nm}^2\text{C}^{-2})$$

The radius of a nucleus:

$$R = R_0(A)^{1/3} \text{ cm} \quad (R_0=1.097 \times 10^{-15} \text{ cm}^{-1})$$

Planck's Quantum Theory:

$$\text{Energy of one photon} = h\nu = \frac{hc}{\lambda} \quad (h=6.62 \times 10^{-34} \text{ Joule-second})$$

Photoelectric Effect:

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

Bohr's Model for Hydrogen like atoms:

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

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

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

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

De-Broglie Wavelength:

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

Wavelength of emitted photon:

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (R=1.0973 \times 10^7 \text{ m}^{-1})$$

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

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

Heisenberg's uncertainty principle:

$$\Delta x \cdot \Delta p > \frac{h}{4\pi} \quad \text{Or} \quad m \Delta x \cdot \Delta v \geq \frac{h}{4\pi} \quad \text{Or} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

Quantum Numbers:

- * Principal quantum number(n)=1,2,3,4....to ∞
- * Orbital angular momentum number 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 $L = \frac{h}{2\pi} \sqrt{\ell(\ell+1)} = \hbar \sqrt{\ell(\ell+1)} \left[\hbar = \frac{h}{2\pi} \right]$

Chemical Thermodynamic

IUPAC Sign convention about Heat and Work:

Work done by the system = Positive

Work done on the system = Negative

1st Law of Thermodynamics

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

Law of equipartition of energy:

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

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

Where f = degrees of freedom for that gas.

F=3 for monoatomic

=5 for diatomic or linear polyatomic

=6 for non-linear polyatomic

Calculation of heat (q):

Total heat capacity:

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

Molar heat capacity:

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

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

Specific heat capacity (s):

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

WORK DONE (w):

Isothermal Reversible expansion/compression of an ideal gas:

$$W = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

Reversible and irreversible isochoric processes.

Since $dV=0$

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

Reversible isobaric processes:

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

Adiabatic reversible expansion:

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

Reversible Work:

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

Irreversible Work:

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

And use $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Free expansion—Always going to be irreversible and since $P_{\text{ext}} = 0$

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

If no. heat is supplied $q=0$

Then $\Delta E=0$ SO $\Delta T=0$.

Application of 1st Law:

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

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

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 = Enthalpy (state function and extensive property)

$$H = U + PV$$

$$\Rightarrow C_p - C_v = R \text{ (Only for ideal gas)}$$

Second Law of Thermodynamics:

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

Entropy(S):

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

Entropy calculation for an ideal gas undergoing a process:

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

$$P_1 V_1 T_1 \qquad P_2 V_2 T_2$$

$$\Delta S_{\text{system}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad (\text{Only for an ideal gas})$$

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

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

Criteria of spontaneity:

- (i) If ΔG_{system} is (-ve) $< 0 \Rightarrow$ process is spontaneous
- (ii) If ΔG_{system} is (+) $> 0 \Rightarrow$ process is non spontaneous
- (iii) If $\Delta G_{\text{system}} = 0 \Rightarrow$ system is at equilibrium.

Physical interpretation of ΔG :

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

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

Standard Free Energy Change (ΔG°):

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

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

4. ΔG_f° for elemental state = 0
5. $\Delta G_f^\circ = G_{\text{Products}}^\circ - G_{\text{Reactants}}^\circ$

Thermochemistry:

Change in standard enthalpy

$$\Delta H^\circ = H_{m,2}^\circ - H_{m,1}^\circ$$

=heat added at constant pressure

$$= C_p \Delta T$$

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

→ Reaction will be endothermic as we have to supply extra heat to reactants to convert it into products

If $H_{\text{products}} < H_{\text{reactants}}$

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

Enthalpy change of a reaction:

$$\begin{aligned}\Delta H^{\circ}_{\text{reactions}} &= H^{\circ}_{\text{products}} - H^{\circ}_{\text{reactants}} \\ &= \text{Positive} \rightarrow \text{endothermic} \\ &= \text{negative} \rightarrow \text{exothermic}\end{aligned}$$

Temperature Dependence of ΔH : (Kirchoff's equation)

For a constant volume 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 $\Delta C_p = C_p(\text{Products}) - C_p(\text{reactants})$

For a constant volume reaction

$$\Delta E_2^{\circ} = \Delta E_1^{\circ} + \int \Delta C_v \cdot dT$$

Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

$$\Delta H_r^{\circ} = \sum v_B \Delta H_{f, \text{products}}^{\circ} - \sum v_B \Delta H_{f, \text{reactants}}^{\circ}$$

v_B is the stoichiometric coefficient.

Estimation of Enthalpy of a reaction from bond Enthalpies:

$$\Delta H = \left(\begin{array}{l} \text{Enthalpy required} \\ \text{to break reactants in} \\ \text{to gaseous atoms} \end{array} \right) - \left(\begin{array}{l} \text{Enthalpy released to} \\ \text{form products from the} \\ \text{gaseous atoms} \end{array} \right)$$

Resonance Energy:

$$\begin{aligned}\Delta H^{\circ}_{\text{resonance}} &= \Delta H^{\circ}_{f, \text{experimental}} - \Delta H^{\circ}_{f, \text{calculated}} \\ &= \Delta H^{\circ}_{c, \text{calculated}} - \Delta H^{\circ}_{c, \text{experimental}}\end{aligned}$$

Solid State

○ Classification of Crystal into Seven System

Crystal System	Unit cell Dimensions and angles	Bravais Example	Lattices
Cubic	$a = b = c ; \alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC	NaCl
Orthorhombic	$a \neq b \neq c ; \alpha = \beta = \gamma = 90^\circ$	SC, BCC, end centred & FCC	S_R (Rhombic Sulfur)
Tetragonal	$a = b \neq c ; \alpha = \beta = \gamma = 90^\circ$	SC, BCC	Sn, ZnO ₂
Monoclinic	$a \neq b \neq c ; \alpha = \gamma = 90^\circ \neq \beta$	SC, end centred	S_M (Monoclinic Sulfur)
Rhombohedral	$a = b = c ; \alpha = \beta = \gamma = 90^\circ$	SC	Quartz
Triclinic	$a \neq b \neq c ; \alpha \neq \beta \neq \gamma \neq 90^\circ$	SC	H ₃ BO ₃
Hexagonal	$a = b \neq c ; \alpha = \beta = 90^\circ ; \gamma = 120^\circ$	SC	Graphite

○ ANALYSIS OF CUBICAL SYSTEM

Property	SC	BCC	FCC
i. atomic radius (r) a = edge length	$\frac{a}{2}$	$\frac{\sqrt{3}a}{4}$	$\frac{a}{2\sqrt{2}}$
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. of voids			
(a) octahedral (Z)	-	-	4
(b) Tetrahedral (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)
(next) ¹	$a\sqrt{2}$	12 (shared by 2 cubes)
(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
(next) ¹	= a	6
(next) ²	= $a\sqrt{2}$	12
(next) ³	= $a \frac{\sqrt{3}}{2}$	24
(next) ⁴	= $a\sqrt{3}$	8

III. Face Centered Cubic (FCC) Structure :

Type of neighbor	Distance	no. of neighbors
nearest	$\frac{a}{\sqrt{2}}$	$12 = \left(\frac{3 \times 8}{2}\right)$
(next) ¹	a	$6 = \left(\frac{3 \times 8}{4}\right)$
(next) ²	$a\sqrt{\frac{3}{2}}$	24
(next) ³	$a\sqrt{2}$	12
(next) ⁴	$a\sqrt{\frac{5}{2}}$	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 :-

$$a_{\text{fcc}} = \frac{4}{\sqrt{3}} (r_{\text{Ca}^{2+}} + r_{\text{S}^{2-}})$$

c. **Zinc Blende (ZnS) C.No.(4:4)**

$$a_{\text{fcc}} = \frac{4}{\sqrt{3}} (r_{\text{Zn}^{2+}} + r_{\text{F}^-})$$

d. **Fluorite structure (CaF₂) C.No. (8 : 4)**

$$a_{\text{fcc}} = \frac{4}{\sqrt{3}} (r_{\text{Ca}^{2+}} + r_{\text{F}^-})$$

Solutions

1. OSMOTIC PRESSURE:

i. $\pi = \rho gh$

Where, ρ = density of solution, h = equilibrium height.

ii. **Van't-Hoff Formula** (For calculation of O.P.)

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

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

$$= C_1 + C_2 + C_3 + \dots$$

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

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

$$\pi = \left(\frac{C_1 V_1 + C_2 V_2}{V_1 + V_2} \right) RT \quad ; \quad \pi = \left(\frac{\pi_1 V_1 + \pi_2 V_2}{RT} \right)$$

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. IInd solution.
- c. **Hypotonic**- IInd solution is hypotonic w.r.t. Ist solution.

Abnormal Colligative Properties (In case of association or dissociation)

VAN'T HOFF CORRECTION FACTOR (i):

$$\begin{aligned} i &= \frac{\text{Exp/Observed/Actual/Abnormal value of colligative property}}{\text{Theoretical value of colligative property}} \\ &= \frac{\text{Exp./Observed no.of particles/Conc.}}{\text{Theoretical no.of particles}} = \frac{\text{Observed molality}}{\text{Theoretical molality}} \\ &= \frac{\text{Theoretical molar mass (formula mass)}}{\text{Theoretical/Observed molar mass (apparent molar mass)}} \end{aligned}$$

- $i > 1 \Rightarrow$ dissociation.
- $i < 1 \Rightarrow$ association.
- $i = \frac{\pi_{\text{exp}}}{\pi_{\text{theor}}}$
- $\therefore \pi = iCRT$
- $\pi = (iCRT)$
- $\pi = (i_1 C_1 + i_2 C_2 + i_3 C_3 \dots) RT$

Relation between i & α (degree of dissociation):

$$i = 1 + (n-1)\alpha \quad ; \text{ where, } n = x + y$$

Relation between degree of association β & i .

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

2. RELATIVE LOWERING OF VAPOUR PRESSURE (RLVP):

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

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

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

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

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

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

Where, n = No. of moles of solute; N = No. of moles of solvent

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

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

(M = molar mass of solvent)

It solute gets associated or dissociated

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

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

○ 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 $\rightarrow \frac{P_1^0 - P_1}{P_1^0} = X_2$

X_2 is the mole fraction of the solvent

- **Ostwald-Walker Method: Experimental or lab determination of**

$$\frac{\Delta P}{P} \text{ or } \frac{\Delta P}{P_s}$$

$$\frac{P - P_s}{P_s} = \frac{\text{Loss in wt. of solvent}}{\text{Loss in wt. of solution}}$$

$$\frac{P - P_s}{P_s} = \frac{\text{Loss in wt. of solvent}}{\text{Gain in wt. of dehydrating agent}}$$

3. ELEVATION IN BOILING POINT:

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

Where, ΔT_b = Boiling point elevation; K_b = Boiling point elevation constant; m = molality of the solution

$$K_b = \frac{RT_b^2}{1000 \times L_{\text{vap}}} \quad \text{OR} \quad K_b = \frac{RT_b^2 M}{1000 \times \Delta H_{\text{vap}}}$$

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

ΔH_{vap} = Enthalpy of vaporization

4. DEPRESSION IN FREEZING POINT

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

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

RAOULT'S LAW FOR BINARY (IDEAL) MIXTURE OF VOLATILE LIQUIDS:

$$P_A = X_A P_A^\circ$$

$$\therefore P_B = X_B P_B^\circ$$

$$\text{If } X_A^\circ > X_B^\circ$$

\therefore A is more volatile than B

$$\therefore \text{B.P of A} < \text{B.P of B}$$

\therefore According to Dalton's law

$$P_T = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

X_A' = mole fraction of A in vapour about the liquid/ solution.

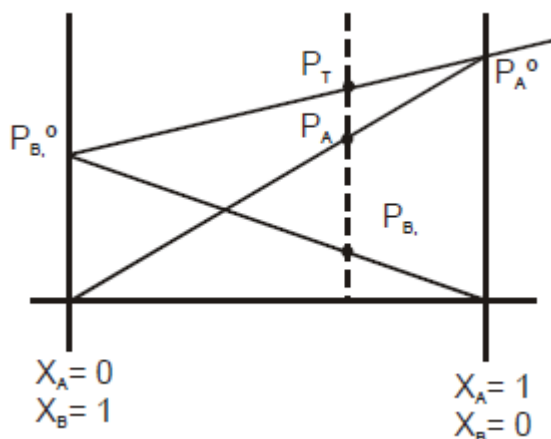
X_B' = mole fraction of B

$$P_A = X_A P_A^\circ = X_A' P_T$$

$$P_B = X_B P_B^\circ = X_B' P_T$$

$$\frac{1}{P_T} = \frac{X_A'}{P_A} + \frac{X_B'}{P_B}$$

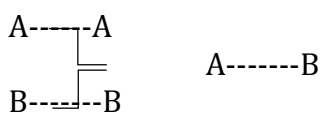
Graphical Representation:



A more volatile than B ($P_A^0 > P_B^0$)

Ideal solutions (mixtures):

Mixtures which follow Raoult's law at all temperature.



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

Eg.

1) Benzene + Toluene

2) Hexane + heptane.

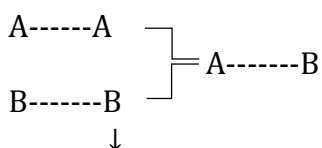
3) $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$

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

a. Positive deviation:-

i. $P_{T,\text{exp}} > (X_A P_A^0 + X_B P_B^0)$

ii.



(Weak force of attraction)

iii. $\Delta H_{\text{mix}} = +ve$ energy absorbed

iv. $\Delta V_{\text{mix}} = +ve$ ($1L + 1L > 2L$)

v. $\Delta S_{\text{mix}} = +ve$

vi. $\Delta G_{\text{mix}} = .ve$

Eg.

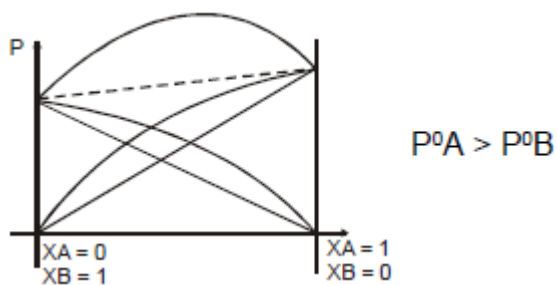
$\text{H}_2\text{O} + \text{CH}_3\text{OH}$

$\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$

$\text{C}_2\text{H}_5\text{OH} + \text{hexane}$

$\text{C}_2\text{H}_5\text{OH} + \text{cyclohexane}$.

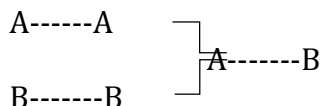
$\text{CHCl}_3 + \text{CCl}_4 \rightarrow$ dipole dipole interaction becomes weak.



b. Negative deviation

i. $P_{\text{exp}} < X_A P_A^0 + X_B P_B^0$

ii.



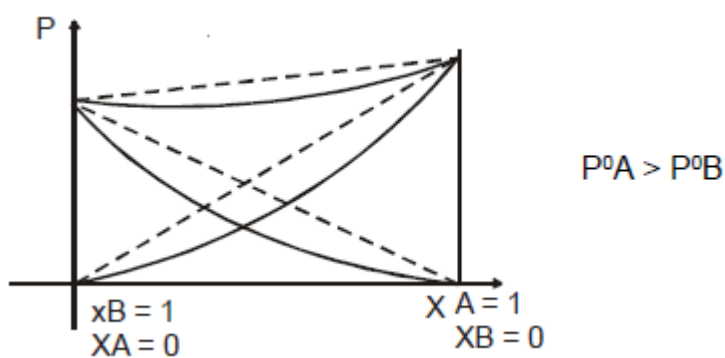
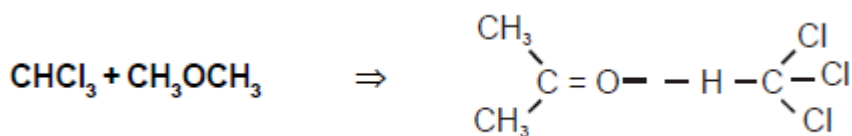
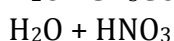
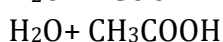
iii. $\Delta H_{\text{mix}} = -ve$

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

v. $\Delta S_{\text{mix}} = +ve$

vi. $\Delta G_{\text{mix}} = -ve$

eg.



Immiscible Liquids:

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

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

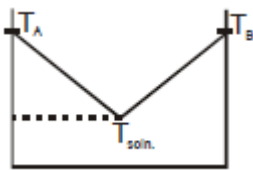
(iii) $P_B = P_B^0 X_B = P_B^0$ [Since, $X_B = 1$].

(iv) $P_{\text{total}} = P_A^0 + P_B^0$

(v) $\frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$

(vi) $\frac{P_A^0}{P_B^0} = \frac{W_A M_B}{M_A W_B}$

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



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

Henry Law:

$$m \propto P$$

$$m = kp$$

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

Equilibrium

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:

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

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

Relation between equilibrium constant & standard free energy change:

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

Reaction Quotient (Q):

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

Degree of Dissociation (α):

$\alpha = \text{no. of moles dissociated} / \text{initial no. of moles taken}$

= fraction of moles dissociated out of 1 mole.

Note: % dissociation = $\alpha \times 100$

Observed molecular weight and Observed Vapour Density of the mixture:

Observed molecular weight

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

$$\alpha = \frac{D-d}{(n-1)d} = \frac{M_r - M_o}{(n-1)M_o} \quad [(\text{Vapour density})_{\text{initial}} = D, (\text{Vapour density})_{\text{eq}} = d]$$

[Theoretical molecular weight = M_r , Observed molecular weight = M_o]

Vapour Pressure of Liquid:

$$\text{Relative Humidity} = \frac{\text{Partial Pressure of H}_2\text{O vapours}}{\text{Vapour pressure of H}_2\text{O at that temp.}}$$

Thermodynamics of Equilibrium:

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

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

IONIC EQUILIBRIUM

1. OSTWALD DILUTION LAW:

- Dissociation constant of weak acid (K_a),

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

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

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

Acidity and pH scale:

$\therefore \text{pH} = -\log[H^+]$ is the activity of H^+ ions = molar concentration for dilute solution.

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

$$\text{pH} = -\log[H^+]; \quad [H^+] = 10^{-\text{pH}}$$

$$\text{pOH} = -\log[OH^-]; \quad [OH^-] = 10^{-\text{pOH}}$$

$$\text{pKa} = -\log K_a; \quad K_a = 10^{-\text{pKa}}$$

$$\text{pKb} = -\log K_b; \quad K_b = 10^{-\text{pKb}}$$

PROPERTIES OF WATER:

1. In pure water $[H^+] = [OH^-]$, so it is Neutral.

2. Molar concentration of water = 55.56 M

3. Ionic product of water (K_w):

$$K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^\circ \text{ (experimentally)}$$

$$\text{pH} = 7 = \text{pOH} \quad \Rightarrow \quad \text{neutral}$$

$$\text{pH} < 7 \text{ or } \text{pOH} > 7 \quad \Rightarrow \quad \text{acidic}$$

$$\text{pH} > 7 \text{ or } \text{pOH} < 7 \quad \Rightarrow \quad \text{Basic}$$

4. Degree of dissociation of water (K_w):

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

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**

$$pK_a + pK_b = pK_w = 14 \quad \text{at } 25^\circ\text{C}$$

$$pK_a \text{ of } H_3O^+ \text{ ions} = -1.74$$

$$pK_b \text{ of } OH^- \text{ ions} = -1.74.$$

○ **pH Calculations of Different Types of Solutions:**

a. Strong acid solution:

- i. If concentration is greater than 10.6M
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⁺] × [OH⁻] = 10⁻¹⁴

c. pH of mixture of two strong acids :

$$\text{Number of H}^+ \text{ ions from I-solution} = N_1V_1$$

$$\text{Number of H}^+ \text{ ions from II-solution} = N_2V_2$$

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

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 :

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

$$\text{if } \alpha \ll 1 \text{ (1-}\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2$$

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

On increasing the dilution ⇒ C ↓ ⇒ α ↑ and [H⁺] ↓ ⇒ pH ↑

g. pH of a solution of a polyprotic weak acid

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

RELATIVE STRENGTH OF TWO ACIDES

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

h. pH of a mixture of two weak acid(both monoprotic) solutions:

$$[\text{H}^+] = \sqrt{K_{a_1} C_1 + K_{a_2} C_2 + K_w}$$

$$C_w K_w = 10^{-14} = K_w$$

$$[\text{H}^+] = \sqrt{C_1 K_{a_1} + C_2 K_{a_2} + 10^{-14}}$$

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

If $[\text{SA}] = C_1$ and $[\text{WA}] = C_2$, then $[\text{H}^+]$ from SA = C_1 and $[\text{H}^+]$ from WA = C_2

Let HA is a weak acid.

$$[\text{H}^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_a C_2}}{2}$$

**** If a strong acid of low conc is added in water then $[\text{H}^+]$ of solution can be calculated as**

$$[\text{H}^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_w}}{2}$$

o. SALT HYDROLYSIS:

Salt of	Type of hydrolysis	K_h	h	pH
a. weak acid & strong base anionic	anionic	$\frac{k_w}{k_a}$	$\sqrt{\frac{k_w}{k_a c}}$	$7 + \frac{1}{2} \text{pk}_a + \frac{1}{2} \log c$
b. strong acid & weak base	cationic	$\frac{k_w}{k_b}$	$\sqrt{\frac{k_w}{k_b c}}$	$7 + \frac{1}{2} \text{pk}_b + \frac{1}{2} \log c$
c. weak acid & weak base	Both	$\frac{k_w}{k_a k_b}$	$\sqrt{\frac{k_w}{k_a k_b c}}$	$7 + \frac{1}{2} \text{pk}_a + \frac{1}{2} \text{pk}_b$
d. Strong acid & strong base	-----do not hydrolysed-----			pH=7

Hydrolysis of polyvalent anions or cations

For $[\text{Na}_3\text{PO}_4] = C$

$$K_{a1} \times K_{h3} = K_3$$

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

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

Generally pH is calculated only using the first step Hydrolysis

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

$$h = \sqrt{\frac{K_{h1}}{C}} \Rightarrow [OH^-] = ch = \sqrt{Kh_1 \times c} \Rightarrow [H^+] = \sqrt{\frac{K_w \times K_{a3}}{C}}$$

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

BUFFER SOLUTION

a. **Acidic Buffer:** e.g. $NH_3OH + NH_4Cl$. (weak base and salt of its conjugate acid).

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

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

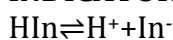
$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Buffer capacity (index):

$$\text{Buffer capacity} = \frac{\text{Total no. of moles of acid / alkali added per litre}}{\text{Change in pH}}$$

$$\text{Buffer capacity} = \frac{dx}{d\Delta pH} = 2.303 \frac{(a+x)(b+x)}{a+b}$$

INDICATOR:



$$\text{Or } [H^+] = H^+ \times \frac{[HIn]}{[In]}$$

$$\therefore pH = pK_{HIn} + \log \frac{[In]}{[HIn]}$$

$$\Rightarrow pH = pK_{HIn} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

○ ISOELECTRIC POINT:

$$[H^+] = \sqrt{K_{a1} K_{a2}}$$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

SOLUBILITY PRODUCT:

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

Redox Reaction and Electrochemistry

ELECTRODE POTENTIAL

For any electrode → oxidation potential(O.P.) = -Reduction potential(R.P.)

$E_{\text{cell}} = \text{R.P. of cathode} - \text{R.P. of anode}$

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

E°_{cell} is always a +ve quality & Anode will be electrode of low R.P.

GIBBS FREE ENERGY CHANGE:

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

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

NERNST EQUATION (Effect of concentration and temp of an emf of cell)

⇒ $\Delta G = \Delta G^{\circ} + RT \ln Q$ (Where Q is reaction quotient)

$$\Delta G^{\circ} = -RT \ln K_{\text{eq}}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log Q$$

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

At chemical equation

$$\Delta G = 0; \quad E_{\text{cell}} = 0$$

$$\circ \quad \log K_{\text{eq}} = \frac{nE^{\circ}_{\text{cell}}}{0.0591}$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n} \log K_{\text{eq}}$$

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

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

CONCENTRATION CELL:

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

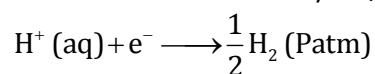
$$E = \frac{0.0591}{2} \log \left(\frac{P_1}{P_2} \right)$$

DIFFERENT TYPES OF ELECTRODES:

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

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

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



$$E = E^\circ - 0.0591 \log \frac{P_H^{\frac{1}{2}}}{[H^+]}$$

3. Oxidation-reduction Electrode $Pt/Fe^{2+}, Fe^{3+}$

As a reduction electrode $Fe^{3+} + e^- \rightarrow Fe^{2+}$

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

4. Metal-Metal insoluble salt Electrode eg. $Ag/AgCl, Cl^-$

as a reduction electrode $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$

$$E_{Cl^-/AgCl/Ag} = E^\circ_{Cl^-/AgCl/A} - 0.0591 \log[Cl^-]$$

CALCULATION OF DIFFERENT THERMODYNAMICS FUNCTION OF CELL REACTION

○ $\Delta G = -n F E_{cell}$

○ $S = - \left[\frac{dG}{dT} \right]_p$ (At constant pressure)

○ $\Delta S = - \left[\frac{d(\Delta G)}{dT} \right]_p = nF \left(\frac{d}{dt} (E_{cell}) \right)_p$

○ $\left[\frac{\partial E}{\partial T} \right]_p =$ Temperature coefficient of e.m.f of the cell.

$$E = a + bT + cT^2 + \dots$$

○ $\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right)_p - E \right]$

○ ΔC_p of cell reaction

$$C_p = \frac{dH}{dT}$$

$$\Delta C_p = \frac{d}{dT} (\Delta H)$$

$$\Delta C_{p} = nFT \frac{d^2 E_{cell}}{dT^2}$$

FARADAY'S LAW OF ELECTROLYSIS:

First Law:

$$w = zq \quad w = Z it \quad Z = \text{Electrochemical equivalent of substance}$$

Second law:

$$W \propto E \quad \frac{W}{E} = \text{Constant}$$

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

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

$$\text{CURRENT EFFICIENCY} = \frac{\text{actual mass deposited/produced}}{\text{Theoretical mass deposited/produced}} \times 100$$

○ **CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe on cathode.**

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{\text{Cu}^{2+}} = E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{\text{Fe}^{2+}}$$

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

CONDUCTANCE:

- Conductance = $\frac{1}{\text{Resistance}}$

- **Specific conductors or conductivity**

(Reciprocal of specific resistance) $\kappa = \frac{1}{\rho}$

K=specific conductance

- **Equivalent conductance:**

$$\lambda_E = \frac{\kappa \times 1000}{\text{Normality}} \quad \text{unit: ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$$

- **Molar conductance:**

$$\lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} \quad \text{unit: ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$$

$$\text{Specific conductance} = \text{conductance} \times \frac{l}{a}$$

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 electrolyte: $\lambda_\infty = n_+ \lambda_{+}^\infty + n_- \lambda_{-}^\infty$ 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 λ_M^0 of weak electrolytes:

$$\lambda_{M(\text{CH}_3\text{COOH})}^0 = \lambda_{M(\text{CH}_3\text{COONa})}^0 + \lambda_{M(\text{HCl})}^0 - \lambda_{M(\text{NaCl})}^0$$

2. To calculate degree of dissociation of a weak 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}

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

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

Absolute ionic mobility:

$$\lambda^0_c \propto \mu_c \quad ; \quad \lambda^0_a \propto \mu_a$$
$$\lambda^0_c = F \mu_c^0 \quad ; \quad \lambda^0_c = F \times \mu_c^0$$

$$\text{Ionic Mobility } \mu = \frac{v \rightarrow \text{Speed}}{(v/\ell) \rightarrow \text{Potential gradient}}$$

Transport Number:

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

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

Chemical Kinetics

CHEMICAL KINETICS & RADIOACTIVITY

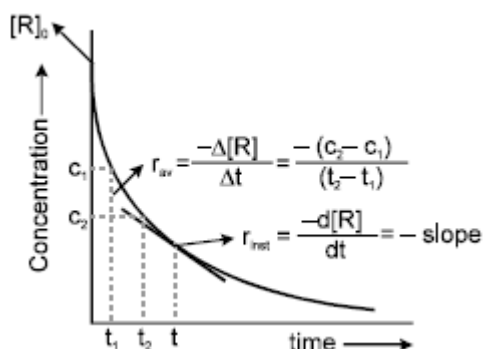
RATE/VELOCITY OF CHEMICAL REACTION:

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

Types of Rates of chemical reaction:

For a reaction $R \rightarrow P$

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



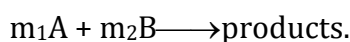
$$R_{\text{instantaneous}} = \lim_{t \rightarrow 0} \left[\frac{\Delta c}{\Delta t} \right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

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 = (conc)^{1-order} time⁻¹

Order of reaction:



$R \propto [A]^p [B]^q$ Where p may or may not be equal to m₁ & similarly q may or may not be equal to m₂.

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:

C₀ or 'a' is initial concentration and C_t or a - x is concentration at time 't'

a. zero order reactions :

$$\text{Rate} = k [\text{conc.}]^0 = \text{constant}$$

$$\text{Rate} = k = \frac{C_0 - C_t}{t} \quad \text{or} \quad C_t = C_0 - kt$$

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

At $t_{1/2}, C_t = \frac{C_0}{2}$, so $kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k} \therefore t_{1/2} \propto C_0$

b. First Order Reactions:

i. Let a 1st order reaction is, $A \longrightarrow \text{Products}$

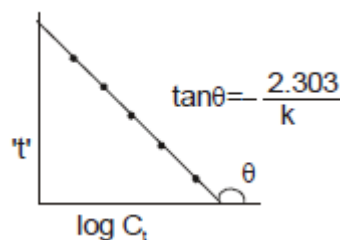
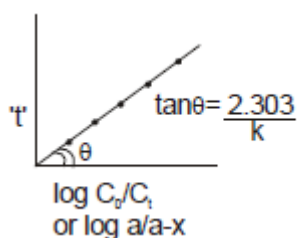
$$t = \frac{2.303}{k} \log \frac{a}{a-x} \text{ or } k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} = \text{Independent of initial concentration}$$

$$t_{\text{avg}} = \frac{1}{k} = 1.44 t_{1/2}$$

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

$A + A \rightarrow \text{Products}$ $A + B \rightarrow \text{Products.}$

$a \quad a$ $a \quad b \quad 0$

$(a-x)(a-x)$ $a-x \quad b-x$

$$\therefore \frac{dx}{dt} = k(a-x)^2 \qquad \frac{dx}{dt} = k(a-x)(b-x)$$

$$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt \qquad k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

d. Pseudo first order reaction:

\therefore For $A+B \longrightarrow \text{Products}$ $[\text{Rate} = K [A]^1 [B]^1]$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Now if 'B' is taken in large excess $b \gg a$.

$$\Rightarrow k = \frac{2.303}{bt} \log \frac{a}{a-x}$$

\therefore 'b' is very large can be taken as constant

$$\Rightarrow kb = \frac{2.303}{bt} \log \frac{a}{a-x}$$

$$\Rightarrow k' = \frac{2.303}{t} \log \frac{a}{a-x}, k \text{ is pseudo first order rate constant}$$

METHODS TO DETERMINE ORDER OF A REACTION

a. Initial rate method:

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

$$[C] = \text{constant}$$

then for two different initial concentrations of A we have

$$r_{01} = k [A_0]_1^a, \quad r_{02} = k [A_0]_2^a$$

$$\Rightarrow \frac{r_{01}}{r_{02}} = \left(\frac{[A_0]_1}{[A_0]_2} \right)^a$$

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

c. Method of half lives:

$$\text{for } n^{\text{th}} \text{ order reaction } t_{1/2} \propto \frac{1}{[R_0]^{n-1}}$$

d. Ostwald Isolation Method :

$$\text{rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$$

MEHODS 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.

$$k = \frac{2.303}{t} \log \frac{P_0(n-1)}{nP_0 - P_t} \text{ \{Formula is not applicable when } n=1, \text{ the value of } n \text{ can be fraction also. \}}$$

b. By titration method:

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

2. Study of acid hydrolysis of an ester.

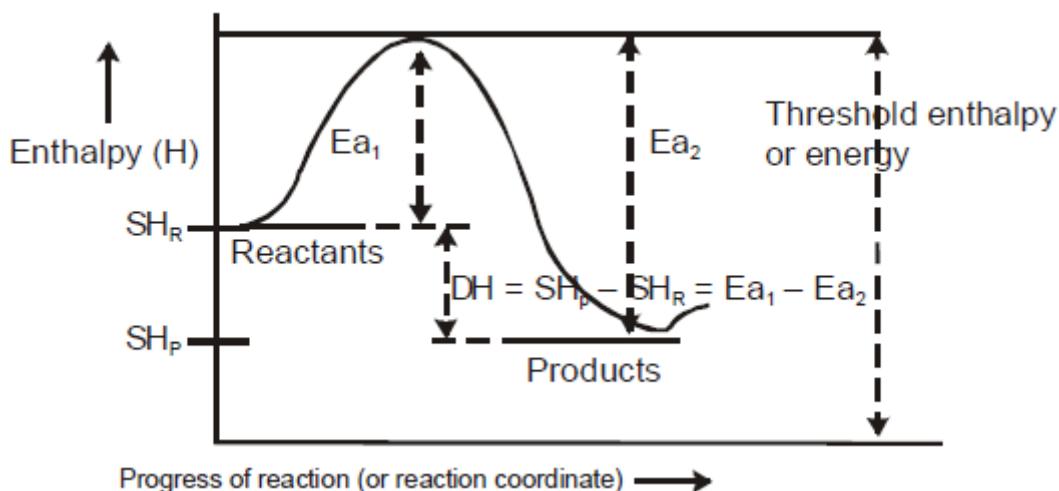
$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

3. *By measuring optical rotation produced by the reaction mixture:*

$$k = \frac{2.303}{t} \log \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

EFFECT OF TEMPERATURE ON RATE OF REACTION.

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



SH_R = Summation of enthalpies of reactants
 SH_P = Summation of enthalpies of products
 DH = Enthalpy change during the reaction
 E_{a1} = Energy of activation of the forward reaction
 E_{a2} = Energy of activation of the backward reaction
 $E_P > E_R$ → endothermic
 $E_P < E_R$ → exothermic

$\Delta H = (E_p - E_r) =$ enthalpy change

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

$E_{\text{threshold}} = E_{af} + E_r = E_b + E_p$

Arrhenius equation

$$k = A e^{-E_a/RT}$$

$$r = k [\text{conc.}]^{\text{order}}$$

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

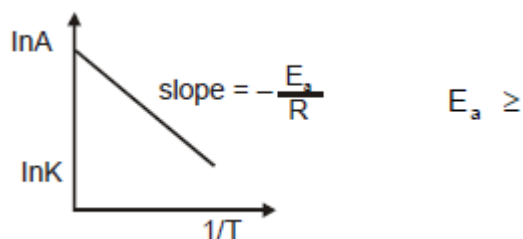
If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have

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

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

0

$$\text{❖ } T \rightarrow \infty, k \rightarrow A$$



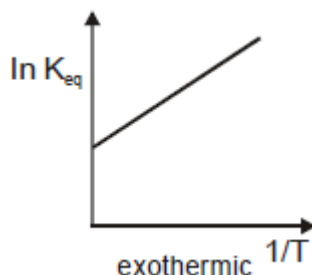
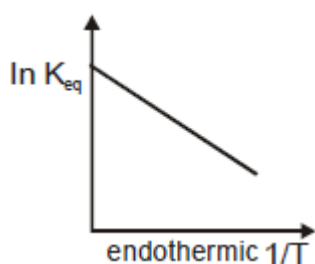
REVERSIBLE REACTIONS

$$K_f = A_f e^{-E_{af}/RT}$$

$$K_b = A_b e^{-E_{ab}/RT}$$

$$K_{eq} = \frac{K_f}{K_b} = \left(\frac{A_f}{A_b} \right) e^{-(E_{af} - E_{ab})/RT}$$

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \ln \left(\frac{A_f}{A_b} \right)$$



$$\frac{[B]}{[C]} = \frac{K_1}{K_2} \Rightarrow E_a = \frac{E_{a1}k_1 + E_{a2}k_2}{k_1 + k_2}$$

ii. REVERSIBLE 1ST ORDER REACTION (both forward and backward)

$$x = \frac{K_f a}{K_f + k_b} (1 - e^{-(k_f + k_b)t})$$

$$k_f + k_b = \frac{1}{t} \ln \left(\frac{x_{eq.}}{x_{eq.} - x} \right)$$

iii. SEQUENTIAL 1ST ORDER REACTION

$$[A] = [A]e^{-k_1 t}$$

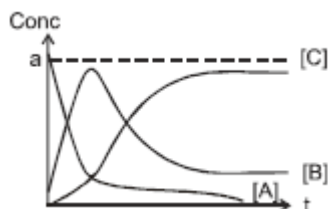
$$X = a(1 - e^{-k_1 t})$$

$$y = \frac{K_1 a}{K_2 - K_1} \{ e^{-k_1 t} - e^{-k_2 t} \}$$

$$T_{B(max)} = \frac{1}{(K_1 - K_2)} \ln \frac{K_1}{K_2}$$

CASE-I

$$K_1 \gg K_2$$



CASE II :

$$K_2 \gg K_1$$

