Chemistry JEE (Main and Advance) Formula

ATOMIC STRUCTURE

- Estimation of closet distance of approach (derivation) of α - particle:

$$R = \frac{4KZe^2}{m_\alpha V_\alpha^{\ 2}}$$

- The radius of a nucleus: $R = R_0 \left(A\right)^{1/3} cm$

- Planck's Quantum theory: energy of one photon $= hv = \frac{hc}{\lambda}$

- Photoelectric effect: $hv = hv_0 + \frac{1}{2} m_e v^2$

- Bohr's Model for Hydrogen like atoms:

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

2. $E_n = -\frac{E_1}{n^2} z^2 = 2.178 \times 10^{-18}$ J/atom= $13.6\frac{z^2}{n^2} eV; E_1 = \frac{-2\pi^2 me^4}{n^2}$

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

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

- De-Broglie wavelength:

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

Wavelength of emitted photon:

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

- No. of photons emitted by a sample of H atoms:

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

- Heisenberg’s uncertainty principle:

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

- 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 $(\ell)=0,1,\ldots\text{to}(n-1)$.

❖ 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 $=\frac{h}{2\pi}\sqrt{\ell(\ell+1)}=\hbar\sqrt{\ell(\ell+1)} \quad \left[\hbar=\frac{h}{2\pi}\right]$.

STOICHIOMETRY

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

Total Number of nucleons.

➢ Y-Map

- Density:

$$\text{Specific gravity } = \frac{\text{density of the substance}}{\text{density of water at } 4^{\circ}\text{C}}$$

- For gases:

- Absolute density (mass/volume) $= \frac{\text{Molar mass of the gas}}{\text{Molar volume of the gas}} \Rightarrow \rho = \frac{PM}{RT}$.
- Vapour density V.D. $= \frac{d_{gas}}{d_{H_2}} = \frac{PM_{gas/RT}}{PM_{H_2/RT}} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2}$
- $M_{gas} = 2\text{V.D}$.

- Mole-mole analysis:

- Concentration terms:

Morality (M):

Morality= $(M) = \frac{w \times 1000}{(Mol.wt \text{ of solute }) \times \text{V}_{\text{inml}}}$

Molality(m):

Molality = $= \frac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 1000 = 1000\text{w}_1 / \text{M}_1\text{w}_2$

- Mole fraction (x):

$\therefore$ Mole fraction of solution $(x_1) = \frac{n}{n+N}$ $\therefore$ 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) $\%\text{w}/\text{v} = \frac{\text{mass of solute in gm}}{\text{mass of solution in ml}} \times 100$

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

- Derive the following conversion:

1. Mole fraction of solute into molarity of solution $M = \frac{x_2 \rho \times 1000}{x_1 M_1 + M_2 x_2}$
2. Molarity into mole fraction $x_2 = \frac{MM_1 \times 1000}{\rho \times 1000 - MM_2}$.
3. Mole fraction into molality $m = \frac{x_2 \times 1000}{x_1 M_1}$.
4. Molality into mole fraction $x_2 = \frac{mM_1}{1000 + m_1}$
5. Molality into molarity $M = \frac{m\rho \times 1000}{1000 + \text{mM}_2}$
6. Molarity into Molality $m = \frac{M \times 1000}{1000\rho - M_2}$

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:

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

- 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 element, equivalent weight (E)= $(E) = \frac{\text{Atomic weight}}{\text{Valency -factor}}$

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

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

- Equivalent weight $(E)=\dfrac{\text{Atomic or moleculear weight}}{\text{v.f.}}$ (v.f. = valency factor)

❖ Concept of number of equivalents:

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

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

- Normality (N) :

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

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:

$\text{N}_1\text{V}_1=\text{N}_2\text{V}_2$
$\text{n}_1\text{M}_1\text{V}_1=\text{n}_2\text{M}_2\text{V}_2$

- Volume strength of H_2O_2:

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

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

$$\text{Morality of } H_2O_2 (M) = \frac{\text{Volume strength of } H_2O_2}{11.2}$$

- Measurement of Hardness :

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

- Calculation of available chlorine from a sample of bleaching powder:

% of $Cl_2 = \frac{3.55 \times x \times V(mL)}{W(g)}$ where $x =$ molarity of hypo solution and $v = m$m. of hypo solution used in titration.

GAEOUS 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, $V \alpha T$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

- Gay-lussac's law:

At constant volume, $\mathrm{P} \alpha T$

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

- Ideal gas equation:

$PV = nRT$

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

- Daltons law of partial pressure:

$P_1 = \frac{n_1 RT}{v}$, $P_2 = \frac{n_2 RT}{v}$, $P_3 = \frac{n_3 RT}{v}$ and so on.

Total pressure $= P_1 + P_2 + P_3 + ...$

Partial pressure = mole fraction × Total pressure

- Amagat's law of partial volume:

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

- Average molecular mass of gaseous mixture:

$$M_{\text{mix}} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$

- 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 :

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

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

- Root mean square speed

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

- Average speed:

$$U_{av}=U_1+U_2+U_3+.....+U_N$$

$$U_{avg}=\sqrt{\frac{8RT}{\pi m}}=\sqrt{\frac{8KT}{\pi m}}$$

K is Boltzmann constant.

- Most probable speed:

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

- Vander wall's equation:

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

- Critical constants

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

- Vander wall equation in virial form :

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

- Reduced Equation of state:

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

THERMODYNAMICS

- Thermodynamic process:

1. Isothermal process: $T=$ constant

$$\mathrm{dT}=0$$

$$\Delta T=0$$

2. Isochoric process: $V=$ constant

$$\mathrm{dV}=0$$

$$\Delta\mathrm{V}=0$$

3. Isobaric process: $P=$ constant

$$\mathrm{dP}=0$$

$$\Delta P=0$$

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

- 1^{st} law of thermodynamics

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

- Law of equitation of energy:

$$U = \frac{f}{2} nRT$$ (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 polyatomic

=6 for non-linear polyatomic

- Calculation of heat (q):

Total heat capacity:

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

- 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):

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

- Work done (w):

❖ Isothermal Reversible expansion/compression of an ideal gas:

$$\mathrm{W} = -\mathrm{nRT}\ln\left(\mathrm{V}_{\mathrm{t}} N_{)}\right)$$

❖ Reversible and irreversible isochoric processes:

Since $dV = 0$

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

❖ Reversible isobaric process:

$$W = P\left(V_f - V_{)}\right.$$

❖ Adiabatic reversible expansion:

$$\Rightarrow \quad T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

❖ Reversible Work:

$$\mathbf{W} = \frac{\mathrm{P}_2 V_2 - P_1 V_1}{\gamma - 1} = \frac{nR\left(T_2 - T_1\right)}{\gamma - 1}$$

❖ Irreversible Work:

$$\mathbf{W} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = \frac{nR\left(T_2 - T_1\right)}{\gamma - 1} nC_v\left(T_2 - T_1\right) = -P_{\mathrm{ext}}\left(V_2 - V_1\right) \text{ and use } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

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

so $\mathrm{dW} = -\mathrm{P}_{\mathrm{ext}} . \ \mathrm{dV} = 0$

If no. heat is supplied $q = 0$

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

- Application of 1st Law :

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

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

- 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)

$H = U + PV$

$\Rightarrow C_p - C_v = R$ (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):

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

- Entropy calculation for an ideal gas undergoing a process:

State A $\overset{irr}{\underset{\Delta s_{irr}}{\rightarrow}}$ State B

$P_1, V_1, T_1 \quad P_2, V_2, T_2$

$$\Delta S_{system} = nc_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$ (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 $(-ve) < 0 \Rightarrow$ process is spontaneous

(ii) (ii) If ΔG_{system} is $> 0 \Rightarrow$ process is non spontaneous

(iii) If $\Delta G_{system} = 0 \Rightarrow$ system is at equilibrium

- Physical interpretation of $\Delta\mathbf{G}$:

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

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

- Standard Free Energy Change $\left(\Delta G^{\circ}\right)$

  1. $\Delta G^{0} = -2.303RT\log_{10}\mathrm{K}$

  2. At equilibrium $\Delta\mathrm{G} = 0$.

  3. The decrease in free energy $(-\Delta G)$ is given as

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

  4. $\Delta\mathrm{G}_{\mathrm{f}}^{0}$ for elemental state $=0$

  5. $\Delta\mathrm{G}_{\mathrm{f}}^{0} = \mathrm{G}_{\text{products}}^{0} - \mathrm{G}_{\text{Reac tants}}^{0}$

- Thermochemistry:

  Change in standard enthalpy

  $\Delta\mathrm{H}^{\circ} = \mathrm{H}_{\mathrm{m},2}^{0} - \mathrm{H}_{\mathrm{m},1}^{0}$

  = heat added at constant pressure. $= \mathrm{C}_{\mathrm{p}}\Delta\mathrm{T}$.

  If $\mathrm{H}_{\text{products}} > \mathrm{H}_{\text{reactants}}$

→ 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 : $\Delta H^{\circ}_{reactions} = H^{\circ}_{products} - H^{\circ}_{reactants}$

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

  = positive –endothermic

  = negative - exothermic

- Temperature Dependence Of ΔH : (Kirchhoff's equation):

  For a constant volume reaction

  $$\Delta H^{\circ}_2 = \Delta H^{\circ}_1 + \Delta C_p \left(T_2 - T_1\right)$$

  where $\Delta C_p = C_p$ (products) $-C_p$ (reactants)

  For a constant volume reaction

  $$\Delta E^0_2 = \Delta E^0_1 + \int \Delta C_V \cdot dT$$

- Enthalpy of Reaction from Enthalpies of Formation:

  The enthalpy of reaction can be calculated by

$\Delta H_r^o = \sum v_B \Delta H_f^o, \text{products} - \sum v_B \Delta H_f^o, \text{reactants}$ v_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

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

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

CHEMICAL EQUILIBRIUM

- At equilibrium:
  - (i) Rate of forward reaction = rate of backward reaction
  - (ii) Concentration (mole/liter) of reactant and product becomes constant
  - (iii) $\Delta G = 0$
  - (iv) $Q = K_{\text{eq}}$

- 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

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

- Relation between K_p & K_x

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

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

- Relation between equilibrium constant & standard free energy change:

$$\Delta G^0 = -2.303RT\log \mathrm{K}$$

- Reaction Quotient (Q) :

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

- Degree of Dissociation (α):

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

= fraction of moles dissociated out of 1 mole

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

- Observed molecular weight and Observed Vapor Density of the mixture:

Observed molecular weight of

$$A_n(g) = \frac{\text{molecular weight of equilibriummixture}}{\text{totalno. of moles}}$$

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

- 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 ℓ nk 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 shifts in the forward direction with increase in temperature
- 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

- Vapor Pressure of Liquid:

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

- Thermodynamics of Equilibrium:

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

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

IONIC EQUILIBRIUM

- OSTWALD DILUTION LAW:

Dissociation constant of weak acid

$(\mathrm{K_a}),\quad \mathrm{K_a} = \dfrac{\left[\mathrm{H^+}\right]\left[\mathrm{A^-}\right]}{[\mathrm{HA}]} = \dfrac{[\mathrm{C}\alpha][\mathrm{C}\alpha]}{\mathrm{C}(1-\alpha)} = \dfrac{\mathrm{C}\alpha^2}{1-\alpha}$

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

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

- Acidity and pH scale

$\therefore \mathrm{pH} = -\log \mathrm{a_{H^+}}$ (where $\mathrm{a_{H^+}}$ is the activity of $\mathrm{H^+}$ ions = molar concentration for dilute solution)

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

$\mathrm{pH} = -\log\left[\mathrm{H^+}\right]; \qquad \left[\mathrm{H^+}\right] = 10^{-\mathrm{pH}}$

$\mathrm{pOH} = -\log\left[\mathrm{OH^-}\right]; \qquad \left[\mathrm{OH^-}\right] = 10^{-\mathrm{pOH}}$

$\mathrm{pKa} = -\log \mathrm{Ka}; \qquad \mathrm{Ka} = 10^{-\mathrm{pKa}}$

$\mathrm{pKb} = -\log \mathrm{Kb}; \qquad \mathrm{Kb} = 10^{-\mathrm{pKb}}$

- PROPERTIES OF WATER:

1. In pure water $\left[\mathrm{H^+}\right] = \left[\mathrm{OH^-}\right]$ so it is Neutral.
2. Moler concentration / Molarity of water $= 55.56\mathrm{M}$.
3. Ionic product of water (K_w) :

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

$pH = 7 = pOH$ $\Rightarrow$ neutral

$pH < 7$ or $pOH > 7$ $\Rightarrow$ acidic

$pH > 7$ or $pOH < 7$ $\Rightarrow$ Basic

4. Degree of dissociation of water:

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

5. Absolute dissociation constant water:

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

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

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

$\Rightarrow$ Note: for a conjugate acid- base pairs

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

pK_a of H_3O^+ ions $= -1.74$

pK_b of OH^- ions $= -1.74$.

➢ - pH Calculations of Different Types of Solutions:

(i) 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

(ii) Strong base solution:

Using similar method as in part (a) calculate first $\left[OH^-\right]$ and then use

$\left[H^+\right]\times\left[OH^-\right]=10^{-14}$

(iii) pH of mixture of two strong acids .:

Number of H^+ ions from I-solution $= N_1 V_1$

Number of H^+ ions from II-solution $= N_2 V_2$

$$\left[H^+\right]=N=\frac{N_1 V_1+N_2 V_2}{V_1+V_2}$$

(iv) pH of mixture of two strong bases:

$$\left[OH^-\right]=N=\frac{N_1 V_1+N_2 V_2}{V_1+V_2}$$

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

If $N_1 V_1 > N_2 V_2$, then solution will be acidic in nature and

$$\left[H^+\right]=N=\frac{N_1 V_1-N_2 V_2}{V_1+V_2}$$

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

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

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

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

if $\alpha < 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_a}{C}}$ (is valid if $\alpha < 0.1$ or 10%)

On increasing the dilution $\Rightarrow \quad C\downarrow \Rightarrow \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

(vii) pH of a solution of a polyprotic weak acid :

$$pH = \frac{1}{2}\left(pK_{a_1} - \log C\right)$$

➢ RELATIVE STRENGTH OF TWO ACIDS

$$\frac{[H^+]\text{furnished by I acid}}{[H^+]\text{furnished by II acid}} = \frac{C_1\alpha_1}{c_2\alpha_2} = \sqrt{\frac{k_{a_1}c_1}{k_{a_2}c_2}}$$

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

* If water is again considered third weak acid in solution of two weak acid then

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2 + K_w}$$

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

$$[H^+] = \sqrt{C_1 K_{a1} + C_2 K_{a2} + 10^{-14}}$$

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

If $[SA]=C_1$ and $[WA]=C_2$, then $\left[H^+\right]$from $SA=C_1$ and $\left[H^+\right]$from $WA=C_2$

Let HA is a weak acid.

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

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

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

- SALT HYDROLYSIS:

Salt of	Types 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				$pH = 7$

- Hydrolysis of polyvalent anions or cations

For $[Na_3PO_4]=C$.

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

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

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

- Generally pH is calculated only using the first step Hydrolysis

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

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

So, $pH = \frac{1}{2}\left[pK_W + pK_{a3} + \log C\right]$

- Hydrolysis of Amphiprotic Anion. (Cation is not Hydrolysed e.g. $NaHCO_3$, NaHS, etc.)

$$pH\left(HCO_3^-\right)=\left(\frac{pK_{a_1}+pK_{a_2}}{2}\right)$$

- Similarly for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions

$$pH_{\left(H_2PO_4^-\right)}=\left(\frac{pK_{a_1}+pK_{a_2}}{2}\right) \quad \text{and} \quad pH_{\left(HPO_4^{2-}\right)}=\left(\frac{pK_{a_2}+pK_{a_3}}{2}\right)$$

$$H_3PO_4\xrightarrow{k_{a1}}H_2PO_4^-\xrightarrow{k_{a2}}HPO_4^{2-}\xrightarrow{k_{a3}}PO_4^{3-}\text{ ionization}$$

$$\xleftarrow[K_{h_1}=\frac{K_w}{K_{a_1}}]{\qquad\qquad} \qquad \xleftarrow[K_{h2}=\frac{K_w}{K_{a2}}]{\qquad\qquad} \qquad \xleftarrow[K_{h1}=\frac{K_w}{K_{a3}}]{\qquad\qquad}$$

The pH of $H_3PO_4=\frac{1}{2}\left(pK_{a1}-\log C\right) \quad \therefore K_{a1}\ggg K_{a2}\gg K_{a3}$

pH of $NaH_2PO_4=\frac{1}{2}\left(pK_{a1}+pK_{a2}\right)$

pH of $Na_2HPO_4=\frac{1}{2}\left(pK_{a2}+pK_{a3}\right)$

pH of $Na_3PO_4=\frac{1}{2}\left(pKw+pKa_3+\log C\right) \quad \therefore$ Sec hydrolysis can neglect

- BUFFER SOLUTION:

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

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

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

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

- 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:

$$\mathrm{HIn \rightleftharpoons H^+ + In^-}$$

Or

$$\mathrm{\left[H^+\right] = k_{HIn} \times \frac{[HIn]}{\left[In^-\right]}}$$

$$\therefore \mathrm{pH = pK_{HIn} + \log\frac{\left[In^-\right]}{[HIn]} \Rightarrow pH{=}pK{+}\log\frac{[ionised\ form]}{[Unionised\ form]}}$$

- SIGNIFICANCE OF INDICATORS

Extent of reaction of different bases with acid (HCl) using two indicators :

	Phenolphthalein	**Methyl orange**

NaOH	$NaHCO_3$ 100% reaction is indicated $NaOH + HCl \rightarrow NaCl + H_2O$	100% reaction is indicated $NaOH + HCl \rightarrow NaCl + H_2O$
Na_2CO_3	50% reaction up to $NaHCO_3$ stage is indicated	$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$ 100% reaction is indicated
$NaHCO_3$	$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ No reaction is indicated	$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ 100% reaction is indicated $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

- ISOELECTRIC POINT

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

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

- SOLUBILITY PRODUCT

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

- CONDITION FOR PRECIPITATION

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

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

ELECTROCHEMISTRY

- ELECTRODEPOTENTIAL

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°_{Cell} = SRP of cathode - SRP of anode.

Greater the SRP value greater will be oxidizing power

- GIBBS FREE ENERGY CHANGE

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

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

$\Rightarrow \Delta G = \Delta G^{o} + RT\ell nQ$ (where Q is reaction quotient)

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

$$E_{cell} = E^{\circ}{}_{cell} - \frac{RT}{nF}\ell nQ$$
$$E_{cell} = E^{\circ}{}_{cell} - \frac{2.303RT}{nF}\log Q$$
$$E_{cell} = E^{\circ}{}_{cell} - \frac{0.0591}{n}\log Q \quad [\text{At 298K}]$$

- At chemical equilibrium

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

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

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

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

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

- CONCENTRATION CELL : A cell in which both the electrodes are made up of same material.

For all concentration cell $\mathrm{E^{0}_{cell}} = 0$.

(a) Electrolyte Concentration Cell :

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

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

(b) Electrode Concentration Cell :

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

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

- DIFFERENT TYPES OF ELECTRODES:

1. Metal-Metal ion Electrode

$$M(s)/M^{n+}. \quad M^{n+} + ne^- \rightarrow M(s) \quad E = E^0 + \frac{0.0591}{n}\log\left[M^{n+}\right]$$

2. Gas-ion Electrode $\mathrm{Pt/H_2(Patm)/H^+(XM)}$

as a reduction electrode $$\mathrm{H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(\ Patm\ ) \quad E = E^\circ - 0.0591\log\frac{P_{H_2}^{\frac{1}{2}}}{\left[H^+\right]}}$$

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

as a reduction electrode $$\mathrm{Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E = E^0 - 0.0591\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]}}$$

4. Metal-Metal insoluble salt Electrode eg. Ag/AgCl, $\mathrm{Cl^-}$

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

- $E_{\mathrm{Cl^-/AgCl/Ag}} = \mathrm{E^0_{Cl^-/AgCl/Ag}} - 0.0591\log\left[\mathrm{Cl^-}\right]$

- CALCULATION OF DIFFERENT THERMODYNAMICS FUNCTION OF CELL REACTION

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

- $S = -\left[\frac{dG}{dT}\right]_p$ (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 cofficient of e.m.f of the cell

$$E = a + bT + CT^2 +$$

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

- ΔCp of cell reaction

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

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

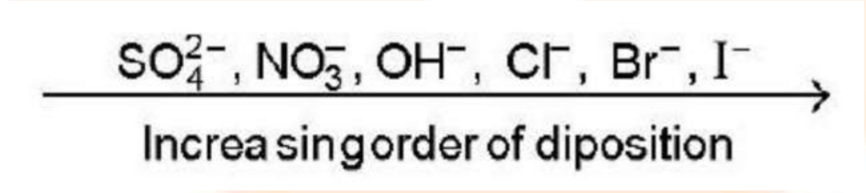
$$\Delta C_p = nFT\frac{d^2E_{cell}}{dT^2}$$

- ELECTROLYSIS:

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

Increasing order of depression

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



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

- FARADAY'S LAW OF ELECTROLYSIS:

- First Law:

$w = zq$ $w = Z$ it $Z =$ Electrochemical equivalent of substance

- Second law

$W \alpha E$ $\frac{W}{E} =$ constant $\frac{W_1}{E_1} = \frac{W_2}{E_2} = \ldots\ldots\ldots$

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

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

- CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe AT CATHODE

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

Condition for the simultaneous deposition of Cu & Fe on cathode

- CONDUCTANCE:

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

- Specific conductance or conductivity:

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

- Equivalent conductance:

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

- Molar conductance:

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

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

- KOHLRAUSCH'S LAW

- Variation of $\lambda_{eq} / \lambda_{\mathrm{M}}$ of a solution with concentration:

(a) Strong electrolyte

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

(b) Weak electrolytes: $\lambda_\infty = n_+\lambda_+^\infty + n_-\lambda_-^\infty$ where λ is the molar conductivity

$\mathrm{n}_+ =$ No of cations obtained after dissociation per formula unit

$\mathrm{n}_- =$ No of anions obtained after dissociation per formula unit

- APPLICATION OF KOHLRAUSCH LAW :

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

$$\lambda^0{}_{M(CH_3COOH)} = \lambda^0{}_{M(CH_3COONa)} + \lambda^0{}_{M(HCl)} - \lambda^0{}_{M(NaCl)}$$

2. To calculate degree of dissociation of a week electrolyte

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

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

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

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

- IONIC MOBILITY : It is the distance travelled by the ion per second under the potential gradient of 1 volts per cm. It's unit is $\mathrm{cm^2 s^{-1} v^{-1}}$.

- Absolute ionic mobility :

$$\lambda_c^0 \propto \mu_c \quad ; \quad \lambda_a^0 \propto \mu_a$$
$$\lambda_c^0 = F\mu_c^0 \quad ; \quad \lambda_a^0 = F \times \mu_a^0.$$

Ionic Mobility $\mu = \frac{v^{\rightarrow speed}}{(V/\ell)_{\rightarrow \text{potential garadient}}}$ speed

- 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

SOLUTION AND COLLIGATIVE PROPERTIES

- OSMOTIC PRESSURE

(a) $\pi = \rho gh$

Where, $\rho =$ density of soln., $h =$ equilibrium height

(b) Vont - Hoff Formula (For calculation of O.P.)

$$\pi = CST$$

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

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

$$= C_1 + C_2 + C_3 +$$

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

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

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

- Types of solutions:

❖ Isotonic solution - Two solutions having same O.P.

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

❖ Hyper tonic- If $\pi_1 > \pi_2$. $\Rightarrow It^{st}$ solution is hypertonic solution w.r.t. 2^{nd} solution

❖ Hypotonic $-1I^{nd}$ solution is hypotonic w.r.t. Ist solution

- Abnormal Colligative Properties : (In case of association or dissociation)
  - VANT HOFF CORRECTION FACTOR (i)

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

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

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

$i > 1 \Rightarrow$ dissociation

$i < 1 \Rightarrow$ association

- $i = \dfrac{\pi_{\text{exp.}}}{\pi_{\text{theor}}}$

  $\therefore \pi = \text{iCRT}$

  $\pi = \left(\text{i}_1\text{C}_1 + \text{i}_2\text{C}_2 + \text{i}_3\text{C}_3 \ldots.\right)\text{RT}$

- 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

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

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

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

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

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

(b) An alternate form $\rightarrow \dfrac{p_1^0 - p_1}{p_1^0} = x_2$.

- Ostwald-Walker Method : Experimental or lab determination of $\dfrac{\Delta P}{P}$ or $\dfrac{\Delta P}{P_S}$

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

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

- ELEVATION IN BOILING POINT

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

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

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

- DEPRESSION IN FREEZING POINT

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

$K_f =$ 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:

$P_A = X_A P_A^0$ $\therefore P_B = X_B P_B^\circ$

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

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

$\therefore$ According to Dalton's Law

$\therefore P_T = P_A + P_B = X_A P_A^0 + X_B P_B^0$

$x_A' =$ mole fraction of A in vapour about the liquid / solution

$x_B' =$ mole fraction of B

$$P_A = X_A P_A^0 = X_A' P_T$$
$$P_B = X_B' P_T = X_B P_B^0$$
$$\frac{1}{P_T} = \frac{X_A'}{P_A^0} + \frac{X_B'}{P_B^0}$$

Graphical Representation:

A more volatile than $B\left(P_A^0 > P_B^\circ\right)$

- Ideal solutions (mixtures): Mixtures which follow Raoul'ts law at all temperature.

$$A\cdots A \Rightarrow \quad A\cdots - B$$
$$B----B$$

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

$: \Delta G_{mx} = -ve$

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) $P_{T,exp} > \left(X_A P_A^0 + X_B P_B^0 \right)$

$$A-----A \qquad > A--------B$$
$$B-----\underset{\downarrow}{B}$$

(ii) weaker force of attraction

(iii) $\Delta H_{mix} = +ve$ energy absorbed

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

(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.

(b) Negative deviation:

(i) $P_T \exp < x_A p^0 + x_B p^0{}_B$

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

strong force of altraction.

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

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

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

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

eg. $H_2O + HCOOH$

$H_2O + CH_3COOH$

$H_2O + HNO_3$

- 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) $\dfrac{P_A^0}{P_B^0} = \dfrac{n_A}{n_B}$

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

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

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.

$$m \alpha p$$
$$m = kp$$
$$m \rightarrow \frac{\text{weight of gas}}{\text{volume of liquid}}$$

SOLID STATE

- Classification of crystal into seven system

Crystal system	**Unit cell dimensions and**	**Bravais Lattice**	**Example**
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 centered and	S_R

		FCC	
Tetragonal	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$	SC,BCC	$SnZnO_2$
Monoclinic	$a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$	SC, end centered	S_M
Rhombohedral	$a = b = c; \alpha = \beta = \lambda \neq 90^\circ$	SC	Quartz
Triclinic	$a \neq b \neq c; \alpha = \beta \neq \lambda \neq 90^\circ$	SC	H_3BO_3
Hexagonal	$a = b \neq c; \alpha = \beta = 90^\circ; \lambda = 120^\circ$	SC	Graphite

- Analysis of Cubical system

property	SC	BCC	FCC
Atomic radius (r)	$\frac{a}{2}$	$\frac{\sqrt{3^a}}{4}$	$\frac{a}{2\sqrt{2}}$
No. of atoms per unit cell (Z)	1	2	4
C.no.	6	8	12
Packing efficiency	52%	68%	74%
(a) Octahedral(Z) (b) Tetrahedral (ZZ)			4 8

a= edge length

- Neighbor Hood of particle

(I) Simple cubic (SC) structure

Type of neighbor	Distance	No. of neighbor
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 neighbor	**distance**	**No. of neighbor**
Nearest	$2r = a\frac{\sqrt{3}}{2}$	8
$(\text{next})^1$	a	6
$(\text{next})^2$	$a\sqrt{2}$	12
$(\text{next})^3$	$a\frac{\sqrt{11}}{2}$	24
$(\text{next})^4$	$a\sqrt{3}$	8

(III) Face centered cubic (FCC) structure:

Type of neighbor	**distance**	**No. of neighbor**
Nearest	$\frac{a}{\sqrt{2}}$	$12 = \left(\frac{3\times 8}{2}\right)$
$(\text{next})^1$	a	$6 = \left(\frac{3\times 8}{4}\right)$

(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 CRYSRALS

C NO.	**Limiting radius ratio** $\left(\frac{r_+}{r_-}\right)$
3	0.155-0.225 (triangular)
4	0.225-0.414 (tetrahedral)
5	0.414-0.732 (octahedral)
6	0.732-0.999(cubic)

- Example of a INOIC 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)

$$a_{fcc} = \frac{4}{\sqrt{3}}\left(r_{Zn^{2+}} + r_{s^{2-}}\right)$$

(d) Fluorite structure (CaF_2) C.No. (8:4)

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

- Crystal Defects (Imperfections)

CHEMICAL KINETIC AND RADIOACTIVITY

- RATE/VELOCITY OF CHEMICALREACTION:

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

- Types of Rates of chemical reaction

For a reaction $R \to P$

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. $)^{\text{order}}$ – differential rate equation or rate expression

Where $\mathrm{K} =$ Rate constant = specific reaction rate = rate of reaction when concentration is unity unit of $K = (\text{ conc })^{1-\text{ order time } -1}$

- Order of reaction

$\mathrm{m_1\,A + m_2\,B} \rightarrow$ 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 '

  - zero order reactions:

Rate $= \mathrm{k[\text{ conc }]^{\circ}} =$ constant

Rate $K = \dfrac{C_0 - C_t}{'t'}$ or $\mathrm{C_t = C_0 - kt}$

Unit of $\mathrm{K = mollit^{-1}sec^{-1}}$, Time for completion $= \dfrac{\mathrm{C_0}}{\mathrm{k}}$

at $\mathrm{t_{1/2}, C_t = \dfrac{C_0}{2}}$, so $\mathrm{kt_{1/2} = \dfrac{C_0}{2} \Rightarrow \quad t_{1/2} = \dfrac{C_0}{2k} \quad \therefore t_{1/2} \propto C_0}$

  - First Order Reactions :

(i) Let a 1^{st} order reaction is, $A \rightarrow$ Products

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

$$\Rightarrow \quad t_{1/2} = \frac{\ell n2}{k} = \frac{0.693}{k} =$$ Independent of initial concentration.

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

Graphical Representation:

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

- ➢ Second order reaction

2nd order reactions	
Two types	
$A + A \rightarrow$ products	$A + B \rightarrow$ products
a a	a b
(a-x) (a-x)	a-x b-x
$\therefore \frac{dx}{dt} = k(a-x)^2$	$\frac{dx}{dt} = k(a-x)(b-x)$
$\Rightarrow \frac{1}{(a-x)} = k\frac{1}{a} = kt$	$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$

- ➢ Psuedo first order reaction:

$\therefore$ For $A + B \rightarrow$ Products [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 $b >> a$.

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

$\because$ ' b ' is very large can be taken as constant

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

- 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

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

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

(c) Method of half lives :

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

(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.

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

(b) By titration method:

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

2. Study of acid hydrolysis of an easter

$$k = \frac{2.303}{\mathrm{t}} \log \frac{\mathrm{V}_\infty - \mathrm{V}_0}{\mathrm{V}_\infty - \mathrm{V}_\mathrm{t}}$$

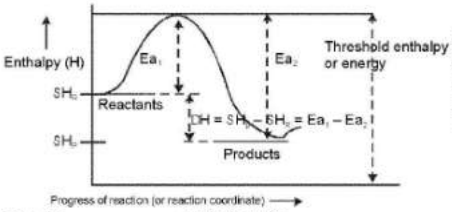
(c) By measuring optical rotation produced by the reaction mixture

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

- EFFECT OF TEMPERATURE ON RATE OF REACTION

T.C. $= \frac{K_t + 10}{K_t} \approx 2$ to 3 (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

$E_p > E_r \longrightarrow$ endothermic
$E_p < E_r \longrightarrow$ exothermic

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

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

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

- ❖ Arhenius equation

$$k = Ae^{-E_a RT}$$

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

$$\frac{\text{dlnk}}{dt} = \frac{E_a}{RT^2}$$

$$\log \text{k} = \left(-\frac{Ea}{2.303R}\right)\frac{1}{T} + \log A$$

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

- ❖ $\text{lnk} = \ln A - \frac{E_a}{RT}$
- ❖ $\text{T} \to \infty, \text{K} \to \text{A}$

➢ REVERSIBLE REACTIONS

$$k_f = A_f e^{-E_{ar}/RT}$$

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

$$k_{eq} = \frac{k_f}{k_b} = \left(\frac{A_f}{A_b}\right) e^{-\left(E_{af} - E_{ab}\right)/RT}$$

IN

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

$$\frac{[B]}{[C]} = \frac{K_1}{K_2} \quad \Rightarrow \quad E_a = \frac{E_{a_1}\mathrm{k}_1 + E_{a_2}\mathrm{k}_2}{\mathrm{k}_1 + \mathrm{k}_2}$$

(II) REVERSIBLE 1st ORDER REACATION (both forward and backward)

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

$$K_f + K_b = \frac{1}{t}\ln\left(\frac{x_{\mathrm{eq.}}}{x_{\mathrm{eq.}} - x}\right)$$

(III) SEQUENTIAL ST ORDER REACTION

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

$$x = a\left(1 - e^{-k_1 t}\right)$$

$$y = \frac{K_1 a}{K_2 - K_1}\left\{e^{-k_1 t} - e^{-k_2 t}\right\} \quad t_{B(\max)} = \frac{1}{\left(K_1 - K_2\right)}\ln\frac{K_1}{K_2}$$

CASE-I $K_1 >> K_2$

CASE II : $\mathrm{K}_2 >> \mathrm{K}_1$