MOLE CONCEPT

SOME USEFUL CONVERSION FACTORS

- 1 Å = 10^{-10} m, 1 nm = 10^{-9} m
- 1 pm = 10^{-12}m
- 1 litre = $10^{-3}\ m^3$ = 1 dm^3
- 1 atm = 760 mm or torr
  = 101325 Pa or Nm^{-2}
- 1 bar = 10^5 Nm^{-2} = 10^5 Pa
- 1 calorie = 4.184 J
- 1 electron volt(eV) = 1.6022×10^{-19}J
- (1 J = 10^7 ergs)
- (1 cal > 1 J > 1 erg > 1 eV)

ATOMIC MASS OR MOLECULAR MASS

Mass of one atom or molecule in a.m.u.

C → 12 amu

H_2O → 18 amu

ACTUAL MASS

mass of one atom or molecule in grams

C → $12 \times 1.6 \times 10^{-24}$ g

H_2O → $18 \times 1.6 \times 10^{-24}$ g

RELATIVE ATOMIC MASS OR RELATIVE MOLECULAR MASS

Mass of one atom or molecule w.r.t. $1/12^{th}$ of ^{12}C atom

C → 12

H_2O → 18

It is unitless

GRAMS ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one mole of atom or molecule

C → 12 g

H_2O → 18 g

It is also called molar mass

DEFINITION OF MOLE

One mole is a collection of that many entities as there are number of atoms exactly in 12 gm of C-12 isotope.

The number of atoms present in exactly 12 gm of C-12 isotope is called Avogadro's number

$[N_A = 6.022 \times 10^{23}]$

1u = 1 amu = (1/12)th of mass of 1 atom of $C^{12} = \frac{1g}{N_A} = 1.66 \times 10^{-24}$ g

For elements

- 1 g atom = 1 mole of atoms = N_A atoms
- g atomic mass (GAM) = mass of N_A atoms in g.
- Mole of atoms = $\frac{Mass\ (g)}{GAM\ or\ Molar\ mass}$

For molecule

- 1 g molecule = 1 mole of molecule = N_A molecule
- g molecular mass (GMM) = mass of N_A molecule in g.
- Mole of molecule = $\frac{Mass\ (g)}{GMM\ or\ Molar\ mass}$

For ionic compounds

- 1 g formula unit = 1 mole of formula unit = N_A formula unit.
- g formula mass (GFM) = mass of N_A formula unit in g.
- Mole of formula unit = $\frac{Mass\ (g)}{GFM\ or\ Molar\ mass}$

1 mole of substance

- Contains 6.022×10^{23} particles
- Weighs as much as molecular mass / atomic mass/ionic mass in grams
- If it is a gas, one mole occupies a volume of 22.4 L at 1 atm & 273 K or 22.7 L at STP

Average or mean molar mass

The average molar mass of the different substance present in the container $M_{avg} = \frac{M_1n_1 + M_2n_2 + ...}{n1 + n2 + ...}$

Here M_1, M_2 are molar mass of substances and n_1, n_2 are mole of substances present in the container.

DENSITIES

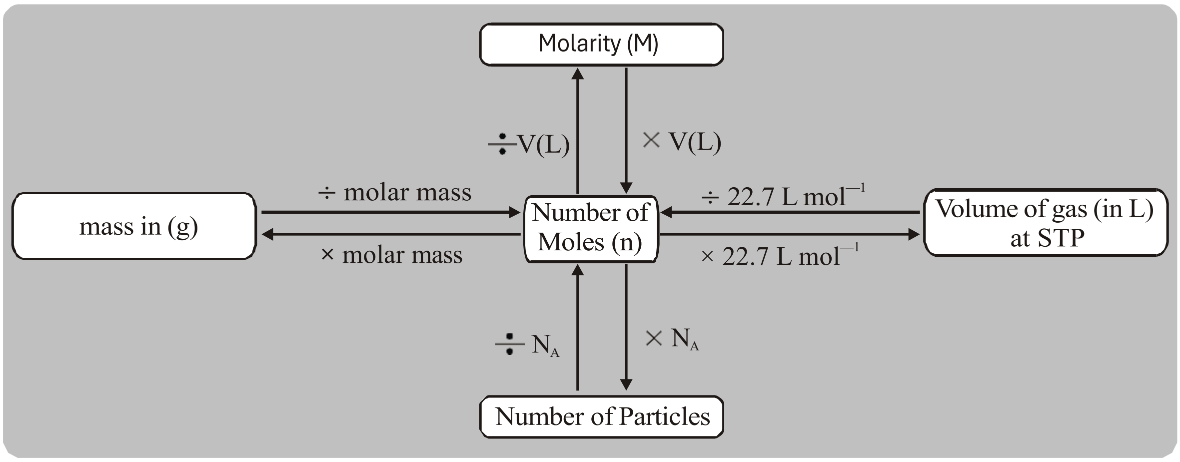
Density = $\frac{Mass}{Volume}$

Relative Density = $\frac{\text{Density of any substance}}{\text{Density of reference substance}}$

VAPOUR DENSITY

Ratio of density of vapour to the density of hydrogen at similar pressure and temperature.

Vapour density = $\frac{Molar\ Mass}{2}$



STOICHIOMETRY BASED CONCEPT

aA + bB → cC + dD

- a,b,c,d, represents the ratios of moles, volumes [for gaseous] molecules in which the reactants react or products formed.
- a,b,c,d, does not represent the ratio of masses.
- The stoichiometric amount of components may be related as

$$\frac{\text{Moles of A reacted}}{a} = \frac{\text{Moles of B reacted}}{b} = \frac{\text{Moles of C reacted}}{c} = \frac{\text{Moles of D reacted}}{d}$$

- Amounts may also be related using POAC method. Moles of reactants and products may be related directly using conservation of suitable atoms.

□ **[Concept of limiting reagent]**

If data of more than one reactant is given then first convert all the data into moles then divide the moles of reactants with their respective stoichiometric coefficient. The reactant having minimum ratio will be L.R. then find the moles of product formed or excess reagent left by comparing it with

L.R. through stoichiometric concept.

□ PERCENTAGE YIELD :

In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical amount of the product. The amount of the product that is actually obtained is called the actual yield. Knowing the actual yield and theoretical yield the percentage yield can be calculate as :

$$\boxed{\%\ \text{yield} = \frac{\textbf{Actual yield}}{\textbf{Theoretical yield}} \textbf{x100}}$$

The percentage yield of any product is always equal to the percentage extent of that reaction.

□ DEGREE OF DISSOCIATION, (α) :

It represents the mole of substance dissociated per mole of the substance taken.

A ➔ n particles; $\alpha = \frac{M_O - M}{(n-1).M}$

where, n = number of product particles per particle of reactant

M_O = Molar mass of 'A'

M = Molar mass of final mixture

Dissociation decreases the average molar mass of system while association increases it.

□ PERCENTAGE PURITY :

The percentage of a specified compound or element in an impure sample may be given as

$$\boxed{\%\ \text{purity} = \frac{Actual\ mass\ of\ compound}{Total\ mass\ of\ sample} \times 100}$$

If impurity is unknown, it is always considered as inert (unreactive) material.

PERCENTAGE DETERMINATION OF ELEMENTS IN COMPOUNDS

- Mass % of an element in a compound

$$= \frac{\text{atomicity of an element} \times \text{atomic mass of an element}}{\text{molecular mass of compound}} \times 100$$

- Methods for organic compounds :

(a) **Liebig's method :** (*For Carbon and hydrogen*)

(w) Organic Compound $\xrightarrow[\text{CuO}]{\Delta} (w_1)CO_2 + H_2O(w_2)$

$\%\text{ of C} = \frac{w_1}{44} \times \frac{12}{w} \times 100$; $\%\text{ of H} = \frac{w_2}{18} \times \frac{2}{w} \times 100$

where w_1 = wt. of CO_2 produced, w_2 = wt. of H_2O produced,
w = wt. of organic compound taken

(b) **Duma's method :** (*for nitrogen*)

(w) Organic Compound $\xrightarrow[\text{CuO}]{\Delta}$ N_2 → (P, V, T given)

use PV = nRT to calculate moles of N_2, n.

$$\therefore\ \%\ of\ N = \frac{n \times 28}{w} \times 100$$

(c) **Kjeldahl's method :** (*for nitrogen*)

(w) $O.C. + H_2SO_4 \rightarrow (NH_4)_2SO_4 \xrightarrow{NaOH} NH_3 + H_2SO_4 \rightarrow$ [molarity and volume (V in L) consumed given]

$$\Rightarrow\ \%\ of\ N = \frac{MV \times 2 \times 14}{w} \times 100$$

where M = molarity of H_2SO_4. Some N containing compounds do not give the above set of reaction as in Kjeldahl's method.

(d) **Sulphur :**

(w) $O.C. + HNO_3 \rightarrow H_2SO_4 + BaCl_2 \rightarrow (w_1)\ BaSO_4$

$$\Rightarrow\ \%\ of\ S = \frac{w_1}{233} \times \frac{32}{w} \times 100\%$$

where w_1 = wt. of $BaSO_4$, w = wt. of organic compound

(e) **Phosphorus :**

$O.C + HNO_3 \rightarrow H_3PO_4 + [NH_3$ + magnesium ammonium molybdate] ➔ $MgNH_4PO_4 \xrightarrow{\Delta} Mg_2P_2O_7$

$$\%\ \text{of P} = \frac{w_1}{222} \times \frac{2 \times 31}{w} \times 100$$

(f) **Carius method :** (Halogens)

O.C. + HNO_3 + $AgNO_3$ ➔ AgX

If X is Cl then colour = white

If X is Br then colour = dull yellow

If X is I then colour = bright yellow

Flourine can't be estimated by this

$$\%\ of\ X = \frac{w_1}{(Mol.wt.of\ AgX)} \times \frac{1 \times (At.wt.of\ X)}{w} \times 100$$

EMPIRICAL AND MOLECULAR FORMULA

- **Empirical formula :** Formula depicting constituent atoms in their simplest ratio.
- **Molecular formula :** Formula depicting actual number of atoms in one molecule of the compound.
- The molecular formula is generally an integral multiple of the empirical formula.
  i.e. molecular formula = empirical formula × n

where $n = \frac{molecular\ formula\ mass}{empirical\ formula\ mass}$

EXPERIMENTAL METHODS TO DETERMINE ATOMIC & MOLECULAR MASSES

- **For determination of atomic mass :**
  Dulong's & Petit's law :
  Atomic weight of metal × specific heat capacity (cal/gm°-C) ≈ 6.4.

  It should be remembered that this law is an empirical observation and this gives an approximate value of atomic weight. This law gives better result for heavier solid elements, at high temperature conditions.

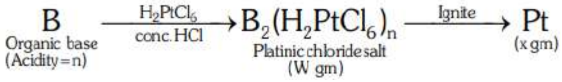
- **Experimental methods for molecular mass determination.**
  (a) **Victor Meyer's Method :**
  Victor -Mayer's method is used to determine molecular weight of volatile compound.

  (b) **Silver Salt Method :**

  $$\text{Organic acid } (H_nA) \xrightarrow{AgNO_3} \underset{(w\ gm)}{Silver\ Salt} \xrightarrow{Ignite} \underset{(x\ gm)}{Ag}$$

  $$\textbf{Molar mass of acid} = \frac{108\times \text{nW}}{\text{x}} - n\times 108 + \text{n}\times 1 = \text{n}\left(\frac{108\text{W}}{\text{x}} - 107\right)\text{gmol}^{-1}$$

  (c) **Chloroplatinate Salt Method :**



$$\underset{\substack{\text{Organic base}\\(\text{Acidity}=n)}}{B} \xrightarrow[\text{conc. HCl}]{H_2PtCl_6} \underset{\substack{\text{Platinic chloride salt}\\(\text{W gm})}}{B_2(H_2PtCl_6)_n} \xrightarrow{\text{Ignite}} \underset{(\text{x gm})}{Pt}$$

$$\textbf{Molar mass of base} = \frac{1}{2}(\textbf{Molar mass of salt} - \textbf{n} \times \textbf{Molar mass of } \mathbf{H_2PtCl_6})$$

$$= \frac{1}{2}\left(\frac{W\times 195\times n}{x} - n\times 410\right) = \frac{n}{2}\left(\frac{w\times 195}{x} - 410\right) gmol^{-1}$$

CONCENTRATION TERMS

Concentration Type	Mathematical Formula	Concept
Percentage by mass	$\%\left(\frac{w}{w}\right) = \frac{Mass\ of\ solute \times 100}{Mass\ of\ solution}$	Mass of solute (in gm) present in 100 gm of solution.
Volume percentage	$\%\left(\frac{v}{v}\right) = \frac{Volume\ of\ solute \times 100}{Volume\ of\ solution}$	Volume of solute (in cm^3) present in 100 cm^3 of solution.
Mass-volume percentage	$\%\left(\frac{w}{v}\right) = \frac{Mass\ of\ solute \times 100}{Volume\ of\ solution}$	Mass of solute (in gm) present in 100 cm^3 of solution.
Parts per million	$ppm = \frac{Mass\ of\ solute \times 10^6}{Mass\ of\ solution}$	Parts by mass of solute per million parts by mass of the solution
Mole fraction	$X_A = \frac{Mole\ of\ A}{Mole\ of\ A + Mole\ of\ B + Mole\ of\ C + ..}$ $X_B = \frac{Mole\ of\ B}{Mole\ of\ A + Mole\ of\ B + Mole\ of\ C + ..}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M = \frac{Mole\ of\ solute}{Volume\ of\ solution\ (in\ L)}$	Moles of solute in one liter of solution.
Molality	$m = \frac{Mole\ of\ solute}{Mass\ of\ solvent\ (Kg)}$	Moles of solute in one kg of solvent

□ **MIXING OF SOLUTIONS :**

It is based on law of conservation of moles.

(i) **Two solutions having same solute :** Final $molarity = \frac{Total\ moles}{Total\ volume} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$

(ii) **Dilution Effect :** Final molarity, $M_2 = \frac{M_1V_1}{V_1 + V_2}$

□ VOLUME STRENGTH OF H_2O_2 SOLUTION :

Labelled as 'volume H_2O_2' means volume of O_2 (in litre) at 1 bar & 273 K that can be obtained from 1 litre of such a sample when it decomposes according to

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

- Volume Strength of H_2O_2 solution = 11.35 × molarity

□ PERCENTAGE LABELLING OF OLEUM :

Labelled as '% oleum' means maximum amount of H_2SO_4 that can be obtained from 100 gm of such oleum (mixture of H_2SO_4 and SO_3) by adding sufficient water. For example, 109 % oleum sample means, with the addition of sufficient water to 100 gm oleum sample 109 gm H_2SO_4 is obtained.

% labelling of oleum sample = (100 + x)%

x = mass of H_2O required for the complete conversion of SO_3 in H_2SO_4

- % of free SO_3 in oleum = $\left(\frac{40}{9} \times x\right)$%

EUDIOMETRY

Some basic assumptions related with calculations are:

1. Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.

$$N_2\,(g) + 3H_2\,(g) \rightarrow\ 2NH_3\,(g)$$

1 vol. 3 vol. 2 vol.

Problem may be solved directly is terms of volume, in place of mole.

The stoichiometric coefficients of a balanced chemical reactions gives the ratio of volumes in which gaseous substances are reacting and products are formed at same temperature and pressure.

2. The volumes of solids or liquids is considered to be negligible in comparison to the volume of gas. It is due to the fact that the volume occupied by any substance in gaseous state is even more than thousand times the volume occupied by the same substance in solid or liquid states.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$$

2 mole 1 mole 2 mole

2 vol. 1 vol. 0 vol.

3. Air is considered as a mixture of oxygen and nitrogen gases only. It is due to the fact that about 99% volume of air is composed of oxygen and nitrogen gases only.

4. Nitrogen gas is considered as an non- reactive gas.

5. The total volume of non-reacting gaseous mixture is equal to sum of partial volumes of the component gases ***(Amagat's law)***.

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

Partial volume of gas in a non-reacting gasesous mixture is its volume when the entire pressure of the mixture is supposed to be exerted only by that gas.

6. The volume of gases produced is often given by certain solvent which absorb contain gases.

Solvent	**Gases absorb**
KOH	CO_2, SO_2, Cl_2
Ammonical Cu_2Cl_2	CO
Turpentine oil	O_3
Alkaline pyrogallol	O_2
water	NH_3, HCl
$CuSO_4/CaCl_2$	H_2O

ATOMIC STRUCTURE

IMPORTANT DEFINITIONS

Proton (m_p) /anode rays

- mass =1.67×10^{-27} kg
- mass = 1.67×10^{-24} g
- mass = 1.00750 amu
- e/m value is dependent on the nature of gas taken in discharge tube.

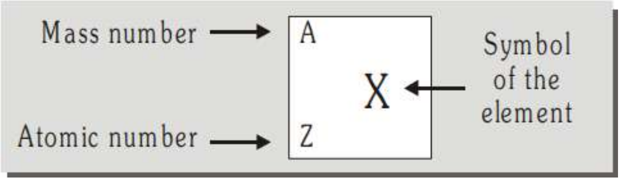
Neutron (m_n)

- mass = 1.67×10^{-27} kg
- mass = 1.67×10^{-24} g
- mass = 1.00850 amu

Electron(m_e) / cathode rays

- mass = 9.1×10^{-31} kg
- mass = 9.1×10^{-28} g
- mass = 0.000549 amu
- e/m of electron is found to be independent of nature of gas & electrode used.

REPRESENTATION OF AN ELEMENT



Terms associated with elements :

- Atomic Number (Z) : = No. of protons
  Electron = Z – C (charge on atom)
- Mass number (A) =Total number of neutron and proton present
  A = Number of proton + Number of Neutrons
- **Isotopes :** Same atomic number but different mass number

  Ex. : ${}_6C^{12}$, ${}_6C^{13}$, ${}_6C^{14}$
- **Isobars :** Same mass number but different atomic number

  Ex. ${}_1H^3$, ${}_2He^3$
- **Isodiaphers :** Same difference of number of Neutrons & protons

  Ex. ${}_5B^{11}$, ${}_6C^{13}$
- **Isotones :** Having same number of neutron

  Ex. ${}_1H^3$, ${}_2He^4$

- **Isosters:** They are the molecules which have the same number of atoms & electrons

  Ex. CO_2, N_2O

- **Isoelectronic:** Species having same no. of electrons

  Ex. Cl^-, Ar

ATOMIC MODELS

- **Thomson :** An atom considered to be positively charged sphere where e^- is embedded inside it.
- **Drawback :** Cannot explain stability of an atom.
- **Rutherford Model of an atoms :**
  Electron is revolving around the nucleus in circular path.
  $R_N = R_0(A)^{1/3}, R_0 = 1.33 \times 10^{-13}\ cm$
  [A = mass number, R_N = Radius of nucleus]

SIZE OF NUCLEUS

- The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.
- Thus, diameter (size) of the atom is 1,00,000 times the diameter of the nucleus.

ELECTROMAGNETIC SPECTRUM

- RW → MW → IR → Visible → UV → X-rays → CR (Radiowaves → Microwaves → Infrared rays → Visible rays → Ultraviolet rays → X-rays → Cosmic rays)
- Wavelength decreases $\longrightarrow$
- Frequency increases $\longrightarrow$
- • $c = v\lambda$ • $\lambda = \frac{c}{v}$ • $\overline{v} = \frac{1}{\lambda} = \frac{v}{c}$

  • $T = \frac{1}{v}$ • $E = \frac{hc}{\lambda} = hv,\ \ h = 6.626 \times 10^{-34} Js$ • E(ev) = $\frac{12400}{\lambda(\text{Å})}$

  • Total amount of energy transmitted $E = nhv = \frac{nhc}{\lambda}$

BOHR'S ATOMIC MODEL

Theory based on quantum theory of radiation and the classical laws of physics

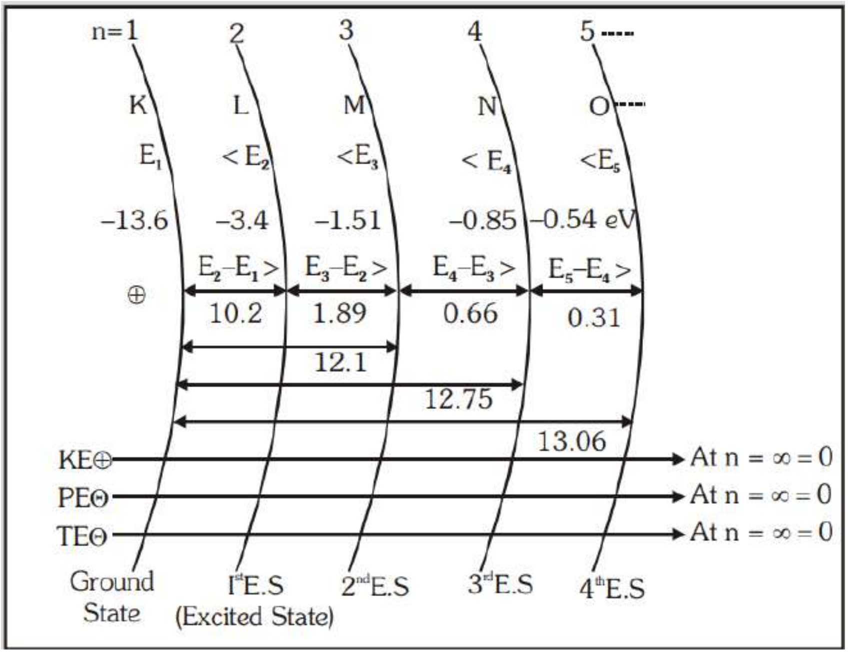
- $\frac{K(Ze)(e)}{r^2} = \frac{mv^2}{r}$
- $mvr = \frac{nh}{2\pi}$ or $mvr = n\hbar$
- Electron remains in stationary orbit where it does not radiate its energy.
- **Radius :** $\boldsymbol{r = 0.529 \times \frac{n^2}{Z}}$ **Å**
- **Velocity :** $\boldsymbol{v = 2.188 \times 10^6 \frac{Z}{n} ms^{-1}}$
- Energy (KE + PE)
  = Total energy = $-13.6 \times \frac{Z^2}{n^2} eV/atom$
- $TE = -\frac{KZe^2}{2r}, PE = \frac{-KZe^2}{r}, KE = \frac{KZe^2}{2r}$

$PE = -2\text{KE}, \text{KE} = -\text{TE}, \text{PE} = 2\text{TE}$

- Revolutions per sec $= \frac{v}{2\pi r}$
- Time for one revolution $= \frac{2\pi r}{v}$
- Energy difference between n_1 and n_2 energy level
  $$\Delta E = E_{n_2} - E_{n_1} = 13.6Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{ eV/atom} = \text{IE} \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$
  where IE = ionization energy of single electron species.
- **Ionization energy** $= \boldsymbol{E_\infty - E_{G.S.} = 0 - E_{G.S.}}$
  $\boldsymbol{E_{G.S.}}$ = Energy of electron in ground state

HYDROGEN SPECTRUM

- **Rydberg's Equation :** $\frac{1}{\lambda} = \bar{\nu} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$
  $R_H \cong 109700\,\text{cm}^{-1}$ = Rydberg constant
- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_α line means $n_2 = n+1$; also known as line of longest λ, shortest v, least E
- Similarly H_β line means $n_2 = n_1 + 2$
- When electrons de-excite from higher energy level (n) to ground state in atomic sample, then number of spectral lines observed in the spectrum $= \frac{n(n-1)}{2}$
- When electrons de-excite from higher energy level (n_2) to lower energy level (n_1) in atomic sample, then number of spectral line observed in the spectrum $= \frac{(n_2-n_1)(n_2-n_1+1)}{2}$
- No. of spectral lines in a particular series $= n_2 - n_1$



DE-BROGLIE HYPOTHESIS

- All material particles posses wave character as well as particle character.
- $\lambda = \frac{h}{mv} = \frac{h}{p}$
- The circumference of the nth orbit is equal to n times of wavelength of electron i.e., $2\pi r_n = n\lambda$
  Number of waves = n = principal quantum number

- Wavelength of electron (λ) $\cong \sqrt{\frac{150}{V(volts)}}$ Å
- $\lambda = \frac{h}{\sqrt{2mKE}}$

HEISENBERG UNCERTAINTY

- According to this principle, " it is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy"
  If one of them is measured with greater accuracy, the other becomes less accurate.
- $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ or $(\Delta x)(\Delta v) \geq \frac{h}{4\pi m}$
  where Δx = Uncertainty in position
  Δp = Uncertainty in momentum
  Δv = Uncertainty in velocity
  m = mass of microscopic particle
- Heisenberg replaced the concept of orbit by that of orbital.

QUANTUM NUMBER

- **Principal Quantum number (By Bohr)**
  ⇒ Indicates = Size and energy of the orbit, distance of e^- from nucleus
  ⇒ Values n = 1, 2, 3, 4, 5....................
  ⇒ Angular momentum = $n \times \frac{h}{2\pi}$
  ⇒ Total number of e^-s in an orbit = $2n^2$
  ⇒ Total number of orbitals in an orbit = n^2
  ⇒ Total number of subshell in an orbit = n

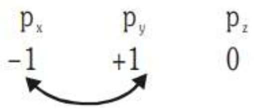
- **Azimuthal/Secondary/Subsidiary/Angular momentum quantum number (ℓ)**
  ⇒ Given by = Sommerfeld
  ⇒ Indicates = Sub shells/sub orbit/sub level
  ⇒ Values ⇒ 0, 1.............(n–1)
  ⇒ Indicates shape of orbital/Sub shell

Value of n	Values of ℓ [Shape]	Initial from word
Eg. If n = 4	ℓ = 0 (s) [Spherical] ℓ = 1 [p] [Dumb bell] ℓ = 2 [d] [Double dumb bell] ℓ = 3 [f] [Complex]	Sharp Principal Diffused Fundamental

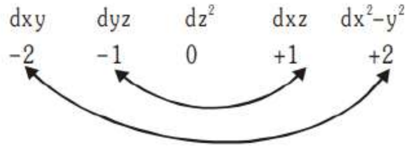
  ⇒ Total no. of e^- s in a suborbit = 2(2l + 1)
  ⇒ Total no. of orbitals in a suborbit = (2l + 1)
  ⇒ Orbital angular momentum = $\sqrt{\ell(\ell+1)}\frac{h}{2\pi} = \sqrt{\ell(\ell+1)}\hbar$
  h = Planck's constant
  ⇒ For H & H like species all the subshells of a shell have same energy.
  i.e. 2s = 2p 3s = 3p = 3d

- **Magnetic Quantum number (m)**
  ⇒ Given by Linde
  ⇒ Indicates orientation of orbitals i.e. direction of electron density.
  ⇒ Value of m = $-\ell$ ....0..............$+\ell$
  ⇒ Maximum no of e's in an orbital = 2 (with opposite spin)

m for p sub shell =



m for d sub shell =



- **Spin Quantum Number (m_s or s)**

  Given by Uhlenback & Goudsmit Values of s = $\pm\frac{1}{2}$

  Total value of spin in an atom = $\pm\frac{1}{2} \times$ number of unpaired electrons

  Spin Angular momentum = $\sqrt{s(s+1)}\frac{h}{2\pi}$

RULES FOR FILLING OF ORBITALS

- **Aufbau principle :** The electrons are filled up in increasing order of the energy in subshells.
  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$
- **(n + ℓ) rule :** The subshell with lowest (n + ℓ) value is filled up first, but when two or more subshells have same (n + ℓ) value then the subshell with lowest value of n is filled up first.
- **Pauli exclusion principle :** Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.
- **Hund's rule of maximum multiplicity :** Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.

CHEMICAL EQUILIBRIUM

REACTION

Reversible Reaction	Irreverssible Reaction
(1). K_c not very large or very small	**(1).** $K_c >>> 1$
(2). Both R and P present at equibilirium	**(2).** [P] >>> [R] at equilibrium
(3). R and P stability comparable	**(3).** Stablility P >>> R

At equilibrium for reaction mix. properties like P, V, T, n, magnetism, colour, density become constant.

- **For gaseous reactions.**

  $K_P = K_C\ (RT)^{\Delta n_g}$

  $K_P > K_C$ if $\Delta n_g > 0$

  $K_P < K_C$ if $\Delta n_g < 0$

  $K_P = K_C$ if $\Delta n_g = 0$

  Units of $K_P = (\text{atm})^{\Delta n_g}$

  Units of $K_C = (\text{M})^{\Delta n_g}$

  $K_P = \frac{A_f}{A_b} e^{-\Delta_r H°/RT}$

  both K_P & K_C depend only on temperature for given reaction.

- For pure solids & pure liquids (solvent) :

  Active mass = 1 [Kinetically]

  Activity = 1 [thermodynamically]

  $\text{Molarity} = \frac{\text{Density}}{\text{Molar mass}} = \text{Constant}$

- **Reaction Quotient (Q_C / Q_P)**

(i) Used to find direction of reaction mixture – Fwd./Bwd.

(ii) $Q_C < K_C$ or $Q_P < K_P \Rightarrow$ FWD.

$Q_C > K_C$ or $Q_P > K_P \Rightarrow$ BWD.

$Q_C = K_C$ or $Q_P = K_P \Rightarrow$ Equilibrium

(iii) $Q_P = Q_C\ (RT)^{\Delta n_g}$

- If

(1) [$K_P >>> 1$ or $K_C >>> 1$]

or

(2) [$K_P <<< 1$ or $K_C <<< 1$]

no need to solve equation but use approximation.

In 1st case $[R]_{eq} \approx 0$

In 2nd case $[P]_{eq} \approx 0$

- **Degree of dissociation, α**

$$\frac{\Delta n}{n_0} = \frac{\Delta P}{P_0} = \frac{\Delta m}{m_0} = \frac{\Delta V}{V_0}$$

\# n, P, m, V → mols, partial pressure, mass, partial volume of reactant respectively.

% dissociation = % reactant converted to product = 100 α

\# $\alpha \le 1$ [Equality for irreversible reaction]

☐ $X_{gas} = \frac{P_{gas}}{P_T} = \frac{V_{gas}}{V_T} = \frac{n_{gas}}{n_T}$

For a reacting mixture of 'n' gases :

$$2VD_{mix} = M_{avg.} = \sum_{i=1}^{n} x_i m_i$$

- $M_{avg.}$ & VD_{mix} is a function of mixture composition.
- For mixture of reacting gas $M_{avg.}$ changes & becomes constant at equilibrium.
- $M_{avg.}$ (or VD_{mix}) $\propto \frac{1}{\text{moles of gases in mixture}}$

- $\frac{(VD)_i}{(VD)_f} = \frac{M_i}{M_f} = \frac{n_f}{n_i} = \frac{P_f}{P_i}$

Used to find 'α' from M_{avg} or VD data for reactions with $\Delta n_g \ne 0$

- On going FWD.

If $\Delta n_g > 0$

$P\uparrow \quad n\uparrow$

$M_{avg.}\downarrow \quad VD\downarrow$

If $\Delta n_g < 0$ $\quad P\downarrow \quad n\downarrow$

$M_{avg.}\uparrow \quad VD\uparrow$

If $\Delta n_g = 0$ $\quad$ P, n, M_{avg}, VD = Constant

- For a reaction with $\Delta n_g \ne 0$

α depends on – K_P or K_C, Temperature, Initial concentration, Initial moles, Initial pressure, volume of vessel

- For a reaction with $\Delta n_g = 0$;

α depends only on - K_P or K_C, Temperature

- K_P or K_C depend on the way of writing a reaction :

I. $R \rightleftharpoons P$; K_C, K_P

$P \rightleftharpoons R$; $1/K_C$, $1/K_P$

II. $C \rightleftharpoons D$; K'_C, K'_P

$\Rightarrow$ $R + C \rightleftharpoons P + D$; $K_C K'_C$ or $K_P K'_P$

III. $R - C \rightleftharpoons P - D$;

or $R + D \rightleftharpoons P + C$; $\frac{K_C}{K'_C}$ or $\frac{K_P}{K'_P}$

IV. $nR \rightleftharpoons nP$; $(K_C)^n$ or $(K_P)^n$

➢ **Relative Humidity (R.H.)**

$$= \left(\frac{\text{Partial pressure of water vapour}}{\text{Aqueous tension}}\right) 100$$

If RH < 100% ⇒ Partial pressure < Aqueous tension ⇒ Unsaturated air sample

If RH ≥ 100% ⇒ Saturated air sample

➢ **Le chetelier Principle**

Case I : [R] increased ⇒ Forward shift

[P] increased ⇒ Backward shift

❑ If R or P is pure solid / Pure liquid ⇒ No effect.

Case II : Total P increased (or V decreased)

If $\Delta n_g > 0$ ⇒ backward

If $\Delta n_g < 0$ ⇒ forward

If $\Delta n_g = 0$ ⇒ no effect

Case III : V Increased

⇒ Same effect as P decreased

If $\Delta n_g > 0$ ⇒ forward

If $\Delta n_g < 0$ ⇒ backward

If $\Delta n_g = 0$ ⇒ no effect

Case IV : T Increased

If $\Delta_r H > 0$ ⇒ forward

If $\Delta_r H < 0$ ⇒ backward

T decreased

If $\Delta_r H > 0$ ⇒ backward

If $\Delta_r H < 0$ ⇒ forward

Case V : Using Catalyst

No effect on K_C, K_P or equilibrium concentration

Only time required to attain equilibrium is lesser.

Case VI : Adding inert gas at constant V.

⇒ No effect

Case VII : Adding inert gas at constant Pressure

⇒ Same effect as Pressure decrease or volume increase

➢ **Thermodynamics state of Equilibrium** :

$$\left.\begin{array}{l} G_{mix} \rightarrow \text{Minimum} \\ \Delta_r G \rightarrow 0 \\ \Sigma V_P G_P = \Sigma V_R G_R \end{array}\right\} \text{at P, T constant}$$

If $\Delta_r G < 0 \Rightarrow \Sigma V_P G_P < \Sigma V_R G_R$

⇒ Reaction shifts forward to attain equilibrium.

If $\Delta_r G > 0 \Rightarrow \Sigma\, V_P G_P > \Sigma\, V_R G_R$

⇒ Reaction shifts backward to attain equilibrium.

If $\Delta_r G = 0 \Rightarrow$ Equilibrium state

❑ $\Delta_r G = \Delta_r G + RT\ \ln(Q)$

$\Delta_r G$ = Standard Gibbs energy of reaction (when all Reactants & Products are in standard states)

➢ **Standard State**

Gas → Ideal gas

Activity=Partial pressure=1 bar ≈ 1 atm.

Solute → Ideal solution

Activity = concentration = 1M

Solid/Liquid → Pure activity = 1

❑ Q contains activity of species i.e., partial pressure in bar (or atm) for gas

molarity for solute is unity for solid or liquid.

❑ At equilibrium $\Delta_r G = 0$ & $Q = K_{eq}$

⇒ $\Delta_r G = -\,RT\ell n\ k_{eq}$

$K_{eq.} = e^{-\Delta_r G^\circ/RT}$

❑ For gaseous homogeneous reaction,

$\Delta_r G = -RT\ \ln K_P$

For homogeneous reaction in solution phase

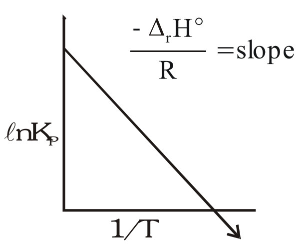
$\Delta_r G = -RT\ \ln K_C$

❑ BP, M.P. & Sublimation point all increase in increasing pressure

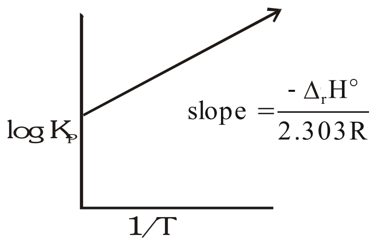
Exception – M.P. of H_2O decrease on increasing pressure

➢ **Von't Hoff Equation** :

$$\frac{d[\ln K_P]}{dT} = \frac{\Delta_r H^\circ}{RT^2}\ ; \qquad \ell n\ K_P = -\frac{\Delta_r H^\circ}{RT} + \ell n\frac{A_f}{A_b}\ ; \qquad \log\frac{K_{P_2}}{K_{P_1}} = \frac{\Delta_r H^\circ}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$



Endothermic Reaction



Exothermic Reaction

IONIC EQUILIBRIUM

➢ ACCORDING TO STRENGTH IONIC CONDUCTORS ARE OF 2 TYPES :

1. **Strong electrolyte** : Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

Ex. Na^+Cl^-, K^+Cl^-, etc.

(a) Strong acid → H_2SO_4, HCl, HNO_3 $HClO_4$, H_2SO_5, HBr, HI

(b) Strong base → KOH, NaOH, $Ba(OH)_2$ CsOH, RbOH

(c) All Salts → NaCl, KCl, $CuSO_4$..........

2. **Weak electrolytes** : Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex.

(a) Weak acid → HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, $B(OH)_3$

(b) Weak base → NH_4OH, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$

➢ ACIDS BASES AND SALTS :

Arrhenius concept :

Arrhenius Acid : Substance which gives H^+ ion on dissolving in water (H^+ donor)

Ex. HNO_3, $HClO_4$, HCl, HI, HBr, H_2SO_4, H_3PO_4 etc.

◆ H_3BO_3 is not Arrhenius acid.

➢ **Arrhenius base** : Any substance which releases OH^- (hydroxyl) ion in water (OH^- ion donor).

◆ First group elements (except Li.) form strong bases

➢ Bronsted - Lowery concept : (Conjugate acid - base concept) (Protonic concept)

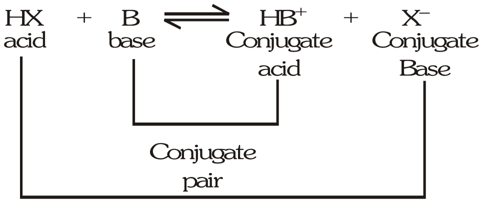
Acid : substances which donate H^+ are Bronsted Lowery acids (H^+ donor)

Base : substances which accept H^+ are Bronsted Lowery bases (H^+ acceptor)

➢ Conjugate acid - base pairs :

In a typical acid base reaction

$$HX + B \rightleftharpoons X^- + HB^+$$



Ex :

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	H_2O	H_3O^+
HSO_4^-	SO_4^{2-}	RNH_2	RNH_3^+
H_2O	OH^-		

➢ LEWIS CONCEPT (electronic concept) :

An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Acid → e^- pair acceptor

Ex. Electron deficient molecules : BF_3, $AlCl_3$
Cations : H^+, Fe^{2+}, Na^+
Molecules with vacant orbitals : SF_4, PF_3

A base is any molecule/ion which has a lone pair of electrons which can be donated.

Base → (One electron pair donor)

Ex. Molecules with lone pairs : NH_3, PH_3, H_2O, CH_3OH
Anions : ^-OH, H^-, $^-NH_2$

➢ IONIC PRODUCT OF WATER :

According to arrhenius concept

$H_2O \rightleftharpoons H^+ + OH^-$ so, ionic product of water, $K_w = [H^+][OH^-] = 10^{-14}$ at 25 (exp.)

Dissociation of water is endothermic, so on increasing temperature K_w increases.

K_w increases with increase in temperature.

Now $pH = -\log[H^+] = 7$ and $pOH = -\log[OH^-] = 7$ for water at 25 C (experimental)

$$\left.\begin{array}{ll} pH = 7 = pOH & \Rightarrow \text{neutral} \\ pH < 7 \text{ or } pOH > 7 & \Rightarrow \text{acidic} \\ pH > 7 \text{ or } pOH < 7 & \Rightarrow \text{Basic} \end{array}\right\} \text{at 25 C}$$

◆ Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

➢ Degree of dissociation of water :

$$H_2O \rightleftharpoons H^+ + OH^- \Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{Total no. of moles initially taken}}$$

$$= \frac{10^{-7}}{55.55} = 18\ \ 10^{-10} \text{ or } 1.8\ \ 10^{-7}\ \% \qquad \text{[at 25 C]}$$

➢ Absolute dissociation constant of water :

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

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

❑ ACIDITY AND pH SCALE :

Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.

So greater then tendency to give H^+, more will be the acidic strength of the substance.

Basic strength means the tendency of a base to give OH^- ions in water.

So greater the tendency to give OH^- ions, more will be basic strength of the substance.

The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale.

pH is defined as negative logarithm of activity of H^+ ions.

∴ $pH = -\log a_{H^+}$ (where a_{H^+} is the activity of H^+ ions)

Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a dilute solution.

The pH scale was marked from 0 to 14 with central point at 7 at 25 C taking water as solvent.

If the temperature and the solvent are changed, the pH range of the scale will also change. For example

0 - 14 at 25 C ($K_w = 10^{-14}$) Neutral point, pH = 7

0 - 13 at 80 C ($K_w = 10^{-13}$) Neutral point, pH = 6.5

pH can also be negative or > 14

➢ **pH Calculation of different Types of solutions :**

(a) **Strong acid solution :**

(i) If concentration is greater than 10^{-6} M.

In this case H^+ ions coming from water can be neglected,

so $[H^+]$ = normality of strong acid solution

(ii) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected.

So $[H^+]$ = normality of strong acid + H^+ ions coming from water in presence of this strong acid

(b) **pH of a weak acid (monoprotic) Solution :**

◆ Weak acid does not dissociated 100 % therefore we have to calculate the percentage dissociation using K_a dissociation constant of the acid.

◆ We have to use Ostwald's Dilution law (as have been derived earlier)

$$\begin{array}{llll} & HA & \rightleftharpoons H^+ & + \quad A^- \\ t = 0 & C & \quad 0 & \quad\; 0 \\ t_{eq} & C(1-\alpha) & \quad C\alpha & \quad\; C\alpha \end{array} \qquad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$$

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

$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$ So pH $= \frac{1}{2}(pK_a - \log C)$

on increasing the dilution $\Rightarrow C\downarrow \; = \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

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

◆ Weak acid and Strong acid both will contribute H^+ ion.

◆ For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.

◆ To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

◆ If the total $[H^+]$ from the acid is more than 10^{-6} M, then contribution from the water can be neglected, if not then we have to take $[H^+]$ from the water also.

➢ **Relative strength of weak acids and bases :**

For two acids of equimolar concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

(d) **pH of a mixture of two weak acid (both monoprotic) solution :**

◆ Both acids will dissociate partially.

◆ Let the acid are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then

$$\begin{array}{lcccc} & HA_1 & \rightleftharpoons H^+ & + & A_1^- \\ t = 0 & C_1 & 0 & & 0 \\ \text{At eq.} & C_1(1-\alpha_1) & C_1\alpha_1 + C_2\alpha_2 & & C_1\alpha_1 \end{array}$$

$$K_{a_1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)}$$

$$\begin{array}{cccc} HA_2 & \rightleftharpoons H^+ & + & A_2^- \\ C_2 & 0 & & 0 \\ C_2(1-\alpha_2) & C_2\alpha_2 + C_1\alpha_1 & & C_2\alpha_2 \end{array}$$

$$K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

(Since α_1, α_2 both are small in comparision to unity)

$$K_{a_1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 \; ; \; K_{a_2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \;\Rightarrow\; \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} + \frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} \;\Rightarrow\; [H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

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

- Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid (H_2A) in water whose concentration is c M.

  In an aqueous solution, following equilbria exist.

If

α_1 = degree of ionization of H_2A in presence of HA^-

K_{a_1} = first ionisation constant of H_2A

α_2 = degree of ionisation of HA^- in presence of H_2A

K_{a_2} = second ionisation constant of H_2A

I step

$$\begin{array}{lcccc} & H_2A + H_2O & \rightleftharpoons HA^- & + & H_3O^+ \\ \text{at eq.} & c(1-\alpha_1) & c\alpha_1(1-\alpha_2) & & (c\alpha_1 + c\alpha_1\alpha_2) \end{array}$$

$$(K_{eq})_1[H_2O] = \frac{[H_3O^+][HA^-]}{[H_2A]} = K_{a_1}$$

$$\therefore \; K_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1-\alpha_2)]}{c(1-\alpha_1)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1} \quad \text{....... (i)}$$

II step

$$\begin{array}{lcccc} & HA^- + H_2O & \rightleftharpoons A^{2-} & + & H_3O^+ \\ \text{at eq.} & c\alpha_1(1-\alpha_2) & c\alpha_1\alpha_2 & & (c\alpha_1 + c\alpha_1\alpha_2) \end{array}$$

$$(K_{eq})_2[H_2O] = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = K_{a_2}$$

$$K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2]}{c\alpha_1(1-\alpha_2)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)]\alpha_2}{1-\alpha_2} \quad \text{...... (ii)}$$

Knowing the values of K_{a_1}, K_{a_2} and c, the values of α_1 and α_2 can be calculated using equations (i) and (ii) After getting the values of α_1 and α_2, $[H_3O^+]$ can be calculated as

$$[H_3O^+]_T = c\alpha_1 + c\alpha_1\alpha_2$$

Finally, for calculation of pH

- If the total $[H_3O^+] < 10^{-6}$ M, the contribution of H_3O^+ from water should be added.
- If the total $[H_3O^+] > 10^{-6}$ M, then $[H_3O^+]$ contribution from water can be ignored.

  Using this $[H_3O^+]$, pH of the solution can be calculated.

Approximation :

For diprotic acids, $K_{a_2} << K_{a_1}$ and α_2 would be even smaller than α_1

$\therefore \quad 1 - \alpha_2 \approx 1$ and $1 + \alpha_2 \approx 1$

Thus, equation (i) can be reduced to $K_{a_1} = \dfrac{C\alpha_1 \times \alpha_1}{1-\alpha_1}$

This is expression similar to the expression for a weak monoprotic acid.

- Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} << K_{a_1}$

SALTS :

Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.

Classification of salts :

(1) Simple salts

(2) Normal salt : (i) Acid salts (ii) Basic salts

(3) Double salts

(4) Complex salts

(5) Mixed salts

TYPES OF SALT HYDROLYSIS :

(1) Hydrolysis of strong acid - weak base [SA - WB] type salt –

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Summary :

(1) $K_h = \dfrac{K_w}{K_b}$

(2) $h = \sqrt{\dfrac{K_h}{C}} = \sqrt{\dfrac{K_w}{K_b \times C}}$

(3) $\left[H^+\right] = Ch = \sqrt{\dfrac{K_w \times C}{K_b}}$

(4) $pH = -\log [H^+]$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

(2) Hydrolysis of [WA – SB] type salt –

Ex. KCN, $NaCN$, K_2CO_3, $BaCO_3$, K_3PO_4

$$NaCN + H_2O \rightleftharpoons NaOH + HCN$$

$$Na^+ + CN^- + H_2O \rightleftharpoons Na^+ + OH^- + HCN$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

Summary :

(1) $K_h = \dfrac{K_w}{K_a}$

(2) $h = \sqrt{\dfrac{K_h}{C}} = \sqrt{\dfrac{K_w}{K_a \times C}}$

(3) $[OH^-] = Ch = \sqrt{\frac{K_w \times C}{K_a}}$ (4) $[H^+] = \sqrt{\frac{K_w \times K_a}{C}}$

(5) $pH = -\log[H^+]$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

(3) Hydrolysis of (WA - WB) type salt :

Ex. NH_4CN, $CaCO_3$, $(NH_4)_2CO_3$, $ZnHPO_3$

- **Summary :**

(1) $K_h = \frac{K_w}{K_a \times K_b}$ (2) $h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}}$

(3) $[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}} = K_a.h$ (4) $pH = -\log[H^+]$

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

(4) Hydrolysis of [SA – SB] type salt –

Ex. NaCl, $BaCl_2$, Na_2SO_4, $KClO_4$ etc.

(i) Hydrolysis of salt of [SA – SB] is not possible

(ii) Solution is neutral in nature (pH = pOH = 7)

(iii) pH of the solution is 7

- BUFFER SOLUTIONS :

A solution that resists change in pH value upon addition of small amount of strong acid or base (less than 1 %) or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

Types of buffer solutions

(A) Simple buffer solution

(B) Mixed buffer solution

- SIMPLE BUFFER SOLUTION :

A salt of weak acid and weak base in water e.g. CH_3COONH_4, $HCOONH_4$, AgCN, NH_4CN.

Buffer action of simple buffer solution

$$\boxed{pH = 7 + \frac{1}{2}pk_a - \frac{1}{2}pk_b}$$

- MIXED BUFFER SOLUTIONS :

(a) Acidic buffer solution :

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

(b) **Basic buffer solution :**

A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of NH_4OH and NH_4Cl.

◆ **Condition for maximum buffer action :**

$[NH_4OH]$: $[NH_4Cl]$

1 1

$$pOH = pK_b + \log\frac{1}{1}$$

$pOH = pK_b$ and $pH = 14 - pK_b$

➢ SOLUBILITY (s) AND SOLUBILITY PRODUCT (K_{sp}) :

This is generally used for sparingly soluble salts. We will be dealing with the solubilities in the following type of solution.

Solubility product (K_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

- **Simple solubility**

Let the salt is $A_x B_y$, in solution in water, let the solubility in H_2O = 's' M, then

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{-x}$$

– xs ys $\therefore$ $K_{sp} = (xs)^x\,(ys)^y = x^x,\ y^y.(s)^{x+y}$

- **Condition of precipitation**
- For precipitation ionic product [IP] should be greater than solubility product k_{sp}.

THERMODYNAMICS

➢ THERMODYNAMICS :

- Study of heat and work interaction between system and surrounding.
- A macroscopic science.
- Thermodynamic laws are experimentally verified.

➢ Important terms and concepts in thermodynamics.

- System - Portion of universe under investigation.
- Surrounding - Anything apart from system.
- Boundary - Real or hypothetical line or surface between system and surrounding.
- Wall - A real boundary.

  Rigid wall - Immovable wall ($w = 0$)

  Non-rigid wall - Movable wall ($w \neq 0$)

  Adiabatic wall - Insulated wall ($q = 0$)

  Diathermic wall - Non-insulated wall ($q \neq 0$)
- State variable - Variable which defines state of system.
- State of system - A condition defined by fixed value of state variables.
- State of thermodynamic equilibrium - A condition in which state variables do not vary with time.

➢ **Extensive state variable** : State variable whose value depends upon size of system.

Examples - mass, volume, charge, mole etc.

➢ **Intensive state variable** : State variable whose value does not depends upon size of system.

Examples - concentration, density, temperature etc.

➢ **Path variable** :

- **Heat** : Mode of energy transfer between system and surrounding due to temperature difference.
- **Work** : Mode of energy transfer between system and surrounding due to difference in generalized force.(Net force).

THE FIRST LAW

(i) Energy of universe is conserved

(ii) Internal energy (U) of a system is state function.

(iii) $\Delta U = q + w$

ΔU = Increase in internal energy of system.
q = Heat absorbed by the system
w = work done on the system

(iv) In a cyclic process $\boxed{\sum_{\text{Cyclic}} \Delta U = 0}$

If a cyclic process involves n steps with heat absorbed and work done on the system, q_i and w_i respectively, then -

$$\sum_{\text{Cyclic}} \Delta U = \sum_{i=1}^{i=n} (q_i + w_i) = \sum_{i=1}^{i=n} q_i + \sum_{i=1}^{i=n} w_i = 0$$

⇒ $Q_{net} = -W_{net}$ (in a cyclic process)

(v) If two states 1 and 2 are connected by n paths involving q_i and w_i, heat and work respectively, then

$$\Delta U = q_1 + w_1 = q_2 + w_2 = \ldots\ldots\ldots\ldots\ q_n + w_n$$

(vi) q and w are path dependent quantities (indefinite quantities) but there sum is a definite quantity (ΔU).

◆ **Enthalpy** : A state function defined by first law

$$H = U + PV$$

(i) Enthalpy is (pressure volume energy + internal energy of system)

(ii) Enthalpy is also called heat content of system.

◆ **Heat absorbed at constant volume and constant pressure.**

$\boxed{q_V = \Delta U}$ Heat absorbed by a system in isochoric process is equal to change in internal energy of system.

$\boxed{q_p = \Delta H}$ Heat absorbed at constant pressure by a system is equal to change in enthalpy.

◆ **Enthalpy change :**

For General process -

$\Delta H = \Delta U + P_2V_2 - P_1V_1$ ....(i)

For Isobaric change -

$\Delta H = \Delta U + P\Delta V$ ....(ii)

For Isochoric change -

$\Delta H = \Delta U + V(\Delta P)$ ....(iii)

For a differential change

$dH = dU + PdV + VdP$ ....(iv)

➢ **Ideal gas processes : (See table page no. 11)**

◆ **Enthalpy of phase transition**

ΔH_{vap} = heat absorbed at constant temperature and pressure to convert one mole liquid into it's vapours.
= molar enthalpy of vapourisation.

ΔH_{fusion}= heat absorbed at constant temperature and pressure to convert one mole solid into liquid.
= molar enthalpy of fusion.

$\Delta H_{sublimation}$ = heat absorbed at constant temperature and pressure to convert one mole solid into it's vapours.
= molar enthalpy of sublimation.

$\Delta H = \Delta U + P(V_f - V_i)$ since phase transtions are isobaric and isothermal processes.

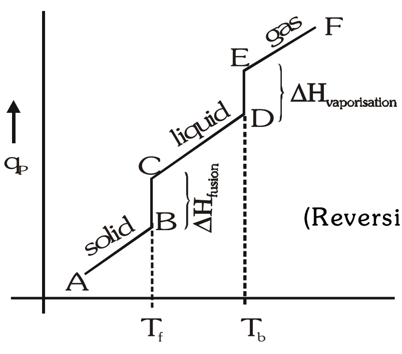
◆ **Relationship between ΔH and ΔU for phase transtions.**

For vapourisation $\Delta H_{vap} = \Delta U_{vap} + RT$

For sublimation $\Delta H_{sublimation} = \Delta U_{sublimation} + RT$

For fusion $\Delta H_{fusion} \cong \Delta U_{fusion}$

◆ **Heating curve at constant pressure :**



(Reversible, isobaric vapourisation at boiling point.)

(Reversible, isobaric, melting at melting point.)

◆ **Enthalpy of reaction ($\Delta_r H$) :** The enthalpy of reaction is heat exchanged at constant pressure and temperature to convert the stoichiometric amount of reactant into product with specified physical state according to balanced chemical reaction at constant temperature and pressure.

for $aA + bB \longrightarrow cC + dD$

$\Delta_r H = q_P =$ enthalpy of reaction

$\Delta_r H = (cH_C + dH_D - aH_A - bH_B)$ where H_A, H_B, H_C, H_D are molar enthalpies of A,B,C and D.

◆ **Relationship between $\Delta_r H$ and $\Delta_r U$**

$\Delta_r H = \Delta_r U + \Delta n_g RT$ (for ideal gas)

$\Delta_r H = \Delta_r U + P(V_f - V_i)$ (for non ideal conditions)

◆ **The stoichiometric coefficient of solids and liquids in not considered in calculation of Δn_g (because $V_S \tilde{} V_L << V_g$)**

◆ **Standard state for**

(i) Ideal gas : 1 bar pressure ; any temperature.

(ii) Solid / Liquid : 1 bar pressure ; any temperature.

(iii) Solute : Molar concentration of 1 mole/L at P = 1 bar.

Standard enthalpy, internal energy change for reaction.

$\Delta_r H$ and $\Delta_r U$ are change in thermodynamics function of a system under standard conditions.

SECOND LAW

➢ **Spontaneous process :**

- A process which takes place on it's own without any external help.
- Spontaneous process ≡ Irreversible process ≡ Natural process.

➢ **Second law** : During a spontaneous process.

- $\Delta S_{universe} > 0$

⇒ $\Delta S_{system} + \Delta S_{surr.} > 0$

- S is a state function. S is measure of disorder of a system.

(A) Change in entropy of system is given by :

$$dS_{system} = \frac{dq_{rev.}}{T}$$

(i) Entropy change for ideal gas process :

- $\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

(ii) Entropy change for system in phase transition :

- $\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T_b}$
- $\Delta S_{fusion.} = \frac{\Delta H_{fusion}}{T_f}$
- $\Delta S_{sublimation} = \frac{\Delta H_{sublimation}}{T_{Sub.}}$

(iii) Entropy change of system for a chemical reaction :

For a reaction -

- $aA + bB \longrightarrow cC + dD$

$$\boxed{\Delta_r S = cS_c + dS_D - aS_A - bS_B}$$

S_A, S_B,S_C and S_D are molar absolute entropies which is obtained by third law.

(B) Entropy change in surrounding :

(i) Ideal gas process : $\Delta S_{surr.} = \frac{-q_{actual}}{T}$

(ii) Phase transition : $\Delta S_{surr.} = \frac{-\Delta H}{T}$

(iii) Chemical reaction : $\Delta S_{surr.} = -\frac{\Delta_r H}{T}$

$$\boxed{\begin{aligned}&\text{For reversible processes : } \Delta S_{system} + \Delta S_{surr.} = 0\\ &\Delta S_{system} = -\Delta S_{surr.}\end{aligned}}$$

$$\boxed{\begin{aligned}&\text{For irreversible processes : } \Delta S_{system} + \Delta S_{surr.} > 0\\ &\Delta S_{total} \geq 0\end{aligned}}$$

◆ **Prediction of sign of $\Delta_r S$ from inspection :**

(i) If $\Delta n_g > 0$; $\Delta_r S > 0$.

(ii) If Solid $\longrightarrow$ liquid, liquid $\longrightarrow$ gas $\Big\}$ $\Delta_r S > 0$

(iii) If cyclisation taken place $\Delta_r S < 0$.

➢ **Gibb's function : $G = H - TS$**

$\Delta G = \Delta H - T\Delta S$ → For isobaric change

$\Delta G = -T(\Delta S_{Total})$

⇒ $(\Delta G)_{T,P} \leq 0$ → **Process spontaneous**

(A) Change in ΔG for phase transition :

(i) For reversible phase transitions : $\Delta G = 0$.

(ii) For irreversible phase transition : $\Delta G_{P,T} = \Delta H_{P,T} - T\Delta S_{P,T}$

(B) Change in ΔG for chemical reaction :

$aA + bB \longrightarrow cC + dD$

$\Delta_r G = cG_C + dG_D - aG_A - bG_B$ .....(i)

$\Delta_r G = \Delta_r H - T\Delta_r S$ .....(ii)

$\Delta_r G = \Delta_r G + RT \ln Q$ .....(iii)

Where, Q ≡ Reaction quotient

➢ ΔG /ΔG and state of chemical equilibrium :

At equilibrium :

- $\Delta G = 0 \Rightarrow G_{product} = G_{reactant}$
- $\Delta G = -RT \ln K_{eq.}$
- At equilibrium the system gibb's function is at minimum value.

➢ Difference between $\Delta_r G$ and $\Delta_r G$:

$\Delta_r G$ = change in Gibb's function when all the reactants and products have arbitrary activities.

$\Delta_r G$ = change in Gibb's function when all the reactants and products are at unit activities.

⇒ All gases at 1 bar pressure.

⇒ All solute at molar concentration 1 M.

➢ Factors on which $\Delta_r G$ depends -

(i) Stoichiometric coefficients of a balanced chemical reaction.

(ii) the temperature.

(iii) the $\Delta_r G$ is independent of actual pressure or concentration of reactants or products.

➢ Gibb's function and non-PV work :

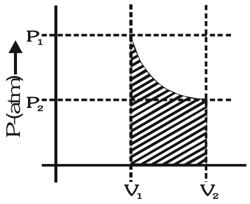
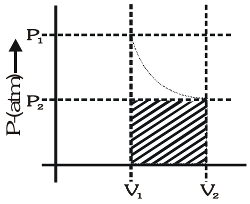
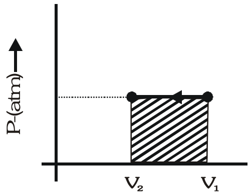
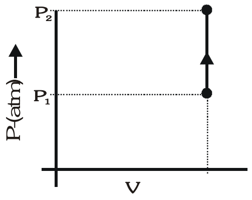
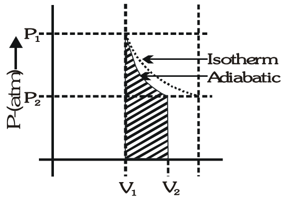
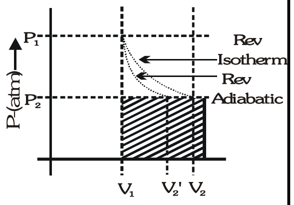
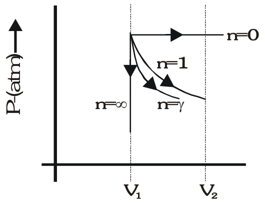
$$-(\Delta G)_{T,\,P} = W_{max}$$

decrease in Gibb's function at constant temperature and pressure is equal to maximum non-PV work obtainable from system reversibly.

$$-\Delta_r G = -\Delta_r H + T\Delta_r S$$

Decrease in Gibb's function = heat given out to surrounding + $T\Delta_r S$.

IDEAL GAS PROCESSES :

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal process	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \left(\frac{V_2}{V_1}\right)$ $q = nRT \ln \left(\frac{P_1}{P_2}\right)$	0	0	
Irreversible isothermal process	$w = -P_{ext}\left(V_2 - V_1\right)$ $= -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$	$q = P_{ext}\left(V_2 - V_1\right)$	0	0	
Isobaric process	$w = -P_{ext}\left(V_2 - V_1\right)$ $= -\ nR\Delta T$	$q = \Delta H = nC_P\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_V\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Reversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ PV^{γ}=constant $TV^{\gamma-1}$ =constant $TP^{1-\gamma/\gamma}$=constant	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Irreversible adiabatic process	$w = nC_V(T_2 - T_1)$ $\frac{P_2V_2 - P_1V_1}{\gamma - 1}$				
Polytropic process	$w = \frac{P_2V_2 - P_1V_1}{n - 1}$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$q = \int_{T_1}^{T_2} C_V dT$ $+ \int_{T_1}^{T_2} \frac{R}{1 - n} dT$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	

V_2 = Final volume V_1 = Initial volume

P_2 = Final pressure P_1 = Final pressure

THERMOCHEMISTRY

- $\Delta_r H = q_P$ = Heat of reaction at constant pressure

  $\Delta_r E = \Delta_r U = q_V$ = Heat of reaction at constant volume.

- For mix. of reacting ideal gases at constant Temperature :

  $\Delta_r H = \Delta_r U + (\Delta n_g)\, RT$.

- **Exothermic Reaction :**

  $H_P > H_R$ $\quad$ $U_P > U_R$
  $\Delta_r H > 0$
  $\Delta_r U > 0$

- **Endothermic Reaction :**

  $H_P < H_R$ $\quad$ $U_P < U_R$
  $\Delta_r H < 0$
  $\Delta_r U < 0$

- **Reversible Phase Transition**

  Isothermal and Isobaric

  Example :

  (a) Melting or Freezing at MP

  (b) Vaporisation or condensation at B.P.

  (c) Sublimation at sublimation point.

  (d) Interconversion of allotropic forms at Transition temperature.

- $S_g >> S_\ell > S_s$; $\quad$ $V_g >> V_\ell > V_s$;
  $V_g >> V_\ell < V_s$ (Water) ; $\quad$ $H_g >> H_\ell > H_s$;
  $U_g >> U_\ell > U_s$; $\quad$ $\Delta H_{sub} >> \Delta H_{vap} > \Delta H_{fus.}$
  At same Pressure and Temperature

  $\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus.}$

- For reversible phase transition.

  $W = -P_{ext}\,[\Delta V]$

  $$\Delta S_{trans.} = \frac{\Delta H_{trans}}{T_{trans}}$$

  $q = \Delta H_{trans}$
  $\Delta U_{trans} = \Delta H_{trans} + w$

- $\Delta_r H = \sum V_P H \text{ (product)} - \sum V_R H \text{ (Reactant)}$

  $\Rightarrow$ V_P, V_R – Stoichiometric coefficient of reactants & products

  $\Delta_r G = \sum V_P G \text{ (product)} - \sum V_R G \text{ (reactants)}$

- **Determining $\Delta_r H$ for reaction :- 3 methods**

  (a) $\Delta_r H = \sum V_P \Delta H_f (P) - \sum V_R \Delta H_f (R)$

  (b) $\Delta_r H = \sum V_R \Delta H_{comb.} (R) - \sum V_P \Delta H_{comb.} (P)$

  (c) $\Delta_r H = \sum \Delta H_{atomisation} (R) - \sum \Delta H_{atomisation} (P)$

- ΔH_f (Element in solid state) = 0.

  $\Delta H_f (CO_2, g) = \Delta H_{comb.}$ (C, grap.)

$\Delta H_f\ (H_2O,\ \ell) = \Delta H_{comb.}\ (H_2,\ g)$

- $aA + bB \longrightarrow cC + dD \quad ; \Delta_r H$

  $\Delta_r H$ = change in enthalpy when

  a mol of A react ; b mol of B react ; c mol of C formed ; d mol of D formed

- $\Delta_r G = \Sigma V_P\ \Delta G_f\ (P) - \Sigma V_R\ \Delta G_f\ (R)$ OR $\Delta_r G = \Delta_r H - T\Delta_r S$

- Gibbs enthalpy is function of P, T.

  $P\uparrow \ \Rightarrow\ G\uparrow$

  $T\uparrow \ \Rightarrow\ G\downarrow$

- $$\left.\begin{array}{l} \Delta H_f\ (H^+,\ aq) = 0 \\ \Delta G_f\ (H^+,\ aq) = 0 \\ E^{\circ}_{H_2 \mid H^+} = 0 \\ S_m\ (H^+,\ aq) = 0 \end{array}\right] \text{By convention}$$

- $$q = \int ms\, dt$$
  $$= \int nC_m\, dt$$
  $$= \int C\, dt$$

  $$\begin{array}{ccccc} mS & = & nC_m & = & C \\ \downarrow & & \downarrow & & \downarrow \end{array}$$

specific	molar	Total
heat	heat	heat
capacity	capacity	capacity

- For strong Acid and strong base

  $\Delta H_{neutr.} = -57.1$ kJ/mol.

  when 1 eq. H^+ (acid) reacts with 1 eq. OH^- (base)

- If acid or base is weak

  $\Delta H_{neut.} = -57.1 + \Delta H_{ionisation} \Rightarrow +ve$

- Heat evolved in SA + SB titration = (no. of eqv. of limiting reagent) 57.1 kJ

- Resonance enthalpy = R.E. < 0 = (Energy of R.H.) – (Energy of stablest R.S.)

- $\Delta_r H$ (Actual) – $\Delta_r H$ (theoretical) = [$\Sigma\ V_P$ RE (P) – $\Sigma\ V_R$ RE (R)

- $\Delta H_{hydration}\ [CuSO_4,\ s]$

  $\Delta H_{solution}\ [CuSO_4,\ s] - \Delta H_{solution}\ [CuSO_4\ 5H_2O,\ s]$

- Enthalpy of atomisation :

  $\Delta H_{atomisation}\ (O_2,\ g) = BE\ (O = O)$

  $\Delta H_{atomisation}\ (C_6H_6,\ \ell) = \Delta H_{vap.} + 3\in (C = C) + 3\in (C - C) + 6\in (C - H)$ $\quad \in$ = Bond enthalpy

  $\Delta H_{atomisation}\ (Fe,\ s) = \Delta H_{sub}$

  $\Delta H_{atomisation}\ (I_2,\ s) = \Delta H_{sub} + \in (I - I)$

LIQUID SOLUTION

- **Vapour Pressure** : Pressure of any volatile substance at any given temperature.
  $T \uparrow \Rightarrow$ V.P. $\uparrow$
  Attractive forces $\uparrow \Rightarrow$ V.P. $\downarrow$

- **Raoult's law** :
  Non volatile solute and volatile solvent solution.

$$\text{If}\begin{cases} B = \text{Non volatile solid} \\ P_B = 0 \end{cases}$$

$$P_A = P_A^{\circ} X_A$$

- **Colligative Properties** : Properties depends on no. of particles of Non volatile solute in solution.

$$\begin{matrix}\text{No. of particle of} \\ \text{Non volatile solute}\end{matrix} \uparrow \Rightarrow \begin{matrix}\text{Colligative} \\ \text{Properties}\end{matrix} \uparrow$$

(1) **Relative lowering of V.P.** :

$$\frac{P_A^{\circ} - P_A}{P_A^{\circ}} = i\frac{n_B}{n_A + n_B} \approx i\frac{n_B}{n_A}$$

Where n_B = mole of Non-volatile solute.
i = Vant Hoff's factor.

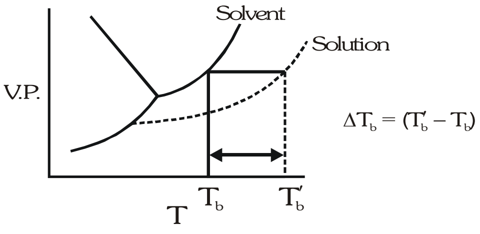
(2) **Elevation in B.P.** :

$\Delta T_b = (T_b' - T_b) = i.\ k_b\ \ m.$

where $K_b = \dfrac{RT_b^2}{1000 \times \ell_v}$

where T_b = B.P. of pure solvent.
ℓ_v = Latent heat of vapourization per gm
K_b = molal elevation constant
M = molar mass

where $\ell_v = \left(\dfrac{\Delta H_{vap}}{M}\right)$



(3) **Depression** in FP.

$\Delta T_f = T_f - T_f' = i\ k_f\ \ m$

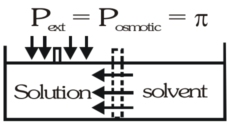
where $k_f = \dfrac{RT_f^2}{1000 \times \ell_f}$

T_f = f.p. of pure solvent
k_f = molal depression contsant
ℓ_f = latent heat of fusion per gm.

(4) **Osmotic presssure** :

$\pi \propto \left(P_A^{\circ} - P_A\right)$

$\pi = iC.\ S.T.$



where π = osmotic pressure
C = molarity (mole/lit)
S = R = const. for solution.

	Sol.(1)		Sol (2)	
If	π_1	=	π_2	Isotonic
If	π_1	>	π_2	$\begin{cases} \text{sol}^n(1) \text{ hypertonic} \\ \text{sol}^n(2) \text{ hypotonic} \end{cases}$

Van't Hoff factor for different Cases of solutes undergoing Ionisation and Association :

Solute	Example	Ionisation/association (x degree)	y*	van'thoff factor	abnormal mol. wt. (m_1')
Non-electrolyte	urea-glucose, sucrose etc.	none	1	1	normal mol.wt. (m_1)
Binary electrolyte A^+B^-	NaCl, KCl, HCl CH_3COOH, $FeSO_4$ etc.	$\underset{1-x}{AB} \rightleftharpoons \underset{x}{A^+} + \underset{x}{B^-}$	2	(1 + x)	$\frac{m_1}{(1+x)}$
Ternary electrolyte A_2B, AB_3	K_2SO_4, $BaCl_2$,	$\underset{1-x}{A_2B} \rightleftharpoons \underset{2x}{2A^+} + \underset{x}{B^{2-}}$	3	(1+2x)	$\frac{m_1}{(1+2x)}$
	$K_3[Fe(CN)_6]$, $FeCl_3$	$\underset{1-x}{AB_3} \rightleftharpoons \underset{x}{A^{3+}} + \underset{3x}{3B^-}$	4	(1+3x)	$\frac{m_1}{(1+3x)}$
Associated Solute	benzoic acid in benzene forming dimer	$2A \rightleftharpoons A_2$ $\underset{(1-x)}{A} \rightleftharpoons \frac{1}{2}\underset{x/2}{A_2}$	$\frac{1}{2}$	$\left(1-\frac{x}{2}\right)=\left(\frac{2-x}{2}\right)$	$\frac{2m_1}{(2-x)}$
	any solute forming polymer A_n	$nA \rightleftharpoons A_n$ $\underset{(1-x)}{A} \rightleftharpoons \frac{1}{n}\underset{x/2}{A_n}$	$\frac{1}{n}$	$\left[1+\left(\frac{1}{n}-1\right)x\right]$	$\left[\frac{m_1}{1+\left(\frac{1}{n}-1\right)x}\right]$
General	one mole of solute giving y mol of products	$A \rightleftharpoons yB$	y	[1+(y−1)x]	$\frac{m_1}{[1+(y-1)x]}$

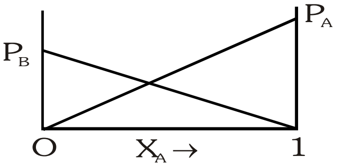
* number of products from one mole solute

Raoult's law :

(1) Volatile binary liquid mix :

Volatile liq.	A	B
Mole fraction	X_A/Y_A	X_B/Y_A ⇒ liq/vapour
V.P. of pure liq.	P_A°	P_B°

Binary liquid solution :

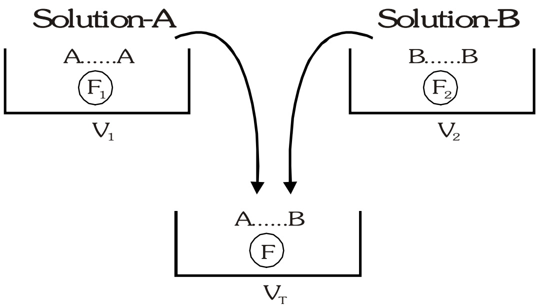


By Raoult's law ⇒ $P_T = P_A^\circ X_A + P_B^\circ X_B = P_A + P_B$ ……(i)

By Dalton's law ⇒ $P_A = Y_A P_T$ ……(ii)

$P_B = Y_B P_T$ ……(iii)

- **Ideal and Non-Ideal solution :**



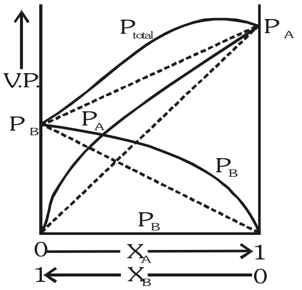
Ideal solution : $\begin{cases} F_1 \simeq F_2 \simeq F \\ V_T = V_1 + V_2 \end{cases}$ ⇒ $\Delta H_{solution} = 0$

Non-Ideal solution :

(1) **Solution showing +ve deviation :**

$F < F_1$ & F_2

$V_T > V_1 + V_2$ ⇒ $\Delta H_{solution} > 0$

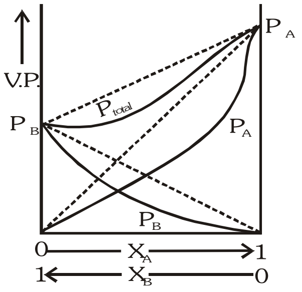


(2) **Solution showing –ve deviation :**

⇒ $F > F_1$ & F_2

⇒ $V_T < (V_1 + V_2)$

⇒ $\Delta H_{solution} < 0$



DEVIATION FROM RAOULT'S LAW

	Positive deviation (ΔH=+ve)	Negative deviation (ΔH=–ve)	Zero deviation (ΔH=0)
(i)	ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(ii)	acetone + carbon disulphide	benzene + chlorform	n-hexane + n-heptane
(iii)	acetone + benzene	nitric acid + chloroform	ethyl bromide + ethyl iodide
(iv)	ethanol + aceton	acetone + aniline	chlorobenzene + bromo benzene
(v)	ethanol + water	water + nitric acid	
(vi)	carbon tetrachloride chloroform	diethyl ether + chloroform	

- **Azeotropic mixtures :**

  Some liquids on mixing form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. Azeotropic mixture cannot be separated by fractional distillation.

- **Types of Azeotropic mixtures**

(i) **Minimum boiling Azeotropic mixtures**

The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviation. For example (95.5%) + water (4.5%) + water boils at 351.15 K.

(ii) **Maximum boiling Azeotropic mixtures**

The mixture of two liquids whose boiling point are more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.

SOLID STATE

- Various type of Criptals :

Some Important Characteristics of Various types of Crystals

Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
Binding forces	Electrostatic attraction between ions	Shared electrons	vander Waals or Dipole-dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
Hardness	Hard	Very hard	Soft Graphite	Hard or soft
Brittleness	Brittle	Intermediate	Low	Low
Melting point	High	Very high	Low	Varying from moderate to high
Electrical Conduction	Semi conductor due to crystal imperfections,conductor in fused state	Non-conductor Graphite is good conductor	Bad conductor	Good conductors
Solubility in Polar solvents	Soluble	Insoluble	Soluble as well as insoluble	Good conductors
Heat of Vaporisation (kj mol^{-1})	NaCl(s) 170-75	Graphite 718-43	NH_3(s) 23.55	Cu(s) 304.59
Heat of fusion (kj mol^{-1})	NaCl 28.45	– –	NH_3 (s) 5.65	Cu(s) 13.016
Example	NaCl, KNO_3 CsCl, Na_2SO_4 ZnS	Diamond, graphite, Quartz (SiO_2), SiC	H_2O(s), CO_2(s), Sulphur, Sugar, Iodine,noble gases	Na, Cu, Ag, Fe, Pt, alloys

THE SEVEN CRYSTAL SYSTEMS

	Name of System	Axes	Angles	Bravais Lattices
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred = 3
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Body centred = 2
3.	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
4.	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred End centred = 4
5.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	Primitive, End - centred = 2
6.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90$	Primitive = 1
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90$ $\gamma = 120$	Primitive = 1 Total = 14

CUBIC UNIT CELL

Unit cell	Relation between r and a	Packing fraction	Co-ordinatin number	Effective number of particle
Simple cubic Body centred	$r = \frac{a}{2}$	52.4%	6	1
cubic	$r = \frac{a\sqrt{3}}{4}$	68%	8	2
Face centred cubic	$r = \frac{a\sqrt{2}}{4}$	74%	12	4

Density : $d = \frac{ZM}{N_{A} \times a^3}$ gm / cm^3

Where Z = effective number of particle

M= molar mass

N_A = Avogarodro's number

a = edge length (cm)

Three dimensional close packing :

- Hexagonal close packing (HCP) :

  Effective number of particle = 6

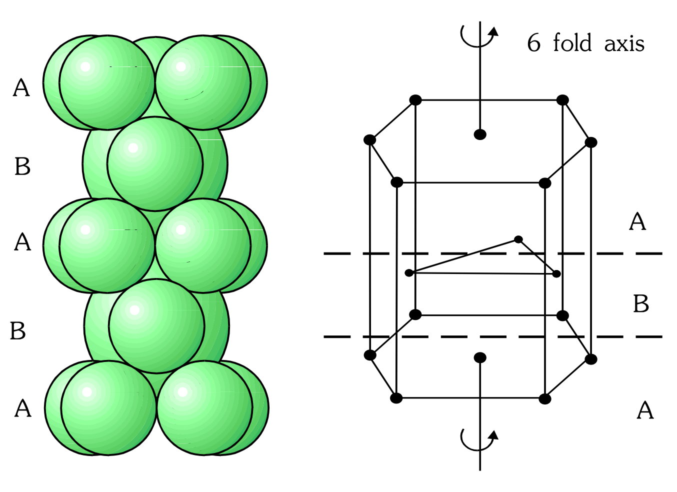
  Effective number of octahedral void = 6

  Effective number of tetrahedral void = 12

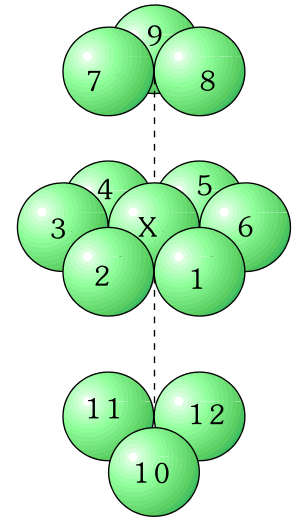
  Packing fraction

  = 74% ; co-ordination number = 12

  $a = \frac{r}{2}$; $b = 4\sqrt{\frac{2}{3}}\,r$



ABABAB... or hexagonal close packing (hcp) of spheres



Coordination number of hcp and ccp structure

- Cubic close packing (CCP) :

  Effective number of particle = 4

  Effective number of octahedral void = 4

  Effective number of tetrahedral void = 8

  Packing fraction = 74% ;

  co-ordination number =12

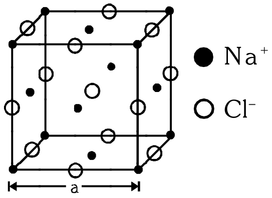
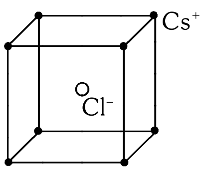
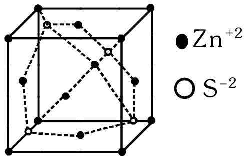
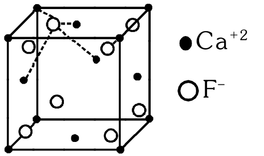
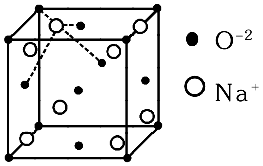
  $$\frac{a\sqrt{2}}{4} = r$$

- Different type of voids and their radius ratio :

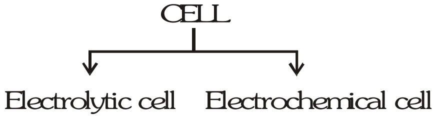
Limiting radius ratio for various types of sites

Limiting radius ratio = r/R	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 - 0.732	4	Square planaer	–
0.414 - 0.732	6	Octahedral	NaCl, MgO_2
0.732 - 1.000	8	Cubic	CsCl

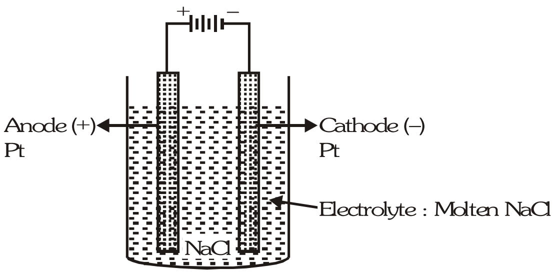
TYPES OF IONIC CRYSTAL

	Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.C.	Examples	
1.	NaCl (1 : 1) (Rock Salt Type)	C.C.P. $Na^+ \rightarrow$ Every element of C.C.P. C.C.P. $Cl^- \rightarrow$ At every OHV	6 : 6	$4Na^+ + 4Cl^-$ $4NaCl$ (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of II–A (Some exception) AgF, AgCl, AgBr, NH_4X	
2.	CsCl Type (1 : 1)	B.C.C. $Cs^+ \rightarrow$ at every corner B.C.C. $Cl^- \rightarrow$ at Body centre or at cubic void	8 : 8	$1Cs^+ + 1Cl^-$ $1CsCl$ (1)	Halides of 'Cs' TlCl, TlBr, CaS	
3.	Zns Type (1 : 1) (Zinc Blende Type) (Sphalerite)	C.C.P. $Zn^{+2} \rightarrow$ Every element of C.C.P. C.C.P. $S^{-2} \rightarrow$ At 50% of T.H.V. or at alternate tetrahedral voild	4 : 4	$4Zn^{+2} + 4S^{-2}$ $4ZnS$ (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI	
4.	CaF_2 Type (1 : 2) (Fluorite Type)	C.C.P. $Ca^{+2} \rightarrow$ Every element of C.C.P. C.C.P. $F^- \rightarrow$ At every T.H.V.	$4Ca^{+2}, 8F^-$ 8 : 4	$4Ca^{+2} + 8F^-$ $4CaF_2$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2 $CaCl_2$, CaF_2	
5.	Na_2O Type (2 : 1) (Antiflourine)	C.C.P. $Na^+ \rightarrow$ At every T.H.V. C.C.P. $O^{-2} \rightarrow$ Every element of C.C.P.	$8Na^+, 4O^{-2}$ 4 : 8	$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S Na_2O, Na_2S K_2O, K_2S	
6.	ZnS Type (1 : 1) (Wurtzite) another geometry of Zns	H.C.P. $Zn^{+2} \rightarrow$ Every element of H.C.P. H.C.P. $S^{-2} \rightarrow$ 50% of T.H.V. or (at alternate T.H.V.)	4 : 4	$6Zn^{+2} + 6S^{-2}$ $6ZnS$ (6)	Same as sphalerite	

ELECTRO CHEMISTRY



- Electrolytic cell : Converts electrical energy into chemical energy



Cathode : $Na^+_{(aq.)} + e \longrightarrow Na(s)$

Anode : $Cl^-_{(aq.)} \longrightarrow \frac{1}{2} Cl_2(g) + e$

- **Deposition of material at any electrode follow faraday's law of electrolysis.**

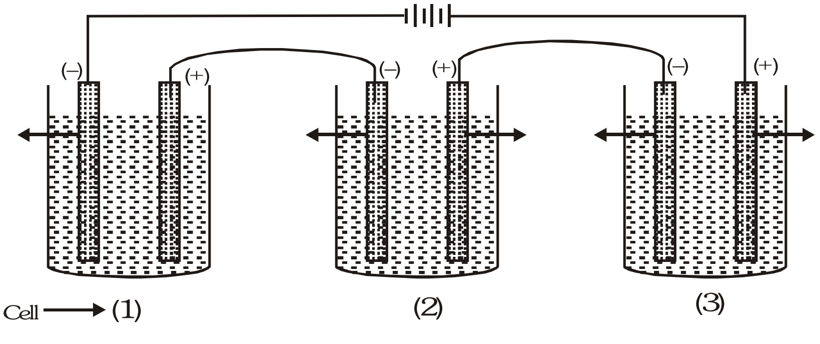
Faraday's Ist Law :

$$w = Z\ it$$

$$w = \frac{M}{n - \text{factor} \times 96500}\ it$$

where w = mass deposite (gm)
M = molar mass
i = current (Amp.)
t = time (sec.)

Faraday's second law :



- At any electrode for material deposited.

$$\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3}$$

Note : Order of discharge potential.

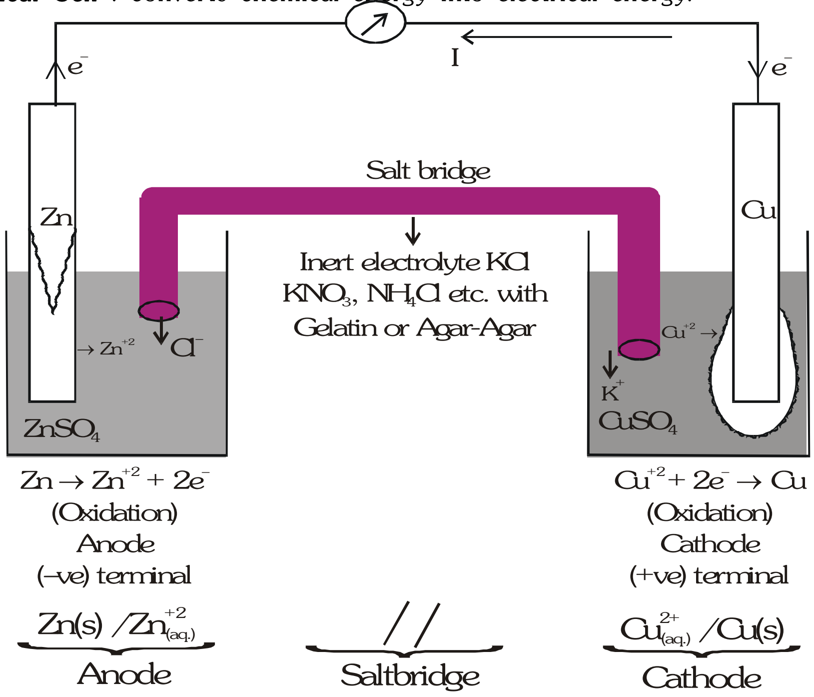
Cathode : $Au^{+3} > Ag^+ > Cu^{+2} > Zn^{+2} > H_2O > Al^{+3} > Mg^{+2} > Na^+ > Li^+$

Anode : $SO_4^{2-} < NO_3^- < H_2O < Cl^- < Br^- < I^-$

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

S. No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(i)	Aqueous NaCl	Pt or Graphite	Cl_2	H_2
(ii)	Fused NaCl	Pt or Graphite	Cl_2	Na
(iii)	Aqueous NaOH	Pt or Graphite	O_2	H_2
(iv)	Fused NaOH	Pt or Graphite	O_2	Na
(v)	Aqueous $CuSO_4$	Pt or Graphite	O_2	Cu
(vi)	Dilute HCl	Pt or Graphite	Cl_2	H_2
(vii)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(viii)	Aqueous $AgNO_3$	Pt of Graphite	O_2	Ag

- **Electrochemical Cell** : converts chemical energy into electrical energy.



- $E_{Cell} = SRP_{cathode} - SRP_{Anode}$

  $= SRP_{cathode} + SOP_{at\ anode}$

  Half cell reaction :

  Anode: $Zn(s) \longrightarrow Zn^{+2}_{(aq.)} + 2e$

  Cathode : $Cu^{+2}_{(aq.)} + 2e \longrightarrow Cus$

- **Cell reaction :** $Zn(s) + Cu^{+2}_{(aq.)} \longrightarrow Zn^{+2}_{(aq.)} + Cu(s)$

$$Q = \frac{[Zn^{+2}]}{[Cu^{+2}]};\ n = 2$$

- Nearest equation :

$$E_{Cell} = E_{\,Cell} - \frac{0.059}{n} \log Q \qquad \text{at 298 K}$$

- Max electrical work done = nFE = –ΔG

  electrical work done = nFE = –ΔG

DIFFERENT TYPE OF ELECTRODES/HALF CELL

Type	Example	Half-cell reaction	Electrode potential (reduction)
Metal - Metal ion	M/M^{n+}	$M^{n+} + ne^- \longrightarrow M(s)$	$E = E + \frac{0.0591}{n} \log [M^{n+}]$
Gas - ion	Pt / H_2 (P atm) / H^+ (XM)	H^+ (aq) + e^- $\longrightarrow \frac{1}{2} H_2$ (P atm)	$E = E - 0.0591 \log \frac{\sqrt{P_{H_2}}}{[H^+]}$
Oxidation - reduction	Pt / Fe^{2+} , Fe^{3+}	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	$E = E - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$
Metal - insoluble salt Anion	Ag/AgCl, Cl^-	AgCl (s) + e^- $\longrightarrow$ Ag (s) + Cl^-	$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag}$ $-0.0591 \log[Cl^-]$
Calomel electrode	$Cl^-(aq)/Hg/Hg_2Cl_2$	$Hg_2Cl_2(s) + 2e^-$ $\longrightarrow 2Hg(l) + 2Cl^-(aq.)$	$E = E - 0.0591 \log [Cl^-]$

- Gibb's Helmhaltz equation :

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]$$

$$\Rightarrow \qquad \Delta H = -nFE + nFT\left[\frac{\partial \Delta G}{\partial T}\right]_P$$

'THE ELECTROCHEMICAL SERIES'

Element	Electrode Reduction Reaction	Standard electrode Reduction potential E^0, Volts
Li	$Li^+ + e \rightarrow Li$	– 3.05
K	$K^+ + e^- \rightarrow K$	– 2.93
Ba	$Ba^{+2} + 2e^- \rightarrow Ba$	– 2.90
Ca	$Ca^{+2} + 2e^- \rightarrow Ca$	– 2.87
Na	$Na^+ + e^- \rightarrow Na$	– 2.71
Mg	$Mg^{+2} + 2e^- \rightarrow Mg$	– 2.37
Al	$Al^{+3} + 3e^- \rightarrow Al$	– 1.66
Mn	$Mn^{+2} + 2e^- \rightarrow Mn$	– 1.18
H_2O	**$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$**	**– 0.828**
Zn	$Zn^{+2} + 2e^- \rightarrow Zn$	– 0.76
Cr	$Cr^{+3} + 3e^- \rightarrow Cr$	– 0.74
Fe	$Fe^{+2} + 2e^- \rightarrow Fe$	– 0.44
Cd	$Cd^{+2} + 2e^- \rightarrow Cd$	– 0.40
Ni	$Ni^{+2} + 2e^- \rightarrow Ni$	– 0.25
Sn	$Sn^{+2} + 2e^- \rightarrow Sn$	– 0.14
Pb	$Pb^{+2} + 2e^- \rightarrow Pb$	– 0.13
H_2	$2H^+ + 2e^- \rightarrow H_2$	0
Cu	$Cu^{+2} + 2e^- \rightarrow Cu$	+ 0.34
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+ 0.54
Hg	$Hg_2^{+2} + 2e \rightarrow 2Hg$	+ 0.79
Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.80
Hg	$Hg^{+2} + 2e^- \rightarrow Hg$	+ 0.85
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.08
O_2	**$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$**	**+ 1.229**
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36
Au	$Au^{+3} + 3e \rightarrow Au$	+ 1.50
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+ 2.87

CONDUCTION IN ELECTROLYTES

	Conductance	Specific Conductivity	Molar Conductivity
Symbol Unit	C Ω^{-1}	κ Ω^{-1} cm^{-1}	Λ_m Ω^{-1} cm^2mol^{-1}
Specific	conductance of volume within electrode	conductance of unit volume	conductance of that volume which contain exactly one mole
Change with concentraction	decrease with decrease in concentration	Decrease with decrease in concentration	Increase with in decrease in concentration
Formula	$C = \frac{1}{R}$	k = C cell constant	$k = \Lambda_m = K \quad V$ V = Volume of solution contain 1 mole of electrolyte
Factors	(i) nature of electrolyte (ii) concentration of electrolyte (iii) Type of cell.	(i) nature of electrolyte (ii) concentration of electrolyte	(i) nature of electrolyte (ii) concentration of electrolyte

- KOHLRAUSEH'S LAW :

$$\Lambda_m^\infty(A_xB_y) = x\lambda_+^\infty + y\lambda_-^\infty$$

$$\Lambda_m^\infty(K_2SO_4) = 2\lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty(Na_3PO_4) = 3\lambda_+^\infty + \lambda_-^\infty$$

$$\Lambda_m^\infty[Fe_2(SO_4)_3] = 2\lambda_+^\infty + 3\lambda_-^\infty$$

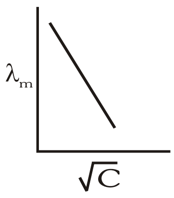
- FORMULA

(1) $R = \rho \frac{\ell}{A}$

(2) $\lambda_m = k \frac{1000}{M}$

(3) $\lambda_{eq.} = k \times \frac{1000}{N}$

(4) for strong electrolyte $\lambda_m = \lambda_{m_\infty} - b\sqrt{C}$



CHEMICAL KINETICS

- Rate of reaction (ROR) $= \dfrac{\text{Rate of disappearance of reactant (appearance of products)}}{\text{Stoichiometric coefficient of reactant (products)}}$

- For a reaction :

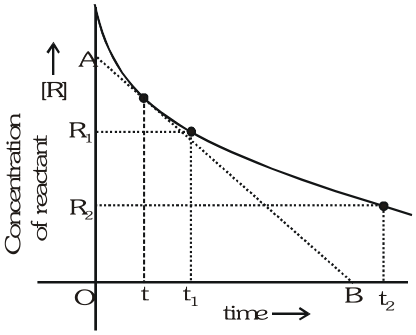
$aA + bB \longrightarrow cC + dD$

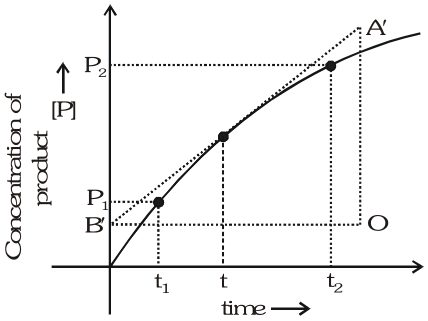
- Instantaneous rate : $-\frac{1}{a}\left(\frac{d[A]}{dt}\right) = -\frac{1}{b}\left(\frac{d[B]}{dt}\right) = \frac{1}{c}\left(\frac{d[C]}{dt}\right) = \frac{1}{d}\left(\frac{d[D]}{dt}\right)$

Relationship between rate of reaction and rate of disappearence of reactant (rate of appearance of product).

◆ Average rate : $-\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[B]}{\Delta t}\right) = \frac{1}{c}\left(\frac{\Delta[C]}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta[D]}{d\Delta t}\right)$

⇒ Graphical method for determining rate :





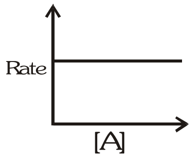
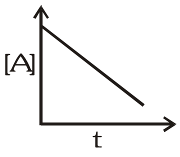
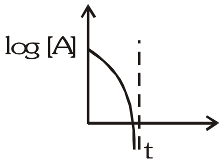
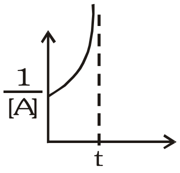
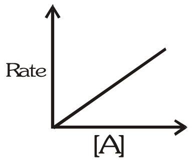
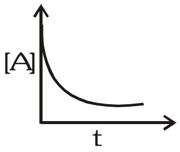
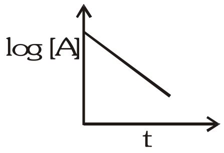
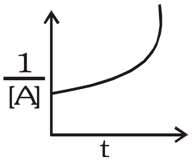
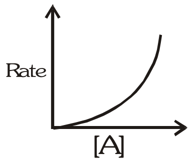
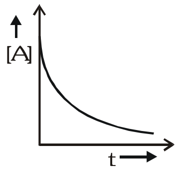
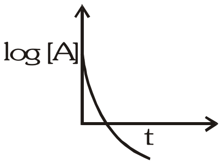
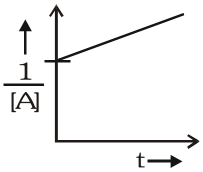
Avg. Rate $= -\left(\frac{[R]_2 - [R]_1}{t_2 - t_1}\right) = \frac{([P]_2 - [P]_1)}{t_2 - t_1}$

Instantaneous rate $= -\left(\frac{OA}{OB}\right) = +\frac{OA'}{OB'} = \pm$ slope of tangent

- **Important kinetic expression for reaction of type $A \longrightarrow B$:**

Order	Zero	1st	2nd	nth
Differential rate law	Rate = k	Rate= k[A]	Rate = $k[A]^2$	Rate = $k[A]^n$
Integrated rate law	$[A_0]-[A]= kt$	$kt = \text{In}\frac{[A]_0}{[A]}$	$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$	$kt = \frac{1}{(n-1)}\left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}\right]$
Half life ($t_{1/2}$)	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$	$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1}-1}{[A_0]^{n-1}}\right]$
($t_{3/4}$)	$t_{3/4}$=1.5 $t_{1/2}$	$t_{3/4}$= 2 $t_{1/2}$	$t_{3/4}$ = 3 $t_{1/2}$	$t_{3/4}$= $(2^{n-1} + 1)$ $t_{1/2}$

- Graphs of various order

Order	Rate vs [A]	[A] vs t	log [A] vs t	$\frac{1}{[A]}$ vs t
Zero order				
First order				
Second order				

Where

$[A]_0 \Rightarrow$ initial concentration

$[A] \Rightarrow$ concentration at time t

$t_{1/2} \Rightarrow$ time taken for initial concentration of reactant to finish by 50%

$t_{3/4} \Rightarrow$ time taken for initial concentration of reactant to finish by 75%

- Monitoring Kinetics Experimently :

The kinetics of reaction can be followed (i.e. order, rate constant etc. can be established) by measuring a property which changes with time.

e.g. (i) Total pressure in a gaseous reaction.

(ii) Volume of a reagent (Acidic, Basic, oxidising or reducing agent)

(iii) Volume of a gaseous mixture (V)

(iv) Optical rotation (R)

For a Reaction -

	$A_n \longrightarrow$	nB	
t = 0	c	0	$c_0 \Rightarrow$ conc. at t = 0
t = t	c – x	nx	$c_t \Rightarrow$ conc. at t = t
t = ∞	0	nc	$c_\infty \Rightarrow$ conc. at t = ∞

For any measurable property X proportional to the concentration of reaction mixture at various times, following relations can be expressed.

In terms of -

(i) X_0 and x	(ii) X_0 and X_t	(iii) X_∞ and X_t	(iv) X_0, X_t, and X_∞
$k = \frac{1}{t}\ln\frac{X_0}{X_0 - x}$	$k = \frac{1}{t}\ln\frac{(n-1)X_0}{nX_0 - X_t}$	$k = \frac{1}{t}\ln\frac{(n-1)X_\infty}{n(X_\infty - X_t)}$	$k = \frac{1}{t}\ln\left(\frac{X_\infty - X_0}{X_\infty - X_t}\right)$

where

$x \Rightarrow$ amount of reactant reacted in time 't'.

$X_0 \Rightarrow$ measured property at t = 0

$X_t \Rightarrow$ measured property at t = t

$X_\infty \Rightarrow$ measured property at t = ∞

➢ Examples : (For Monitoring Kinetics Experimently)

(i) Inversion of cane sugar :

$$\underset{\substack{\text{Sucrose}\\ \text{dextro-rotatory}\\ (+66.5\ )}}{C_{12}H_{22}O_{11}\ (aq)} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{Glucose}\\ \text{dextro-rotatory}\\ (+52.5\ )}}{C_6H_{12}O_6(aq)} \quad + \quad \underset{\substack{\text{Fructose}\\ \text{laevo-rotatory}\\ (-92\ )}}{C_6H_{12}O_6(aq)}}_{\text{(Laevo-rotatory)}}$$

$$\boxed{k = \frac{2.303}{t}\log\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)}$$

r_0 = rotation at time, $t = 0$

r_t = rotation at time, $t = t$

r_∞ = rotation at time, $t = \infty$

(ii) **Acidic hydrolysis of ethyl acetate :**

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\boxed{k = \frac{2.303}{t}\log\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)}$$

V_0 = Volume of NaOH solution used at time, $t = 0$

V_t = Volume of NaOH solution used at time, $t = t$

V_∞ = Volume of NaOH solution used at time, $t = \infty$

Note : Here NaOH acts as a reagent. Acetic acid is one of the product the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution.

➢ Important characteristics of first order reaction :

◆ $t_{1/2}$ is independent of initial concentration.

◆ In equal time interval, reactions finishes by equal fraction.

	$t = 0$	$t = t$	$t = 2t$	$t = 3t$ ....
Reactant conc.	a_0	a_0x	a_0x^2	a_0x^3........

x = fraction by which reaction complete in time 't'.

◆ Graph of ln[A] vs t is straight line with slope = $\frac{k}{2.303}$

◆ Graph of [A] vs t is exponentially decreasing.

➢ Zero order :

- $t_{1/2}$ of zero order is directly proportional to initial concentration.
- In equal time interval, reaction finishes by equal amount.

$t = 0$	$t = t$	$t = 2t$	$t = 3t$ .....
C_0	$C_0 - x$	$C_0 - 2x$	$C_0 - 3x$ ....

- Graph of [A] vs t is straight line.

A zero order reaction finishes in $\boxed{t = \frac{[A]_0}{k}}$

➢ Temperature dependence :

– Arrhenious equation : $k = A.e^{-Ea/RT}$

– E_a = minimum energy over and above the avg. energy of reactant which must be possesed by reacting molecule for collision to be succesful.

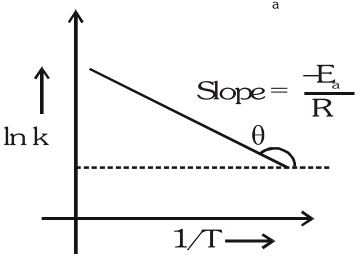
– A = frequency factor - proportional to number of collisions per unit volume per second.

– $e^{-Ea/RT}$ = Fraction of collision in which energy is greater than E_a.

– A and E_a are constant i.e. do not vary with temperature

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

Graph : Graphical determination of E_a.

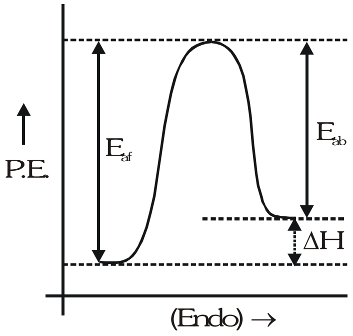


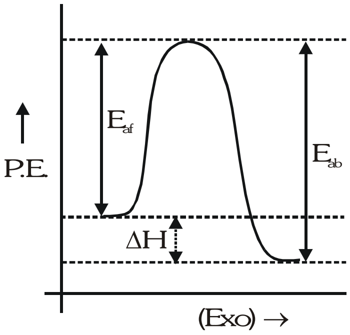
Temperature coefficient $= \frac{k_{T+10}}{k_T}$

By default T = 298 K

Variation of rate constant with temparture ⇒ $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

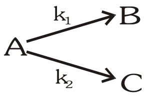
➢ **Endothermic and exothermic reactions :**





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

➢ **Parallel reaction :**



(i) Rate = $(k_1 + k_2)$ [A] - (differential rate law)

(ii) $\frac{k_1}{k_2} = \frac{[B]}{[C]}$

(iii) $t_{1/2} = \frac{0.693}{k_1 + k_2}$

(iv) % of B = $\frac{k_1}{k_1 + k_2} \times 100$; % of C = $\frac{k_2}{k_1 + k_2} \times 100$

(v) $[A] = [A]_0 \, e^{-(k_1 + k_2)t}$

➢ **Pseudo-order reaction :**

Rate law → rate = $k\,[A]^m\,[B]^n$

Pseudo rate law :

rate = $k_1\,[A]^m$

[B] assumed constant in two cases :

(i) B in large excess (ii) B → CATALYST

NUCLEAR CHEMISTRY

- **All nuclear reactions are first order :**

  Two types of nuclear reaction : (a) Artifical radioactivity(b) Radioactivity (spont.)

  First order

  $\lambda t = 2.303 \log \frac{N_0}{N_t}$

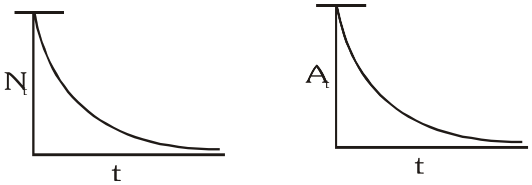
  $\lambda \rightarrow$ Decay constant

  $N_0 \rightarrow$ Initial nuclei

  $N_t \rightarrow$ Nuclei at 't'

  Activity = $A_t = \frac{-dN_t}{d_t} = \lambda N_t$; Nuclei/sec.

  A_t = Rate of decay



  $\Rightarrow \quad t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$

- **α decay** = ^4_2He Particles at high velocity

  $^A_ZX \rightarrow {}^{A-4}_{Z-2}Y + \alpha$

  To ↓ size of large nuclei

- **β decay** = $^0_{-1}e$ at high velocity

  $^A_ZX \rightarrow {}^A_{Z+1}P + {}^0_{-1}e$

  \# To ↓ $\frac{n}{P}$ ratio.

  \# Nuclear change in β decay

  $^1_0n \longrightarrow {}^1_1P + {}^0_{-1}e$

- **γ-decay :**

  Photons from excited nuclei after α – or β – decay

  No effect on n/p ratio

  High energy e/m radiation.

  Mean life , $t_{avg} = \frac{1}{\lambda}$

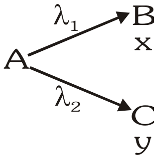
- **Parallel decay :**

  $t = 0 \quad N_0$

  $t = t \quad N_0 - x - y$

  $\lambda_{eff.} = \lambda_1 + \lambda_2$

  $\frac{1}{t_{eff.}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}$



  $\lambda \rightarrow$ No dependence on temp.