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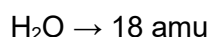
SOME BASIC CONCEPTS OF CHEMISTRY

SOME USEFUL CONVERSION FACTORS

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

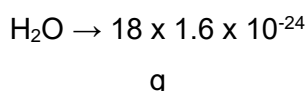
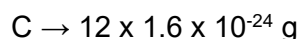
ATOMIC MASS OR MOLECULAR MASS

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



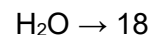
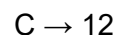
ACTUAL MASS

Mass of one atom or molecule in grams



RELATIVE ATOMIC MASS OR RELATIVE MOLECULAR MASS

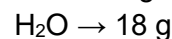
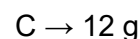
Mass of one atom or molecule w.r.t. $1/12^{\text{th}}$ of ^{12}C atom



It is unitless

GRAMS ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one atom or molecule



It is also called molar weight

DEFINITION OF ONE MOLE

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

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

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 = $\frac{\text{Mass (g)}}{\text{GAM or molar mass}}$

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 = $\frac{\text{Mass (g)}}{\text{GMM or molar mass}}$

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 = $\frac{\text{Mass (g)}}{\text{GFM or molar mass}}$

1 mole of substance

Contains 6.022×10^{23} particles

Weight as much as molecular weight / atomic ionic / weight in grams

If it is a gas, one mole occupies a volume of 22.4 L at 1 atm & 273 K

Average or mean molar mass

The average molar mass of the different substance present in the container $M_{\text{avg}} = \frac{M_1 n_1 + M_2 n_2 + \dots}{n_1 + n_2 + \dots}$

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 = $\frac{\text{Mass}}{\text{Volume}}$, unit: g/cc

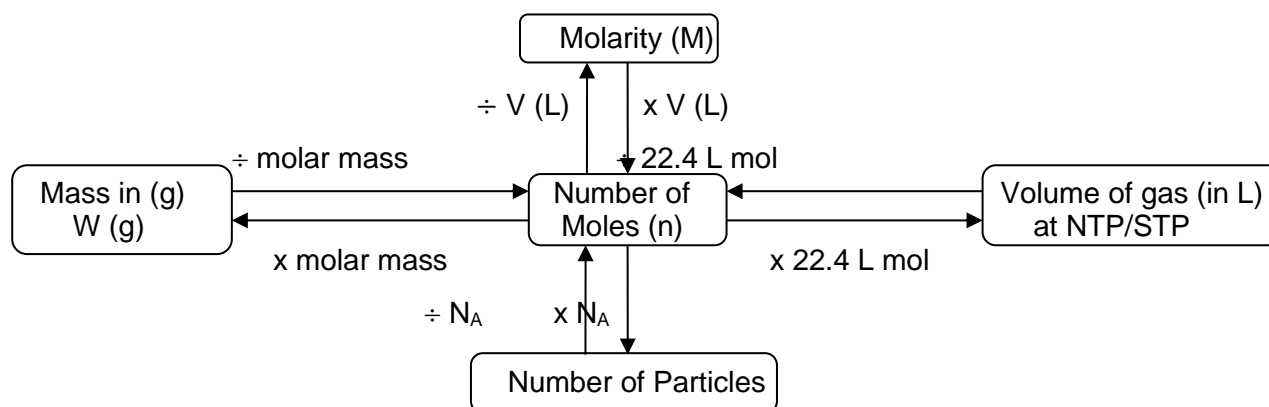
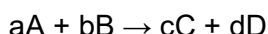
Relative Density = $\frac{\text{Density of any substance}}{\text{Density of reference substance}}$

VAPOUR DENSITY

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

Vapour Density = $\frac{\text{Molar Mass}}{2}$

* Mass % of an element in a compound = $\frac{\text{atomicity of an element} \times \text{atomic mass of an element}}{\text{molecular mass of compound}} \times 100$

➤ **STOICHIOMETRY BASED CONCEPT****[Concept of limiting reagent]**

- 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.

➤ **HOW TO FIND L.R.**

- **Case I:** If data of only one reactant is given then treat that reactant as L.R. and other reactants as excess reagent.
- **Case II:** 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.

➤ **EQUIVALENT WEIGHT**

• Equivalent weight = $\frac{\text{molar weight}}{\text{valency factor (VF)}}$

• V.F. for elements = Valency

Ex.: Na = 1, Al = 3, N₂ = 6, O₂ = 4, H₂ = 2

V.F. for ionic compounds (salts)

= total charge on cation / anion

Ex.: Na₂⁺¹ CO₃⁻² → V.F. = +1 x 2 = 2

K₄⁺¹ [Fe(CN)₆] = V.F. = +1 x 4 = 4

V.F. for acids = No. of replaceable H⁺ ions

HCl = 1, H₂SO₄ = 2, H₃PO₄ = 3

H₃PO₃ = 2, H₃PO₂ = 1

- V.F. for bases = No. of replaceable OH⁻
- NaOH = 1, Ba(OH)₂ = 2, Ca(OH)₂ = 2, Al(OH)₃ = 3

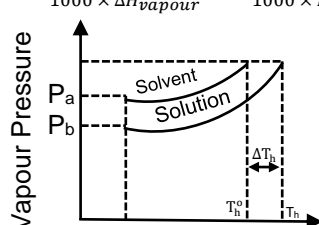
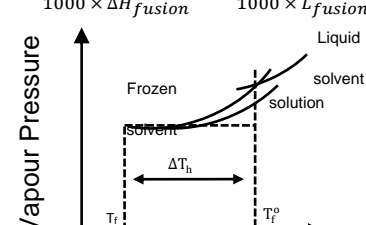
- Dulong & Petit's law only for solids (except Be, B, Si, C)
Atomic mass x specific heat (in Cal / grams °C) = 6.4
- Victor-Mayer's method is used to determine molecular weight of volatile compound.

SOLUTIONS

Normality (N) $= \frac{\text{No. of Gram Equivalent of solute}}{\text{Volume of solution (L)}}$	Molarity (M) $= \frac{\text{No. of Moles of solute}}{\text{Volume of solution (L)}}$	Relation b/w M&N $N = M \times \text{Valency Factor}$	% by Mass (w/W) $= \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 100$
Formality (F) $= \frac{\text{Mass of solute (g)}}{\text{Formula mass of solute (g)} \times \text{volume of solution (L)}}$	Strength of solution (S) $= \frac{\text{Mass of solute (g)}}{\text{Volume of solution (L)}}$	Relation b/w m & X $\frac{X_B}{X_A} = \frac{M \times (M.wt)_A}{1000}$	% mass by volume (w/V) $= \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 100$
PPM (by mass) $= \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 10^6$	PPM (by volume) $= \frac{\text{Volume of solute (g)}}{\text{Volume of solution (g)}} \times 10^6$	PPM (by w/V) $= \frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 10^6$	

COLLIGATIVE PROPERTY

Of dilute solution depends upon relative number of particles of solute & do not depend upon nature of solute particles.

Liquid – Liquid System Liquid: Volatile solvent (A) & volatile solute (B) $P'_A = X_A P_A^0$ & $P'_B = P'_B = X_B P_B^0$ $P_{\text{total}} = P'_A + P'_B = P_A^0 X_A + P_B X_B$ $P_{\text{total}} = (P_B^0 + P_A^0) X_B + P_A^0$ $P'_A = Y_A P_T$ & $P'_B = P_B = Y_B P_T$ (Dalton law of gaseous mixtures) $P'_A = P_A^0 X_A = Y_A P_T$ $P'_B = P_B^0 X_B = Y_B P_T$ (Y_A & Y_B : mole fraction in vapour phase)	Raoult's law	Solid Liquid System Solid: Non – volatile solute (B) & Liquid: volatile solvent (A) $P_{\text{total}} = P_A^0 X_A = \frac{n_A}{n_A + n_B} \times P_A^0$ ($\because P_B^0 = 0$) Relative lowering in vapour pressure $(RLVP) = \frac{P_A^0 - P_S}{P_A^0} = X_B$ Lowering of vapour pressure $= \Delta P = P_A^0 - P_S$ Derived from RLVP: $\frac{P_A^0 - P_S}{P_S} = \frac{n_B}{n_A}$	Van't Hoff Factor (i) $\frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{\text{Calculated Molar Mass}}{\text{Observed Molar Mass}}$ For $i = 1$: Neither Association nor Dissociation Eg.: Sugar, Glucose, Urea etc. Dissociation ($i > 1$) $i = 1 + (n-1)\alpha$ n = total no. of ions α = Degree of dissociation Association ($i < 1$) $i = 1 - \alpha + \alpha/n$ n = No. of solute particles asso. α = Degree of Association
Relative Lowering of Vapour Pressure (RLVP) For dilute solution ($n_B \ll n_A$) $\frac{P_A^0 - P_S}{P_A^0} \approx i \times \frac{n_B}{n_A}$ $\Delta P \propto \frac{n_B}{n_A}$ RLVP depends upon relative number of solute particles		Elevation in Boiling Point (ΔT_b) $\Delta T_b = (T_b)_{\text{solution}} - T_b^0 = i \times m \times K_b$ K_b = molal elevation constant or ebullioscopic constant For a solvent $K_f = \frac{RT_b^{02} \times M.wt}{1000 \times \Delta H_{\text{vapour}}} \quad K_b = \frac{RT_b^{02}}{1000 \times L_{\text{vapour}}}$ 	Depression in Freezing Point (ΔT_f) $\Delta T_f = (T_f^0) - (T_f)_{\text{solution}} = i \times m \times K_f$ K_f = molal depression constant or Cryoscopic constant For a solvent $K_f = \frac{RT_f^{02} \times M.wt}{1000 \times \Delta H_{\text{fusion}}} \quad K_f = \frac{RT_f^{02}}{1000 \times L_{\text{fusion}}}$ 

Osmotic Pressure (π) Osmosis: Net flow of solvent molecules from dilute solution to concentrated solution through semi-permeable membrane. $\pi = h d g$ For dilute solution: $\pi = I \times CRT$	* Isotonic solution: $\pi_1 = \pi_2$ (Primary condition) at constant T; $C_1 = C_2$ (Secondary condition)	* when $\pi_1 > \pi_2$ or $C_1 > C_2$ The solution 1 is called hypertonic solution Solution 2 is called hypotonic solution
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% of Volume (v/V)

$$= \frac{\text{Volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$$

Molality (m)

$$= \frac{\text{No. of moles of solute}}{\text{Amount of solvent (g)}} \times 1000$$

Mole Fraction

A → Solvent; B → Solute

$$X_A = \frac{\text{Moles of solvent}}{\text{Moles of solute} + \text{Moles of solvent}} \quad X_B = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

$$X_A + X_B = 1$$

Volume Strength of H₂O₂ be 'XV'

$$M = \frac{X}{11.2}; S = \frac{X}{5.2} \times 17$$

$$N = \frac{X}{5.6}; \% (w/V) = \frac{X}{5.6} \times \frac{17}{10}$$

Dilution

$$M_1V_1 = M_2V_2; N_1V_1 = N_2V_2$$

I: when acid-acid or base-base mixed

$$N_g = \frac{N_1V_1 + N_2V_2 + N_3V_3 + \dots}{V_1 + V_2 + V_3 + \dots}$$

II: a) Complete Neutralisation

$$N_A V_A = N_B V_B \quad (A \rightarrow \text{Acid}; B \rightarrow \text{Base})$$

$$N_B = \frac{N_A V_A}{V_A + V_B} \quad (N_B \text{ is the normality of salt})$$

b) Incomplete Neutralisation

$$N_B = \frac{|N_A V_A - N_B V_B|}{V_A + V_B}$$

Azeotropic Mixture: Binary mixtures having same composition in liquid & vapour phase & boil at a constant temperature. These mixtures are formed only by Non-ideal solutions. They are of two types:

a) Minimum boiling azeotrope: Show large positive deviation from Raoult's law.

b) Maximum boiling azeotrope: Show large negative deviation from Raoult's law.

Components of mixture are separated by azeotropic distillations.

Henry Law: According to Henry Law at constant temperature.

Partial pressure of Gas (P) ∝ Solubility of gas in liquid.

Partial pressure of Gas (P) ∝ Mole fraction of gas dissolved (X).

$$P = K_H \times X \quad (K_H : \text{Henry's constant})$$

Depends upon nature of gas, temperature & nature of liquid

$$T \uparrow = K_H \uparrow \text{ Solubility (X)} \downarrow$$

Best method to determine molecular weight of macromolecules like protein is osmotic pressure because osmotic pressure can be easily measured at room temperature.

- M, F, N & % by volume, % w/V are temperature dependent terms.
- K₀ & K₁ are characteristics property of solvent.

Reverse Osmosis: When (External Pressure) > Osmotic Pressure then solvent molecules move from solution to solvent.

Cryoscopic constant is maximum for camphor & it is the best solvent for determination of molar mass of solute by depression in freezing point.

Ethylene Glycol is usually added to water in the radiator to lower its freezing point. It is called anti-freeze. NaCl & CaCl₂ does the same work to clear snow from the roads.

Gases which can react with solvent do not follow Henry's law.

- 0.91% W/V NaCl solution is isotonic with blood.

- When density ≤ 1 ⇒ m > M

When density > 1 ⇒ m < M

Konowaloff's Rule: the vapour phase is richer in more volatile component than the less volatile component.

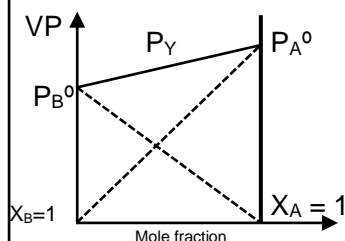
IDEAL SOLUTION

Obey Raoult's Law

$$(VP)_{\text{observed}} = (VP)_{\text{calculated}}$$

$$(BP)_{\text{observed}} = (BP)_{\text{calculated}}$$

$$(A - A) = (A - B) = (B - B)$$



$$\Delta H_{\text{mix}} = 0 \quad \Delta V_{\text{mix}} = 0$$

$$\Delta S_{\text{mix}} > 0 \quad \Delta G < 0$$

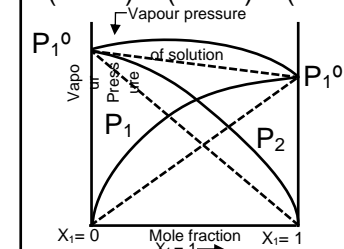
**NON-IDEAL SOLUTION
POSITIVE DEVIATION**

Do not Obey Raoult's Law

$$(VP)_{\text{observed}} > (VP)_{\text{calculated}}$$

$$(BP)_{\text{observed}} < (BP)_{\text{calculated}}$$

$$(A - A) = (B - B) > (A - B)$$



$$X_2 = 1 \quad \Delta H_{\text{mix}} > 0 \quad \Delta V_{\text{mix}} > 0$$

$$\Delta S_{\text{mix}} > 0 \quad \Delta G < 0$$

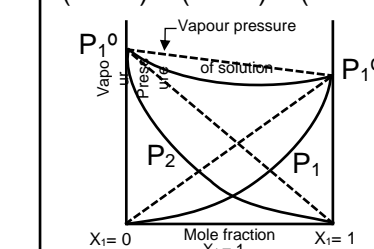
**NON-IDEAL SOLUTION
NEGATIVE DEVIATION**

Do not Obey Raoult's Law

$$(VP)_{\text{observed}} < (VP)_{\text{calculated}}$$

$$(BP)_{\text{observed}} > (BP)_{\text{calculated}}$$

$$(A - A) = (A - B) < (B - B)$$



$$X_2 = 1 \quad \Delta H_{\text{mix}} < 0 \quad \Delta V_{\text{mix}} < 0$$

$$\Delta S_{\text{mix}} > 0 \quad \Delta G < 0$$

REDOX REACTIONS

- Stock notations** Expressing the oxidation state of a metal by Roman numerals like I, II, III etc. within parenthesis is called Stock notation.

e.g. FeSO_4 = Iron (II) sulphate;

Na_2CrO_4 = Sodium chromate (VI) etc.

- Valency** of an element is only a number and as such there is no positive or negative sign attached to it. It can neither be zero nor fractional. Oxidation number, on the other hand, refers to charge and hence has either positive or negative sign. It can also be zero or fractional. For example, oxidation state of C in CH_2Cl_2 is zero while that of Fe in Fe_3O_4 is $8/3$ and of S in $\text{Na}_2\text{S}_2\text{O}_3$ is 2.0.

*** Valence factor of reducing agent (R.A.):**

= Increasing in O.N. per unit formula of R.A.

= No. of electrons loss by unit formula of R.A.

*** Valence factor of oxidation agent (O.A.):**

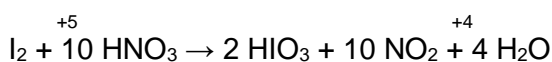
= Decreasing in O.N. per unit formula of O.A.

= No. of electrons gain by unit formula of O.A.

- The oxidation number of metals in amalgams and metal carbonyls, i.e. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ etc. is zero.
- A substance acts only as an oxidising agent if the oxidation number of one of its element is in its highest oxidation state and as a reducing agent if the oxidation number of one of its elements is in its lowest oxidation state. However, if the oxidation number of one of the elements of a substance is in its intermediate oxidation state. It can act both as an oxidising as well as a reducing agent.

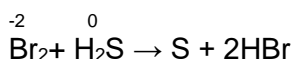
For example:

- * The O.N. of N in HNO_3 i.e. +5 is the maximum, therefore, it can act only an oxidising agent by accepting one or more electrons. For example,



Here, the O.N. of N decreases from +5 in HNO_3 to +4 in NO_2 and hence it acts an oxidising agent.

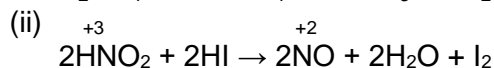
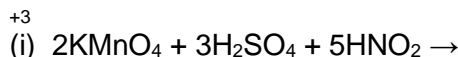
- * The O.N. of S in H_2S , i.e., -2 is the minimum and hence it can act only as a reducing agent by losing one or more electrons. For example,



Hence the O.N. of S increase from -2 H_2S to 0 in elemental sulphur and hence it acts as a reducing agent.

- * The O.N. of N in HNO_2 i.e., +3 is neither maximum (i.e., +5) nor minimum (i.e. -3), therefore, it can act both as an oxidising as well as a reducing agent.

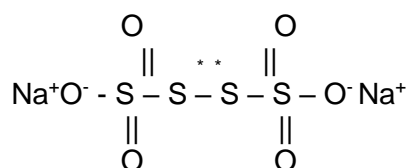
For example:



In equation (i), the O.N. of N increases from +3 in HNO_2 to +5 in HNO_3 , therefore, it acts as a reducing agent.

In equation (ii), the O.N. of N decreases from +3 in HNO_2 to +2 in NO , therefore, it acts as an oxidising agent.

- Redox reactions** are also called electron-transfer reactions since electrons are transferred from the reductant to the oxidant.
- Oxidation is also called de-electronation while reduction is called electronation.
- If a compound contains two or more atoms of the same element, all of them may or may not have same oxidation number e.g.
 - $\text{Na}_2\text{S}_2\text{O}_3$, one S-atom has oxidation number = -2 while the other has oxidation number = +6
 - In CaOCl_2 i.e., $\text{Ca}(\text{OCl})\text{Cl}$ (bleaching powder), oxidation number of one Cl = -1 while oxidation number of the other Cl = +1.
 - In Fe_3O_4 i.e., $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ oxidation of number of one Fe = +2 while that of each of the other two = +3.
 - In NH_4NH_3 , oxidation no. of N of NH_4^+ = -3 while that of N in NO_3^- = +5.
 - In $\text{Na}_2\text{S}_4\text{O}_6$ (sodium tetrathionate) having the structure



The oxidation number of both S^* is equal to 0 (pure covalent nature) and other to sulphur atoms have O.No. = +5

ELECTROCHEMISTRY

Resistance

$$(R) = \frac{V}{I}$$

Unit of R: Ohms

$$\text{Conductance (G)} = \frac{1}{R}$$

Unit of G: mho, ohm⁻¹ or Siemen's

$$\text{Cell constant (G}^*) = \frac{\ell}{A}$$

Unit of G*: cm⁻¹

Resistivity

Or

Specific Resistance (ρ)

$$R = \rho \frac{\ell}{A}$$

Unit of ρ : ohm cm

Specific conductance / conductivity

$$K (\text{Kappa}) = \frac{1}{\rho} = \frac{\ell}{A \times R} = G \times G^*$$

Conductance of 1 cm³ (m³) solution of an electrolyte is called conductivity.Unit of K: ohm⁻¹ cm⁻¹

Debye-Huckel

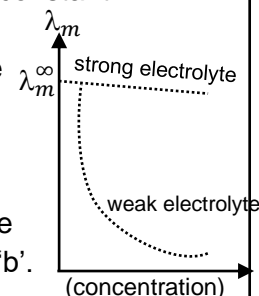
Onsager Equation

For strong electrolytes:

$$\lambda_m = \lambda_m^\infty - b\sqrt{C}$$

b: Debye Huckel Onsager constant

At constant temperature for a given solvent all electrolytes of same type have same 'b'.



GALVANIC CELL

Device in which spontaneous redox reaction ($\Delta G < 0$) is used to convert chemical energy into electrical energy.

Eg: Daniel Cell

At anode: (-ve) oxidation $\text{Zn(s)} \rightarrow \text{Zn}^{+2}(\text{aq}) + 2\text{e}^-$ **At cathode:** (+ve) reduction $\text{Cu}^{+2}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$ **Cell Reaction:** $\text{Zn(s)} + \text{Cu}^{+2}(\text{aq}) \rightarrow \text{Zn}^{+2}(\text{aq}) + \text{Cu(s)}$ **Current flow:** Anode \rightarrow Cathode (Internal circuit)
Cathode \rightarrow Anode (External circuit)

- $[\text{Zn}^{+2}]$ ions in anode solution \uparrow
 $[\text{Cu}^{+2}]$ ions in cathode solution \downarrow
- Mass of Zn rod \downarrow while Mass of Cu rod \uparrow

Cell Representation

Anode	Anode half cell electrolyte (concentration)	Cathode half cell electrolyte (concentration)	Cathode
Zn(s)	ZnSO ₄ (aq) C ₁ M	CuSO ₄ (aq) C ₂ M	Cu(s)

TRICK

L \rightarrow Left
O \rightarrow Oxidation
A \rightarrow Anode
N \rightarrow Negative

$$E^\circ_{\text{cell}} = \text{SRP (cathode)} - \text{SRP (anode)}$$

Reduction Potential = oxidation potential

NERNST EQUATION

- $E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{product}]}{[\text{reactant}]}$
- At $T = 298 \text{ K} \Rightarrow E = E^\circ - \frac{0.0591}{n} \log_{10} \frac{[\text{product}]}{[\text{reactant}]}$
- For metals: If $[\text{Mn}^{n+}] \uparrow \Rightarrow E_{\text{oxid}} \uparrow \Rightarrow E_{\text{oxid}} \downarrow$
If $[\text{Mn}^{n+}] \downarrow \Rightarrow E_{\text{oxid}} \downarrow \Rightarrow E_{\text{oxid}} \uparrow$
- $W_{\text{electrical}} = \Delta G = -nFE_{\text{cell}}$
If $E_{\text{cell}} = +ve \Rightarrow \Delta G = -ve \Rightarrow$ Cell reaction is spontaneous
If $E_{\text{cell}} = -ve \Rightarrow \Delta G = +ve \Rightarrow$ Cell reaction is non-spontaneous
- At Equilibrium: $E_{\text{cell}} = 0 \Rightarrow \Delta G = 0$
 $E^\circ_{\text{cell}} = \frac{0.0591}{n} \log_{10} K_{\text{eq}}$ [K_{eq} : Equilibrium constant]
 $\Delta G^\circ = -2.303 RT \log_{10} K$
- Concentration cell: $E^\circ_{\text{cell}} = 0$
 $E_{\text{cell}} = -\frac{0.0591}{n} \log_{10} \frac{[\text{product}]}{[\text{reactant}]}$
- Electrode potential is an intensive property.
- In salt bridge, electrolytes used are KCl, KNO₃, NH₄NH₃
KCl / NaCl / NH₄Cl etc. cannot be used in salt bridge when solution contains Pb²⁺, Hg₂²⁺, Ag⁺, Cu⁺² because they react to form precipitate.

Molar conductance

$$\lambda_m = \mu = \Lambda_m = K \times V$$

$$\text{unit of } \lambda_m = \text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$$

$$\lambda_m = \frac{K \times 1000}{M}$$

Equivalent**Conductance** (λ_{eq} or Λ_{eq})

$$\lambda_{eq} = K \times V = \frac{K \times 1000}{N}$$

$$\text{Unit of } \lambda_{eq} \rightarrow \text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$$

$$\text{Dilution } \uparrow \Rightarrow \text{concentration } \downarrow$$

$$\Rightarrow K \downarrow \Rightarrow (G, \Lambda_m, \Lambda_{eq}) \uparrow$$

Electrolytic Conductance \uparrow

Solvation /
Hydration of ions \downarrow

Inter Ionic Interactions \downarrow Temperature \uparrow Dilution \uparrow **Kohlrausch Law**

$$\lambda_{eq}^{\infty} = \lambda_{eqc}^{\infty} + \lambda_{eqa}^{\infty}$$

$$\text{For } A_xB_y: A_xB_y \rightarrow xA^{y+} + yB^{x-}$$

$$\lambda_m^{\infty} = x\lambda_{m_c}^{\infty} + y\lambda_{m_a}^{\infty}$$

$$\alpha = \frac{\lambda_{eq}}{\lambda_{eq}^{\infty}} = \frac{\lambda_m}{\lambda_m^{\infty}}$$

$$K_a = \frac{ca^2}{(1-\alpha)}; \text{ If } \alpha \leq 5\% \text{ then } K_a = c\alpha^2$$

$$\Lambda_m^{\infty} (\text{saturated}) = \Lambda_m^{\infty} = \frac{K \times 1000}{S}$$

S \rightarrow Solubility**ELECTROCHEMICAL SERIES**

is the arrangement of elements in order of increasing standard reduction potential values

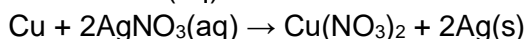
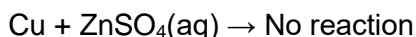
Value of SRP increases

Tendency to get reduce themselves \uparrow Oxidising Power \uparrow Reactivity of metal \downarrow

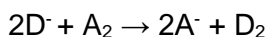
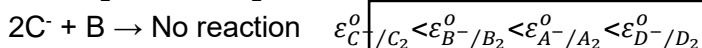
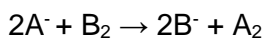
Reactivity of halogens \uparrow

 \uparrow Value of SOP \uparrow Tendency to get oxidize themselves \uparrow Reducing Power \uparrow

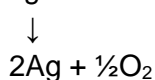
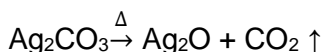
- Oxidising Power \propto SRP $\propto \frac{1}{SOP}$ [Maximum SRP $\rightarrow F_2 (+2.87V)$]
- Reducing Power \propto SOP $\propto \frac{1}{SRP}$ [Maximum SOP $\rightarrow Li (+3.05V)$]
- Metals which are placed above in series can easily displace metal ion from their aqueous solution which are placed below in series.

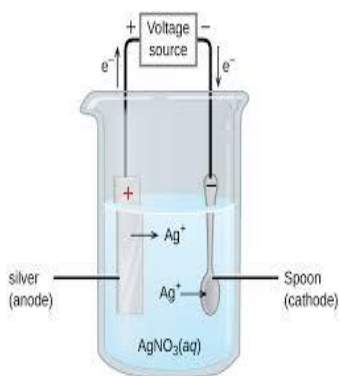


- Non-metals which are placed below in series can easily displace anions of non-metal which are placed above in series.



- Metal placed above H_2 \rightarrow displace $H_2(g)$ from aqueous solution of acid.
- Metals placed above Mg \rightarrow displace $H_2(g)$ from cold water.
- Metals from Mg to Cr \rightarrow displace $H_2(g)$ from hot water.
- Metals Fe \rightarrow displace $H_2(g)$ when react with steam
- Oxides of metal which are placed below to copper are thermally unstable & easily reduced to metal when heated.



Electrolytic Cell

- Device in which non-spontaneous redox reaction ($\Delta G > 0$) is used to convert electrical energy into chemical energy.
- Cation (+ve) \rightarrow Cathode (-ve) \rightarrow Reduction
- Anion (-ve) \rightarrow Anode (+ve) \rightarrow Oxidation
- Sign of cathode & anode are opposite in Galvanic cell & Electrolytic cell.
- D.C. source is used for electrolysis.

$$\text{Efficiency of cell } (\eta) = \frac{\Delta G}{\Delta H} = \frac{\eta FE}{\Delta H}$$

Faraday's Law**1st Law:**

When Electricity is passed through an electrolyte then
 $W \propto Q$; $W = Z \times I \times t$

Z (Electrochemical Equivalent):

Weight of substance in gram discharged by 1C charge

$$W = \frac{E \times i \times t}{96500}$$

If same amount of charge is passed through different solution of electrolyte then

$$\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3} = \frac{w_4}{E_4} \dots \text{constant}$$

S.No.	Electrolyte	Electrode	Product at anode	Product at cathode	PH change
1.	Fused/molten NaCl	Pt or Graphite	Cl ₂	Na	No change
2.	Aqueous NaCl	Pt or Graphite	Cl ₂	H ₂	pH \uparrow
3.	Dilute NaCl	Pt or Graphite	O ₂	H ₂	No change
4.	Aqueous NaCl	Hg	Cl ₂	Reduction of Na; H ₂ \uparrow	No change
5.	Fused NaOH	Pt or Graphite	O ₂	Na	No change
6.	Aqueous CuSO ₄	Pt or Graphite	O ₂	Cu	pH \downarrow
7.	Aqueous CuSO ₄	Cu	Cu oxidizes to Cu ⁺²	Cu	No change
8.	Aqueous CuCl ₂	Cu	Cu oxidizes to Cu ⁺²	Cu	No change
9.	Aqueous AgNO ₃	Pt or Graphite	O ₂	Ag	pH \downarrow
10.	Aqueous AgNO ₃	Ag	Ag ⁺	Ag	No change
11.	Aqueous NiSO ₄ /Ni (NO ₃) ₂	Ni	Ni ⁺²	Ni	No change
12.	Aqueous NiSO ₄	Pt or Graphite	O ₂	Ni	pH \downarrow
13.	Aqueous Na ₂ SO ₄	Pt or Graphite	O ₂	H ₂	No change
14.	Dilute H ₂ SO ₄	Pt or Graphite	O ₂	H ₂	No change

Corrosion

- Corrosion is the process of change of metal surface into salts like oxides, sulphides, carbonates etc. due to attack of atmospheric gases.
- Rust is hydrated ferric oxide $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
- Factors which enhance corrosion are
 - Pressure of impurities is metal.
 - Presence of moisture (Eg. rainy season)
 - Presence of electrolyte (Eg. saline water)
- Corrosion can be prevented by Barrier protection (oil/grease), sacrificial protection (Galvanisation), Electrical protection.
- H_2O_2 fuel cell was the source of drinking water & electrical energy in Appollo Moon flight.
- Mercury cell gives constant voltage throughout its life.
- Dry cell have short life because acidic NH_4Cl corrodes Zn container

Cell

- Primary cells cannot be recharged. Eg. Dry Cell & Mercury Cell
- Secondary cells can be recharged.
- Eg. Ni-Cd Cell & Lead storage battery.
- Fuel cell produce energy from the combustion of fuels which can be converted into electrical energy. Eg.: $\text{H}_2\text{-O}_2$ fuel cell.

Name of the cell/battery	Anode	Cathode	Electrolyte
Dry Cell	Zinc	Graphite; MnO_2 + C (touching cathode)	NH_4Cl + ZnCl_2 (touching anode)
Mercury cell (used in watches, hearing aids)	Zinc/mercury Amalgum	Paste of H_2O & carbon	Paste of KOH & ZnO
Lead storage battery	Lead	Lead Dioxide	H_2SO_4 (38%)
Ni-Cd cell	Cadmium	Nickel Dioxide	KOH solution
$\text{H}_2\text{-O}_2$ fuel cell.	Porous carbon containing catalysts (H_2 passed)	Porous carbon containing catalysts (O_2 passed)	Concentrated aq. NaOH solution

- Reactions in lead storage battery during discharge:
- At anode: $\text{Pb}_{(s)} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_{4(s)} + 2\text{e}^-$
- At cathode: $4\text{H}^+ + \text{PbO}_{2(s)} + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_{4(s)} + 2\text{H}_2\text{O}$
- Complete reaction: $\text{Pb}_{(s)} + \text{PbO}_{2(s)} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_{4(s)} + 2\text{H}_2\text{O}$

The EMF of a cell is found by adding oxidation potential & reduction potential of the half-cell reaction.
But the electrode potential of a half-cell from two other half cells cannot be found by simply adding their electrode potential.

Given 1) $\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$, $E = 0.337\text{V}$
 2) $\text{Cu}^{+2} + \text{e}^- \rightarrow \text{Cu}$, $E = 0.153\text{V}$
 Aim 3) $\text{Cu} + \text{e}^- \rightarrow \text{Cu}$, $E = ?$

Subtracting 1-2 will not give the desired result. We have to calculate their free energy change.
 Let ΔG°_1 , ΔG°_2 & ΔG°_3 be free energy changes of the above three reactions. Then $\Delta G^\circ_1 - \Delta G^\circ_2 = \Delta G^\circ_3$
 i.e. $(-2 \times F \times 0.3337) - (-1 \times F \times 0.153) = -1 \times F \times E^\circ_{\text{Cu}^+/\text{Cu}}$ ($\Delta G^\circ = -nFE^\circ$)
 This gives $E^\circ_{\text{Cu}^+/\text{Cu}} = 0.521\text{V}$

BEHAVIOUR OF GASES

GAS LAW

- Boyle's law:** $V \propto \frac{1}{P}$ ($n, T = \text{const}$) $P_1 V_1 = P_2 V_2$
- Charle's law:** $V \propto T$ ($n, P = \text{const}$) $\frac{V_2}{V_1} = \frac{T_2}{T_1}$
- Gay lussac's law:** $P \propto T$ ($n, V = \text{const}$) $\frac{P_2}{P_1} = \frac{T_2}{T_1}$
- Avogadro's law:**
 $V \propto \text{moles} \propto \text{number of molecules}$ ($P, T = \text{const}$)
 Ideal gas equation $PV = nRT$
 $R = 0.0821 \text{ lit atm mol}^{-1} \text{ K}^{-1}$
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ or $8.314 \text{ N x m K}^{-1} \text{ mol}^{-1}$
 $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$
 $R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$

GRAHAM'S DIFFUSION LAW

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}; r \propto \frac{1}{\sqrt{VD}}; r \propto \frac{1}{\sqrt{M_w}} \quad (P, T = \text{constant})$$

$$VD = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{M_w}{2}$$

Rate of diffusion

$$r = \frac{\ell_{\text{diffused gas}}}{t_{\text{timetaken}}}; r = \frac{V_{\text{diffused gas}}}{t_{\text{timetaken}}}; r = \frac{n_{\text{diffused gas}}}{t_{\text{timetaken}}}$$

(Where, ℓ = distance travelled by diffused gas)

KINETIC GAS EQUATION: $PV = \frac{1}{3} Mn V_{\text{rms}}^2$

DALTON'S LAW OF PARTIAL PRESSURE

$$P_{\text{mixture}} = P_1 + P_2 + P_3 \dots \dots \dots (T \text{ \& } V \text{ const})$$

Partial pressure

$$P_{\text{moist gas}} = P_{\text{drygas}} + P_{\text{watervapours}}$$

It is applicable for non reacting gases.

Methods of determination of partial pressure (P_A & P_B are partial pressure)

- From ideal gas equation
 $P_A V = n_A RT$ & $P_B V = n_B RT$
- In the form of mole fraction.
 $P_A = X_A P_T$ & $P_B = X_B P_T$
 $P_A = \frac{n_A}{n_t} P_T$ & $P_B = \frac{n_B}{n_t} P_T$
 $[X_A + X_B = 1]$
- In the form of volume fraction
 $P_A = \frac{V_A}{V} P_T$ & $P_B = \frac{V_B}{V} P_T$
- If individual pressure and individual volume are given
 $P_A = \frac{V_A}{V} P_1$ & $P_B = \frac{V_B}{V} P_2$

P_1, P_2 = pressure of gases before mixing

P_A, P_B = pressure of gases after mixing

AVERAGE KINETIC ENERGY (KE_{av})

$$KE_{\text{av}} = \frac{3}{2} nRT \quad (n \text{ moles})$$

$$KE_{\text{av}} = \frac{3}{2} RT \quad (1 \text{ mol or } N_A \text{ molecules})$$

$$KE_{\text{av}} = \frac{3}{2} KT \quad (1 \text{ molecule})$$

$$K = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$$

K is called Boltzman's constant

$$V_{\text{rms}} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \dots + V_n^2}{n}} \quad V_{\text{av}} = \frac{V_1 + V_2 + V_3 + \dots + V_n}{n}$$

$$V_{\text{rms}} = \sqrt{\frac{3RT}{M_w}} \quad V_{\text{av}} = \sqrt{\frac{8RT}{\pi M_w}} \quad V_{\text{mp}} = \sqrt{\frac{2RT}{M_w}}$$

$$V_{\text{rms}} = \sqrt{\frac{3PV}{M_w}} \quad V_{\text{av}} = \sqrt{\frac{8PV}{\pi M_w}} \quad V_{\text{mp}} = \sqrt{\frac{2PV}{M_w}}$$

$$V_{\text{rms}} = \sqrt{\frac{3P}{d}} \quad V_{\text{av}} = \sqrt{\frac{8P}{\pi d}} \quad V_{\text{mp}} = \sqrt{\frac{2P}{d}}$$

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

$$= 1 : 0.92 : 0.82$$

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

$$= 1 : 1.128 : 1.224$$

$$\text{Compressibility factor } (z) = \frac{(V_m)_{\text{obs}}}{V_1} = \frac{P(V_m)_{\text{obs}}}{RT}$$

If $z = 1$, the gas show ideal gas behavior.

If $z > 1$, the gas show positive deviation.

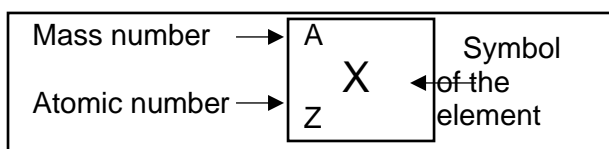
If $z < 1$, the gas show negative deviation.

ATOMIC STRUCTURE

IMPORTANT DEFINITIONS

Proton(m_p) / anoderays	Neutron (m_n)	Electron (m_e)/cathode rays
mass = 1.67×10^{-27} kg	mass = 1.67×10^{-27} kg	mass = 9.1×10^{-31} kg
mass = 1.67×10^{-24} g	mass = 1.67×10^{-24} g	mass = 9.1×10^{-28} g
mass = 1.00750 amu	mass = 1.00850 amu	mass = 0.000549 amu
e/m value is dependent on the nature of gas taken in discharge tube.		e/m of electron is found to be independent of nature of gas & electrode used.

REPRESENTATION OF AN ELEMENTS



Terms associated with elements:

- Atomic Number (Z) : = No. of protons
Electrons = 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.: ${}_6\text{C}^{12}$, ${}_6\text{C}^{13}$, ${}_6\text{C}^{14}$
- Isobars:** Same mass number but different atomic number
Ex.: ${}_1\text{H}^3$, ${}_2\text{He}^3$
- Isodiaphers:** Same difference of number of Neutrons & protons
Ex.: ${}_5\text{B}^{11}$, ${}_6\text{C}^{13}$
- Isotones:** Having same number of neutron
Ex.: ${}_1\text{H}^3$, ${}_2\text{He}^4$
- 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.
 $R_N = R_0(A)^{1/3}$, $R_0 = 1.33 \times 10^{-13}\text{cm}$
[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 →
- Frequency increases →
 $c = v\lambda$, $\lambda = \frac{c}{v}$, $\bar{v} = \frac{1}{\lambda} = \frac{v}{c}$
- $T = \frac{1}{v}$, $E = \frac{hc}{\lambda} = hv$, $h = 6.626 \times 10^{-34}\text{Js}$
- $E(\text{ev}) = \frac{12400}{\lambda(\text{\AA})}$
- Total amount of energy transmitted $E = nh\nu = \frac{nhc}{\lambda}$

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 $mvr = nh$
- Electron remains in stationary orbit where it does not radiate its energy.

- **Radius:** $r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$

- **Velocity:** $v = 2.188 \times 10^6 \frac{Z}{n} \text{ ms}^{-1}$

- Energy (KE + PE)

$$= \text{Total energy} = -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom}$$

- $TE = -\frac{KZe^2}{2r}$, $PE = \frac{-KZe^2}{r}$, $KE = \frac{KZe^2}{2r}$

$$PE = -2KE, KE = -TE, PE = 2TE$$

- 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

$$\Delta E = E_{n_2} - E_{n_1} = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV} = IE \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where IE = ionization energy of single electron species.

- **Ionization energy** = $E_\infty - E_{G.S.} = 0 - E_{G.S.}$

$E_{G.S.}$ = Energy of electron in ground state

HYDROGEN SPECTRUM

- **Rydberg's Equation:** $\frac{1}{\lambda} = \bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \times Z^2$

$$R_H \cong 109700 \text{ cm}^{-1} = \text{Rydberg constant}$$

- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_α line means $n_2 = n_1 + 1$; also known as line of longest λ , shortest ν , least E
- Similarly H_β line means $n_2 = n_1 + 2$
- When electron 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 special lines in a particular series = $n_2 - n_1$

Hydrogen

Spectrum

(n2)

(n1)

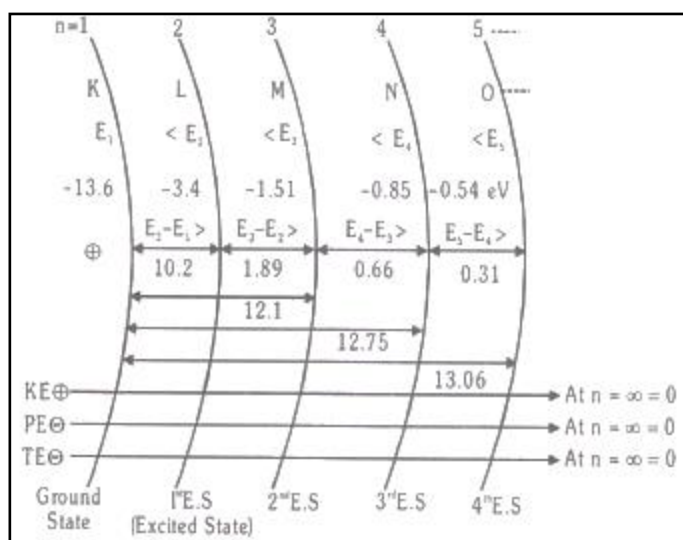
Lyman → Any higher orbit → 1 [Found in U.V. region]

Balmer → Any higher orbit → 2 [Found in visible region]

Paschen → Any higher orbit → 3 [Found in I.R. region]

Brackett → Any higher orbit → 4 [Found in I.R. region]

Pfund → Any higher orbit → 5 [Found in I.R. region]



DE-BROGLIE HYPOTHESIS

- All material particles possess wave character as well as particle character.
- $\lambda = \frac{h}{mv} = \frac{h}{p}$
- The circumference of the n^{th} orbit is equal to n times of wavelength of electron i.e. $2\pi r_n = n\lambda$
Number of waves = n = principle quantum number
- Wavelength of electron (λ) $\cong \sqrt{\frac{150}{V(\text{volts})}} \text{ \AA}$
- $\lambda = \frac{h}{\sqrt{2mKE}}$

HEISENBERG UNCERTAINTY PRINCIPLE

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.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad (\Delta x) (\Delta v) \geq \frac{h}{4\pi m}$$

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

In an atom each shell, sub shell, orbital and electron are designated by a set of 4 quantum numbers.

Principal Quantum Number (By Bohr)

- Indicates = Size and energy of the orbit, distance of e^- from nucleus
- Values $n = 1, 2, 3, 4, 5, \dots$
- 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 sub shell in an orbit = n

Azimuthal Secondary / Subsidiary / Angular momentum quantum number (ℓ)

- Given by = Sommerfeld
- Indicates = Sub shells / sub orbit / sub level
- Values $\Rightarrow 0, 1, \dots, (n-1)$
- Indicates shape of orbital / sub shell

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

- Total no. of e^- s in a sub orbit = $2(2\ell+1)$
- Total no. of orbitals in a sub orbit = $(2\ell+1)$
- 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 sub shells 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 $m = -\ell, \dots, 0, \dots, +\ell$
- Maximum no. of e^- s in an orbital = 2 (with opposite spin)

m for p sub shell = $p_x p_y p_z$

$-1 \quad +1 \quad 0$

m for d sub shell = $dx^2dyz \quad dz^2dxz \quad dx^2-y^2$

$-2 \quad -1 \quad 0 \quad +1 \quad +2$

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 = $\pm \frac{1}{2} \times \text{number of unpaired electrons}$

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 sub shells.
 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$
- ($n + \ell$) rule:** The sub shell with lowest ($n + \ell$) value is filled up first, but when two or more sub shells have same ($n + \ell$) value then the sub shell with lowest value of n is filled up first.
- Pauli exclusive 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 sub shell in such a way as to give maximum number of unpaired electrons with parallel spin.

CHEMICAL KINETICS

HOW TO GENERATE RATE LAW EXPRESSION

RATE OF REACTION



Instantaneous or Average Rate of Reaction

$$\text{ROR} = -\frac{1}{n_1} \frac{d[A]}{dt} = -\frac{1}{n_2} \frac{d[B]}{dt} = \frac{1}{n_3} \frac{d[C]}{dt} = \frac{1}{n_4} \frac{d[D]}{dt}$$

- * Rate of Disappearance of A = $-d[A]/dt$
- * Rate of Disappearance of B = $-d[B]/dt$
- * Rate of Appearance of C = $+d[C]/dt$
- * Rate of Appearance of D = $+d[D]/dt$
- * Unit of ROR = $\text{mol L}^{-1} \text{time}^{-1}$
- * ROR is always positive

Rate Law (Experimental Expression)

$$\text{Rate} = K[A]^x [B]^y$$

Where K = Rate constant or Specific reaction rate

x = order of reaction w.r.t. A
y = order of reaction w.r.t. B
x+y = n (overall order of reactions)

- * Order is an experimental quantity
- * It may be 'O' +ve, -ve or fractional
- * Unit of K = $[\text{mol L}^{-1}]^{1-n} \times \text{time}^{-1}$
= $(\text{atm})^{1-n}$

K depends upon temperature, catalyst & nature of reactant.

EXPERIMENTAL OBSERVATIONS

For the reaction $\text{OCl}^- + \text{I}^- \xrightarrow{\text{OH}^-} \text{OI}^- + \text{Cl}^-$ the experimental observations are given below:

Exp.	[OCl ⁻]	[I ⁻]	[OH ⁻]	d[OI ⁻]/dt
1	0.0017	0.0017	1.0	1.75
2	0.0034	0.0017	1.0	3.50
3	0.0017	0.0034	1.0	3.50
4	0.0017	0.0017	0.5	3.50

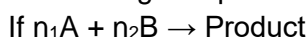
from experimental observations :
Rate Law = $K[\text{OCl}^-] [\text{I}^-] / [\text{OH}^-]$
Order = 1

MOLECULARITY

- Molecularity is the total number of reacting species participating in an elementary reaction.
- It is a theoretical quantity & have only integer values (i.e. 1, 2, 3)
- Molecularity > 3 is very rare.

ELEMENTARY REACTIONS

These type of reactions complete in single step.



$$\text{Rate Law} = K[A]^{n_1} [B]^{n_2}$$

$$\text{Order} = n_1 + n_2$$

For elementary reaction fractional order is not possible.

In elementary reaction molecularity is equal to its order.

Zero order reactions can never be elementary reaction.

PSEUDO FIRST ORDER REACTION

Reactions having order = 1 and molecularity > 1

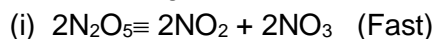
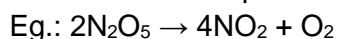
Eg :

- Hydrolysis of Ester in acidic medium.
- Inversion of cane sugar.

Reactant taken in excess can't affect order of reaction.

COMPLEX REACTIONS

These types of reactions complete in multi-step:



Here rate law is written in terms of slowest step (R.D.S.) which must be free from intermediates.

$$\text{Rate law} = K[\text{N}_2\text{O}_5], \text{ Order} = 1$$

Molecularity of each reaction step is defined separately.

Total molecularity of complex reaction is not defined.

If not defined is not in the option then molecularity is equal to order of reaction. (Then in this case molecularity will be 1)

ZERO ORDER REACTIONS

Eg.: 1. Decomposition of gases on metal surface.

2. Photochemical Reaction

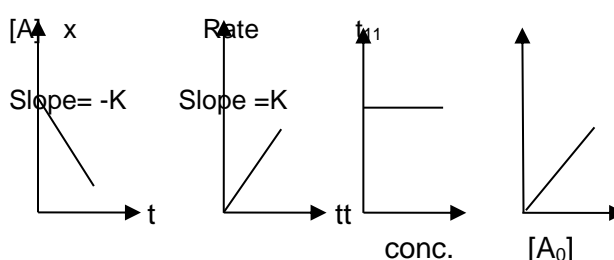
Differential Rate Equation:

$$R = -d[A]/dt = K[A]^0$$

Integrated Rate equation:

$$[A]_1 = [A]_0 - Kt; \quad x = Kt$$

$$t_{1/2} = t_{50\%} = \frac{[A]_0}{2K}; \quad t_{100\%} = \frac{[A]_0}{K} = 2t_{1/2}$$

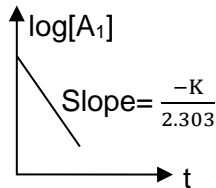
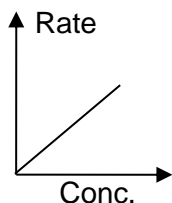
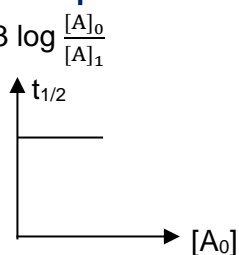


FIRST ORDER REACTION

- Eg. 1. All Radioactive decay
2. Pseudo First order reaction

Differential Rate Equation

$$r = -d[A]/dt = K[A]^1 \quad Kt = 2.303 \log \frac{[A]_0}{[A]_1}$$

**Integrated Rate Equation**

$$t_{1/2} = t_{50\%} = \frac{0.693}{K}$$

$$t_{3/4} = t_{75\%} = 2t_{1/2}$$

nth ORDER REACTION

$$Kt = \frac{1}{(n-1)} \left[\frac{1}{[A]_1^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]; n \neq 1$$

$$Kt_{1/2} = \frac{1}{(n-1)} \left[\frac{2^{n-1}-1}{[A]_0^{n-1}} \right]; n \neq 1$$

$$T_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

It is half life method to determine order of reaction

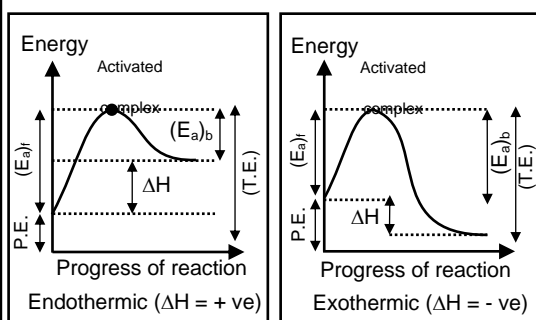
Hydrolysis of ester in alkali medium is second order reaction.

COLLUSION THEORY

For Effective collision following two conditions must be satisfied:

Reacting molecules must possess a minimum amount of energy known as Threshold Energy (TE)

Proper orientation of collision.
TE = Potential energy of reactant + Activation Energy (E_a)



$$\Delta H = (E_a)_f - (E_a)_b = H_P - H_R$$

Factors Affecting Activation Energy

(a) Nature of reactant (b) Catalyst

Positive Catalyst $\Rightarrow \downarrow$ T.E. $\Rightarrow \downarrow$ $E_a \Rightarrow \uparrow$ Rate
Negative Catalyst $\Rightarrow \uparrow$ T.E. $\Rightarrow \uparrow$ $E_a \Rightarrow \downarrow$ Rate

FACTORS AFFECTING RATE OF REACTION

Nature of Reactant

Radiation

Concentration

Pressure

Catalyst

Temperature

TEMPERATURE

(a) Temperature co-efficient (μ): By

Default $T = 25^\circ\text{C}$ & $\mu = 2$ is taken

$$\mu = \frac{K_{T+10}}{K_T} - 2 \text{ to } 3$$

$$\frac{r_2}{r_1} = \frac{K_2}{K_1} = \mu^{\Delta T/10}$$

(b) $K = Ae^{-E_a/RT}$ (Arrhenius Eqⁿ)

A = Arrhenius constant / Frequency factor / pre-exponential factor

E_a = Activation Energy

R = Gas Constant

T = Temperature (K)

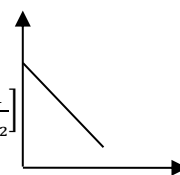
$e^{-E_a/RT}$ = Boltzmann factor

$K/A = e^{-E_a/RT}$ = Fraction of molecules having energy $\geq E_a$

$$\log_{10} K = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\text{Slope} = \frac{-E_a}{2.303R}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$



THERMODYNAMICS

DEFINITION

Deals with interaction of one body with another in terms of energy.

System: Part of universe under investigation

Surrounding: Rest part of universe except system

Boundary: Divide system & surrounding

SYSTEM

Open	Closed	Isolated
Energy and matter can exchange	Only energy can exchange	Neither energy nor matter

State Function	Path Function
Properties which depends only on initial & final state of system & not on process or path. e.g. U, H etc.	Depends on path or process. e.g. work, heat

THERMODYNAMIC PROPERTIES

Extensive	Intensive
Properties which are dependent of matter (size & mass) present in system. e.g. Mass, volume, heat capacity etc.	Properties which are independent of matter (size & mass) present in system. e.g. Pressure, temperature, melting point, density etc.

PROCESSES

Isothermal	Isochoric	Isobaric	Adiabatic	Cyclic
T = const.	V = const.	P = const.	No heat exchange $dq = 0$	Initial & final state of system are same

Reversible	Irreversible
<ul style="list-style-type: none"> * Slow process * At any time system and surrounding are in equilibrium * $P_{\text{sys}} = P_{\text{surr}} \pm dP$ 	<ul style="list-style-type: none"> * Fast process * No equilibrium between system and surrounding * $P_{\text{sys}} = P_{\text{surr}} \pm \Delta P$

INTERNAL ENERGY (U)

Sum of all molecular energies. It is state function, depends on temperature and extensive property.

For Ideal gas: $\Delta U = nC_V \Delta T$

For chemical reaction:

$$\Delta_r E = \sum E_{\text{prod}} \neq 0 \text{ at given } T$$

HEAT (q)

Energy exchange due to temperature difference:

$$q = CAT, \quad q = nC_m \Delta T, \quad q = ms \Delta T$$

C = heat capacity

C_m = molar heat capacity

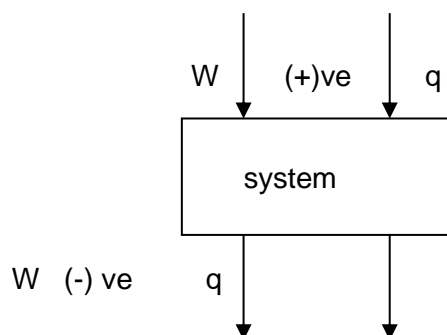
s = specific heat capacity

m = amount of substance

WORK (W)

Reversible	Irreversible
$W_{\text{rev}} = \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$	$W_{\text{irr}} = -P_{\infty} (V_2 - V_1)$

SIGN CONVENTION



FIRST LAW OF THERMODYNAMICS (FLOT)

Law of conservation of energy
 $\Delta U = q + W$

WORK DONE IN VARIOUS PROCESS

Isochoric	Isobaric	Free expansion
$W = 0$	$W = -P_{\text{ex}} (V_2 - V_1)$	$P_{\text{ext}} = 0$
$\Delta U = q = nC_v\Delta T$		$W = 0, \Delta U = 0, q = 0$

Isothermal

$dT = 0; \Delta U = 0$ (for inert gas); $q = -W$

Reversible Isothermal

$$W_{\text{rev, iso}} = nRT \ln \left(\frac{V_2}{V_1} \right) = nRT \ln \left(\frac{P_1}{P_2} \right)$$

Irreversible Isothermal

$$W_{\text{irr, iso}} = P_{\text{ext}} \left[\frac{nRT}{P_2} - \frac{nRT}{P_1} \right]$$

Adiabatic:

$$Q = 0 \Rightarrow \Delta U = W = nC_v\Delta T \Rightarrow W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

$$\gamma = \frac{C_p}{C_v} \Rightarrow C_p = \text{molar heat capacity at constant P.}$$

$$C_p - C_v = R \Rightarrow C_v = \text{molar heat capacity at constant V.}$$

For Reversible adiabatic:

$$PV^\gamma = \text{constant (Ideal gas)}$$

$$TV^{\gamma-1} = \text{constant (Ideal gas)}$$

Enthalpy (H)

State function, extensive property, constant pressure, depend on temperature.

$$H = U + PV$$

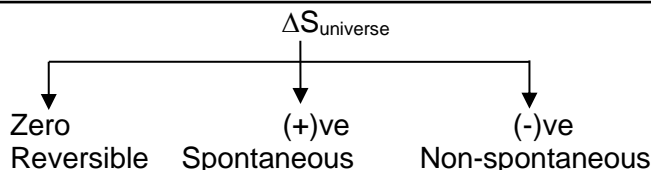
$$\Delta H = nC_p\Delta T = q_p \text{ (Ideal Gas)}$$

For reaction: $\Delta H = \Delta U + \Delta n_g RT$

SECOND LAW OF THERMODYNAMICS (SLOT)

In an irreversible process (spontaneous process) entropy of universe increases.

$$\Delta S_{\text{system}} + \Delta S_{\text{sun}} = \Delta S_{\text{univ}}$$



ENTROPY (S)

State function, extensive property measurement of randomness a disorderness.

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

$$S \uparrow \text{ as temperature } \uparrow; \Delta S = \frac{q_{\text{rev}}}{T}$$

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = nC_p \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{P_1}{P_2} \right)$$

Reversible phase transformation:

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{MP}}}; \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{BP}}}$$

For chemical reaction:

$$\Delta_r S = \sum S(\text{product}) - \sum S(\text{Reactant})$$

Gibbs free energy (G) & spontaneity

G: State function; extensive property

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{ (at constant T \& P)}$$

$\Delta G < 0$: Spontaneous process

$\Delta G = 0$: At equilibrium

$\Delta G > 0$: Non-spontaneous

ΔG : Measurement of Non=pV work (useful work)

$$\Delta_r G = \sum \Delta_f G^0(\text{prod}) - \sum \Delta_f G^0(\text{react})$$

$$\Delta G = \Delta G^0 + RT \ln Q \text{ (Rev. Rxn)}$$

At equilibrium $\Delta G = 0, Q = K$

$$\Delta G^0 = -RT \ln K$$

$\Delta_1 H$	$\Delta_1 S$	$\Delta_1 G$	Description
—	+	—	Reaction spontaneous at all temperatures.
—	—	—	(at low T) Reaction spontaneous at low temperature.
—	—	+	(at high T) Reaction non-spontaneous at high temp.
+	+	+	(at low T) Reaction spontaneous at low temp.
+	+	—	(at high T) Reaction spontaneous at high temp.
+	—	+	(at all T) Reaction non-spontaneous at all temp.

THERMOCHEMISTRY (ENERGIES)

ENTHALPY OF REACTION (ΔH_B)

Amount of heat evolved or absorbed during a reaction at constant pressure.

ENTHALPY OF FORMATION ($\Delta_f H$) (May be endothermic or exothermic)

Change in enthalpy when one mole of a substance is formed from its constituent elements present in standard state.

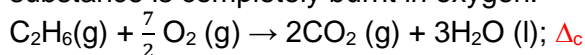
* For elements $\Delta_f H^0 = 0$ (for standard state)

$$\Delta_f H^0 [\text{O}_2(\text{g})] = 0, \quad \Delta_f H^0 = S_{8(\text{rhombic})} = 0$$

$$\Delta_f H^0 [\text{P}_4(\text{white})] = 0, \quad \Delta_f H^0 = C_{(\text{graphite})} = 0$$

ENTHALPY OF COMBUSTION ($\Delta_c H$) (always exothermic)

Change in enthalpy when 1 mole of a substance is completely burnt in oxygen.

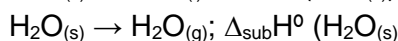
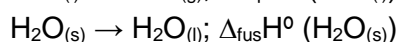
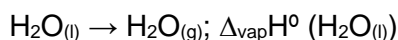
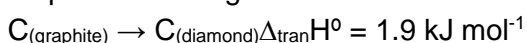


$$\Delta_r H^0 = \sum \Delta_c H^0 (\text{react.}) - \sum \Delta_c H^0 (\text{prod.})$$

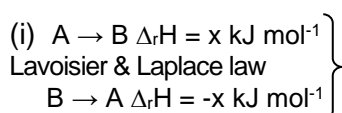
$$\text{Calorific value} = \frac{\Delta H_{\text{comb}}}{\text{molecular wt}}$$

ENTHALPY OF TRANSITION

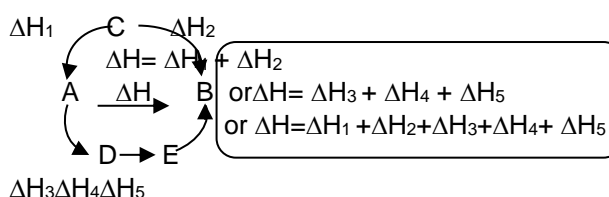
Enthalpy change when one mole of one allotropic form changes to another.



LAWS OF THERMOCHEMISTRY



(ii) Hess Law of Constant Heat summation



BOND ENTHALPY (always endothermic)

Average amount of enthalpy required to dissociate one mole gaseous bond into separate gaseous atoms.

$$\Delta_r H = \left(\text{Sum of bond enthalpy of gaseous reactant} \right) - \left(\text{Sum of bond enthalpy of gaseous product} \right)$$

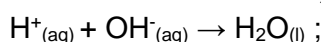
RESONANCE ENERGY

$$\Delta H^0_{\text{resonance}} = \Delta_f H^0 (\text{experimental}) - \Delta_f H^0 (\text{calculated})$$

$$= \Delta_c H^0 (\text{calculated}) - \Delta_c H^0 (\text{experimental})$$

ENTHALPY OF NEUTRALIZATION (ΔH_{neut}) (always exothermic)

Change in enthalpy when one gram equivalent of an acid is completely neutralized by one g-equivalent of a base in dilute solution.



$$\Delta H = -13.7 \text{ kCal eq}^{-1} = 57.3 \text{ kJ eq}^{-1}$$

In case of weak acid/base or both $|\Delta H^0_N| < 13.7 \frac{\text{Kcal}}{\text{eq}}$

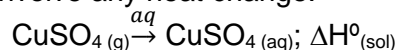
and the difference is enthalpy of ionisation of weak species except in case of HF when $|\Delta H_N| > 13.7$ due to hydration of F^- .

ENTHALPY OF ATOMISATION (ΔH_{atom}) (always endothermic)

Change in enthalpy when one mole of gaseous molecules converts into gaseous atoms.

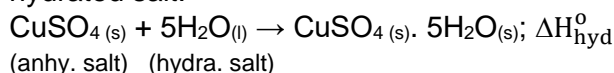
ENTHALPY OF SOLUTION (ΔH_{sol}) (may be endo or exothermic)

Change in enthalpy when 1 mol of a substance is dissolved in excess of water so that further dilution does not involve any heat change.



ENTHALPY OF HYDRATION (ΔH_{hydra}) (always exothermic)

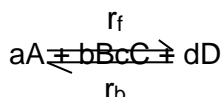
Enthalpy change when 1 mol of anhydrous salt combine with requisite amount of water to form hydrated salt.



CHEMICAL EQUILIBRIUM

- ♦ Equilibrium represents the state of a process in which the measurable properties like: temperature, pressure, color, concentration of the system do not show any change with the passage of time.
- ♦ Equilibrium is a dynamic process, chemical equilibrium can be approached from both sides.
- ♦ The state of equilibrium is not affected by the presence of catalyst. It only helps to attain the equilibrium state in less or more time.
- ♦ Equilibrium can be attained both in homogeneous & heterogeneous system.

Consider a reversible reaction,



AT EQUILIBRIUM STATE

Rate of forward reaction (r_f)
= Rate of backward reaction (r_b)

So, at equilibrium,

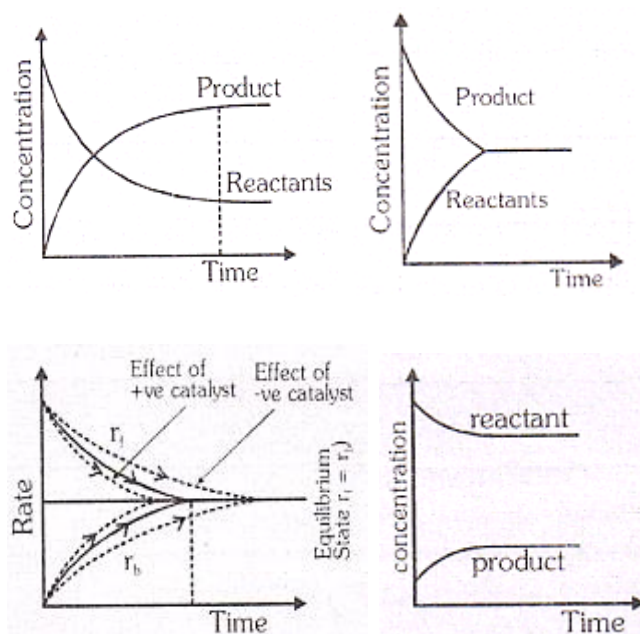
$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{K_f}{K_b} \quad \text{In terms of active mass}$$

$$K_P = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad \text{In terms of partial pressure}$$

$$K_X = \frac{[X_C]^c [X_D]^d}{[X_A]^a [X_B]^b} \quad \text{In terms of mole fraction}$$

- ♦ Partial pressure of solid is taken as unity & in calculation of partial pressure of solids, their number of moles are not considered.
- $K_P = K_C (RT)^{\Delta n_g}$ then $K_P = K_C$
 when $\Delta n_g = 0$ then $K_P = K_C$
 when $\Delta n_g > 0$ then $K_P > K_C$
 when $\Delta n_g < 0$ then $K_P < K_C$
- While determining Δn_g take only gaseous species.
- The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

GRAPHS



♦ Unit of Equilibrium constant:

$$K_C = (\text{mol L}^{-1})^{\Delta n_g}; \quad K_P = (\text{atm})^{\Delta n_g}$$

♦ Application of K_C or K_P

- More is the value of K_P or K_C more is the extent of reaction.
- Stability of reactant increases when value of K decreases
- Stability of product increases when value of K increases.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

Equilibrium constant depends upon temperature & way of writing the reaction

(i) Temperature:

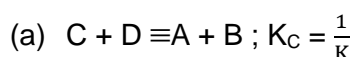
Let K_1 & K_2 be equilibrium constant at T_1 & T_2 then

$$\text{Log} \left(\frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

(Van't Hoff equation)

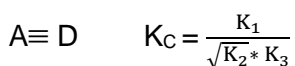
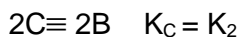
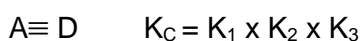
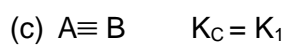
(ii) Way of writing the reaction:

For $A + B \rightleftharpoons C + D$ $K_C = K$ then



when $n = 2$, then $K_C'' = K^{1/3}$

$n = \frac{1}{3}$ then $K_C'' = K^{1/3}$



♦ Predicting the direction of reaction :

Reaction Quotient (Q) is expressed in the same way as for equilibrium constant, except that the concentrations may not necessarily be at equilibrium.

In general, for the reversible reaction:



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

$$Q = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad (\text{in terms of pressure})$$

If $Q = K_{eq}$ then system is in equilibrium.

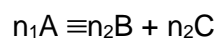
If $Q > K_{eq}$ the system proceed in backward direction to attain equilibrium.

If $Q < K_{eq}$ the system proceed in forward direction to attain equilibrium.

♦ Degree of Dissociation (α)

$$\frac{\text{No. of moles of reactant dissociated}}{\text{No. of mole of reactant present initially}}$$

♦ Degree of Dissociation from Vapour Pressure



$$\alpha = \frac{n_1}{\Delta n} \left(\frac{D_r D_0}{D_0} \right) ; \Delta n = (n_2 + n_3) - (n_1)$$

$$D_T = \text{theoretical vapour density} = \frac{\text{Molecular Weight}}{2}$$

D_0 = observed vapour density

PHYSICAL EQUILIBRIUM

Physical reaction:

Those reactions in which change in only & only physical states of substances takes place without any chemical change.

(i) **Ice-water system (melting of ice):**



(more volume) (less volume)

It is an endothermic process & there is decrease in volume. Thus, the favourable conditions for melting of ice are high temperature, & High-pressure.

(ii) **Water-Water vapour system (vapourisation of water):**



(less volume) (more volume)

It is an endothermic process & there is increase in volume. Thus, the favourable conditions for vaporization of water are high temperature, & low-pressure.

(iii) **Solubility of gases in liquids:**



When a gas dissolve in liquid, there is decrease in volume. Thus, increase in pressure will favour the dissolution of a gas in liquid.

LE-CHATELIER'S PRINCIPLE

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

Le-Chatelier's principle is applicable for both chemical and physical equilibrium

CHEMICAL EQUILIBRIUM

S. No	Effect due to change in		$\Delta n_g = 0$ $A \rightleftharpoons B$	$\Delta n_g > 0$ $A \rightleftharpoons 2B$	$\Delta n_g < 0$ $2A \rightleftharpoons B$
a)	Concentration	(i) $\uparrow [A]$ (ii) $\downarrow [A]$	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
b)	Pressure	(i) \uparrow in pressure (ii) \downarrow in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
c)	Temperature	(i) \uparrow in Endothermic (ii) \uparrow in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
d)	Dissociation	(i) \uparrow in pressure (ii) \uparrow in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Increases	Dissociation Increases Dissociation Decreases
e)	Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Increases Unchanged	Dissociation Decreases Unchanged

IONIC EQUILIBRIUM

ACID	Base
<p>Strong</p> <p>Weak</p> <p> HClO_4 HI HBr HClO_3 H_2SO_4 H_3PO_4 HCl H_3PO_2 H_3BO_3 HNO_3 H_3PO_3 HF H_2S Almost all organic acid Like: acetic acid oxalic acid </p>	<p>Strong</p> <p>Weak</p> <p> <u>Group-1 hydroxide</u> except LiOH like NaOH NH_4OH KOH Zn(OH)_2 RbOH Al(OH)_3 <u>Group-2 hydroxide</u> except Be(OH)_2 Cu(OH)_2 and Mg(OH)_2 etc. **Ca(OH)_2 Sr(OH)_2 Ba(OH)_2 </p>

ACID BASE THEORIES

ARRHENIUS CONCEPT

Acid:

Which produce H^+ ion in aqueous solution.
 e.g. HCl , H_2SO_4 , HClO_4 , H_3PO_4 , CH_3COOH
 but H_3BO_3 IS NOT A Arrhenius acid.



Base:

Which produce OH^- ion in aqueous solution.
 e.g. NaOH , Mg(OH)_2 , Ba(OH)_2

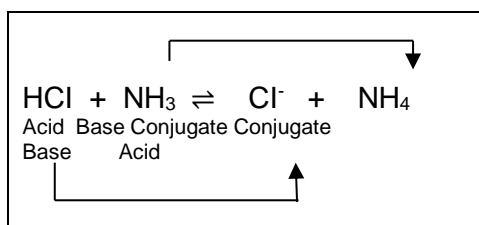
Major Limitation:

Defined only in water solvent.

BRONSTED-LOWRY CONCEPT

Acid: Which gives H^+ in any solvent.

Base: which accepts H^+ in any solvent



- To find conjugate base of any Acid \rightarrow Remove one H^+
- To find conjugate acid of any Base \rightarrow add one H^+
- Water is Amphoteric solvent (can accept as well as lose H^+)



Major Limitation:

Does not explain acidic behaviour of aprotic acids
 e.g. SO_2 , SO_3 , CO_2 , AlCl_3 , SiCl_4

LEWIS THEORY

ACID

TYPES OF LEWIS ACID

1. **Having Incomplete octet:**
BF₃, BCl₃, B(OH)₃, AlCl₃ etc.
2. **Having vacant d-orbitals:**
SF₄, SF₆, SnCl₂, SnCl₄ etc.
3. **Having multiple bonds between atoms of different EN:**
CO, SO₂, SO₃ etc.
4. **Cations:**
Ag⁺, Li⁺, Al³⁺, Mg²⁺
false cations (which cannot act as Lewis acid) :
NH₄⁺, H₃O⁺, PH₄⁺ etc.

Lewis acid is an electron pair acceptor



BASE

TYPES OF LEWIS BASE

1. **Neutral molecule having lone pair**
NH₃, R - NH₂, R₂ - NH,
H - - H, R -
2. **Anions:**
O²⁻, SO₄²⁻, CO₃²⁻, Cl⁻, Br⁻, I⁻, CH₃COO⁻ etc.
 - All the Lewis bases are Bronsted bases but all the Lewis acids are not Bronsted acids.
 - All Arrhenius acids are Bronsted acid but it is not so for bases.

Lewis base is an electron pair donor

OSTWALD'S DILUTION LAW

(Only for weak electrolytes)

$$\alpha \propto \sqrt{\text{dilution}} \quad \text{dilution} \uparrow \Rightarrow \alpha \uparrow$$

EXPLANATION OF WATER

K_w = Ionic product of water

$$pK_w = \text{Ph} + \text{pOH}$$

K = dissociation constant of water

$$K = \frac{K_w}{[\text{H}_2\text{O}]} \quad [\because [\text{H}_2\text{O}] = 55.5]$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

OSTWALD'S DILUTION LAW



FOR PURE WATER

1. [H⁺] = [OH⁻]
2. Ph = POH
3. (PH)_{pure water} = $\frac{pK_w}{2}$
 - pH of an acidic solution is always less than pH of pure water.
 - pH of a basic solution is always greater than pH of pure water

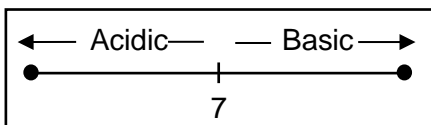
DIFFERENT VALUES AT DIFFERENT TEMPERATURE

At 25° C

1. K_w = 10⁻¹⁴

2. (pH)_{pure water} = (pOH)_{pure water} = 7

3. Ph + pOH = 14

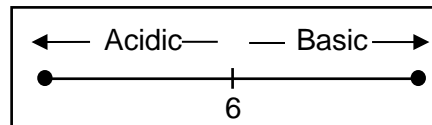
on increasing temperature $K_w \uparrow$ on increasing temperature
(pH)_{pure water} decreases

At 90° C

1. K_w = 10⁻¹²

2. (pH)_{pure water} = (pOH)_{pure water} = 6

3. Ph + pOH = 12



pH OF DIFFERENT SOLUTIONS

Type I: Single Substances

CASE-1**Strong Acid:**

$$[H^+] = N_{\text{Acid}} + 10^{-7}$$

(from water)

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

We neglect smaller values

$$(\text{in } N_{\text{acid}} + 10^{-7})$$

If it is atleast 100 times smaller than other.

CASE-2**Strong Base:**

$$[OH^-] = N_{\text{Base}} + 10^{-7}$$

(from water)

We can neglect smaller values. If it is atleast 100 times smaller than other.

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

$$\text{pH} = \text{pK}_w - \text{pOH}$$

CASE-3**Weak Acid:**

(for monobasic acid)

$$[H^+] = \sqrt{K_a C}$$

K_a = dissociation constant of acid

C: Initial concentration of acid

CASE-4**Weak Base:**

$$[OH^-] = \sqrt{K_b C}$$

K_b = dissociation constant of base

C: Initial concentration of base

Type II: More than one substance (Non-reacting)

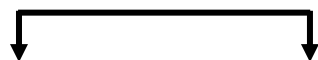
CASE-5: (SA)_I + (SA)_{II}

Initially same Beaker
(If individual volume is not given)

Initially in different beaker
(individual volume is given)

$$[H^+] = N_1 + N_2$$

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

CASE-6: (SB)_I + (SB)_{II}

Same Beaker
(Initially)

Different Beaker
(Initially)

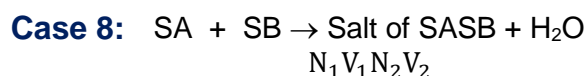
$$[OH^-] = N_1 + N_2$$

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

CASE-7: SA + WA or SB + WB

We can ignore $[H^+]$ / $[OH^-]$ coming from weak part as compared to strong part due to common ion effect

Type III: More than one substance (Reacting)

**a) If $N_1 V_1 = N_2 V_2$**

Then salt of SASB is left in beaker after reaction.

Salt of SASB:

- Does not hydrolyse
- Solution remain neutral ($\text{pH} = 7$ at 25°C)

b) If $N_1 V_1 > N_2 V_2$

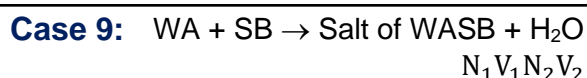
Then SA + salt of SASB is left in solution among which only SA is the contributing substance towards Ph.

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

c) If $N_1 V_1 < N_2 V_2$

Then SB + salt of SASB is left in solution among which only SB is contributing substance towards Ph.

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

**a) If $N_1 V_1 = N_2 V_2$ [left :- salt of WASB]**

Salt of WASB : Anionic hydrolysis

$$\Rightarrow K_h = \frac{K_w}{K_a}; h = \sqrt{\frac{K_h}{C}}$$

$$\Rightarrow \text{pH} = 7 + \frac{1}{2} [\text{pK}_a + \log C] (\text{pH} > 7)$$

b) If $N_1 V_1 > N_2 V_2$

[left: WA + salt of WASB] Acidic buffer

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} ([C] \text{ in normality})$$

Case 10: $\text{SA} + \text{WB} \rightarrow \text{Salt of SAWB} + \text{H}_2\text{O}$
 $N_1 V_1 N_2 V_2$

- a) If $N_1 V_1 = N_2 V_2$ [left : salt of SAWB]
Salt of SAWB : Cationic hydrolysis

$$K_h = \frac{K_w}{K_b}; h = \sqrt{\frac{K_h}{C}}$$

$$\text{pH} = 7 - \frac{1}{2} [\text{p}K_b + \log C]; [\text{pH} < 7]$$

- b) If $N_1 V_1 < N_2 V_2$
 [left: WB + salt of SAWB] basic buffer

$$\text{pOH} = \text{p}K_b + \log \left(\frac{[\text{salt}]}{[\text{base}]}\right)$$

Case 11: $\text{WA} + \text{WB} \rightarrow \text{Salt of SASB} + \text{H}_2\text{O}$
 $N_1 V_1 N_2 V_2$

If $N_1 V_1 = N_2 V_2$ [left: - salt of WAWB]

Salt of WAWB:

Cationic anionic or anionic cationic hydrolysis

$$K_h = \frac{K_w}{K_a \cdot K_b}; h = \sqrt{K_h}$$

$$\text{pH} = 7 + \frac{1}{2} [\text{p}K_a - \text{p}K_b]$$

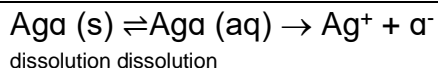
Ph & h is independent of 'C'

[pH can > 7, < 7 or = 7 depends on value of K_a & K_b]

SOLUBILITY (s) & Solubility Product (K_{sp})

Solubility:

The maximum amount of solute that can be dissolved in a particular amount of solvent at a given temperature is called solubility (s). It is generally expressed in molarity.



Solubility Product (K_{sp}):



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

depends only on temperature.

Expression of K_{sp} : $\text{A}_x \text{B}_y \rightleftharpoons x\text{A}^{+y} + y\text{B}^{-x}$

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

$$\text{In terms of 'S' } K_{sp} = (xS)^x (yS)^y$$

Ionic Product [Q_{sp}]



In Q_{sp} the concentration taken are at any time but in K_{sp} the concentration are at equilibrium time / saturation time.

Applications:

1. If $Q_{sp} < K_{sp}$ [unsaturated]
2. If $Q_{sp} = K_{sp}$ [saturated]
3. If $Q_{sp} > K_{sp}$ [super saturated/ppt. will form]

Effect of common ion

- Presence of common ion decreases the solubility but has no effect on K_{sp} as it depends only on temperature.

Effect of odd ion

- Presence of odd ion increases the solubility but has no effect on K_{sp} .

Group	Radicals	Condition for precipitation (Group reagent)	Forms of precipitation
Zero	Na^+ , K^+ , NH_4^+	1-2 drops of CH_3COOH	-----
First	Pb^{+2} , Hg^{+1} (Hg_2^{+2}), Ag^+	By mixing of dilute HCl	AgCl , Hg_2Cl_2 , PbCl_2
Second	Pb^{+2} , Cu^{+2} , Hg^{+2} , Cd^{+2} , Bi^{+3} , As^{+3} , Sb^{+3} , Sn^{+2} , Sn^{+4}	H_2S gas passed in the presence of acidic medium	Sulphide PbS , HgS , CuS , CdS , SnS , SnS_2 , As_2S_3 , Sb_2S_3 , Bi_2S_3
Third	Al^{+3} , Cr^{+3} , Fe^{+3}	NH_4OH mixed in the presence of NH_4Cl	Hydroxide $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$
Fourth	Zn^{+2} , Ni^{+2} , Mn^{+2} , Co^{+2}	H_2S gas passed in the presence of basic medium	Sulphide MnS , ZnS
Fifth	Ba^{+2} , Sr^{+2} , Ca^{+2}	$(\text{NH}_4)_2\text{CO}_3$ mixed in the presence of NH_4Cl	Carbonate BaCO_3 , SrCO_3 , CaCO_3
Sixth	Mg^{+2}	By mixing of Na_2HPO_4	Hydrogen phosphate (MgHPO_4)

Name of indicator	Colour in acidic medium	Colour in basic medium	Working of pH range of indicators
Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
Methyl red	Red	Yellow	4.2 to 6.2
Phenol red	Yellow	Red	6.2 to 8.2
Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

ACID-BASE TITRATION

Type of titration	pH range of titration	Suitable indicators
SA / SB	3 – 11	All indicators (MeOH, HPh etc.)
SA / WB	3 – 7	Methyl Orange (MeOH) and Methyl red
WA / SB	7 – 11	Phenolphthalein (HPh)
WA / WB	6.5 – 7.5	Phenol red

KEY POINTS



Buffer Capacity

$$\frac{\text{No. of moles of } \frac{\text{acid}}{\text{base}} \text{ added per litre}}{\text{change in pH of buffer solution}}$$



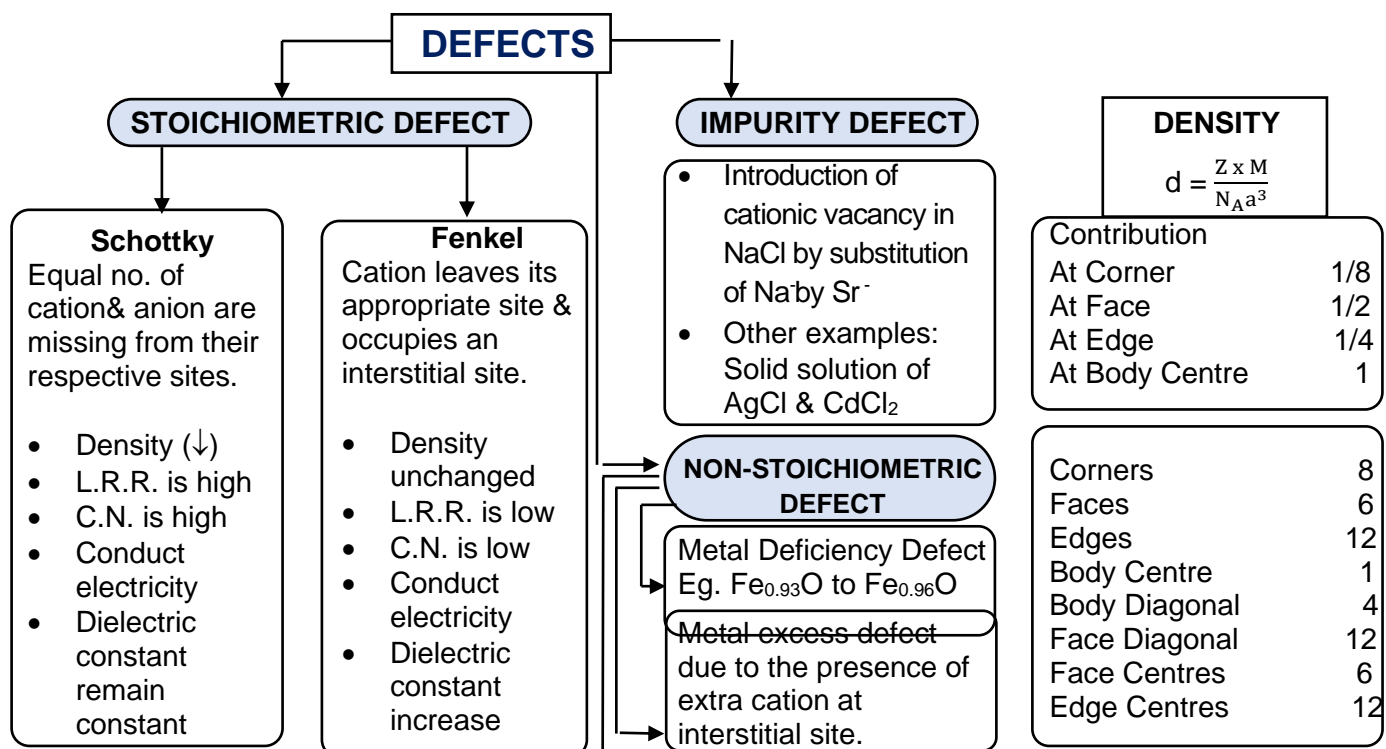
Maximum buffer action when
[salt] = [acid]



pH of Amphiprotic species:
(NaHPO_4 , NaHCO_3) which can donate as well as accept H^+

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

SOLID STATE



Metal excess defect due to anionic vacancies (anion is absent from its site which is occupied an electron). This site is called F-centre.

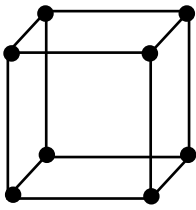
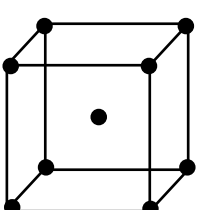
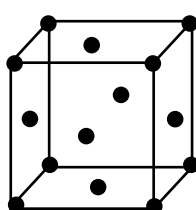
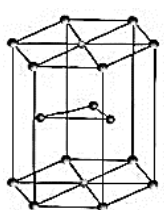
Limiting Radius Ratio	Coordination No. of cation	Geometry of Void	Void found in	Location of Void	No. of Void per atom	Example
$0.155 \leq r/R < 0.225$	3	Plane Trigonal	-----	-----	---	Boron oxide (B_2O_3)
$0.225 \leq r/R < 0.414$	4	Tetrahedral	FCC, HCP	On body diagonal at $\sqrt{3}a/4$ distance from corner of the unit cell.	2	ZnS, SiO_2 , Na_2O , CaF_2
$0.414 \leq r/R < 0.732$	6	Octahedral	FCC, HCP	Body centre & edge centre	1	NaCl, MgO
$0.732 \leq r/R < 1.000$	8	Cubical	SCC	Body centre	1	CaCl

Classification of solid on the basis of nature of order of arrangement of constituent particles.

CRYSTALLINE	AMORPHOUS
These solids have definite characteristic shape.	These solids have irregular shape.
Definite melting point & heat of fusion.	Indefinite melting point & heat of fusion.
Cleavage surfaces are smooth.	Cleavage surface are irregular.
Anisotropic in nature.	Isotropic in nature.
Long range order.	Short range order.
Ex. : NaCl, Quartz, Metal, Diamond etc.	Ex. : Glass Quartz Glass, Rubber, Plastics etc.

Name of system	Axis	Angles	Bravais Lattices
1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	SCC, BCC, FCC
2. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SCC, BCC
3. Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SCC, BCC, FCC, ECC
4. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	SCC, ECC
5. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	SCC
6. Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	SCC
7. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	SCC

S.No.	Type of Ionic Crystal	Geometry	Coordination Number	No. of Formula per U.C.	Examples
1	NaCl (1 : 1) (Rock Salt Type)	Cl ⁻ : Every element CCP of CCP Na ⁺ : At Every OHV	6 : 6	$4\text{Na}^+ + 4\text{Cl}^-$ 4NaCl (4)	<ul style="list-style-type: none"> Halides of (Li, Na, K, Rb); Oxides & sulphides of Alkaline earth metals, (some exception) AgF, AgCl, AgBr, NH₄X
2	CsCl Type (1 : 1)	Cl ⁻ : At Every corner BCC Type Cs ⁺ : At Body centre	8 : 8	$1\text{Cs}^+ + 1\text{Cl}^-$ 1CsCl (1)	<ul style="list-style-type: none"> Halides of 'CS' TlCl, TlBr, CaS
3	ZnS Type (1 : 1) (Zinc Blende Type) (Sphalerite)	S ²⁻ : Every element CCP of CCP Zn ²⁺ : At 50% of THV or At Alternate THV	4 : 4	$4\text{Zn}^{+2} + 4\text{S}^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
4	CaF ₂ Type (1 : 2) (Fluorite Type)	Ca ²⁺ : Every element CCP of CCP F ⁻ : At Every THV		$4\text{Ca}^{+2} = 8\text{F}^{-1}$ 4CaF_2 (4)	BaCl ₂ , BaF ₂ , SrCl ₂ , SrF ₂ , CaCl ₂ , CaF ₂
5	Na ₂ O Type (2 : 1) (Antifluorite Type)	Na ⁺ : At every THV CCP O ²⁻ : Every element of CCP		$8\text{Na}^+ + 4\text{O}^{-2}$ $4\text{Na}_2\text{O}$ (4)	Li ₂ O, Li ₂ S, Na ₂ O, Na ₂ S, K ₂ O, K ₂ S
6	ZnS Type (1 : 1) (Wurtzite) another geometry of ZnS	S ²⁻ : Every element HCP of HCP Zn ²⁺ : 50% of THV or at alternate THV	4 : 4	$6\text{Zn}^{+2} + 6\text{S}^{-2}$ 6ZnS (6)	Same as Sphalerite

S.No.	Content	SCC	BCC	FCC / CCP	HCP
1	Geometry				
2	Arrangement	AAAA Packing but not close packing	ABAB Packing but not close packing	ABCABC Close packing or CCP packing	ABAB Close packing
3	No. of atoms / UC	1	2	4	6
4	Coordination No.	6	8	12	12
5	a & r relation	$r = a/2$	$r = \sqrt{3}a/4$	$r = \sqrt{2}a/4$	----
6	Packing Efficiency	$\pi/6$ or 52.4%	$\sqrt{3}\pi/8$ or 68%	$\pi/3\sqrt{2}$ or 74%	$\pi/3\sqrt{2}$ or 74%
7	Example	Mn	IA; Group: V & Cr, Ba, Fe	Ca, Sr, Al Group: Co, Ni, Cu All inert gases except He	Remaining d-block elements, Be & Mg

SURFACE CHEMISTRY

Classification based on interaction of phases:

LYOPHILIC AND LYOPHOBIC SOLS

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols (solvent – liking).

For example: dispersion of gelatin, starch, gum and proteins in water.

Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called Lyophobic colloidal (Solvent hating) solutions.

COMPARISON OF LYOPHIBIC AND LYOPHILIC SOLS

S.No.	Property	Lyophilic sol (Emulsoid)	Lyophobic sol (suspensoid)
1	Preparation	Can be easily prepared by shaking or warming the substance with solvent	Cannot be prepared easily. Special methods are required
2	Stability	Are more stable	Are less stable
3	Reversibility	Are reversible	Are irreversible
4	Viscosity	Viscosity is much higher than that of solvent	Viscosity is nearly same as that of the solvent
5	Surface tension	Surface tension is usually low.	Surface tension is almost same as that of solvent
6	Hydration or solvation	These are highly solvated as the particles have great affinity for solvent	These are less solvated as the particles have less affinity for solvent
7	Charge	The particles have little charge or no charge at all	The particles carry a characteristic charge either positive or no negative
8	Visibility	Particles cannot be seen under microscope	Particles can be seen under microscope
9	Coagulation or precipitation	Precipitated by high concentration of electrolytes	Precipitated by low concentration of electrolytes
10	Tyndall effect	Less scattering	More scattering
11	Migration in electric field	May or may not migrate as they may or may not carry charge	Migrate towards anode or cathode as these particles carry charge
12	General Ex.	Mostly of Organic nature Ex. Gelatin, Starch, Gum, Albumin & Cellulose Solution	Mostly of Inorganic nature Ex. Transition metal salt in water like Gold, As etc.

PEPTIZATION

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed as Peptization. The electrolyte used is called a **Peptizing Agent**.

Hardy Schulze Rule: This rule states that the precipitating effect of an ion on dispersed phase opposite charge increases with the valency of the ion.

The higher the valency of the flocculating ion, the greater is its precipitating power. Thus for the precipitation of As_2S_3 sol (-ve) the precipitating power of Al^{3+} , Ba^{2+} , and Na^+ ions is in the order

$\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$

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

$[\text{Fe}(\text{CN})_6]^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

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

$$\text{Flocculation value} \propto \frac{1}{\text{Flocculation power}}$$



GOLD NUMBER

The number of **milligrams** of a hydrophilic colloid that will just prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 10% NaCl solution is known as **Gold number** of that protector (Lyophillic colloid).

The precipitation of the gold sol is indicated by a colour change from red to blue when the particle size just increases.

The **smaller the gold number** of a protective Lyophillic colloid, **greater is its protection power**.

Note: Gelatin and starch have the maximum & minimum protective powers.

Protection Capacity $\propto \frac{1}{\text{Protection number}}$
(Gold number)

TYPES OF COLLOIDS ACCORDING TO THEIR SIZE

Multi Molecular	Macro Molecular	Associated Colloids
Formation by aggregation of a large number of atoms or smaller molecules of substance	Formation by aggregation of big size molecules. These are polymers with high molecular mass.	These are the substances which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal solutions. These associated particles are also called micelles.
Ex.: Gold sol (Au), Sulphur sol (S ₈)	Ex.: Starch, Cellulose, Protein etc.	Ex.: Soap & Detergent

COMPARISON OF PHYSI-SORPTION AND CHEMI-SORPTION

	Physical Adsorption	Chemical Adsorption (Activated ad.)
1	It is caused by intermolecular Vander Waal's forces.	It is caused by chemical bond formation.
2	It is not specific.	It is highly specific.
3	It is reversible.	It is irreversible.
4	Heat of adsorption is low. -20 to -40 KJ/mol	Heat of adsorption is high. -80 to -240 KJ/mol
5	No appreciable activation energy is involved.	High activation energy is involved.
6	It forms multimolecular layers on adsorbent surface.	It forms unimolecular layer under high pressure.

GENERAL CHARACTERISTICS OF CATALYSIS

Critical temperature increases
Ease of liquification increases
Extent of adsorption increases
(true for physisorption)

(i) A catalyst remains unchanged in mass and chemical composition but can change their physical state. (ii) Only a very small amount of catalyst is sufficient to catalyse a reaction. (iii) A catalyst does not initiate a reaction. (iv) Solid catalyst is more efficient when used in finely divided form. (v) Generally catalyst does not change the nature of products.	(vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time. (vii) The catalyst are generally specific in nature. (viii) Change rate constant of reaction. (ix) Does not change free energy of reaction. (x) Participate in mechanism of reaction.
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