



## A. Electron

- Lorentz coined the term electron. It was discovered in cathode ray experiment by J.J. Thomson
- Mass of electron =  $9.11 \times 10^{-31}$  kg
  - Radius of electron =  $4.28 \times 10^{-14}$  cm
  - Volume of 1 electron =  $3.28 \times 10^{-40}$  cm<sup>3</sup>

## B. Proton - Goldstein (1886)

- e/m ratio for canal ray depends upon nature of gas
- Mass of 1 proton =  $1.67 \times 10^{-27}$  kg
  - Radius of proton =  $1.53 \times 10^{-13}$  cm
  - Volume of proton =  $1.5 \times 10^{-38}$  cm<sup>3</sup>

## C. Neutron - Chadwick (1932)

- Discovered it in experiment of  $\alpha$  particle on B as well as Be
- Mass =  $1.675 \times 10^{-27}$  kg

## D. Rutherford $\alpha$ -scattering (1909)

- Gold foil of  $10^{-4}$  mm was bombarded with  $\alpha$ -particle
- The scattering of  $\alpha$ -particle is perfectly elastic
- Scattering is directly proportional to atomic number of source
- Density of nucleus is constant  $10^{14}$  g/cm<sup>3</sup>

## E. Limitations of Rutherford Model

1. Does not obey Maxwell's law for electrodynamics
2. Could not explain the emission of various spectral lines
3. Could not suggest for discontinuous nature of spectrum

## F. For Electromagnetic Radiation Word

### Gamma XUVIMR

- |                |                |                 |
|----------------|----------------|-----------------|
| Gamma          | X = X-ray      | U = Ultraviolet |
| V = Visible    | I = Infrared   |                 |
| M = Micro Wave | R = Radio Wave |                 |

Frequency is decreasing from gamma to radio wave

## G. Bohr's Model

Based on quantization of energy as per Planck's theory

1. When electron jumps from higher to lower shell, emission spectrum is generated.
2. Absorption spectrum is formed when electron goes from lower shell to higher shell
3. Valid for 1 electron system
4. Radius =  $\frac{h^2}{4\pi^2 me^2} = 0.52\text{\AA}$  for H  
 $r_{n \text{ H like atom}} = r_n \text{ H/Z}$   
Radius of nth shell of H =  $0.529 \times n^2 \text{\AA}$
5. Velocity =  $\frac{2\pi e^2}{nh}$  =  $2.18 \times 10^8 \text{ cm/sec}$   
 $V_{n \text{ H like atom}} = V_{n \text{ H like atom}} \times Z$

## Structure of Atom

$$6. \text{ Energy} = \frac{2\pi^2 me^4}{n^2 h^2}$$

$$E_T = \frac{-13.6}{n^2} \text{ eV}, \frac{-21.77 \times 10^{-19}}{n^2} \text{ J}$$

for H-like atom

$$E_T = \frac{-21.77 \times 10^{-12} \times Z^2}{n^2} \text{ erg}$$

$$E_T = 13.6 Z^2 \text{ eV}$$

$$7. \text{ Lyman series} = \text{U.V.} \quad n_1 = 1$$

$$\text{Balmer series} = \text{Visible} \quad n_1 = 2$$

$$\text{Paschen} = \text{near IR} \quad n_1 = 3$$

$$\text{Brackett} = \text{IR} \quad n_1 = 4$$

$$\text{Pfund} = \text{far IR} \quad n_1 = 5$$

$$\frac{1}{\lambda} = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

## H. The Ratio of mth and nth Lines

The ratio of mth and nth lines of Lyman series can be written as

$$\frac{\lambda_m}{\lambda_n} = \left( \frac{m+1}{n+1} \right)^2 \times \frac{(n+1)^2 - 1}{(m+1)^2 - 1}$$

## I. Number of Spectral Lines

Number of spectral lines =  $\Sigma n_i - n_j$

i.e. suppose electron jumps from 5 → 2

$$\Sigma(5 - 2) = \Sigma 3 = 1 + 2 + 3 = 6$$

## J. Sommerfeld Model

Studied line spectrum

Electron revolves around the nucleus in elliptical shell

$$\frac{n}{k} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

Limitations of Bohr-Sommerfeld Model :

1. Could not explain the spectrum of poly electronic system
2. Could not explain the behaviour of electron in applied electric and magnetic field

$$K. \quad \lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

## L. Heisenberg Uncertainty

$$\Delta X \cdot \Delta P = \hbar$$

$$\Delta X \cdot \Delta P = \frac{\hbar}{2\pi}$$

## M. Schrodinger Equation

$$\Delta^2 \psi + \frac{8\pi^2 m}{h^2} (E - v) \psi = 0$$

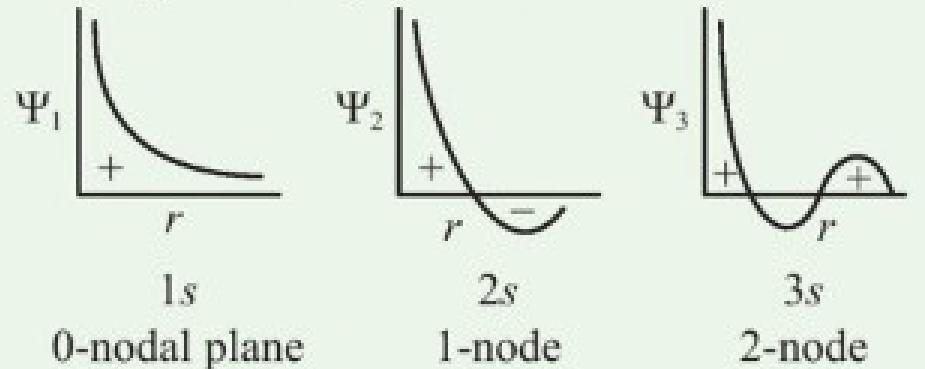
$$\frac{d^2 \psi}{dx^2} + \frac{d^2 \psi}{dy^2} + \frac{d^2 \psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - v) \psi = 0$$

$\Psi$  = amplitude function;  $\Psi^2$  = probability density

defined orbital as 3-dimensional region in which probability of finding electron is maximum

## Nodal Plane

Probability of finding an electron is zero



- Number of nodal planes increase with increase in value of principal quantum number
- Number of radial (spherical) nodes =  $n - l - 1$
- Number of angular (planar) nodes =  $l$

## Quantum Number

Principal quantum number =  $n$

- Indicates size
- Permitted value is 1 to 7
- Theoretically it can be up to infinite
- Non-permitted value = zero, negative fractional

Azimuthal or angular quantum number =  $l$

$$l = 0 = s \quad 1 = p \quad 2 = d \quad 3 = f$$

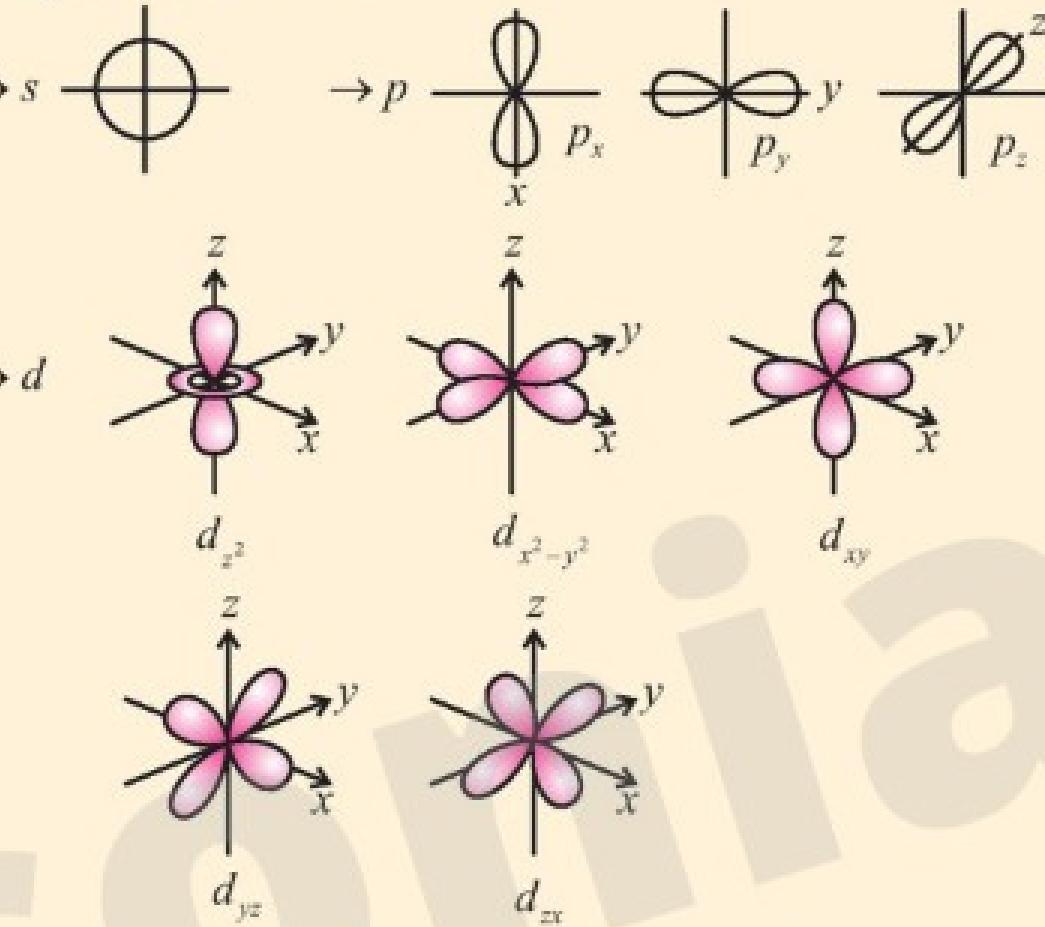
Permitted value =  $(n - 1)$  to zero

Non-permitted value = -ve and fractional indicate shape of subshell

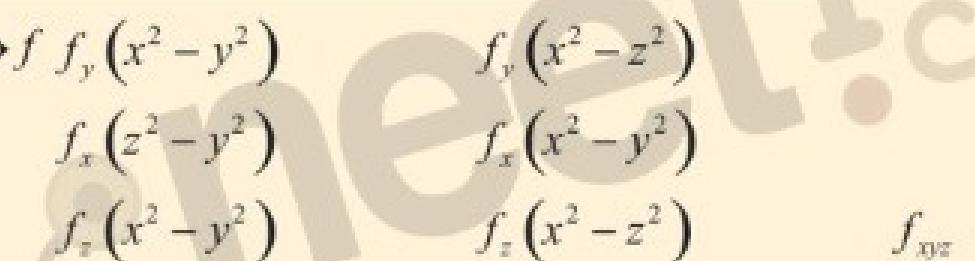
## Magnetic Quantum Number = $m_l$

- It indicates the number of orbitals in a subshell
- Permitted value =  $-l$  to  $+l$   
i.e. for  $p$ -subshell  
 $l = -1, 0, +1$
- Non-permitted value = fractional
- Spin quantum number
- Indicates rotation of electron around its own axis
- For electron, permitted value is  $\pm \frac{1}{2}$
- For photon, permitted value is  $\pm 1$

## Shape of Orbitals



# Structure of Atom



## Pauli's Exclusion Principle

- It is impossible for 2 electrons of an atom to have all their 4 quantum numbers same

It leads to following results :

1. Maximum number of electrons in a shell can be  $2n^2$
2. Maximum number of electrons in a subshell can be 2, 6, 10, 14
3. Maximum number of electrons in an orbital can be 2

## Aufbau Principle

- German Word - Meaning is building up or increasing order
- Electron enters in orbital of lowest energy
- Lower the  $(n + 1)$ , lower will be the energy
- If  $(n + 1)$  is same, lower value of  $n$ , lower the energy
- Energy of orbital for H-atom or He<sup>+</sup>  
 $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$
- The energy of orbitals other than H-atom depends upon  $(n + 1)$  value and varies as  
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$   
 $4f < 5d < 6p < 7s < 5f < 6d$

## Hund's Rule

Pairing of electron in a subshell cannot take place unless and until each orbital is filled with single electron with parallel spin. e.g.



## Compton Effect

When a monochromatic X-Ray was made to fall on lighter elements such as Carbon, it was noticed that scattered X-rays have longer wavelength from incident - X-rays.

$$\lambda_{\text{scattered}} \text{ X-ray} > \lambda_{\text{incident}} \text{ X-ray}$$

It is due to interaction of photons and electrons

## Spin Magnetic Moment

$$\mu_{\text{effective}} = \sqrt{4s(s+1)} \quad \mu_{\text{effective}} = \sqrt{n(n+2)} \quad \text{B.M.}$$

$$\rightarrow \text{Angular Momentum in an orbital} = \frac{\hbar}{2\pi} \sqrt{l(l+1)}$$

$$\rightarrow \text{Stopping potential} = \frac{1}{2} mv^2 = eV_0$$

## Exceptional Electronic Configuration

Cr = 24 = [Ar] 4s <sup>1</sup> , 3d <sup>5</sup>	Pd = 46 = [Kr] 5s <sup>0</sup> , 4d <sup>10</sup>
Cu = 29 = [Ar] 4s <sup>1</sup> , 3d <sup>10</sup>	Ag = 47 = [Kr] 5s <sup>1</sup> , 4d <sup>10</sup>
Nb = 41 = [Kr] 5s <sup>1</sup> , 4d <sup>4</sup>	Gd = 64 = [Xe] 6s <sup>2</sup> , 5d <sup>1</sup> , 4f <sup>7</sup>
Mo = 42 = [Kr] 5s <sup>1</sup> , 4d <sup>5</sup>	Tb = 65 = [Xe] 6s <sup>2</sup> , 4f <sup>9</sup>
Ru = 44 = [Kr] 5s <sup>1</sup> , 4d <sup>7</sup>	Pt = 78 = [Xe] 5s <sup>2</sup> , 5p <sup>6</sup> , 6s <sup>1</sup> , 5d <sup>9</sup>
Rh = 45 = [Kr] 5s <sup>1</sup> , 4d <sup>8</sup>	Au = 79 = [Xe] 5s <sup>2</sup> , 5p <sup>6</sup> , 6s <sup>1</sup> , 5d <sup>10</sup>

## Kinetic Theory of Gases

$$PV = \frac{1}{3} mnv^2 \text{ rms}$$

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

3 word in rms so 3 is in equation

$$U_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

2 word in mp so 2 is in equation

$$U_{\text{avg}} = \sqrt{\frac{2.5RT}{M}}$$

average of 3 and 2

rms = Root Mean Square

mp = Most Probable

$$C_{\text{rms}} = \sqrt{\frac{U_1^2 + U_2^2 + U_3^2}{n}}$$

$$C_{\text{rms}} = \sqrt{\frac{n_1 U_1^2 + n_2 U_2^2 + n_3 U_3^2}{n_1 + n_2 + n_3}}$$

$$C_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

$$C_{\text{mp}} < C_{\text{avg}} < C_{\text{rms}}$$

$$\text{K.E./Mol} = \frac{3}{2} PV = \frac{3}{2} RT$$

$$\text{K.E./Molecule} = \frac{3}{2} \frac{R}{N} T$$

$$K = \frac{R}{N} = \frac{8.314 \times 10^7}{6.023 \times 10^{23}} = 1.38 \times 10^{-16} \text{ erg}$$

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^+}$$

$\lambda$  = Mean free path

$N^+$  = Number of molecule per unit volume

$\sigma$  = Diameter

Real Gas	Ideal Gas
1. Obeys gas law only at low pressure and high temperature	1. Obeys gas law under all the condition $P$ and $T$
2. All are real gases	2. None of the gas present in the Universe
3. Not negligible at all conditions	3. Volume occupied by one molecule is negligible in comparison to total volume
4. Attraction among gaseous molecule should not be neglected at H.P. and L.T.	4. No attractive or repulsive force

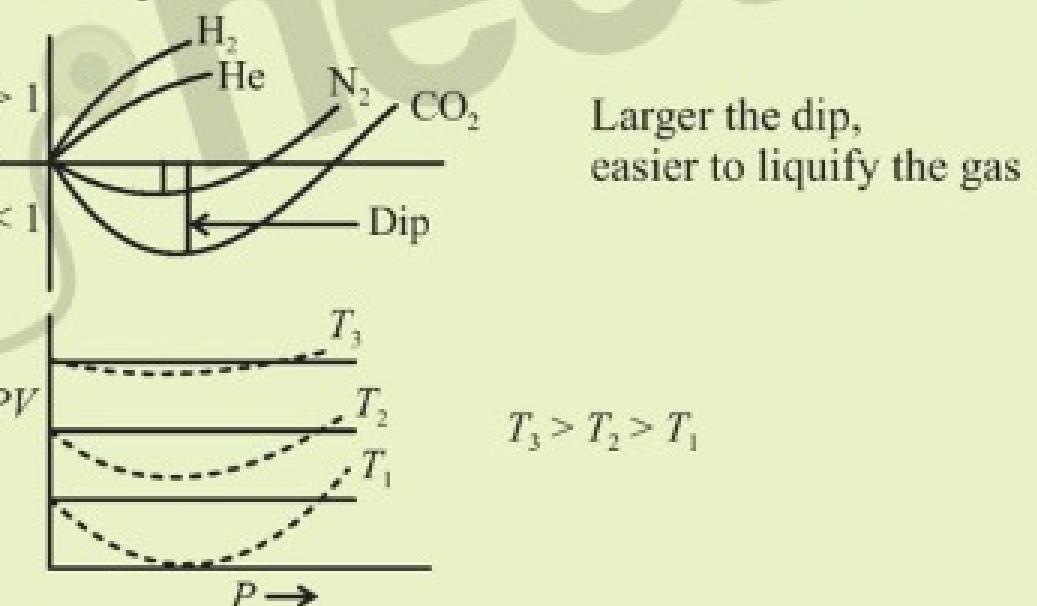
## States of Matter

### Compressibility Factor

$$Z = \frac{PV}{nRT}$$

$$V_M > 22.4$$

$Z > 1$  Repulsion;  $Z < 1$  Attraction



### Effect of Pressure

→ At very low pressure =  $PV \approx RT, Z \approx 1$

→ Low pressure =  $PV < RT, Z < 1$

→ At moderate pressure =  $PV = RT, Z \approx 1$

→ At high pressure =  $PV > RT, Z > 1$

### Boyle's Temperature

Temperature at which gas obeys ideal gas nature. Below this temperature,  $Z$  decreases to minimum then increases with increase in pressure

$$T_b = \frac{a}{R_b} \quad a, b = \text{Van der Waals' Constant}$$

### Van der Waals' Correction

Two points of K.T. were defective :

1. Volume occupied by gaseous molecule is negligible as compared to total volume of gas at all conditions.
2. The force of attraction among gaseous molecules are negligible at all conditions.

### Volume Correction

Real or compressible or ideal volume of gas

= Actual volume of container – volume occupied by  $N$  molecules in motion

Real volume =  $(V - b)$ ,  $b = 4 NV$

### Pressure Correction

Real pressure of gas = Pressure developed due to collision + Pressure loss due to attraction

$$P + P', P' = \frac{a}{V^2}$$

$$\left( P + \frac{a}{V^2} \right)$$

$$\left( P + \frac{a}{V^2} \right) |V - b| = RT$$

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

## Van der Waals' Constant $a, b$

$a$  = Indicates attractive force among gaseous molecule

$a$  = Changes with change in temperature rapidly

$a$  = Increase with increase in polarity

Value of ' $a$ ' for a gas is nearly 100 times higher than ' $b$ '

$a = 4.17, b = 0.037$

$b$  = Indicates molecular volume

$b$  = Does not change with small change in temperature

Unit of ' $a$ ' = atm Litre<sup>2</sup> mol<sup>-2</sup>

Newton m<sup>4</sup> mol<sup>-1</sup>

Unit of ' $b$ ' = Litre mol<sup>-1</sup>

m<sup>3</sup> mol<sup>-1</sup>

Higher the value of ' $a$ ' easier to liquify the gas

→ If two gases have same value of ' $b$ ' then gas with larger value of ' $a$ ' can liquify easily.

→ If two gases have same value of ' $a$ ', smaller value of ' $b$ ' will liquify easily.

## Van der Waals' Correction

At low pressure, volume of gas becomes more. So ' $b$ ' can be ignored

$$\left( P + \frac{a}{V^2} \right) V = RT$$

$$PV = RT - \frac{a}{V}$$

$$Z = 1 - \frac{a}{RTV}$$

$$Z < 1$$

→ At high pressure, volume becomes low, so ' $b$ ' cannot be ignored.  $a/V^2$  becomes negligible in comparison to  $P$

$$P(V - b) = RT, P_v = R_T + P_b$$

$$Z = 1 + \frac{P_b}{R_T}, Z > 1$$

→ At high temperature  $V$  being large, so  $a/V^2$  and  $b$ , both may be neglected

$$PV = RT$$

## Critical Phenomenon

$T_c$  = Critical Temperature,

maximum temperature upto which a gas can be liquefied

$$T_c = \frac{8a}{27Rb}$$

$P_c$  = Critical Pressure,

Minimum pressure at critical temperature needed to liquefy a gas

$$P_c = \frac{a}{27Rb^2}$$

$V_c$  = Critical Volume,

Volume at given  $P_c$  and  $T_c$

$$V_c = 3b$$

## States of Matter

### Value of $Z$ at Critical Process

$$Z = \frac{P_c V_c}{RT_c} = \frac{3}{8} \text{ or } 0.375$$

### Joule Thomson Effect

$$\mu_\pi = \left( \frac{\delta T}{\delta P} \right)_H$$

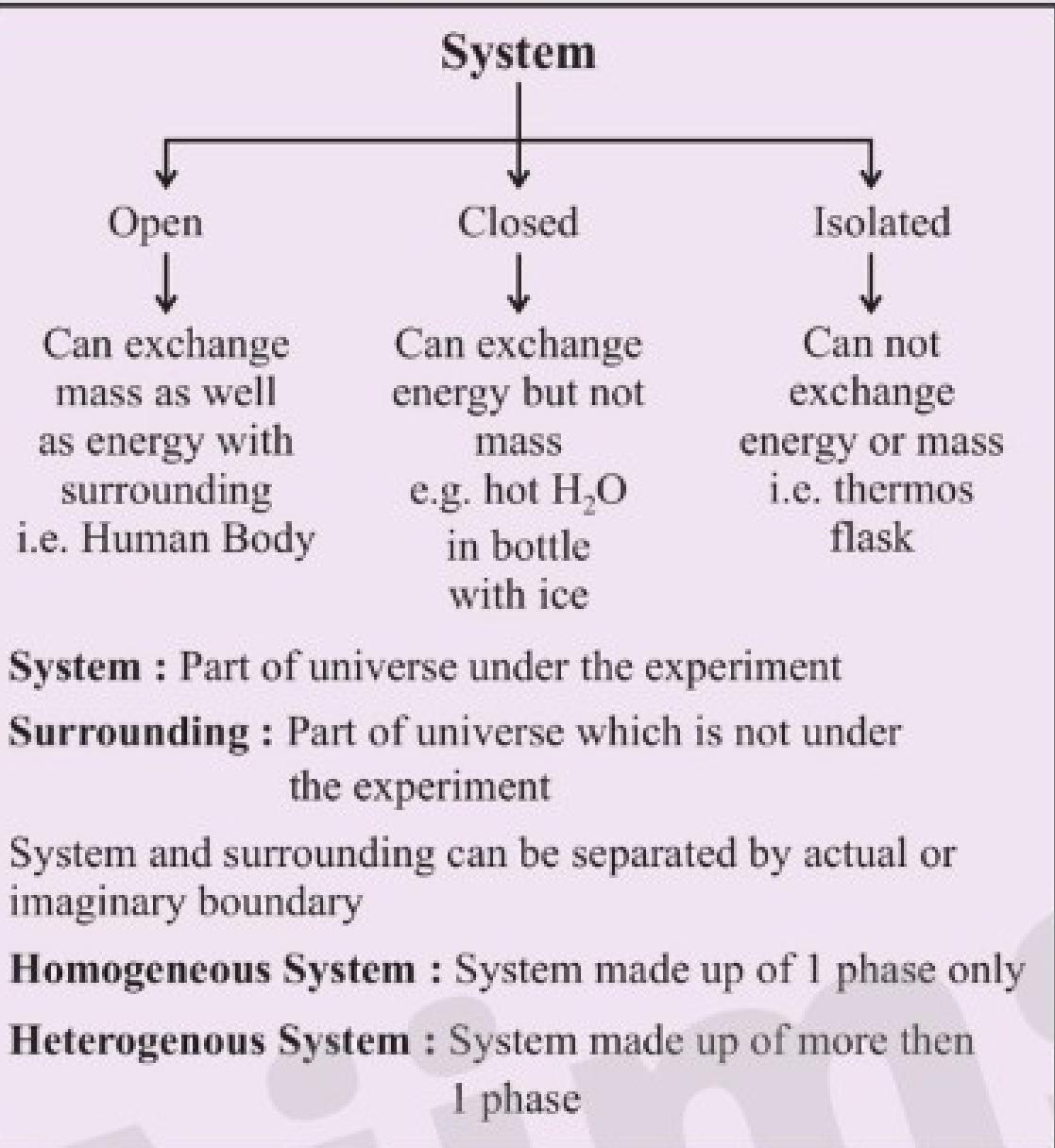
$\mu_\pi$  = Positive = Cooling Effect

$\mu_\pi$  = Negative = Heating Effect

### Inversion Temperature

Characteristic temperature of each gas above this temperature, shows heating and below shows cooling effect

$$T_i = \frac{2a}{Rb}$$



## Thermodynamics Properties

**Intensive Properties :** Do not depend on mass  
e.g. Pressure, Temperature, Density, MP, BP

**Extensive Properties :** Depend on mass  
e.g. Heat capacity, Enthalpy, Entropy

## Thermodynamic Processes

**Isothermal :** Temperature remain constant  
 $d_T = 0, \Delta U = 0$

**Isobaric :** Pressure remain constant  
 $d_p = 0$

**Isochoric :** Volume remain constant

$$d_V = 0$$

**Adiabatic :** System does not exchange heat with surrounding

$$d_q = 0$$

### Reversible Process

- System and surrounding are in equilibrium
- Very small gap between driving and opposing force

### Irreversible Process

- Which proceed in one direction only
- Gap between driving and opposing force is large
- All natural processes are irreversible

## Enthalpy

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V, \Delta H = \Delta U + \Delta nR\Delta T$$

$$\Delta H = f(T, P) \quad dH = \left(\frac{\delta H}{\delta T}\right)_P dT + \left(\frac{\delta H}{\delta P}\right)_T dP$$

$$\Delta H = \int C_p dT$$

### Kirchoff's Equation

$$\int d\Delta r H = \int \Delta n C_p dT$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_p (T_2 - T_1)$$

**Zeroth Law:** Two systems in thermal equilibrium with 3rd system are also in thermal equilibrium with each other.

# Thermodynamics

## Internal Energy

The sum of all microscopic form of energy

$$U = U_{\text{translational}} + U_{\text{rotational}} + U_{\text{vibrational}} + U_{\text{bonding}} + U_{\text{electronic}}$$

**U** = State function and extensive property

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

$$dU = \left(\frac{\delta U}{\delta T}\right)_V dT + \left(\frac{\delta U}{\delta V}\right)_T dV$$

$$dU = nC_{Vm} (T_2 - T_1) \text{ at constant volume}$$

## First Law of Thermodynamics

$$\Delta U = q + w$$

Work done on the system = Positive

Work done by the system = Negative

**Heat :** The energy that flows into or out of a system because of difference in temperature between system and surrounding

### Types of Work

Mechanical =  $PV$  work

Electrical = non  $PV$  work

In thermodynamics only mechanical work is considered

$$dW = -P_{\text{ext}} dV, \quad W = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

Work done in isothermal reversible process

$$W = -nRT \ell n\left(\frac{V_2}{V_1}\right) = -nRT \ell n\left(\frac{P_1}{P_2}\right)$$

$$W = -2.303 nRT \log\left(\frac{V_2}{V_1}\right)$$

$$W = -2.303 nRT \log\left(\frac{P_1}{P_2}\right)$$

Work done in isothermal irreversible process

$$W = -P_{\text{ext}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

In case of free expansion

$$P_{\text{ext}} = 0, W = 0$$

### Adiabatic Process

$$q = 0$$

$$\Delta U = W = nC_V(T_2 - T_1)$$

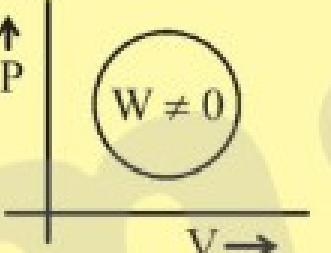
$$\frac{P_2V_2 - P_1V_1}{(\gamma - 1)}, \text{ where } \gamma = \frac{C_p}{C_v}$$

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

For irreversible process

$$\frac{T_2 - T}{(\gamma - 1)} = -P_{\text{ext}} \left( \frac{T_2}{P_2} - \frac{T_1}{P_1} \right)$$

Work done = area under PV diagram



For clockwise = It is negative

For anti clockwise = It is positive

**Heat Capacity :** Between any two temperatures, the quantity of heat required to raise the temperature of the system from lower to higher temperature divided by the temperature difference.

$$C = \frac{da}{dT}, qV = \Delta U$$

$$C_V = \left( \frac{q}{T_2 - T_1} \right)_V = \left( \frac{\Delta U}{T_2 - T_1} \right)_V$$

$$C_P = \left( \frac{\delta H}{dT} \right)_P$$

$$\gamma_{\text{mix}} = \frac{n_1 C_{P_1} + n_2 C_{P_2} + \dots}{n_1 C_{V_1} + n_2 C_{V_2} + \dots}$$

Reversible Adiabatic process

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

$$PV^\gamma = \text{Constant}$$

$$T^\gamma P^{1-\gamma} = \text{Constant}$$

### Second Law of Thermodynamics

- No cyclic engine is possible which take heat from one single source.
- In irreversible process, entropy of universe increases
- In reversible process, entropy remains constant

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$$

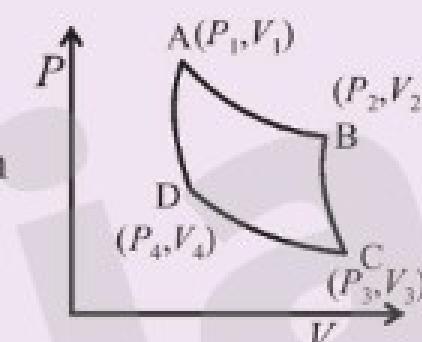
$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0$$

### Carnot Cycle

AB = Isothermal reversible expansion

$$W_{AB} = -nRT \ln \left( \frac{V_2}{V_1} \right)$$



## Thermodynamics

BC = Adiabatic reversible expansion

$$W_{BC} = C_V (T_1 - T_2)$$

CD = Isothermal reversible expansion

$$W_{CD} = -nRT_1 \ln \left( \frac{V_4}{V_3} \right) (T_2 > T_1)$$

DA = Adiabatic reversible expansion

$$W_{DA} = C_V (T_2 - T_1)$$

### Carnot Efficiency ( $\eta$ ) Calculation

$$\frac{-W_{\text{total}}}{q_2} = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$$

### Calculation of Entropy

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

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

→ Reversible and irreversible isothermal expansion / contraction

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

→ Isobaric heating or cooling

$$\Delta S = nC_P \ln \left( \frac{T_2}{T_1} \right)$$

→ Isochoric heating or cooling

$$\Delta S = nC_V \ln \left( \frac{T_2}{T_1} \right)$$

### Adiabatic Process

$$\Delta S = nC_V \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right) \quad (\text{Irreversible process})$$

$\Delta S = 0$ , reversible adiabatic compression and expansion

$$\Delta S = \frac{\Delta H}{T} \quad \text{For phase transformation}$$

$$\Delta S = \sum S_P^0 - \sum S_R^0$$

## Third Law of Thermodynamics

At absolute zero, entropy of an absolute crystal

## Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G$  = Negative for spontaneous reaction

$\Delta G = 0$  for equilibrium

$$\Delta G^{\circ} = \sum \Delta G_p^{\circ} - \sum \Delta G_r^{\circ}$$

$$\Delta G = -RT \ln K, \Delta G = -2.303 RT \log K_{eq}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$\Delta G = W_{max}$  (for a reversible change at constant  $P$  and  $T$ )

$$\Delta G^{\circ} = -nE^{\circ}F, E^{\circ} = \text{Standard cell potential}$$

## Thermochemistry

### Enthalpy of Formation :

It is change in energy when one mole of substance is formed from its constituents in standard states

e.g. Graphite is standard form, not diamond

→ For calculation of other enthalpies, one mole of reactant is taken as reference

### Enthalpy of Transition :

It is enthalpy change, when one mole of reactant changes from one allotropic form to another allotropic form

### Enthalpy of Neutralization :

Equivalent weight of acid/base is considered for strong acid and strong base

$$\rightarrow \Delta H_{neutralization}^{\circ} = -13.7 \text{ k cal or } 57.2 \text{ KJ}$$

## Hess Law of Constant Heat Summation

Total heat change during the complete course of a reaction is same, whether the reaction occurs in one step or in several steps

→ Hess's law is application of first law of thermodynamics

### Bomb Calorimeter :

Is used to measure enthalpy of combustion of organic compound

$$q = m\Delta ST$$

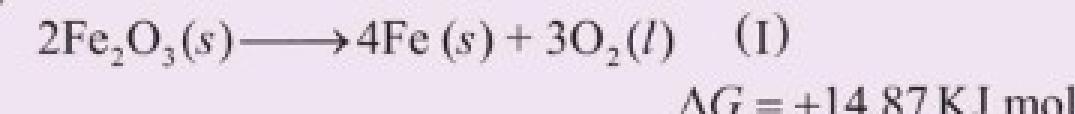
$q$  = Heat,  $m$  = Mass,  $\Delta S$  = Specific heat,  $T$  = Temperature

# Thermodynamics

### Coupled Reaction :

Some non-spontaneous reactions ( $\Delta G = +ve$ ) can be made spontaneous by coupling these reactions with other reactions which have high negative value of  $\Delta G$

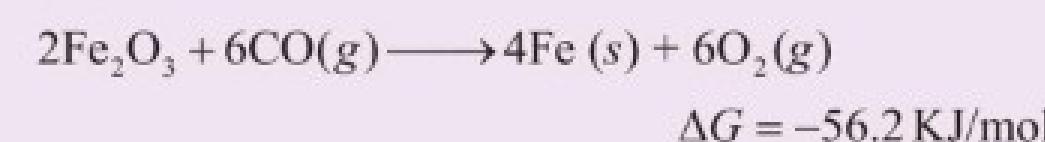
e.g.



It becomes spontaneous when it is coupled with



$$(\text{I}) + (\text{II}) \times 3$$



## System

- Irreversible reactions
- Occur in one direction
- These do not attain equilibrium
- Reversible reactions
- Occur in both directions
- These attain equilibrium

## Law of Mass Action

Guldberg and Waage proposed this law; the rate at which a substance reacts is directly proportional to its active mass raised with suitable powers.

$$r_f = K_f [A]^x [B]^y$$

$$r_b = K_b [C]^m [D]^n$$

$r_f, r_b$  = rate of forward and backward reaction respectively

$$K_c = \frac{K_f}{K_b} = \frac{[C]^m [D]^n}{[A]^x [B]^y}$$

$K_c$  = Equilibrium constant

1. At equilibrium,  $\Delta G$  is has minimum value

2.  $K_c$  does not changes with time

3. Value of  $K_c$  does not depends on initial conc. of reactant or products

4.  $K_c$  value does not changes due to catalyst

If reaction is carried out in gaseous phase,  $K_p$  is used in place of  $K_c$ , where P indicates the pressure at equilibrium

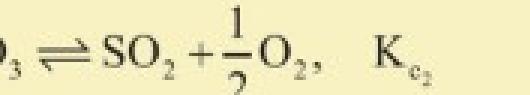
$$5. K_p = K_c (RT)^{\Delta n}$$

$R$  = Universal gas constant

$T$  = Temperature in Kelvin

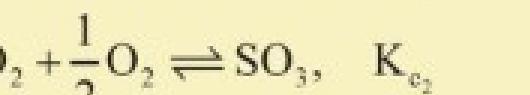
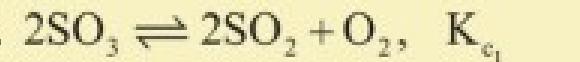
$\Delta n$  = Number of moles of gaseous products – number of moles of gaseous reactants

6. Higher value of  $K_c$  indicates reaction will proceed in forward direction



reaction between  $K_{c_1}$  and  $K_{c_2}$

$$K_{c_1} = (K_{c_2})^2$$



reaction between  $K_{c_1}$  and  $K_{c_2}$

$$K_{c_1} = \sqrt{\frac{1}{K_{c_2}}}$$

## Equilibrium

9.  $K_c/K_p$  variation with temperature is given by

Arrhenius equation

$$= 2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[ \frac{T_2 - T_1}{T_1 \times T_2} \right]$$

$\Delta H = Ea(f) - Ea(b)$  = Heat of reaction

$$\frac{d}{dt} \ln K_c = \frac{\Delta H}{RT^2} = \text{Van't Hoff isochore}$$

(A) If  $\Delta H = 0$

$K_2 = K_1$  = No effect of temperature on  $K_c$  or  $K_p$

(B) If  $\Delta H = \text{Positive}$

$K_2 > K_1$  = Equilibrium constant increases with increase in temperature

(C) If  $\Delta H = \text{Negative}$

$K_2 < K_1$  = Equilibrium constant decreases with increase in temperature



$\Delta G$  = Negative or  $K > 1$

Forward reaction is thermodynamically feasible

$\Delta G$  = Positive or  $K < 1$

Backward reaction is feasible

11. Factors affecting equilibrium constant

(A) Effect of Pressure

No impact if  $\Delta n = 0$

If  $\Delta n \neq 0$ , increase in pressure

Will favour the reaction in the direction having lesser number of moles of gaseous components

(B) Temperature

Increase in temperature

Will favour the reaction in the endothermic direction and vice versa

(C) Addition of inert gas at equilibrium at constant pressure

If  $\Delta n = 0$ , there is no impact of introduction of inert gas at  $K_c$  or  $K_p$

If  $\Delta n \neq 0$ , introduction of gas at constant pressure increase volume. So, reaction will move in the direction having more number of moles of gaseous components

(D) Addition of inert gas at equilibrium at constant pressure does not have any impact on  $K_c$

12. Factors affecting degree of dissociation

Degree of Dissociation =  $\alpha$

$$= \frac{\text{Moles dissociated at any temperature}}{\text{Total moles present or dissolved initially}}$$

(A)  $\alpha$  increases with increase in temperature

(B)  $\alpha$  increases with increase in dilution for weak electrolyte

### 13. Ostwald's Dilution Law

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \text{for weak electrolyte } 1 - \alpha \approx 1$$

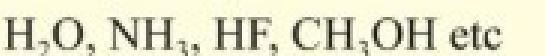
$$K_a = C\alpha^2, \quad \alpha = \sqrt{\frac{K_a}{C}}$$

14. Higher the value of  $K_a$ , stronger will be the acid

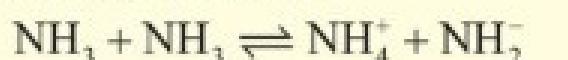
$$-\log K_a = PK_a$$

Higher the  $PK_a$ , weaker will be the acid

### 16. Autoprotolysis



Show autoprotolysis, which confirm the conducting nature of solvent



### 17. Common Ion Effect

The phenomenon in which degree of dissociation of a weak electrolyte is suppressed by addition of a substance having one ion common to weak electrolyte

18. All Arrhenius acids are Bronsted acids, but all Arrhenius bases are not Bronsted bases

19. All Bronsted bases are Lewis bases, but all Bronsted acids are not Lewis acids

$$20. \text{ pH} = -\log[\text{H}^+]$$

pH = changes with change in temperature at 40°C.

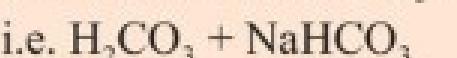
pH of water becomes 6.8 because scale shifts from 14 to 13.6

$$21. \text{ pH of } 10^{-8} \text{ N HCl} = 6.97$$

$$22. \text{ pH} + \text{pOH} = 14$$

### 23. Buffer Solution

(a) Weak acid with its conjugated base



(b) Weak bases and its conjugated acid



### 24. pH of Buffer Solution

$$\text{pH} = \text{PK}_a + \log \frac{[\text{Conjugated Base}]}{[\text{Acid}]}$$

$$\text{pOH} = \text{PK}_b + \log \frac{[\text{Conjugated Acid}]}{[\text{Base}]}$$

### 25. Buffer Capacity

$$= \frac{\text{Moles of acid or base added to 1 litre of buffer}}{\text{Change in pH}} \\ = \frac{n}{\Delta \text{pH}}$$

26. pH of buffer does not change by itself or on dilution

### 27. Solubility Product



$$K = \frac{[A^{y+}]^x [B^{x-}]^y}{[A_x B_y]_s}$$

$$\frac{K_s(A_x B_y)_s}{K_{sp}} = [A^{y+}]^x [B^{x-}]^y$$

$K_{sp} > K_{\text{ionic product}}$  = Solution is unsaturated

$K_{sp} < K_{\text{ionic product}}$  = Precipitate will form

## Equilibrium

### 28. Salt Hydrolysis

(A) Salt of S.A. + S.B. i.e. NaCl, KNO<sub>3</sub> are neutral and do not undergo salt hydrolysis pH = 7

(B) Salt of S.A. + W.B.

e.g. NH<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub> etc.

Cations undergo hydrolysis

pH of such salt is lesser than 7

$$K_H = Ch^2, \quad h = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{K_w}{K_b C}}$$

$$\text{pH} = \frac{1}{2} [\log K_b - \log K_w - \log c] \\ = \frac{1}{2} [pK_w - \log c - pK_b]$$

### (C) Salt of S.B. + W.A.

e.g. KCN, CH<sub>3</sub>COOHa etc.

Anion undergoes hydrolysis

pH is greater than 7

$$h = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{K_w}{K_b C}}$$

$$\text{pOH} = \frac{1}{2} [\log K_a - \log K_w - \log c] \\ = \frac{1}{2} [pK_w - \log c - pK_a]$$

### (D) Salt of W.A. + W.B.

e.g. CH<sub>3</sub>COONH<sub>4</sub>, BeC<sub>2</sub>O<sub>4</sub> etc.

Both cation and anion undergo hydrolysis

pH nearly equal to 7

$$K_H = \frac{K_w}{K_a \cdot K_b}, \quad h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

$$\text{pH} = \frac{1}{2} [pK_w + pK_a - pK_b]$$

### 29. Methyl orange is pH indicator which acts in pH of 3.1

to 4.5. It has yellow colour in alkaline medium and pink red in acidic medium

### 30. Phenol phthalein as an indicator works in pH range 8 to 9.8, has pink colour in alkaline and colourless in acidic medium

- Elements having in between oxidation number will act as both oxidising and reducing agent
- Calculated oxidation number cannot exceed the group number
- If calculated oxidation number is higher than group number, it indicates the presence of peroxide linkage
- Number of peroxide linkage is  

$$= \frac{\text{Calculated oxidation number} - \text{Group number}}{2}$$

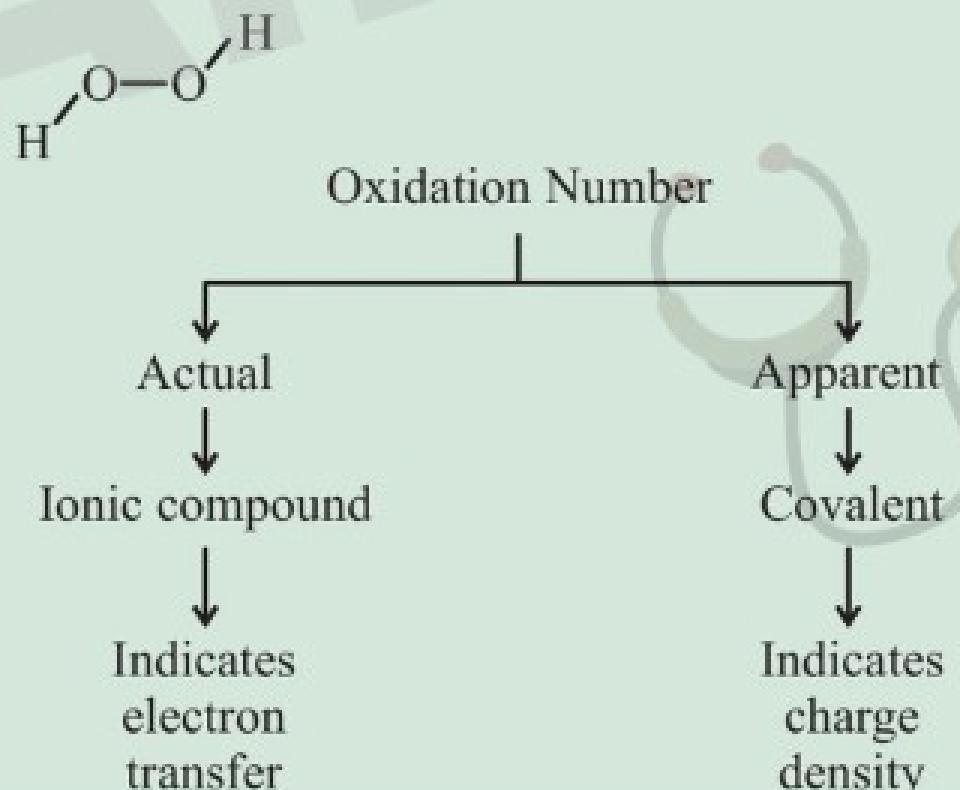
Calculated peroxide linkage cannot be fractional. If calculated peroxide linkage is fractional, then convert to nearest whole number

i.e.  $\text{H}_2\text{O}_2$

Calculated oxidation number of H = 2

$$\text{Peroxide linkage} = \frac{2-1}{2} = 0.5$$

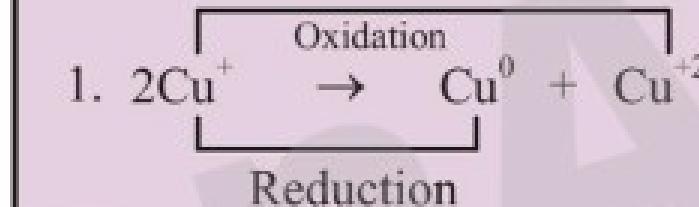
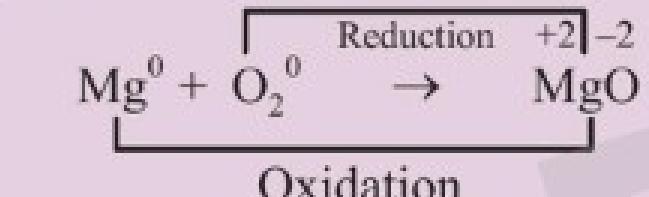
But 0.5 bond cannot exist. So it will be 1



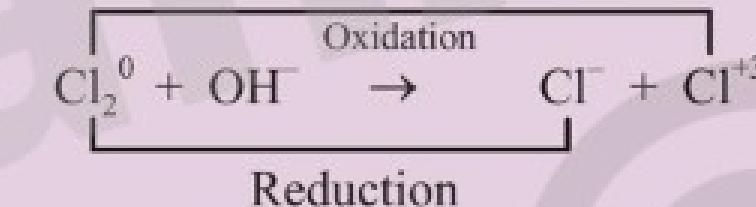
## Redox Reaction

### Type of Redox

In Inter-molecular redox, two substances react; one undergoes oxidation and second undergoes reduction



Same element undergoes oxidation as well as reduction



2. Auto redox = Disproportionation

3. Intra-molecular Redox

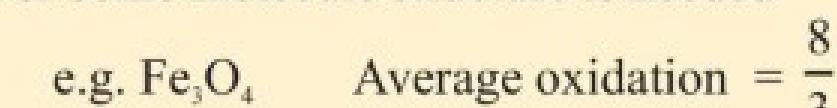


One atom of a molecule gets oxidised and 2nd atom gets reduced



Average oxidation number is not valid for all molecules.

For some molecule structure is needed



But oxidation number cannot be fractional

Actually its  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ,



$$\text{So total charge on Fe} = \frac{2 \times 1 + 3 \times 2}{3} = \frac{8}{3}$$

## Oxidation

(a) Loss of Electron



(b) Loss of Hydrogen



(c) Loss of Electropositive Element



(d) Gain of Oxygen



(e) Gain of Electronegative Element



(f) Increase in oxidation number



Reduction = Opposite of oxidation

## Oxidising Agent

→ Itself undergoes reduction

→ Assists in oxidation

## Reducing Agent

→ Itself undergoes oxidation

→ Assists in reduction



$A^+$  underwent reduction

So will act as oxidising agent as it helped  $B^-$  to get oxidised

## Redox Reaction

### Rules to Calculate Oxidation Number

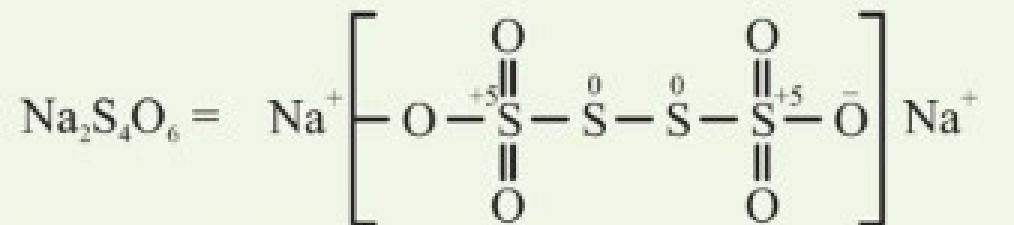
1. Sum of all oxidation numbers is equal to zero in molecules
2. Sum of individual oxidation numbers is equal to charge present in ions
3. Group I and group II elements always show +1 and +2 respectively
4. Halogen generally shows -1
5. Oxygen generally shows
  - 2 Normal oxide =  $O^{-2}$
  - 1 Peroxide =  $O_2^{-2}$
  - 1/2 Superoxide =  $O_2^{-1}$
  - +1 in  $O_2F_2$
  - +2 in  $OF_2$
6. Oxidation number of elements in alloy, metal carbonyl and amalgam is zero  
i.e. oxidation number of iron in steel is zero
7. Maximum oxidation number is equal to number of valence electrons
8. Minimum oxidation number = (valence electron) - 8
9. Elements with minimum oxidation number will act as reducing agent
10. Elements with maximum oxidation number will act as oxidising agent

$B^+$  underwent oxidation, so will act as reducing agent, as it helped  $A^+$  to get reduced.

$$KI_3 = I = \frac{-1}{3}$$

But again fractional cannot be permitted  
So, actually it is

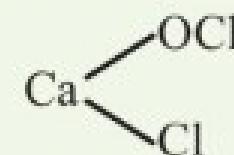
$$KI^{-1} \cdot I_2^0 = \frac{\text{total charge}}{\text{total atom}} = \frac{-1}{3}$$



Average = S = 2.5

But actually it is +5 on 2 and zero on 2 atom

$CaOCl_2$  = one Cl is having -1 another is having +1



### Valency

No negative sign can be used

Usually fixed

Always whole number

Never zero except for noble gases

### Oxidation Number

Can be +ve or -ve

Variable for some element (*d, f, p*)

May be whole or fractional

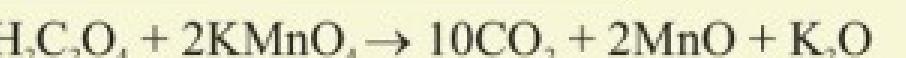
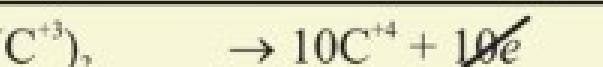
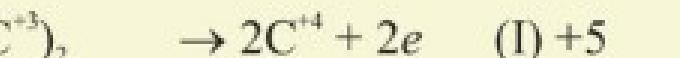
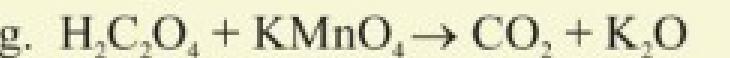
May be zero

## Balancing of Equation

### [In neutral medium]

- Balance each half equation atom wise except H and O
- Balance each half equation charge wise by adding electron
- Cancel electron by multiplying by suitable number

### 4. Add both part



Balance O-atom using  $H_2O$  on desired side



### [Acidic Medium]

All steps are same, except the last step of O, H to balance H and oxygen

Add X  $H_2O$  on oxygen deficient side and 2X on opposite side

### [Basic Medium]

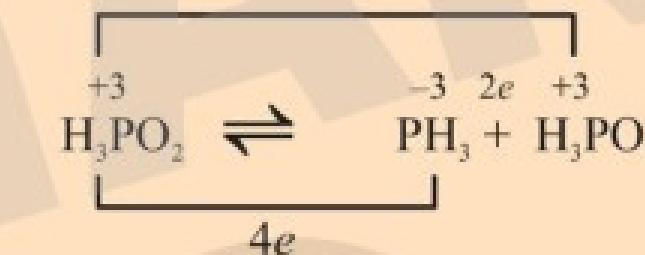
Add X  $H_2O$  on oxygen rich side and 2X  $OH^-$  on opposite side

$$\text{Equivalent closing disproportionation} = \frac{\text{Mol Weight}}{\text{Valency factor}}$$

Valency factor in disproportionation

$$\text{Valency factor} = \frac{n_1 \times n_2}{n_1 + n_2}$$

e.g. Equivalent weight of  $H_3PO_2$  when 1+ disproportionate into  $PH_3$  and  $H_3PO_3$



$$\text{Valency factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{4 \times 2}{4 + 2} = \frac{8}{6} = \frac{4}{3}$$

$$\text{Equivalent Weight} = \frac{\text{Mol Weight}}{\frac{4}{3}}$$

## Redox Reaction

### Redox Titration

$$NV = \frac{W}{E} \times 1000$$

$$\text{Milli Moles} = \frac{\text{Weight of Substance}}{\text{Mol Weight of Substance}} \times 1000$$

$$\text{Equivalent Weight of OA} = \frac{\text{Mol Weight}}{\text{Number of electrons accepted per molecule}}$$

### Iodimetric Titration

Iodine being moderate oxidising agent, it can be used to titrate reducing agent



$I_2$  acts as self indicator with starch solution

### Iodometric Titration

$I^-$  ion is weak reducing agent, therefore will reduce strong oxidising agent



## 1. Solids

Crystalline Solid	Amorphous Solid
(a) The internal arrangement of particles is well defined or long range order	(a) The internal arrangement of particles is not well defined or short range order
(b) They possess sharp melting point	(b) They do not possess sharp melting point
(c) Give a regular cut, when cut with a sharp edge knife	(c) Amorphous solid give irregular cut

## 3. Unit Cell

The smallest 3D portion of a crystal lattice, when repeated again and again, gives the entire crystal lattice

# Solid State

## 2. Classification of Crystalline Solids

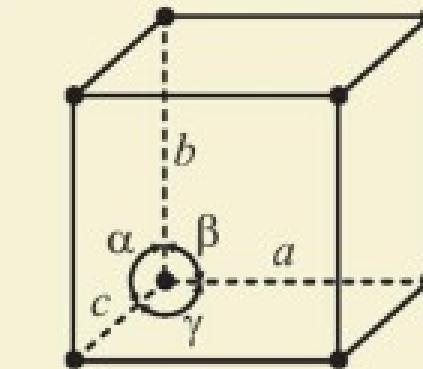
Type of Solid	Constituent Particles	Binding/Attraction Force	Example	Physical Nature	Electrical Properties
1. Ionic Solid	Positive and negative ions network systematically arranged	Ionic bonds and coulombic forces	NaCl, ZnS, CaF <sub>2</sub> , LiF, BaSO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub>	Hard and brittle, high melting points, high heats of fusion	Poor thermal and electrical conductors
2. Molecular Solid					
(a) Non-polar Solid	Molecules	van der Waal's force (London dispersion)	F <sub>2</sub> , Cl <sub>2</sub> , Ar, CH <sub>4</sub> , CO <sub>2</sub>	Soft, very low melting point, low heat of fusion	Insulator
(b) Polar Solid	Molecules	Dipole-dipole forces	HCl, SO <sub>2</sub>	Soft, low melting point, low heat of fusion	Insulator
(c) H-bonded Solid	Molecules	H-bonding	H <sub>2</sub> O, NH <sub>3</sub>	Hard, low melting point, low heat of fusion	Insulator
3. Covalent or network Solid	Atoms connected in covalent bond network	Covalent bonds	Diamond, Quartz, Silica	Very hard, very high melting point	Poor thermal and electrical conductors
4. Metallic Solid	Cations in a sea of delocalised electron	Metallic bonds (Positive ions and delocalised electrons)	All metallic elements, for example Cu, Fe, Zn, etc.	soft to very hard, low to very high melting points, malleable and ductile	Excellent thermal and electrical conductors

#### 4. Seven Primitive Unit Cells

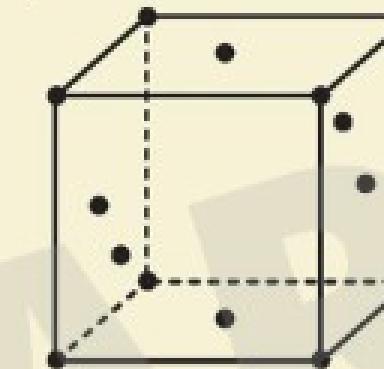
System	Primitives or axial distance	Interfacial or axial angles	Maximum elements of symmetry	Examples
1. Cubic a. Simple b. Face centred c. Body centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Nine planes, thirteen axes, one centre	NaCl, KCl, CaF <sub>2</sub> , ZnS, Pb, Ag, Hg, Diamond, Alums
2. Monoclinic a. Simple b. End face centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	One plane, one axis	Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O, CaSO <sub>4</sub> · 2H <sub>2</sub> O, Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O, monoclinic Sulphur
3. Orthorhombic a. Simple b. f.c.c c. b.c.c d. End face centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Three planes, three axes	Rhombic Sulphur, BaSO <sub>4</sub> , KNO <sub>3</sub> , PbCO <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub>
4. Tetragonal a. Simple b. Body centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Five planes, five axis	TiO <sub>2</sub> , ZnO <sub>2</sub> , Sn, SnO <sub>2</sub> , NiSO <sub>4</sub>
5. Hexagonal (Simple)	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Seven planes, seven axis	Mg, PbI <sub>2</sub> , CdS, ZnO, HgS, Graphite
6. Rhombohedral or Trigonal (Simple)	$a = b = c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Seven planes, seven axis	Calcite, NaNO <sub>3</sub> , ICl
7. Triclinic (Simple)	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	No plane, no axis	CuSO <sub>4</sub> · 5H <sub>2</sub> O, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , H <sub>3</sub> BO <sub>3</sub>

#### 5. Structure

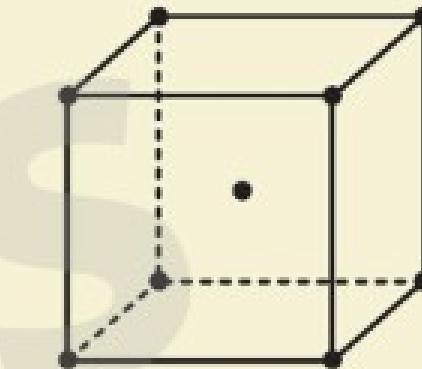
1. Cubic :  $a = b = c, \alpha = \beta = \gamma = 90^\circ$



(i) Simple

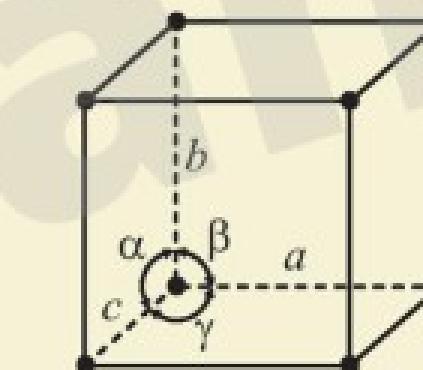


(ii) Face-centred

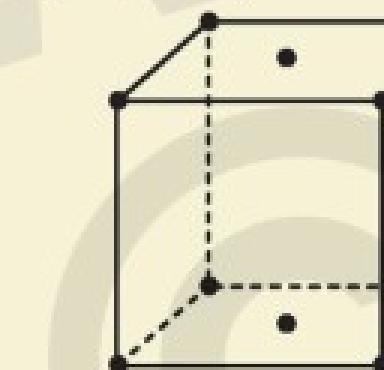


(iii) Body-centred

2. Monoclinic :  $a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$



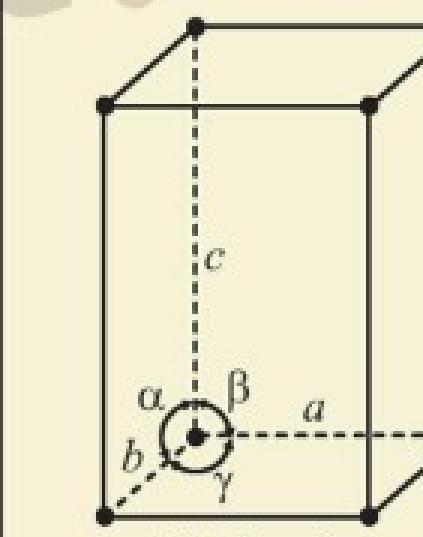
(iv) Simple



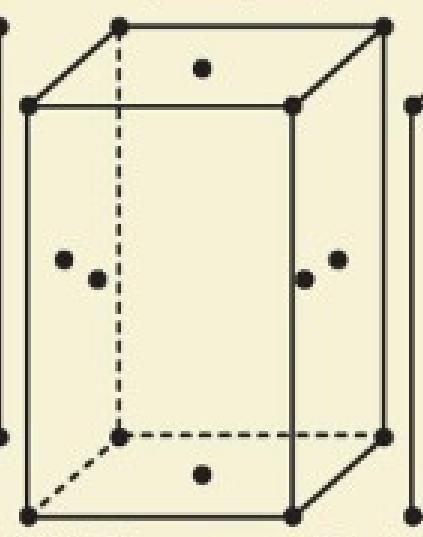
(v) End face-centred

## Solid State

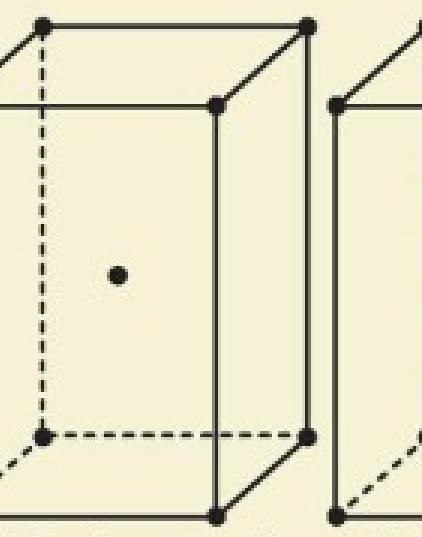
3. Orthorhombic :  $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$



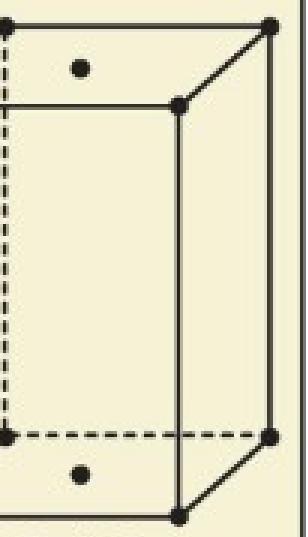
(vi) Simple



(vii) Face-centred

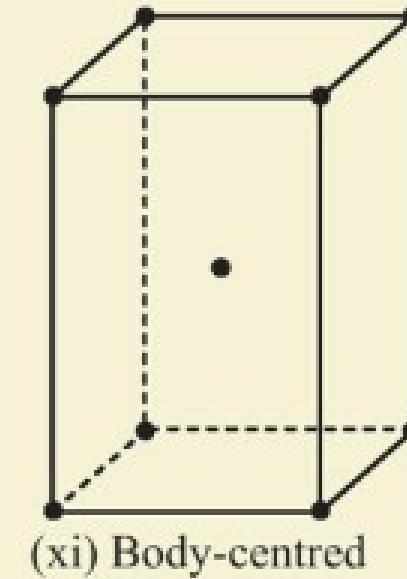
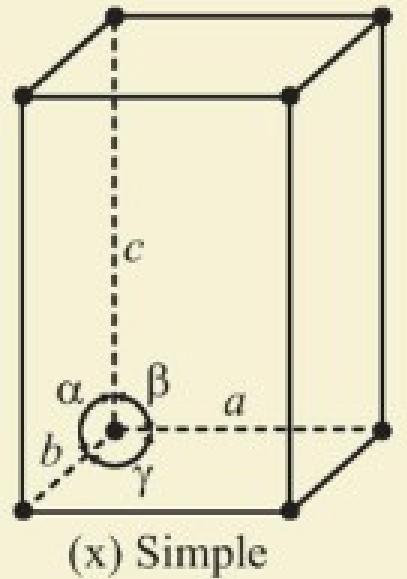


(viii) Body-centred

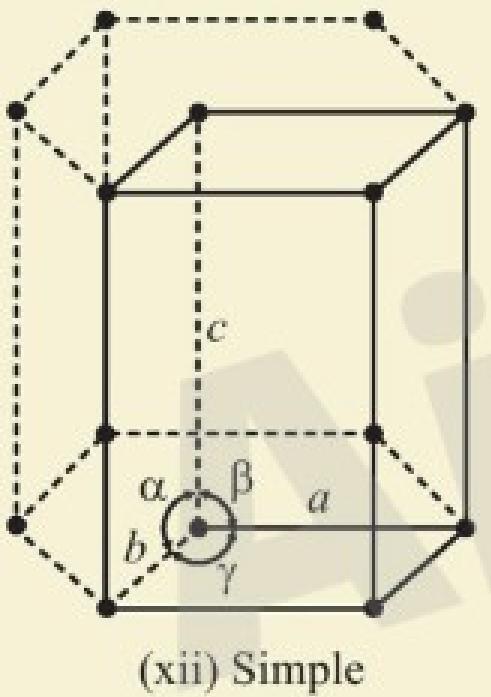


(ix) End face-centred

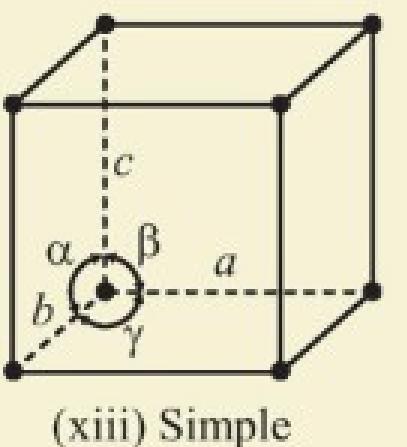
4. Tetragonal :  $a = b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$



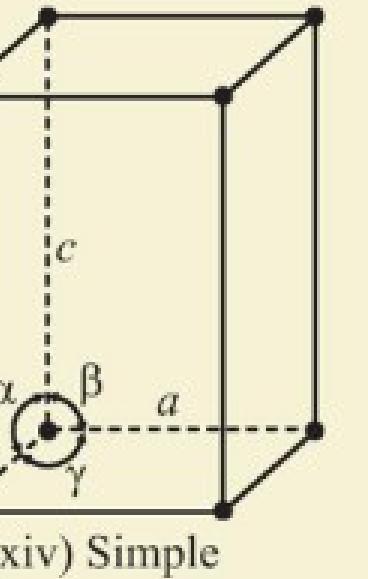
5. Hexagonal :  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ;  $\gamma = 120^\circ$



6. Rhombohedral :  $a = b = c$ ,  $\alpha = \gamma = 90^\circ$ ;  $\beta \neq 90^\circ$



7. Triclinic :  $a \neq b \neq c$ ,  $\alpha \neq \beta \neq \gamma \neq 90^\circ$



8. Density of Lattice Matter

$$d = \frac{n \times M}{a^3 \times N_A}$$

$n$  = Number of atoms per unit volume

$M$  = Mass of the crystal

$a^3$  = Volume

$N_A$  = Avogadro number

9. Packing Fraction

$$= \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of unit cell}}$$

(a) In S.C.C.

$$r = \frac{a}{2}, V = \frac{4}{3} \pi r^3$$

$$\text{P.F.} = \frac{\frac{\pi a^3}{6}}{a^3} = \frac{\pi}{6} = 0.52$$

52% is occupied and 48% is empty

(b) In F.C.C.

$$r = \frac{a}{2\sqrt{2}}, V = \frac{4}{3} \pi r^3 \times \frac{4}{\text{Number of atom/cell}}$$

$$V = \frac{\sqrt{2} \pi a^3}{6}, \text{ P.F.} = \frac{\sqrt{2} \frac{\pi a^3}{6}}{a^3} = \frac{\sqrt{2} \pi}{6} = 0.74$$

74% is occupied and 26% is empty

(c) In B.C.C.

Volume of atoms in unit cell

$$= 2 \times \frac{4}{3} \pi r^3 = 2 \times \frac{4}{3} \pi \times \left( \frac{\sqrt{3}a}{4} \right)^3$$

$$\text{P.F.} = \frac{\sqrt{3} \pi a^3}{8a^3} = \frac{\sqrt{3} \pi}{8} = 0.68$$

68% is occupied and 32% is empty

## Solid State

6. Radius of Atom

$$\text{In S.C.C.} = \frac{a}{2} = r$$

$$\text{In F.C.C.} = r = \frac{a}{2\sqrt{2}}$$

$$\text{In B.C.C.} = r = \frac{\sqrt{3}a}{4}$$

7. Number of atoms per unit cell (n)

$$\text{B.C.C.} = 2 = 8 \times \frac{1}{8} + 1 \times 1 = 2$$

$$\text{S.C.C.} = 1 = 8 \times \frac{1}{8} = 1$$

$$\text{F.C.C.} = 4 = 6 \times \frac{1}{2} + 1 \times 1 = 4$$

## 10. Radius Ratio

$$= \frac{\text{Radius of cation } (r^+)}{\text{Radius of anion } (r^-)}$$

**Summary of the four kinds of packing for spheres**

Structure	Packing pattern	Co-ordination number	Packing efficiency (%)	Unit Cell
1. Simple cubic	<i>AAAA</i>	6	52	Primitive cubic
2. Body centred cubic or bcc	<i>ABAB</i>	8	68	Body centred cubic
3. Hexagonal closest packing	<i>ABAB</i>	12	74	Non cubic
4. Cubic closest packing or fcc	<i>ABCABC</i>	12	74	Face centred cubic

# Solid State

## 11. Bragg's Equation

$$n\lambda = 2d \sin \theta$$

$d$  = Distance between planes in a crystal

$\lambda$  = Wavelength of X-ray

## 12. Schottky Defects

These defects are created when one positive and one negative ion are missing from their respective positions, leaving behind a pair of holes.

- Common in high co-ordination number where size of cations and anions are almost equal
- Density decreases
- Number of defects increase with increase in temperature

## 13. Frenkel Defects

These defects are created when an ion leaves its correct lattice site and occupies interstitial site

- More common in ionic composition having low co-ordination number

## 14. Conductors

- Conductors do not have forbidden gap
- Semiconductors have small forbidden gap
- Insulators have large forbidden gap

## 15. Doping

It is the process to mix impurity with pure semi conductor [intrinsic semi conductor] to prepare extrinsic semi conductors, which are having higher conductivity

16. Generally 1 atom is doped in  $10^{18}$  atoms to prepare an extrinsic semi conductor
17. If group 14 elements are doped with group 15 elements, *n* type semi conductor is formed. Crystal becomes conductor due to present of electrons. Electrons conduct electricity
18. When group 14 elements are doped with group 13 element, *p* type semi conductor is formed and holes conduct electricity

## 19. $\text{YBa}_2\text{Cu}_3\text{O}_7$ is a super conductor at 90 K

## 20. Magnetic Properties

(a) **Diamagnetic** : Substances which are feebly repelled by the magnetic field.

- They do not have any unpaired electrons
- Non metallic elements (except O, S), inert gases, metals of group 2, etc. are example of diamagnetic substances

(b) **Paramagnetism** : Substances which are weakly attracted by magnetic field are paramagnetic in nature

- They have unpaired electrons
- eg :  $\text{TiO}_2$ ,  $\text{VO}_2$ ,  $\text{CuO}$ ,  $\text{O}_2$  and  $\text{FeSO}_4$

(c) **Ferromagnetism** : Substances which are strongly attracted by magnetic field are ferromagnetic in nature

- They have permanent dipole moment
- eg : Fe, CO, Ni and  $\text{CrO}_3$
- They have magnetic properties even in absence of magnetic field

(d) When actual magnetic moments is lesser than theoretical value of magnetic moment, then it is ferromagnetism

eg,  $\text{Fe}_3\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$

(e) **Antiferromagnetic** : In spite of having unpaired electron, they have zero dipole moment

eg,  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$

## 21. Curie's Temperature

Temperature above which ferromagnetic substances becomes paramagnetic. This happens due to non-alignment of electron at higher temperature.

## 22. Piezo-electricity

When some crystals which align to produce net dipole moment on application of pressure.

**Pyro-electricity** : Some crystals on heating produce electricity

## 1. Solubility

$$= \frac{\text{Mass of Solute}}{\text{Mass of Solvent}} \times 100$$

2. Solubility of  $\text{NH}_4\text{Cl}$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$  etc. (endothermic dissolution) increases with increase in temperature

3.  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$  etc. (exothermic dissolution)  
Solubility of such compounds decreases with increase in temperature

4.  $\text{I}_2$  gets dissolved in  $\text{KI}$ , due to formation of complex  
 $\text{I}_2 + \text{KI} \rightarrow \text{KI}_3$

## 5. Hygroscopic Substances

Those substances that absorb moisture from atmosphere

## 6. Deliquescent Substances

Crystalline substances that absorb more mass of moisture from atmosphere and pass in solution form.  
e.g.  $\text{NaOH}$ ,  $\text{MgSO}_4$

## 7. Efflorescent Substances

Crystalline substances that give up their water of crystallisation to atmosphere and change into dehydrated or partially dehydrated form.  
e.g.  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

## 8. Henry's Law

The mass of gas dissolved per unit volume of solvent is directly proportional to its partial pressure.

$$a \propto P; a = K.P.$$

→ Henry's law is valid for non reacting gases at low concentration and low pressure

$$S = K_H \cdot P_{(g)}$$

$S$  = Solubility of gas (mol/litre)

$P'_{(g)}$  = Partial pressure of gas

$$P' = K_H \cdot X_{(g)}$$

$P'$  = Partial pressure

$X_{(g)}$  = Mole fraction of gas

9. To minimize the impact of dissolution of more  $\text{N}_2$  in blood of deep sea divers,  $\text{N}_2$  in the gas cylinder is replaced by  $\text{He}$ .

## 10. Osmosis

Movement of solvent particles from higher concentration to lower concentration through a semi permeable membrane

**Exo-osmosis :** Outward osmotic flow of water from a cell containing an aqueous solution through a semi permeable membrane i.e. grape in concentrated  $\text{NaCl}$  solution

**Endo-osmosis :** Inward flow of water into cell containing aqueous solution through a semi permeable membrane. i.e. grape in water

# Solutions

## 11. Natural Semipermeable Membrane

Skin around white of an egg, membrane around R.B.C., Pigs bladder

## 12. Artificial Semipermeable Membrane

Gelatinous  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$

## 13. Osmotic Pressure

$$\pi = h\rho g$$

$h$  = height of liquid in capillary;  $\rho$  = density of liquid;  
 $g$  = gravity

$\pi v = n \cdot S \cdot T$        $n$  = number of mole;  $C$  = Molarity;

$\pi = C \cdot S \cdot T$        $S$  = Solution concentration value equal to  $R$   
 $T$  = Temperature in Kelvin

→ Two solutions of different substances having same osmotic pressure at same temperature are said to be isotonic to each other.

$$\pi_1 = \pi_2$$

So,  $C_1 = C_2$  when temperature is same

## 14. Vapour Pressure

Pressure exerted by the vapour of solvent when they are in dynamic equilibrium with its liquid at a temperature

$$2.303 \log_{10} \frac{P_2}{P_1} = \frac{\Delta H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$\Delta H$  = Latent heat of vapourization per mole;

$T_1, T_2$  = Temperature;  $P_1, P_2$  = Pressure

Vapour pressure can be calculated by

(a) Barometric Method

(b) Manometric Method

## 15. Raoult's Law

$$(i) P_M = P'_A + P'_B + \dots$$

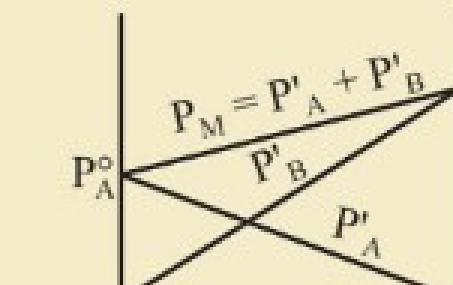
$P_M$  = Vapour pressure of mix

$P'_A, P'_B$  = Partial vapour pressure of components A and B

$$(ii) P'_A = P_A^\circ \cdot X_A$$

$$P'_B = P_B^\circ \cdot X_B$$

$P_A^\circ, P_B^\circ$  = Vapour pressure of solvents A and B



$X_A = 1$	$X_A = 0$
$X_B = 0$	$X_B = 1$

Relative lowering of vapour pressure is directly proportional to mole fraction of solute

$$P^\circ - P_S \propto \text{loss in mass of solvent}$$

## 16. Ideal Solutions

- (a) Obeys Raoult's Law
- (b)  $\Delta V_{\text{mixing}} = 0$
- (c)  $\Delta H_{\text{mixing}} = 0$

Solvent-Solvent and Solute-Solute interactions are almost of the same type as Solvent-Solute interaction  
→ Polarity of solute and solvent is almost same

e.g.,  $C_6H_6 - C_6H_5CH_3$ ;  $C_6H_6 - CCl_4$   
*n*-hexane – *n*-heptene

## 17. Non-Ideal Solutions

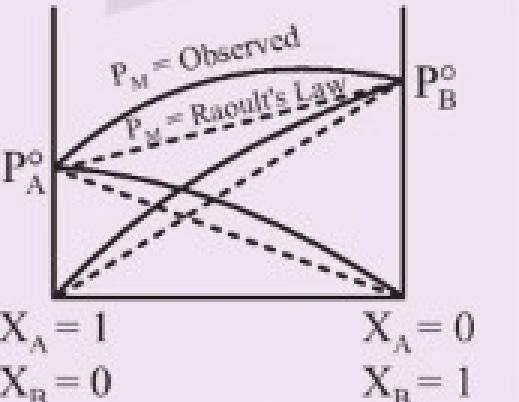
- (a) They do not obey Raoult's Law
- (b)  $\Delta H_{\text{mixing}} \neq 0$
- (c)  $\Delta V_{\text{mixing}} \neq 0$

Non-ideal can be divided into

- (1) Solutions showing +ve deviation
- (2) Solution showing -ve deviation

### Solution with +ve deviation

Vapour pressure of solution is higher than expected  
→ Solute-solvent interaction is weak than solute-solute or solvent-solvent



e.g., hexane and ethanol

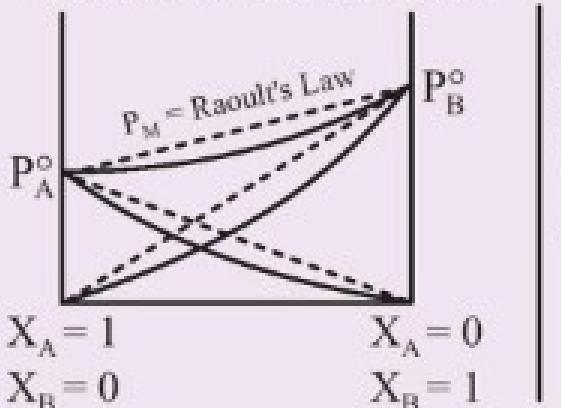
Hexane reduces inter molecular forces in ethanol

$$\Delta V_{\text{mixing}} = +ve \quad \Delta H_{\text{mixing}} = -ve$$

$$P_M (\text{observed}) > P_M (\text{expected})$$

### Solution with -ve deviation

Vapour pressure of solution is lesser than expected  
→ Solute-solvent interaction is stronger than solute-solute or solvent-solvent



Such solutions form maximum boiling Azeotropes

e.g., acetone and chloroform, develop attraction due to polarity

$$\Delta H_{\text{mixing}} = -ve \quad \Delta V_{\text{mixing}} = +ve$$

$$P_M (\text{Observed}) < P_M (\text{Raoult's Law})$$

## Solutions

### 18. Azeotropes

Constant boiling mixture

→ They cannot be separated by boiling

**Minimum Boiling Azeotropes** have boiling point of mixture lower than either of the component

Component	%Mass	Boiling Point		
		A	B	Azeotropes
$H_2O + C_2H_5OH$	95.97	373	351.3	351.2

Lower than either component ←

### Maximum Boiling Azeotropes

Boiling point of mixture is higher than either component

Component	Boiling Point		
	A	B	Azeotropes
$H_2O + HCl$	373	353	381.6
$H_2O + HNO_3$	373	359	393.5
Phenol + Aniline	455.2	457.4	459.2

### 19. Elevation in boiling point is directly proportional to molality

$$\Delta T_b = K_b \times \text{molality}$$

$$\Delta T_b = \frac{K_b \times w \times 1000}{m \times W};$$

$$\Delta T_f = \frac{K_f \times w \times 1000}{m \times W}$$

$\Delta T_f$  = depression in freezing point

$$K = \frac{RT^2}{1000L} = \frac{0.02T^2}{L \text{ (in cal)}}$$

$$K_b = \frac{RT_b^2}{1000L} \quad K_f = \frac{RT_f^2}{1000L_f}$$

$$\Delta H = L \cdot M \quad K_f = \frac{RT_f^2 \times M}{1000 \Delta H_f}$$

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad \Delta S_f = \frac{\Delta H_f}{T_f}$$

$$K_b = \frac{RT_b M}{1000 \Delta S_v} \quad K_f = \frac{RT_f M}{1000 \Delta S_f}$$

### 20. Abnormal colligative properties – (Dissociation)

Experimental C.P. > Normal C.P.

C.P.  $\propto$  molar mass

Experimental molar mass < normal molar mass

Experimental C.P.  $\propto$  number of particles after dissociation

Van't Hoff Factor (*i*)

$$\frac{\text{Exp C.P.}}{\text{Normal C.P.}} = \frac{\text{Normal Mass}}{\text{Exp Mass}} \propto \frac{i-1}{n-1}$$

*a* = degree of dissociation; *i* = Van't Hoff factor;

*n* = number of ions given by molecule

$$21. \text{Van't Hoff Coefficient} = (g) = \frac{i}{n}$$

In case of Association

Such solutes which associate in a solvent show a decrease in number of particles present in a solution

Experimental C.P. < Normal C.P.

Experimental Mass > Normal Mass

$$nA \rightleftharpoons (A)_n$$

$$t = 0 \quad 1 \quad 0$$

$$t = t' \quad 1 - \alpha \quad \alpha/n$$

$$\text{Particles after association} = 1 - \alpha + \left( \frac{\alpha}{n} \right)$$

$$\text{Van't Hoff Factor} = i = \left( 1 - \alpha + \frac{\alpha}{n} \right)$$

<b>1. E.M.F.</b>	<b>Cell Potential</b>	<b>Chemical Cell</b>	<b>Concentration Cell</b>	<b>6. Nernst Equation</b>
The potential difference between two electrodes when no current is flowing in the circuit is called e.m.f.  E.m.f. is the maximum voltage	The potential difference between two half cells when electric current flows through the emf cell is called cell potential  Cell potential is always less than maximum voltage	Net chemical change  $Zn   ZnSO_4 \parallel CuSO_4   Cu$  Anode = $Zn \rightarrow Zn^{+2} + 2e$ Cathode = $Cu^{+2} + 2e \rightarrow Cu$	No net change in composition of electrolyte  $M   M_{C_1}^+ \parallel M_{C_2}^+   M$  $M \rightarrow M_{C_1}^+ + e$  $M_{C_1}^+ + e \rightarrow M$  $M_{C_1}^+ \rightarrow M_{C_2}^+$	$M \rightleftharpoons M^{+n} + ne$  $E_{OP\ M/M^{+n}} = E_{OP} - \frac{0.059}{n} \log \frac{[M^{+n}]}{M}$  $H_2 \rightleftharpoons 2H^+ + 2e^-$  $E_{OP} = E_{OP} - \frac{0.059}{n} \log \frac{[H^+]^2}{p_{H_2}}$  E.m.f. of cell = $E_{OP} + E_{RP}$  $E = \frac{0.059}{n} \log K_e$ (or $K_p$ )  $E = E.m.f.; K_e = \text{equilibrium constant}$
<b>2. Electrolytic Cell</b>	<b>Electrochemical Cell</b>		Where $C_1$ and $C_2$ are concentrations of electrolyte of same metal. Cell will work only when $C_2 > C_1$	
Passage of current brings in chemical change  Electrical energy is converted into chemical energy	A chemical change bring in passage of current  Chemical energy is converted into electrical energy	Electrode having high standard oxidation potential works as anode	The electrode having more dilute solution works as anode	<p>7. Emf is additive for the process in which half reactions are added to yield an overall redox reaction</p> <p>8. Emf is not additive when half cell reactions yield a 3rd half cell reaction</p>

→ More the discharge potential of ion lesser is its tendency to get discharged. So during electrolysis of aq. NaCl, at cathode  $H_2$  will be released whereas  $Na^+$  will remain in ionic form

| **3. Rust is hydrated ferric oxide  $[Fe_2O_3 \cdot XH_2O]$** |
| **4. Faraday's Law of Electrolysis** |
| 1<sup>st</sup> Law :  $m = z \cdot I \cdot t$   $z$  = Electrochemical equivalent i.e. mas of substance deposited by one coulomb charge 1 Faraday Charge (F) = Charge on one mole of electron  $1.602 \times 10^{-19} \times 6.023 \times 10^{23} = 96500 \text{ C}$   $\frac{W}{E} = \frac{it}{96500}$   $W$  = Weight of atoms or ions deposited  $E$  = Equivalent weight of atoms or ions  $i$  = Current;  $t$  = Time in seconds |
| **5.  $M \rightleftharpoons M^{+n} + ne$** |
$\frac{M	M^{+n}}{\text{O.P.}} = \text{Positive}$	$M$  will have tendency to get oxidised
$\frac{M	M^{+n}}{\text{O.P.}} = \text{Negative}$	With negative value of oxidation potential   $M \rightarrow M^{+n}$  will not take place  $M^{+n} \rightarrow M$  will be favourable
	Element having higher positive oxidation potential will act as anode	
	Oxidation takes place at anode	
**9.  $E_3^o = \frac{n_1 E_1^o + n_2 E_2^o}{n_3}$**		
If  $n_1 = n_2 = n_3$		
$E_3^o = E_1^o + E_2^o$		
**10. Salt bridge is used to eliminate liquid junction potential or electrical double layer.**		
→ Salt bridge consists of semi solid paste of gelatin or Agar Agar saturated with an electrolyte  $KNO_3$ ,  $NH_4NO_3$  or  $KCl$		
→ Salt bridge is not needed if precipitate forms		
**11. Normal hydrogen electrode is known as primary reference electrode.**		
$Pt H_2 \text{ gas}	HCl \text{ at } 25^\circ C \quad E^o = 0$	
$1 \text{ bar} = a = 1$		
$H_2 \rightarrow 2H^+ + 2e$		

### A. Primary Cells cannot be recharged

e.g., Dry Cell, Mercury Cell, Leclanche Cell

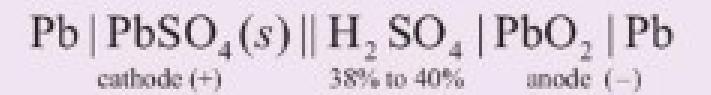


$\text{NH}_3$  formed is not liberated as a gas but combines with  $\text{Zn}^{+2}$  to form  $\text{Zn}(\text{NH}_3)_4^{+2}$

The emf of mercury cell is 1.35 V, so used in hearing aids and watches

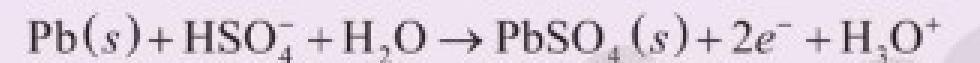
### B. Secondary Cells: Which can be recharged

e.g., Lead Storage Battery



#### Discharging

At anode



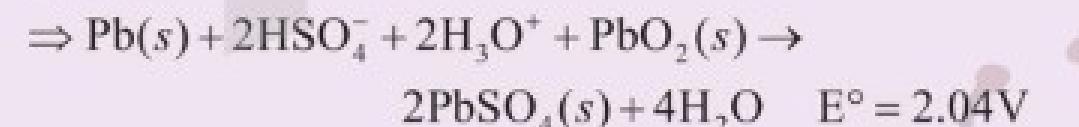
$$E_{\text{OP}} = +0.356\text{V}$$

At cathode

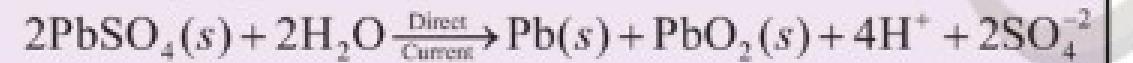


$$E_{\text{RP}} = +1.685\text{V}$$

Overall



#### Recharging



### 12. Fuel Cells



→ Fuel cells are more efficient (70% - 75%)

→ Do not cause pollution

→ High cost of fuel cell is a negative factor

### 14. Conductivity of Solutions

Conductivity (K)

$$K = \frac{1}{R} \cdot \frac{l}{a}$$

$\frac{1}{R}$  = Conductance

$\frac{l}{a}$  = Cell Constant

$$K = \text{S cm}^{-1}$$

Equivalent Conductivity

$$\Lambda_{\text{eq}} = \frac{K \times 1000}{N} \quad N = \text{Normality}$$

Molar Conductivity

$$\Lambda_m = \frac{K \times 1000}{M} \quad M = \text{Molarity}$$

$$\alpha = \frac{\pi_{\text{eq}}(V)}{\pi_{\text{eq}}(a)} \quad \alpha = \text{Degree of dissociation}$$

## Electrochemistry

### 13. Electrochemical Series

An electrochemical series is one in which elements are placed in order of their decreasing tendency to lose electron

→ It is measured in terms of O.P.

→ Higher the  $E_{\text{OP}}^\circ$ , easier to replace elements from their salts which are having lesser  $E_{\text{OP}}^\circ$

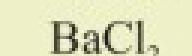
→ Change in oxidation number can cause different position for the same element in electrochemical series i.e.,

$\text{Fe}^{+2}$  has higher  $E_{\text{OP}}^\circ$  than H, whereas  $\text{Fe}^{+3}$  has lesser  $E_{\text{OP}}^\circ$  than H

### 15. Kohlrausch Law

Molar conductivity at infinite dilution is equal to the sum of ionic conductivities of its component ions at infinite dilution

$$\Lambda_{\text{electrolyte}}^\alpha = \lambda_{\text{cation}}^\alpha + \lambda_{\text{anion}}^\alpha$$



$$\Lambda_{\text{M BaCl}_2}^\alpha = \lambda_{\text{Ba}^{+2}}^\alpha + \lambda_{\text{Cl}^-}^\alpha$$

$$\Lambda_{\text{eq BaCl}_2}^\alpha = \frac{1}{2} \lambda_{\text{Ba}^{+2}}^\alpha + \lambda_{\text{Cl}^-}^\alpha$$

Transport number of cation

$$= \frac{\text{Current carried by cation}}{\text{Total current carried by cation and anion}}$$

## 1. Elementary Reactions

Those reactions which can take place in one step

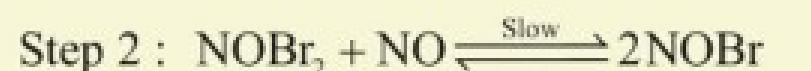
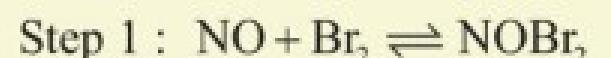
## 2. Complex Reactions

Those reactions which can take place in multiple steps, and slowest step is known as rate determining step

→ Write the rate expression for reaction



which is supposed to have the mechanism



Rate expression is derived by slowest step

$$\text{Rate} = K[\text{NOBr}_2][\text{NO}]$$

But  $\text{NOBr}_2$  is reaction intermediate, so it is not appearing in main reaction

$$K_c = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]} = [\text{NOBr}_2] = K_c[\text{NO}][\text{Br}_2]$$

$$R = K \cdot K_c [\text{NO}]^2 \cdot [\text{Br}_2]$$

$$R = K^1 [\text{NO}]^2 [\text{Br}_2]$$

## 3. Rate of Reaction



$$-\frac{1}{2} \frac{d}{dt} [\text{A}] = -\frac{d}{dt} [\text{B}] = \frac{1}{2} \frac{d}{dt} [\text{C}] = \frac{1}{3} \frac{d}{dt} [\text{D}]$$

## 4. Factors Affecting Rate of Reaction

- (a) Nature of reactant
- (b) Concentration of reactant
- (c) Catalyst
- (d) Temperature
- (e) Exposure to light

# Chemical Kinetics

## 5. Rate Constant

$K$  = Velocity constant or specific rate constant

$n\text{A} \rightarrow \text{Product}$

$$R = \frac{dX}{dt} = K[A]^n$$

Unit of rate constant depends on order of reaction

Variation of  $K$  with temperature is given by

Arrhenius equation

$$\frac{d}{dT} \ln K = \frac{E_a}{RT^2}$$

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

$$\ln K = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

$A$  = Integration constant

When graph is plotted between  $\ln K$  and  $1/T$ , a

straight line with slope  $= -\frac{E_a}{R}$  and intercept  $= \ln A$

$e^{\frac{-E_a}{RT}}$  = Boltzmann factor

$$= \frac{K_2}{K_1} = \frac{K_T + 10}{K_T}$$

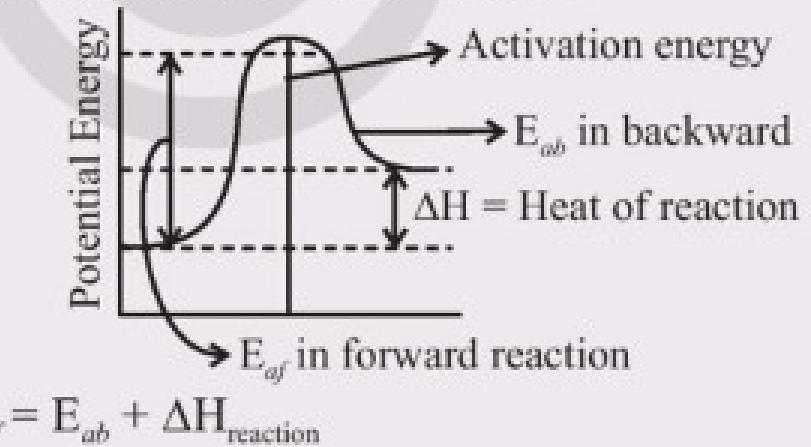
$\frac{K_2}{K_1}$  = Temperature coefficient when  
 $T_2 = 35^\circ\text{C}$ ,  $T_1 = 25^\circ\text{C}$

→ Larger the activation energy, smaller is the value of rate constant

→ When  $T = \infty$ ,  $K = Ae^0$ ,  $K = A$

→  $E_a = 0$ ,  $K = A$

6. Presence of catalyst lowers the activation energy both in forward and backward reaction



## 7. Molecularity

Number of reactants taking part in elementary step of a chemical reaction which collide simultaneously to bring the change as represented by a balanced chemical equation



Molecularity = 1



Molecularity = 3

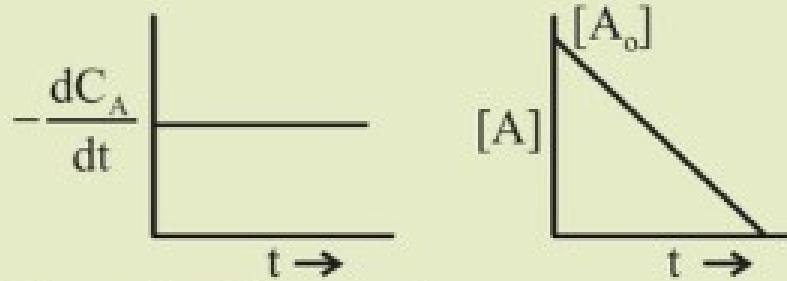
Molecularity  $\geq 3$  are rare

## 8. Order = Experimental Value

Zero - Order Reaction

$$A_0 - kt = 0, t = \frac{[A]_0}{K}$$

$$\frac{dx}{dt} = K[A]^0, dx = K dt, x = Kt$$



Example of zero-order

1. Decomposition of HI on gold surface
2. Reaction between H<sub>2</sub> and Br<sub>2</sub> to give HBr over water
3. Decomposition of gases on metal surface

1st Order Reaction

$$\frac{dx}{dt} = K(a-x) = t_2 = \frac{2.303}{K} \log \frac{[A]_0}{[A]}$$

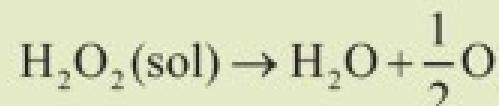
$$t_{1/2} = \frac{0.693}{K} \quad t_{1/2} = \text{Half life}$$

$$\text{The mass left in 'n' halves} = \frac{[A]_0}{2^n}$$

e.g., 1. Decomposition of N<sub>2</sub>O<sub>5</sub>



2. Decomposition of H<sub>2</sub>O<sub>2</sub>



4. Decomposition of azoisopropane

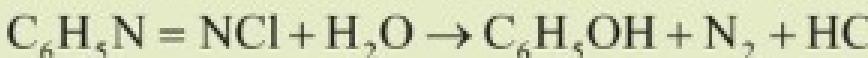


5. Hydrolysis of Ester



6. All radioactive decays

7. Decomposition of Benzene diazonium chloride



2nd Order Reaction

$$\frac{dx}{dt} = K(a-x)^2 \quad \frac{d[A]_t}{dt} = K[A]^2$$

$$\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}, \text{ for a graph plotted between } \frac{1}{[A]_t} \text{ vs } t,$$

gives a straight line with slope K and intercept  $\frac{1}{[A]_0}$

$$Kt_{1/2} = \frac{1}{[A]_0} \quad t_{1/2} \propto [A]_0^{-1}$$

## Chemical Kinetics

e.g., 1. Thermal decomposition of acetaldehyde



2. Saponification of an ester



3. Reaction between persulphate and iodide ion



4. Thermal decomposition of nitrous oxide



5. Thermal decomposition of NO<sub>2</sub>



6. Hydrogenation of C<sub>2</sub>H<sub>4</sub>



3rd Order Reaction

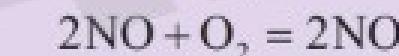
$$R = \frac{dx}{dt} = K[\text{reactant}]^3$$

$$\frac{dx}{dt} = K(a-x)^3$$

$$K = \frac{x \cdot (2a-x)}{t \cdot 2a^2 (a-x)^2}$$

$$Kt = \frac{3}{2a^2}$$

$$t_{1/2} = \frac{3}{2K[A]_0^2}$$



Order	Unit of K	t <sub>1/2</sub> Values
0	Mol Litre <sup>-1</sup> Time <sup>-1</sup>	t <sub>1/2</sub> = A <sub>0</sub> /2K
1	Time <sup>-1</sup>	t <sub>1/2</sub> = 0.693/K
2	Litre Mol <sup>-1</sup> Time <sup>-1</sup>	t <sub>1/2</sub> = 1/K
n <sup>th</sup>	(Litre) <sup>n-1</sup> Mol <sup>(1-n)</sup> Time <sup>-1</sup>	t <sub>1/2</sub> = [A] <sub>0</sub> <sup>(1-n)</sup>

Fractional Order Reaction

1. Reaction between H<sub>2</sub> and D<sub>2</sub>

$$r = K_{\text{PH}_2} (P_{\text{O}_2})^{1/2}$$

2. Conversion of para hydrogen into ortho hydrogen at high temperature

$$\text{Rate} = K_{(\text{PH}_2)^s}$$

3. Thermal decomposition of pure CH<sub>3</sub>CHO



$$\text{Rate} = K [\text{CH}_3\text{CHO}]^s$$

### Negative Order Reactions



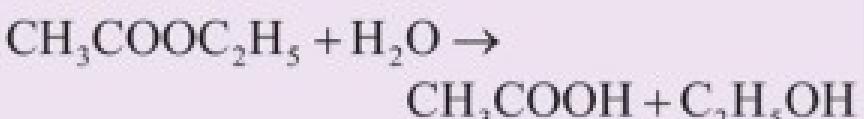
$$R = K[\text{O}_3]^{\frac{1}{2}}[\text{O}_2]^{\frac{1}{2}}$$

Overall positive, but w.r.t.  $\text{O}_2$ , it is a negative order reaction

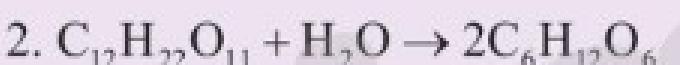
### 9. Pseudo Unimolecular Reactions

The reactions having molecularity  $\geq 2$ , but order is one

1. Hydrolysis of Ester



$$R = K[\text{Ester}]^1[\text{H}_2\text{O}]^0$$

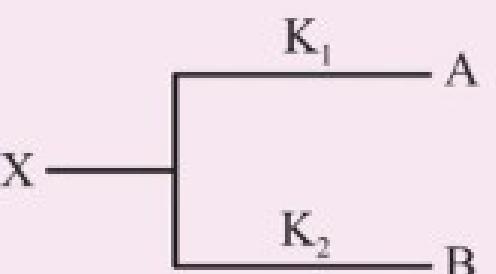


$$R = K[\text{Sugar}]^1[\text{H}_2\text{O}]^0$$

Molecularity = 2, Order = 1

### 10. Parallel Reaction

Some reaction undergo chemical changes following 2 or more different path to yield 2 or more products



$$K_{\text{avg}} = K_1 + K_2$$

$$K_{\text{avg}} \times \text{Fractional Yield of A} = K_1$$

$$K_{\text{avg}} \times \text{Fractional Yield of B} = K_2$$

### Collision Theory

- All collisions do not lead to chemical reactions
- There must a threshold energy associated with colliding molecule to bring change
- Threshold energy and proper orientation during collision leads to product formation
- Activation energy = Threshold energy – Energy of colliding molecules
- Energy of activated complex is higher than that of reactants and products
- The rate of photo chemical reaction is  $K \times I_{\text{abs}}$

## Chemical Kinetics

### Chemiluminescence

It is the emission of light as a result of chemical reaction at ordinary temperature  
e.g., Glow worms

### Fluorescence

Some substances when exposed to light or radiation, absorb light and immediately start re-emitting the energy  
e.g.,  $\text{CaF}_2$

### Phosphorescence

There are some substances which continue to glow for some time even after the source of light is cut off  
e.g.,  $\text{ZnS}$

**A.**

Physical Adsorption	Chemical Adsorption
Reactant molecules are absorbed on surface by weak vander Waal's force	Reactant molecules are absorbed by free valencies
Reversible with temp usually occurs at low temp	Irreversible with temp at high temp
Weak, multilayer non directional and non specific	Strong unilayer directional and specific
Exothermic; about 20-40 kJ/mole heat is given out	Exothermic; about 80-100 kJ/mole heat is given out
Does not require activation energy	Requires activation energy

Adsorption	Absorption
Binding of molecule to a surface	Uptake of molecules into interior of another substance
H <sub>2</sub> O is adsorbed in silica gel	H <sub>2</sub> O is absorbed in CaCl <sub>2</sub>
For adsorption, ΔG = -ve ΔH = -ve (Exothermic) ΔS = -ve because adsorption of gaseous molecule on the surface is in more ordered manner	

**B. Adsorption of Gases on Solids**

- Nature of adsorbent - Transition metals are good adsorbents for gases because of vacant or half filled d-orbitals and high charge/size ratio
  - Activated charcoal
  - Metal oxides like silica gel and aluminium oxide, clay etc.
- Nature of adsorbate - Easily liquefiable gases  
eg, HCl, NH<sub>3</sub> are absorbed to greater extent than others i.e., H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>

**C. Freundlich Adsorption**

$$\frac{X}{m} = Kp^{1/n}$$

1. At Low Pressure

$$\frac{X}{m} \propto p$$

2. At Very High Pressure

$$\frac{X}{m} = Kp^\circ \quad \text{Independent of pressure}$$

3. At Moderate Range of Pressure

$$\frac{X}{m} = Kp^{1/n}$$

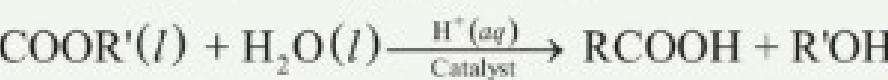
$$\log \frac{X}{m} = \log K + \frac{1}{n} \log p$$

**Surface Chemistry****D. Application of Adsorption**

- Gas mask
- To create high vacuum by charcoal
- Used in chromatography

**E. Homogeneous Catalyst**

When reactant and catalyst are in same physical state

**F. Heterogeneous Catalyst**

When reactants and catalyst have different physical state

**G. Negative Catalyst**Acetanilide or glycerine or H<sub>3</sub>PO<sub>4</sub> act as negative catalyst because

- they retard the rate of reaction (decomposition of H<sub>2</sub>O<sub>2</sub>)
- the oxidation of benzaldehyde to benzoic acid is retarded by diphenylamine

**H. Catalytic Poisoning**

The phenomenon in which presence of foreign substance even in small amounts decreases or ruins the activity of catalyst

eg,

- CO acts as poison for Fe in Haber's process  
BaSO<sub>4</sub> acts as poison for Pd in Rosenmund's reaction

**I. Autocatalysis**

The phenomenon in which either of the product formed during reaction acts as catalyst for the reaction

eg,

- The colour of KMnO<sub>4</sub> disappears slowly on treating it with oxalic acid but becomes faster after some time due to formation of Mn<sup>+2</sup>, which acts as auto catalyst
- The decomposition of HNO<sub>3</sub> by Cu is autocatalyzed by NO<sub>2</sub>

# Surface Chemistry

## J. Catalytic Promoter

The phenomenon in which presence of a foreign substance in small amount increases the activity of catalyst

eg,

Mo acts as promoter for Fe in Haber's process  
 Cu and Te acts as promoter for Ni in the Hydrogenation of oil  
 HCl or H<sub>2</sub>O acts as promoter for AlCl<sub>3</sub> in the decomposition of Paraffins

## K. Enzyme Catalysis

1. Highly specific in nature
2. Enzyme catalyzed reactions are normally hydrolytic in nature
3. Enzyme catalyzed reaction - takes place with release of gases
4. Need optimum pH

### Co-enzyme or activations

The activity of enzyme is increased in the presence of non protein or metal ion etc.

## L. Inhibitors

Non protein or metal ion which is present in enzyme which reduces the activity of enzyme

### Induced Catalyst

Ability to influence the rate of other reaction which does not occur under ordinary condition

eg,

The reduction of HgCl<sub>2</sub> by oxalic acid is slow but becomes faster if reduction is made in mixture of KMnO<sub>4</sub> and HgCl<sub>2</sub> where both are reduced, reduction of KMnO<sub>4</sub> induces the reduction of HgCl<sub>2</sub>

## M.

Properties	Lyophilic Solutions	Lyophobic Solutions
Nature	D.P. has more affinity for D.M.	Less affinity for D.M.
Preparation	Solutions are formed by intermixing	Specific methods are needed
Concentration of solution	More concentration of D.P. in Solution	Less concentration of D.P. in Solution
Stability	More stable	Less stable
Viscosity	More viscous than D.M.	Same as D.M.
Surface tension	Much lesser than D.M.	Same as D.M.
Reversibility	Reversible with temp	Irreversible
Charge	Charge on solution particle depends upon pH of solution	Independent of pH
Tyndall Effect	Less scattering	More scattering
Solvation	Higher degree of solvation	Lower degree of solvation
True Solution	Colloidal solution	Suspension
Size 1 m $\mu$ to 10A°	Size of D.P. 1 m $\mu$ to 200 m $\mu$	- 200 m $\mu$

DM is water = Hydrosols  
 DM is alcohol = Alcosols  
 DM is benzene = Benzosols  
 DM is air = Aerosols

## N. Preparation of Colloidal Solutions (Lyophobic)

**Peptization :** The phenomenon of converting fresh precipitate into colloidal solution by the action of solute or solvent

The solute or solvent used in this process is known as peptizing agent

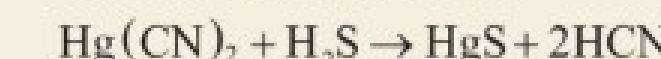
eg, Freshly precipitated Fe(OH)<sub>3</sub> is passed in colloidal state by the action of FeCl<sub>3</sub> (aq)

## O. Bredig Arc Method

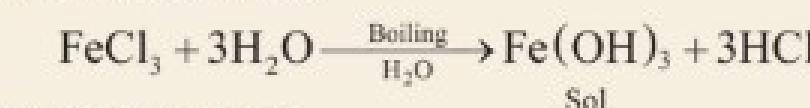
Purple of cassius is obtained by this method  
 By condensation



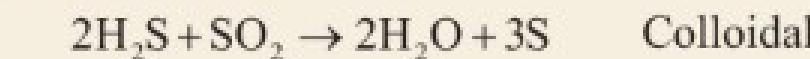
## P. Double Decomposition



## Q. Hydrolysis



## R. Oxidation



## S. Reduction



## T. Physical Properties of Collidal Solution

1. Heterogeneity
2. Diffusibility
3. Filterability
4. Non-setting Nature
5. Viscosity and Surface Tension

## U. Tyndall Effect

Based on scattering of light  $\propto \frac{1}{\lambda^4}$  larger the dispersed phase particle, more will be the scattering

## V. Application of Tyndall Effect

1. Blue colour of sky and sea water
2. Visibility of tails of comets
3. Twinkling of stars
4. Visibility of sharp ray of sunlight entering through a slit in dark room

### Brownian Motion

- Smaller the particle, the more rapid is the movement
- This movement increases with increase in temp
- Origin of charge on sol

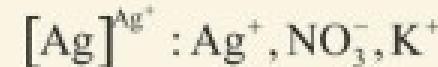
1. Due to friction between D.P. and D.M.
2. Due to electron captured by sol particle
3. Nature of dispersed phase  
i.e.,



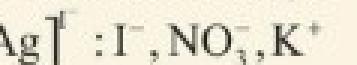
Undergoes aggregation to form sol particles, thus charge is negative

### 4. Preferential ion adsorption theory

Addition of KI drop by drop to dilute solution of  $\text{AgNO}_3$ , give rise to +ve solution of  $\text{AgI}$



If  $\text{AgNO}_3$  is added drop by drop in KI solution, it gives rise to -ve solution of  $\text{AgI}$



## W. Zeeta Potential

The potential difference set up across the surface of two oppositely charged layers just in contact with each other is known as electro kinetic potential or zeeta potential

## X. Cataphoresis or Electrophoresis

Migration of colloidal particle under the influence of electrical field

Solution particles carry charge and thus move towards opposite electrodes

# Surface Chemistry

## Y. Electro-osmosis

The movement of D.M. under the influence of electrical field when the D.P. are prevented from moving is known as electro-osmosis

**Coagulation** : The separation of D.M. and D.P. or destabilisation of solution is known as ageing

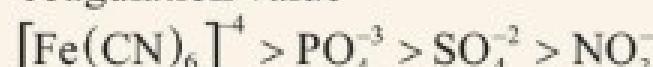
## Z. Cataphoresis

Colloidal particles under the influence of electric field move to opposite electrode

## A1. Hardy-Schulze Rule

Coagulation of solution by opposite ion

- Greater is the valence of effective ion, more is its coagulating power
- Higher is the coagulating power, lesser is the coagulation value



Coagulation power for +ve solution

## B1. Gold Number

Min mass of lyophilic substance in milligram, which prevents the coagulation of 10 ml gold solution against 1 ml of 10% NaCl

More is the gold number less is the protective power of lyophilic colloidal solution

## C1. Application of Coagulation

1. Removal of smoke from air by cottrell's precipitator
2. Sewage water disposal
3. Delta formation
4. Artificial rain
5.  $\text{FeCl}_3$  stops bleeding from cut

## D1. Emulsion

For dispersion of liquid droplets in mother liquid, the two liquid should be immiscible

Type of Emulsion

**Water in oil** : W/O i.e. butter cream

**Oil in Water** : O/W i.e. milk can be diluted with  $\text{H}_2\text{O}$

## E1. Emulsifying Agent

Emulgents/Emulsifiers are used to stabilize the emulsion

**Gels** : Liquid dispersing in solid i.e. curd, jelly

**Liquid rich gels** are known as Jellies

## F1. Non-Elastic Gels

Irreversible, on dehydration changes into powder form and cannot be regenerated into gels on addition of water

**Elastic gels** : Reversible

**Weeping of gels** : Spontaneous outcome of internal liquid without disturbing gel structure

## G1. Swelling

Gels on keeping in contact with their d.p. take in considerable amount of it and swell up

## H1. Kraft Temperature

It is the min temp above which miscelles formation takes place

## I1. Surfactants

The property to lower the surface tension of liquid