THERMODYNAMICS

The word thermodynamics implies flow of heat. Thermodynamics is **the study of the relations between heat, work, temperature, and energy**. The laws of thermodynamics describe how the energy in a system changes.

The term **thermodynamics** is derived from Greek word, **`Thermos'** meaning heat and **`dynamics'** meaning flow. Thermodynamics deals with the inter-relationship between heat and work.

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation.

Chemical thermodynamics is the study of the interrelation of heat and work with chemical reactions.

Different Branches of Thermodynamics

Thermodynamics is classified into the following four branches:

- **Classical Thermodynamics**
- **Statistical Thermodynamics**
- **Chemical Thermodynamics**
- **Equilibrium Thermodynamics**

Classical Thermodynamics

In classical thermodynamics, the behaviour of matter is analyzed with a macroscopic approach. Units such as temperature and pressure are taken into consideration, which helps the individuals calculate other properties and predict the characteristics of the matter undergoing the process.

Statistical Thermodynamics

In statistical thermodynamics, every molecule is under the spotlight, i.e. the properties of every molecule and how they interact are taken into consideration to characterize the behaviour of a group of molecules.

Chemical Thermodynamics

Chemical thermodynamics is the study of how work and heat relate to each other in chemical reactions and changes of states.

Equilibrium Thermodynamics

Equilibrium thermodynamics is the study of transformations of energy and matter as they approach the state of equilibrium.

Laws of Thermodynamics

There are four laws of thermodynamics and are given below:

- **Zeroth law of thermodynamics**
- **First law of thermodynamics**
- **Second law of thermodynamics**
- **Third law of thermodynamics**

Zeroth Law of Thermodynamics

The Zeroth law of thermodynamics states that if two bodies are individually in equilibrium with a separate third body, then the first two bodies are also in thermal equilibrium with each other.
This means that if system A is in thermal equilibrium with system C and system B is also in equilibrium with system C, then system A and B are also in thermal equilibrium.

First Law of Thermodynamics

First law of thermodynamics, also known as the law of conservation of energy, states that energy can neither be created nor destroyed, but it can be changed from one form to another.

Second Law of Thermodynamics

The second law of thermodynamics says that the entropy of any isolated system always increases.

Third Law of Thermodynamics

Third law of thermodynamics states that the entropy of a system approaches a constant value as the temperature approaches absolute zero.

Macroscopic system and its properties: If as system contains a large number of chemical species such as atoms, ions, and molecules, it is called macroscopic system.

Extensive properties: These properties depend upon the quantity of matter contained in the system. Examples are; mass, volume, heat capacity, internal energy, enthalpy, entropy, Gibb's free energy.

Intensive properties: These properties depend only upon the amount of the substance present in the system, for example, temperature, refractive index, density, surface tension, specific heat, freezing point, and boiling point.

Endothermic process is a process where heat is absorbed from the surroundings.

Exothermic process is a process where heat is released to the surroundings.

The System and the Surroundings

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.

The universe = the system + the surroundings

Types of the System

We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System

In an open system, there is exchange of energy and matter between system and surroundings.

2. Closed System

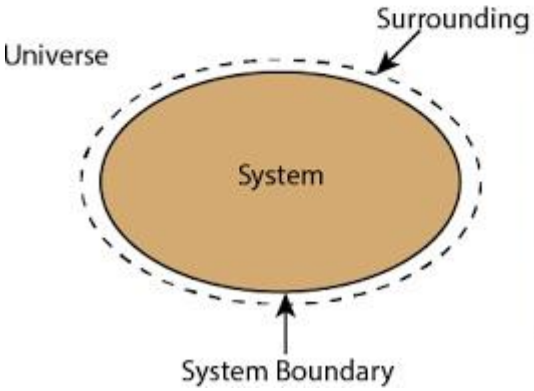
In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.

3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings.

Thermodynamic System

Open system	**Closed system**	**Isolated system**
Mass transfer (yes)	Mass transfer (yes)	Mass transfer (No)
Heat transfer (yes)	Heat transfer (No)	Heat transfer (No)



The Four Types of Thermodynamic Processes

The four types of thermodynamic process are isobaric, isochoric, isothermal and adiabatic.

- Isobaric process in which the pressure (P) is kept constant ($\Delta P = 0$).
- Isochoric process in which the volume (V) is kept constant ($\Delta V = 0$).
- Isothermal process in which the temperature (T) is kept constant ($\Delta T = 0$).
- Adiabatic process in which the heat transfer is zero ($Q=0$).

Concepts of Partial molar properties

1. Partial molar properties are defined as the properties which are the quantities change with number of moles.
2. Several extensive properties like volume, free energy, enthalpy, entropy depends on number of mole.

Partial molar volume and its significance

Eg 1) 100ml H_2O + 10ml H_2O = 110ml volume.

Eg 2) 10,000 ml MeOH + 18 ml H_2O = 10,018 ml actual volume but experimental volume is 10,014 ml.

In eg (1) there are no molecular interactions because both are a water molecule that’s why volume is not changed.

In eg (2) actual volume is 10,018 ml but experimentally it gives 10,014 ml only because methanol and water both are different molecules. So some molecular interactions are there that’s why gives 10,014 ml.

This change in volume in binary system is called Partial molar volume.

- G. N. Lewis introduces a new property X which is defined as function of temperature, pressure and number of moles.
- $X = f(T, P \text{ and } n_1, n_2)$

Taking partial differentiation on both sides

$$dx = \left(\frac{\partial x}{\partial T}\right)_{P,\, n1,n2,\, \ldots..ni} dT + \left(\frac{\partial x}{\partial P}\right)_{T,\, n1,\, n2\ldots ni} dP + \left(\frac{\partial x}{\partial n1}\right)_{T,P,\, n2,n3...ni} dn_1 + \left(\frac{\partial x}{\partial n2}\right)_{T,P,n1,n3,\ldots.ni} dn_2$$

We know that $(\frac{\partial x}{\partial n1})_{T, P, n2, n3..,ni} = X_1$ and $(\frac{\partial x}{\partial n2})_{T, P, n1} = X_2$

Then

$dx = (\frac{\partial x}{\partial T})_{P, n1,n2, ...ni} dT + (\frac{\partial x}{\partial P})_{T, n1, n2...ni} dP + X_1 dn_1 + X_2 dn_2$

At constant temperature and pressure, i.e. dT= 0 and dP= 0

Then $dX= X_1 dn_1 + X_2 dn_2$

Integration on both sides

$\int dx = \int X1\, dn1 + \int X2\, dn2$

$\int dx = X_1 \int dn1 + X_2 \int dn2$

$X = X_1 n_1 + X_2 n_2$

The above equation represents the partial molar properties of binary system.

If the system having I components then the above equation changes to

$X = X_1 n_1 + X_2 n_2 + X_3 n_3 + X_4 n_4 + \ldots\ldots.. + X_i n_i$

Significance of Partial molar properties:

1. Partial molar properties always measures for binary system only.
2. The sum of products of number of moles and partial molar property equal to thermodynamic property.

Partial molar volume $V = V_1 n_1 + V_2 n_2$

Partial molar energy $E = E_1 n_1 + E_2 n_2$

Partial molar Gibbs free energy $G = G_1 n_1 + G_2 n_2$.

Determination of Partial molar properties:

Partial molar properties are determined by 3 methods.

1. Graphical method
2. Intercept method
3. Apparent molar volume method

1. Graphical method:

According to definition of partial molar properties

$\left(\frac{\partial x}{\partial ni}\right) = X_{\mathrm{i}}$ (I = 1, 2, 3, ….i)

For binary system X = $X_1 n_1 + X_2 n_2$

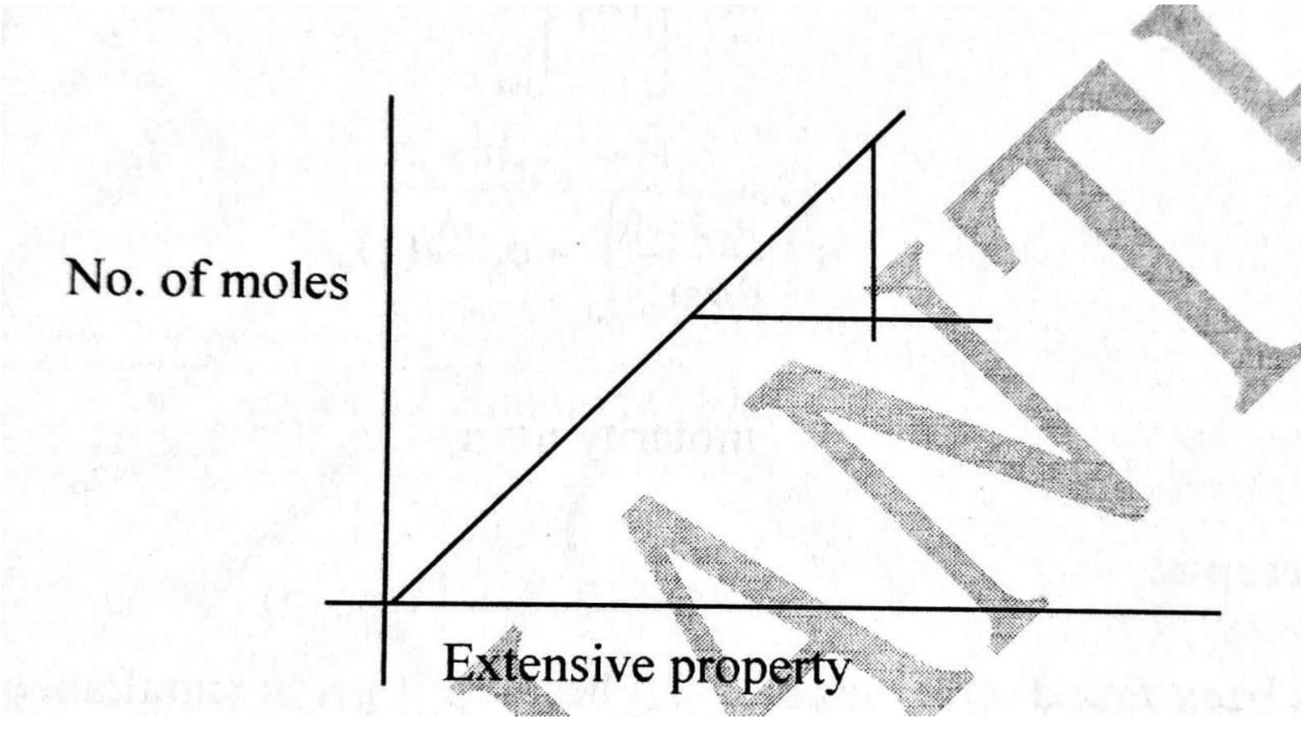
Where x = any extensive property

n_1, n_2 = number of moles of components 1 & 2

X_1, X_2 = partial molar properties of components 1 & 2

For the experimental determination of X_1, take differentiation of X w.r.t. to n_1

- $dx/dn_1 = X_1\, dn_1/\, dn_1 + X_2\, dn_2/dn_1$
- $dx/dn1 = X_1 + 0$,
- this equation in the form of y = mx + c



Limitation: This method is not of much use as the exact slope cannot be determined.

2. Intercept method:

The method of intercept is more useful because we can measure the partial molar quantities of both components in a binary system.

- This method gives more accurate values of partial molar quantities.
- For this method a new property, mean molar property of solution (x). This is definded as extensive property of solution divided by total number of moles in a system.

Mathematically it is represented as $x = X / n_1 + n_2$

$$x\,(n_1 + n_2) = X$$

Differentiating w.r.t. to n_2 at constant n_1

$[\frac{d}{dn2}\left(x\,(n1\ +\ n2)\right)]_{n1} = [dx/dn_2]_{n1}$ [we know $d/dx\,(uv) = u\,dv/dx + v\,du/dx$]

$x\,\frac{d}{dn2}(n1\ +\ n2) + (n1\ +\ n2)\frac{dx}{dn2} = [dx/dn_2]_{n1}$

$x\,(0 + 1) + (n1\ +\ n2)\frac{dx}{dn2} = [dx/dn_2]_{n1}$

$x + (n1\ +\ n2)\frac{dx}{dn2} = X_2$ -------------------- (1)

Mole fraction of component 1 is $N_1 = n_1/ n1\ +\ n2$ ---------- (2)

Take differentiation on both sides w.r.t. to n_2 at constant n_1

$(dN_1/dn_2)_{n1} = d/dn_2\,(n_1/ (n_1 + n_2))_{n1}$

$= n_1\, d/dn_2\,[(n_1+n_2)^{-1}]_{n1}$ [since $\frac{d}{dx}X^n = n\,x^{n-1}$]

$= n_1\,[-1/ (n_1 + n_2)^2]_{n1}$

$[dN_1/dn_2]_{n1} = [- n_1/(n_1 + n_2).\ 1/ (n_1 + n_2)]_{n1}$ -------------- (3)

substitude eq (2) in eq (3), we get

$[dN_1/dn_2]_{n1} = [-N_1.\ 1/ (n_1 + n_2)]_{n1}$

$[n_1 + n_2/ dn_2]_{n1} = [- N_1 / dN_1]_{n1}$

Take differentiation with x

$[dx/dn_2\ (n_1+n_2)]_{n1} = [-N_1\ dx/dN_1\ ]_{n1}$ -----------------(4)

Substitute eq (4) in eq (1), we get

- $x + [-N_1\ dx/dN_1]_{n1} = X_2$
- $x - N_1\ [dx/dN_1]_{n1} = X_2$

$x = X_2 + N_1\ [dx/dN_1]_{n1}$

3. Apparent molar volume method:

- Suppose X be the value of any extensive property for a mixing of n_1 moles of component 1 and n_2 moles of component 2.
- X_1 is the value of property per mole of pure component 1.then the apparent molar value can be represented by ϕ_x of component 2.

Mathematically it can be represented as

- $x = n_1X_1 + n_2X_2$
- $x = n_1X_1 + n_2\phi_X$
- $x - n_1X_1 = n_2\phi_X$
- differentiating w.r.t to n_2
- $\frac{d}{dn2}(x-n_1X_1) = \frac{d}{dn2}(n_2\ \phi_X)$
- $\frac{dx}{dn2} - X_1\ \frac{dn1}{dn2} = n_2\ \frac{d\emptyset x}{dn2} + \phi_x\ \frac{dn2}{dn2}$
- $\frac{dx}{dn2} - 0 = n_2\ \frac{d\emptyset x}{dn2} + \phi_x$
- $\frac{dx}{dn2} = m\ \frac{d\emptyset x}{dm} + \phi_x$
- $\frac{dx}{dn2} = \frac{d}{dm}(\phi_x\ m)$
- $X_2 = \frac{d}{dm}(\phi_x\ m)$
- $X_2\ dm = d\ (\phi_x\ m)$
- Integration on both sides with suitable limits
- $\int_0^m x2\ dm = \int_0^m d\ (\phi x\ m)$
- $\int_0^m x2\ dm = \phi_x\ m$
- $\frac{1}{m}\int_0^m x2\ dm = \phi_x$

Chemical Potential:

1. The amount of change in free energy is known as chemical potential.

2. It is denoted by μ i.e. $\frac{\partial G}{\partial ni}$ = $G_i = \mu_i$
3. Chemical potential is also known as partial molar free energy.
4. Chemical potential is an intensive property.
5. According to definition of partial molar property

$$G = f (T, P, n_1, n_2)$$

Differentiating on both sides

$$dG = (\frac{\partial G}{\partial T})_{P, n1, n2}\, dT + (\frac{\partial G}{\partial P})_{T, n1, n2}\, dP + (\frac{\partial G}{\partial n1})_{T, P, n2}\, dn_1 + (\frac{\partial G}{\partial n2})_{T, P, n1}\, dn_2$$

We know that $(\frac{\partial G}{\partial n1})_{T, P, n2} = G_1 = \mu_1$

$(\frac{\partial G}{\partial n2})_{T, P, n1} = G_2 = \mu_2$ then we get

$$dG = (\frac{\partial G}{\partial T})_{P, n1, n2}\, dT + (\frac{\partial G}{\partial P})_{T, n1, n2}\, dP + \mu_1\, dn_1 + \mu_2\, dn_2$$

At constant temperature and pressure, dT=0 and dP =0 then we get

$dG = \mu_1\, dn_1 + \mu_2\, dn_2$ ---------for binary system

$dG = \mu_1\, dn_1 + \mu_2\, dn_2 +$ -------------- $+ \mu_i\, dn_i$ -------for I component system

This is the mathematical representation of chemical potential.

Variation chemical potential with Temperature:

According to 2nd law of thermodynamics

$$dG = VdP – SdT$$

At constant pressure (dP = 0)

$$dG = - SdT$$

Differentiating w.r.t. to temperature

$$\frac{\partial G}{\partial T} = - S \frac{\partial T}{\partial T}$$

$$\frac{\partial G}{\partial T} = - S$$

Differentiating w.r.t. to n_i

$\partial^2 G / \partial T \partial n_i = - S_i$ ------------- (1)

According to definition of chemical potential

$\frac{\partial G}{\partial ni} = \mu_i$

Differentiating w.r.t. to temperature

$\partial^2 G / \partial T \partial n_i = \frac{\partial \mu i}{\partial T}$ --------- (2)

Compare eq (1) and eq(2), we get

$\frac{\partial \mu i}{\partial T} = -S_i$

Where S_i = partial molar entropy of i components.

Variation chemical potential with Pressure:

According to 2nd law of thermodynamics

dG = VdP – SdT

At constant temparature (dT = 0)

dG = VdP

Differentiating w.r.t. to pressure

$$\frac{\partial G}{\partial P} = V \frac{\partial P}{\partial P}$$

$$\frac{\partial G}{\partial P} = V$$

Differentiating w.r.t. to n_i

$$\frac{\partial 2G}{\partial P \partial ni} = \frac{\partial V}{\partial ni}$$

$\frac{\partial 2G}{\partial P \partial ni} = V_i$ --------- (1)

According to definition of chemical potential

$\frac{\partial G}{\partial ni} = \mu_i$

Differentiating w.r.t. to pressure

$\frac{\partial 2G}{\partial P \partial ni} = \frac{\partial \mu i}{\partial P}$ ------- (2)

Compare eq(1) and eq(2), we get

$\frac{\partial \mu i}{\partial P} = V_i$

Where V_i = partial molar volume of i components.

<u>Gibbs – Duhem equation and its significance:</u>

Gibbs – Duhem equation describes the relationship b/w changes in chemical potential for component in a thermodynamic system.

According to definition of partial molar property

$$G = f(T, P, n_1, n_2)$$

Differentiating on both sides

$dG = (\frac{\partial G}{\partial T})_{P, n1, n2}\, dT + (\frac{\partial G}{\partial P})_{T, n1, n2}\, dP + (\frac{\partial G}{\partial n1})_{T, P, n2}\, dn_1 + (\frac{\partial G}{\partial n2})_{T, P, n1}\, dn_2$

We know that $(\frac{\partial G}{\partial n1})_{T, P, n2} = G_1 = \mu_1$

$(\frac{\partial G}{\partial n2})_{T, P, n1} = G_2 = \mu_2$ then we get

$dG = (\frac{\partial G}{\partial T})_{P, n1, n2}\, dT + (\frac{\partial G}{\partial P})_{T, n1, n2}\, dP + \mu_1\, dn_1 + \mu_2\, dn_2$

At constant temperature and pressure, dT=0 and dP =0 then we get

$dG = \mu_1\, dn_1 + \mu_2\, dn_2$ ---------for binary system

$dG = \mu_1\, dn_1 + \mu_2\, dn_2 +$ -------------- $+ \mu_i\, dn_i$ -------for I component system ------(1)

Integration on both sides

$\int dG = \int \mu 1\, dn1 + \int \mu 2\, dn2 +$ ------------ $+ \int \mu i\, dni$

$\int dG = \mu_1 \int dn1 + \mu_2 \int dn2 +$ ------------ $+ \mu_i \int dni$

$G = \mu_1 n_1 + \mu_2 n_2 +$ --------- $+ \mu_i n_i$

Take differentiation on both sides

$dG = (\mu_1\, dn_1 + \mu_2\, dn_2 + \text{-------------} + \mu_i\, dn_i) + (n_1\, d\mu_1 + n_2\, d\mu_2 + \text{-----} + n_i\, d\mu_i)$ ----(2)

Compare eq(1) and eq(2), we get

$(\mu_1\, dn_1 + \mu_2\, dn_2 + \text{--} + \mu_i\, dn_i) = (\mu_1\, dn_1 + \mu_2\, dn_2 + \text{--} + \mu_i\, dn_i) + (n_1\, d\mu_1 + n_2\, d\mu_2 + \text{-} + n_i\, d\mu_i)$

$0 = n_1\, d\mu_1 + n_2\, d\mu_2 + \text{-----} + n_i\, d\mu_i$

$0 = \sum_0^i ni\ d\mu i$

This is the Gibbs - Duhem equation.

Significance:

- Gibbs – Duhem equation is helpful in calculating the partial molar quantities of binary system.
- Gibbs – Duhem equation cannot be used for small thermodynamic system.
- Ti is also helpful in calculating the partial vapour pressure of a system.

SOLUTIONS

Solution is defined as homogeneous mixture of two or more components.

- In a solution the component which is having large proportion is called **solvent**.
- In a solution the component which is having small proportion is called **solute**.

Ideal solutions: a solution of two or more substances is said to be ideal, if it obeys Raoults law at all temperatures and concentrations.

- Ex: benzene + toluene
- n-hexane + n-heptane
- Chlorobenzene and Bromobenzene
- Ethyl Bromide and Ethyl Iodide

Non ideal solutions: a solution of two or more substances is said to be non ideal, if it does not obeys Raoults law at all temperatures and concentrations.

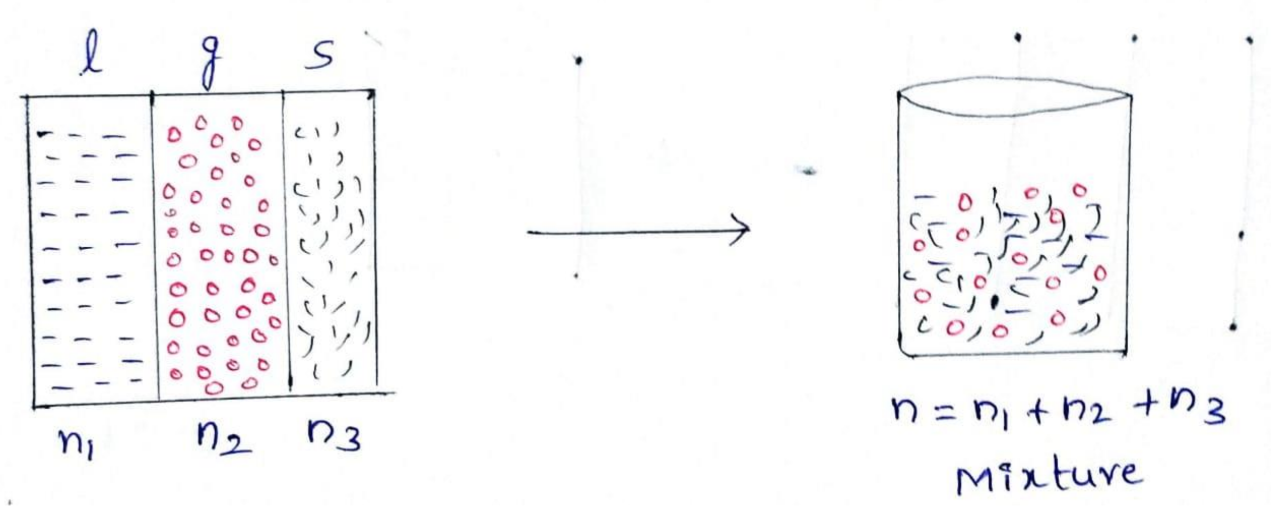
- Ex: water + ethanol
- Chloroform and Benzene (negative deviation from raoults law)
- Acetone and Benzene (positive deviation from raoults law)

Thermodynamic properties of ideal solutions mixing quantities:

When two or more substances are mixed there occurs a change in measurable properties of components always takes place spontaneously.

1. Free Energy Mixing of Ideal Gases:

The formation of mixture from the pure components always takes place spontaneously.



Let us consider a vessel with three compartments and each compartment contains pure substance.

For the pure substance free energies are written as

- $n_1\mu_1 = G_1$
- $n_2\mu_2 = G_2$
- $n_3\mu_3 = G_3$

Where n_1, n_2, n_3 = Number of moles of components 1, 2, 3.

μ_1, μ_2, μ_3 = chemical potentials of components 1, 2, 3.

For initial free energy is $G_{initial} = G_1 + G_2 + G_3$

$G_{initial} = n_1\mu_1 \text{ (Pure)} + n_2\mu_2 \text{ (Pure)} + n_3\mu_3 \text{ (Pure)}$

$G_{final} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3$

Change in free energy for mixing

$\Delta G_{mixing} = G_{final} - G_{initial}$

$\Delta G_{mixing} = (n_1\mu_1 + n_2\mu_2 + n_3\mu_3) - (n_1\mu_1 \text{ (Pure)} + n_2\mu_2 \text{ (Pure)} + n_3\mu_3 \text{ (Pure)})$

$\Delta G_{mixing} = n_1 (\mu_1 - \mu_1 \text{ pure}) + n_2 (\mu_2 - \mu_2 \text{ pure}) + n_3 (\mu_3 - \mu_3 \text{ pure})$ -------- (1)

We know that $\mu_i = \mu_i^0 + RT \ln X_i$

$\mu_i - \mu_i^0 = RT \ln X_i$

$\mu_1 - \mu_1^0 = RT \ln X_1$

$\mu_2 - \mu_2^0 = RT \ln X_2$

$\mu_3 - \mu_3^0 = RT \ln X_3$

Where μ_1^0, μ_2^0, μ_3^0 = chemical potentials of pure components.

Substitute the above values in eq(1), we get

$\Delta G_{mixing} = n_1 (RT \ln X_1) + n_2 (RT \ln X_2) + n_3 (RT \ln X_3)$

$\Delta G_{mixing} = RT [n_1 \ln X_1 + n_2 \ln X_2 + n_3 \ln X_3]$ ---------- (2)

According to definition of mole fraction $x_i = \frac{ni}{N}$

$n_i = x_i N$

- $n_1 = x_1 N$
- $n_2 = x_2 N$
- $n_3 = x_3 N$

Substitute the above values in eq(2), we get

$\Delta G_{mixing} = RT [x_1 N \ln X_1 + x_2 N \ln X_2 + x_3 N \ln X_3]$
$\Delta G_{mixing} = NRT [x_1 \ln X_1 + x_2 \ln X_2 + x_3 \ln X_3]$
$\Delta G_{mixing} = NRT [\sum_0^i xi \ln xi]$

2. Entropy mixing of ideal gases:

We know that $\Delta G_m = G_f - G_i$

According to second law of thermodynamics $dG = VdP - SdT$

At constant pressure dP=0

Then dG = - SdT

Differentiating w.r.t. to temperature

$\frac{\partial G}{\partial T}$ = - S $\frac{\partial T}{\partial T}$

$\frac{\partial G}{\partial T}$ = - S ------- (1)

$\frac{\partial G1}{\partial T}$ = - S_1 ------ (2) Initial

$\frac{\partial G2}{\partial T}$ = - S_2 ---- (3) Final

(3) – (2) $\frac{\partial G2}{\partial T} - \frac{\partial G1}{\partial T}$ = - S_2 + S_1

$\frac{\partial}{\partial T}$ (G_2-G_1) = - (S_2-S_1)

$\frac{\partial}{\partial T}$ (ΔG) = - ΔS

For mixing $\frac{\partial}{\partial T}$($\Delta G_{mix}$) = -$\Delta S_{mix}$

We know that ΔG_{mix} = NRT [$\sum_0^i xi \ln xi$]

$\frac{\partial}{\partial T}$ NRT [$\sum_0^i xi \ln xi$] = -ΔS_{mix}

NR $\sum_0^i xi \ln xi$ = -ΔS_{mix}

ΔS_{mix} = - NR $\sum_0^i xi \ln xi$

This above equation represents the entropy mixing of ideal gases.

3. Enthalpy mixing of ideal gases:

We know that ΔG = ΔH - TΔS

For mixing $\Delta G_m = \Delta H_m - T\Delta S_m$

$\Delta H_m = \Delta G_m + T\Delta S_m$

$$\Delta H_m = NRT\ [\ \sum_0^i xi \ln xi] - NRT\ [\ \sum_0^i xi \ln xi] = 0.$$

❃⁑*Vapor – Pressure Raoults Law

Lowering of vapor pressure: The difference between vapor pressure of pure solvent (P_0) and vapor pressure solution (P_s) is called lowering of vapor pressure.

Vapor pressure of pure solvent = P_0

Vapor pressure of solution = P_s

Lowering of vapor pressure = $P_0 - P_s$

Relative Lowering of vapor pressure: The ratio between lowering of vapor pressure ($P_0 - P_s$) and vapor pressure of pure solvent (P_0) is called relative lowering of vapor pressure.

Relative Lowering of vapor pressure = $\frac{P0 - Ps}{P0}$

Statement: The relative lowering of vapor pressure of a solution is equal to mole fraction of Non volatile solute is called Raoults Law.

Mathematically Raoults law can be represented by

$$\frac{P0 - Ps}{P0} = X_2$$

Where P_0 = Vapor pressure of pure solvent

P_s = Vapor pressure of solution

X_2 = Mole fraction of Non volatile solute

Proof: By the definition of chemical potential $\mu_i = \mu_i^0 + RT \ln X_i$

Chemical potential of solution phase $\mu_1(liq) = \mu_1^0\ (liq) + RT \ln X_1$ ------ (1)

Chemical potential of vapor phase $\mu_1(g) = \mu_1^0\ (g) + RT \ln P_s$ ------ (2)

At equilibrium chemical potential of solution phase and vapor phase must be equal.

$\mu_1(liq) = \mu_1(g)$

$\mu_1^0\ (liq) + RT \ln X_1 = \mu_1^0\ (g) + RT \ln P_s$ $\qquad \because X_1 + X_2 = 1 \rightarrow X_1 = 1 - X_2$

μ_1^0 (liq) + RT ln (1 – X_2) = μ_1^0 (g) + RT ln P_s -------- (3)

When X_2 = 0 and P = P_0

Then μ_1^0 (liq) + RT ln (1 – 0) = μ_1^0 (g) + RT ln P_0

μ_1^0 (liq) + RT ln (1) = μ_1^0 (g) + RT ln P_0

μ_1^0 (liq) + 0 = μ_1^0 (g) + RT ln P_0

μ_1^0 (liq) = μ_1^0 (g) + RT ln P_0 -------- (4)

(3) - (4) μ_1^0 (liq) + RT ln (1 – X_2) - μ_1^0 (liq) = μ_1^0 (g) + RT ln P_s - μ_1^0 (g) + RT ln P_0

RT ln (1 – X_2) = RT ln P_s - RT ln P_0

RT ln (1 – X_2) = RT (ln P_s - ln P_0)

ln (1 – X_2) = ln P_s - ln P_0

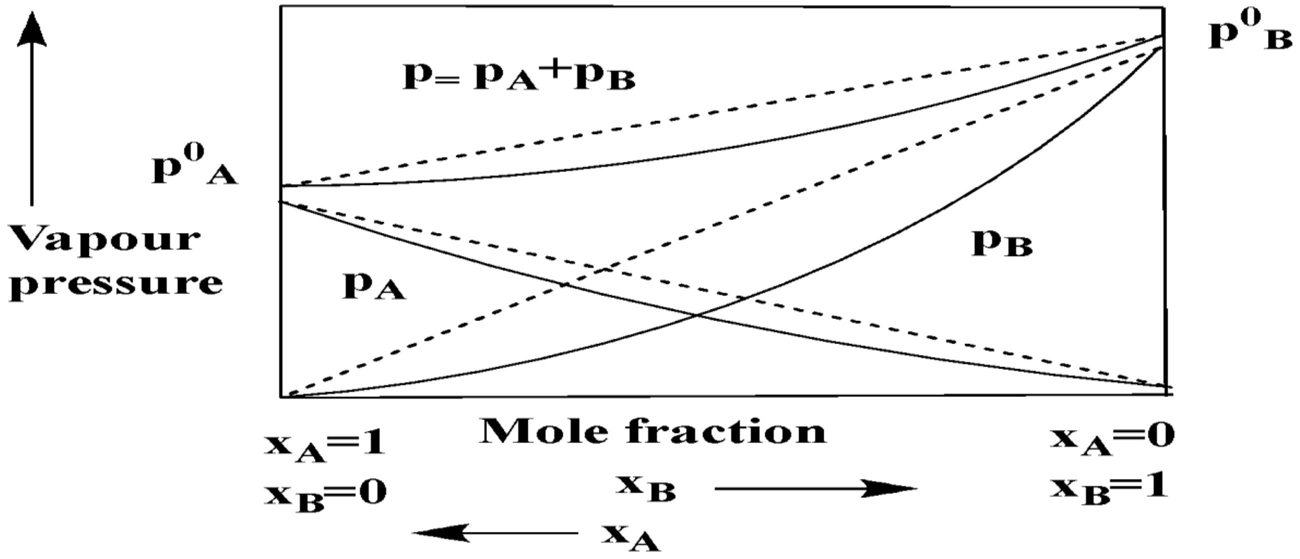
ln (1 – X_2) = ln $(\frac{Ps}{Po})$

$1 - X_2 = \frac{Ps}{P0}$

$1 - \frac{Ps}{P0} = X_2$

$\frac{P0 - Ps}{P0} = X2$

Graphical Representation:



⁂⁎❁⁎**Vapor-Pressure Henrys Law**

The solubility of a gas in a liquid is directly proportional to pressure of the gas. It is called Henrys law.

(OR)

The mass of gas dissolved in a given liquid at constant temperature is directly proportional to pressure of the gas it is called Henrys law.

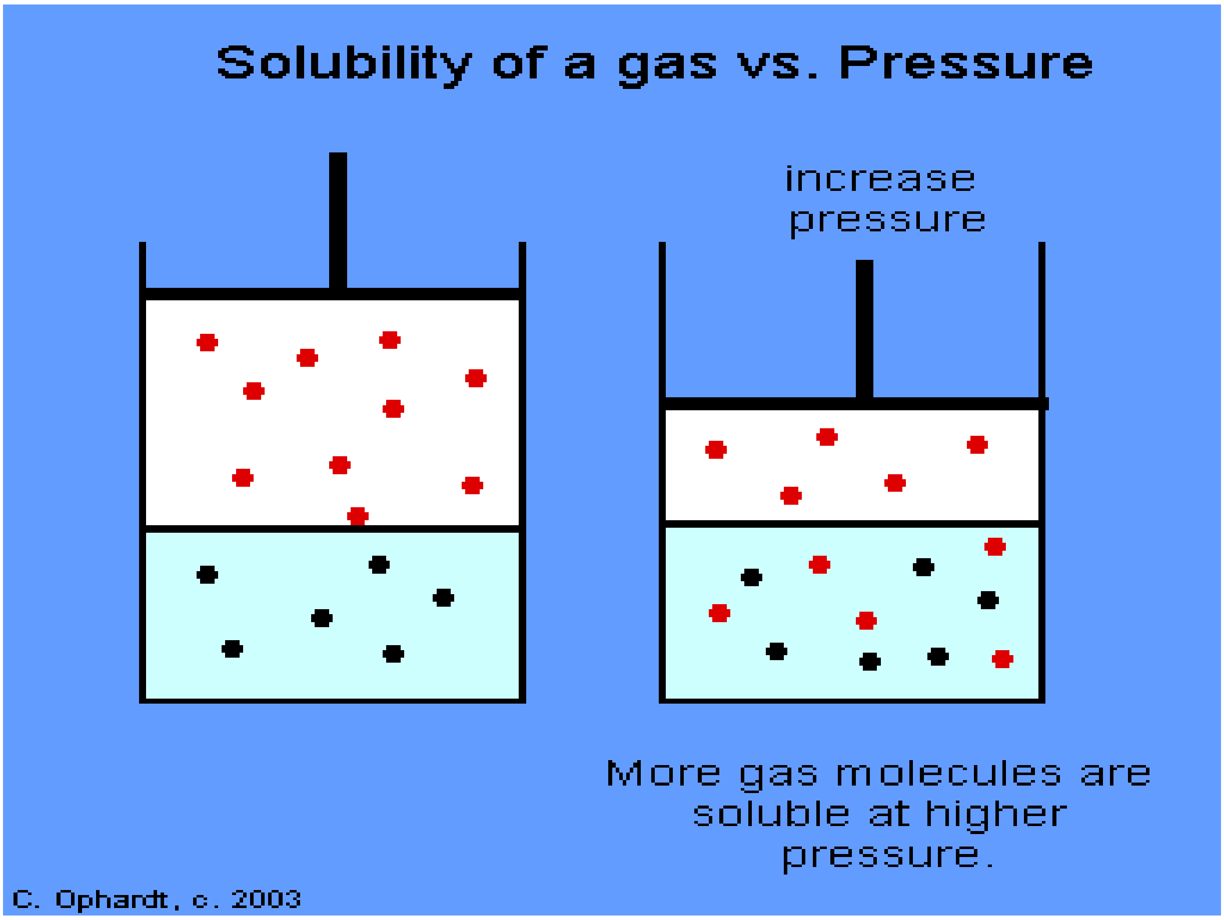
$$M \propto P$$

$$M = KP$$

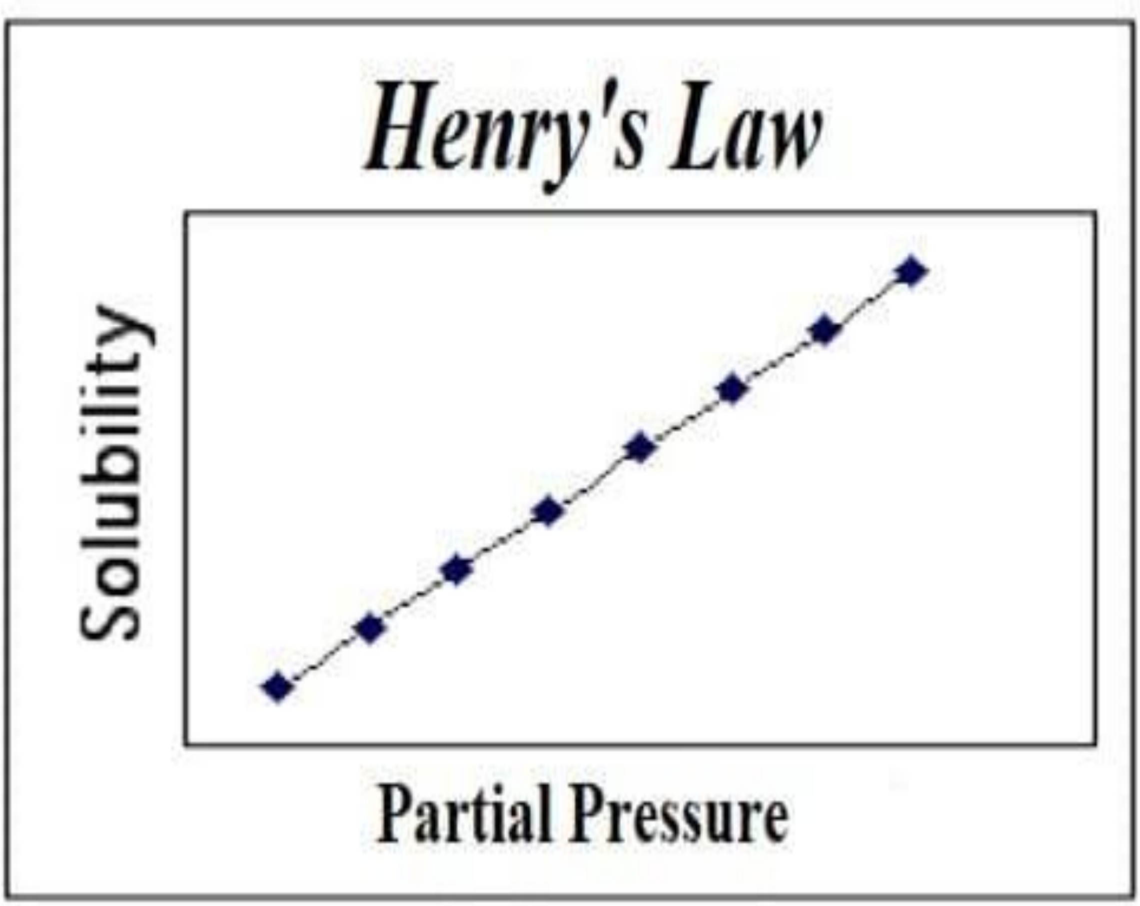
Where K= Henrys constant

M = mass of the gas

P = pressure of the gas



If Henrys law is valid, graph is drawn between solubility of gas v/s pressure of the gas at constant temperature should be a straight line.



Limitations:

→This law is valid for the following conditions.

1. Temperature should be constant throughout the experiment.

2. Pressure is not too low.

3. Gas is not highly soluble.

4. The gas does not disassociate in solvent.

Ex (1): Henrys law is valid for the solubility of HCl and NH_3 in Benzene because both gases are sparingly soluble.

Ex (2): Henrys law is not valid for the solubility of HCl and NH_3 in water because both gases are highly soluble in nature.

Non-ideal solutions

Concept of Fugacity

Fugacity and Fugacity coefficient:

We know that dG = VdP - SdT

At constant Temperature dG = VdP ---------- (1)

For ideal gas PV = nRT

For 1 mole of ideal gas PV = RT

$$V = \frac{RT}{P} \quad \text{--------- (2)}$$

From equations (1) and (2) $dG = \frac{RT}{P}\ dP$

Integrate w.r.t. to Pressure with suitable limits

$$dG = RT\ \int_{P1}^{P2} dP/P \quad \text{---------- (3)}$$

This equation is not applicable to incase of gases in order to remove this difficulty Lewis introduced a new function fugacity (f).

→Fugacity does not depend on the nature of the gas.

→Fugacity is not a physical property.

⁂ P = f

$$dG = RT\ \int_{f1}^{f2} df/f$$

$$dG = RT\ lnf$$

Significance of fugacity (or) fugacity coefficient:

In general the fugacity of real gas is related to its pressure by an equation

Fugacity α P

$f \alpha\ p$

$$f = \emptyset\, p$$

$$\frac{f}{p} = \emptyset$$

Where $\emptyset = fugacity\ coefficient$

Determination of Fugacity:

Fugacity is determined by the following methods

1. Graphical method

2. Approximation calculation method

1. Graphical method:

We know that fugacity of real gas dG = RT ln f -------- (1)

From ideal gas equation dG = VdP - SdT

At constant Temperature dG = VdP ---------- (2)

From equations (1) and (2) RT ln f = VdP -------- (3)

In case of real gases a new function (α) is defined as

$$\alpha = \frac{RT}{P} - V$$

Where α = constant over a range of pressure which are not too high

$$V = \frac{RT}{P} - \alpha \quad \text{------- (4)}$$

Substitute eq (4) in eq (3) $RT \ln f = (\frac{RT}{P} - \alpha)\, dP$

$$RT \ln f = \frac{RT}{P} dP - \alpha\, dP$$

Integrate w.r.t to Pressure $RT \ln f = RT \int_0^P \frac{dP}{P} - \int_0^P \alpha\, dP$

$$RT \ln f = RT\ [\int_0^P \frac{dP}{P} - \frac{1}{RT} \int_0^P \alpha\, dP]$$

$$\ln f = \ln P - \frac{1}{RT}\int_0^P \alpha \, dP$$

$$\ln f - \ln P = -\frac{1}{RT}\int_0^P \alpha \, dP$$

$$\ln \frac{f}{p} = -\frac{1}{RT}\int_0^P \alpha \, dP$$

To know the value of fugacity we should know the value of $\int_0^P \alpha \, dP$.

→A graph is drawn between $\frac{\alpha}{RT}$ v/s P.

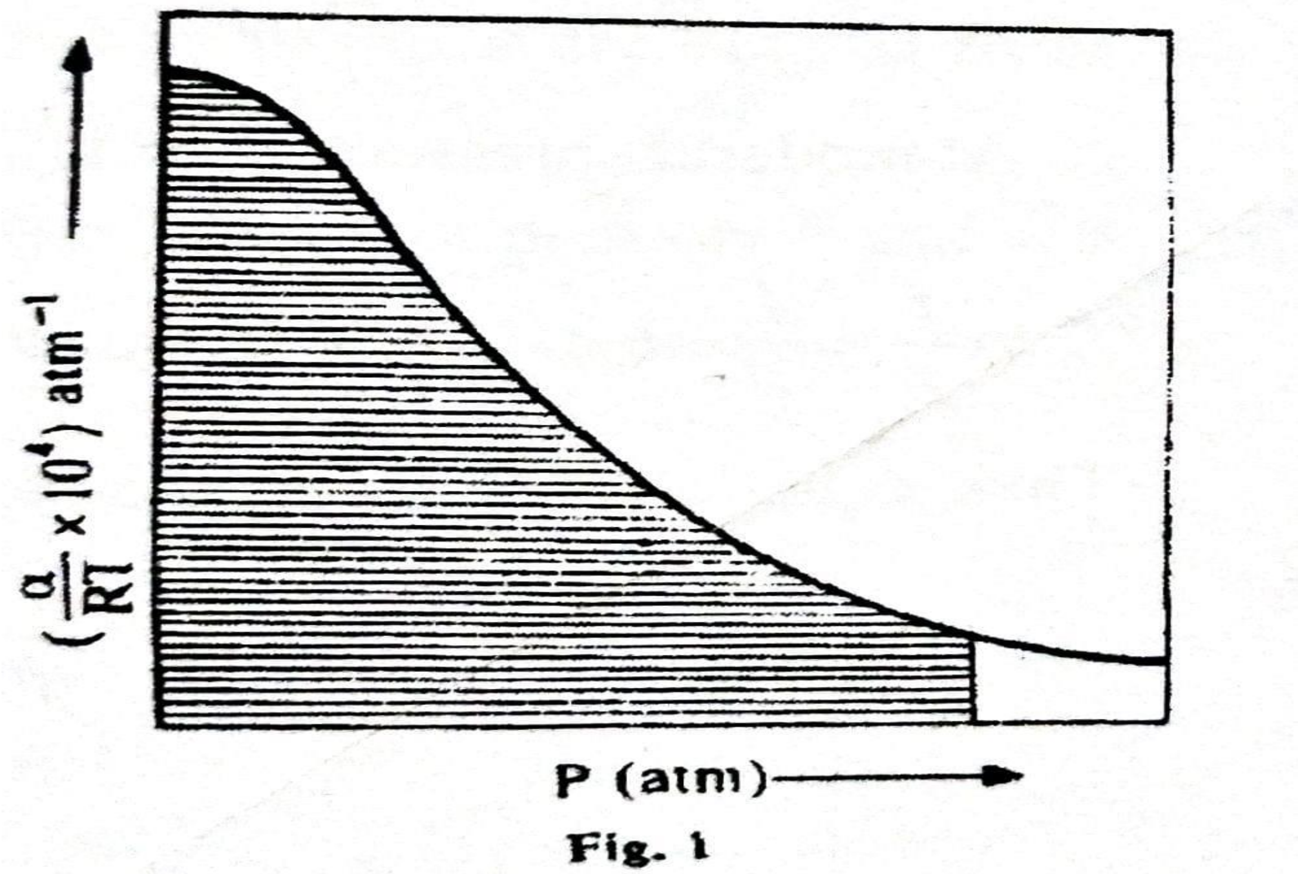


Fig. 1

The area under the curve gives the value of $\int_0^P \alpha \, dP$.

From this value we can calculate the fugacity.

2. Approximation Calculation method:

According to the definition of fugacity

$$\ln\frac{f}{P} = -\frac{1}{RT}\int_0^P \alpha\, dP$$

→α is a constant over a range of pressure which is not too high.

$$\ln\frac{f}{P} = -\frac{\alpha}{RT}\int_0^P dP$$

$$\ln\frac{f}{P} = -\frac{\alpha}{RT}P \text{ ----- (1)}$$

For moderate pressure $\frac{f}{P} = 1$ ∵ when X→ 1

$\ln\frac{f}{P} = \frac{f}{P} - 1$ ------ (2) ln X = X-1

Compare eq(1) and eq(2) $\frac{f}{P} - 1 = -\frac{\alpha P}{RT}$ -------- (3)

We know that $\alpha = \frac{RT}{P} - V$ --------- (4)

Substitute eq(4) in eq(3) $\frac{f}{P} - 1 = -\frac{\frac{RT}{P} - V}{RT} P$

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

$$\frac{f}{P} - 1 = -\frac{RT}{RT} + \frac{PV}{RT}$$

$$\frac{f}{P} - 1 = -1 + \frac{PV}{RT}$$

$$\frac{f}{P} = \frac{PV}{RT}$$

$$f = P^2V/RT$$

From this we can calculate the accurate value of fugacity.

Activity and Activity Coefficient:

Activity term is used to replace concentration term in non ideal solutions.

For ideal solution $\mu_i = \mu_i^0 + RT \ln X_i$ ---------- (1)

μ_i = chemical potential of ith component for ideal gas

X_i = mole fraction of ith component for ideal solution

For Non ideal solution $\mu_i = \mu_i^0 + RT \ln a_i$ --------- (2)

μ_i = chemical potential of ith component for non ideal solution

a_i = activity of ith component for non ideal solution

Compare eq (1) and eq (2) $a_i \alpha x_i$

$$a_i = \gamma x_i$$

Where γ = activity coefficient

For ideal solutions $\gamma = 1$

$$1 = \frac{ai}{xi}$$

$\rightarrow a_i = x_i$

For non ideal solutions $\gamma < 1$ or $\gamma > 1$.

Determination of activity coefficient

1. Determination of activity coefficient from vapor pressure measurements:

I. Activity of solvent:

P_1 = let the vapor pressure of solvent

P_1^0 = vapor pressure of pure solvent

Suppose the vapor pressures are not too high know pressure is replaced by fugacity

$P_1/P_1^0 = f_1/f_1^0 = \gamma$

Hence the activity of solvent in a solution can be easily determined by knowing the values of P_1 & P_1^0.

II. Activity of solute:

If the solute is volatile its activity may be calculated as similar to activity of solvent.

If the solute is Non volatile activity of solute is calculated by the following procedure.

Activity = activity X Pressure

$\rightarrow a = \gamma P$

$\rightarrow a \propto P$

From this equation we can calculate the activity of solute from vapor pressure measurements.

2. by using Gibbs-Duhem equation:

This method is more accurate method to determine the activity of solution.

For binary compounds $n_1\, d\mu_1 + n_2\, d\mu_2 = 0$ -------- (1)

Where n_1, n_2 = number of moles of components 1 & 2.

μ_1, μ_2 = chemical potential of components 1 & 2.

According to chemical potential $\mu_1 = \mu_1^0 + RT \ln a_1$

$$\mu_2 = \mu_2^0 + RT \ln a_2$$

Where a_1, a_2 are activities of two components.

Differentiating w.r.t. to a

$\rightarrow d\mu_1 = 0 + RT\, d \ln a_1$ and $d\mu_2 = 0 + RT\, d \ln a_2$

$\rightarrow d\mu_1 = RT\, d \ln a_1$ and $d\mu_2 = RT\, d \ln a_2$ ----------- (2)

Substitute eq (2) in eq (1)

$\rightarrow n_1 (RT d\ln a_1) + n_2 (RT d\ln a_2) = 0$

$\rightarrow RT (n_1 d\ln a_1 + n_2 d\ln a_2) = 0$

→ $n_1 d\ln a_1 + n_2 d\ln a_2 = 0$

→ $n_1 d\ln a_1 = - n_2 d\ln a_2$

→$\frac{n1}{n2} = -\frac{dlna2}{dlna1}$

→$\frac{n1}{n2} = -\frac{lna2}{lna1}$

CHEMICAL EQUILIBRIUM

⁎ What is Chemical Equilibrium and write the characteristics of chemical equilibrium?

In a chemical reaction chemical equilibrium is the state in which concentrations of reactants and products must be equal.

Ex: $aA + bB \leftrightarrow cC + dD$

Where a, b, c, d are staichometry coefficients.

A, B are reactants and C, D are products.

$$rate\ of\ reaction = \frac{products}{reactants}$$

Rate of reaction = $[C]^c [D]^d / [A]^a [B]^b$

Characteristics of chemical equilibrium:

→Chemical equilibrium is also known as dynamic equilibrium.

→Chemical equilibrium is represented as K_c.

→Chemical equilibrium is formed only in closed vessel.

→At chemical equilibrium catalyst is not affected.

→At chemical equilibrium ΔG^0, $\Delta S = 0$.

❁⁂ Effect of Temperature on equilibrium constant – Van,t Hoff equation

Vant hoff equation is the combination of Gibbs – Helmholtz equation and Vant hoff isotherm equation.

We know that by the definition of free energy G = H – TS

When a small change is considered ΔG = ΔH - TΔS -------- (1)

We know that dG = VdP – SdT

At constant Pressure dP = 0

Then dG = - SdT

Differentiating w.r.t. to Temperature $\left(\frac{dG}{dT}\right) = -s\frac{dT}{dT}$

$$\left(\frac{dG}{dT}\right) = -s$$

Initial state $\frac{dG1}{dT} = -S1$ ----- (2)

Final state $\frac{dG2}{dT} = -S2$ ----- (3)

Eq (2) – Eq (3)

$$\frac{dG2}{dT} - \frac{dG1}{dT} = -S2 - (-S1)$$

$$\frac{d}{dT}(G2 - G1) = -(S2 - S1)$$

$\frac{d}{dT}(\Delta G) = -\Delta S$ ------ (4)

Substitute eq (4) in eq (1)

$$\Delta G = \Delta H - T(-\frac{d}{dT}\Delta G)$$

$$\Delta G = \Delta H + T\ \frac{d}{dT}\ \Delta G$$

This is known as Gibbs Helmholtz equation.

According to Vant Hoff isotherm equation

→$\Delta G = -RT\ln K$

→$\ln K = -\frac{1}{R}\left(\frac{\Delta G}{T}\right)$

Differentiating w.r.t. to Temperature

→$\frac{d}{dT} lnK = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta G}{T}\right)$ ------- (5)

We know that $\Delta G = \Delta H - T\Delta S$

Dividing with T

→$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$

Differentiating w.r.t. to Temperature

$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = -\Delta H/T^2 + 0$ -------- (6)

Substitute eq (6) in eq (5)

→$\frac{d}{dT} lnK = -\frac{1}{R}(-\Delta H/T^2)$

$$\boxed{\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (4)}$$

→Equation 4 is known as differential form of van't Hoff equation.

→On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2.

$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta H^\circ}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$[\ln K]_{K_1}^{K_2} = \frac{\Delta H^\circ}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

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

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{T_2-T_1}{T_2T_1}\right]$$

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\left[\frac{T_2-T_1}{T_2T_1}\right] \quad \text{............ (5)}$$

Equation 5 is known as integrated form of van’t Hoff equation.

Phase equilibrium – Derivation of Phase rule from the concept of Chemical Potential

The phase rule describes the possible number of degrees of freedom in an enclosed system at equilibrium, in terms of the number of separate phases and the number of chemical constituents in the system. It was deduced by J.W Gibbs in the 1870s. Today, the phase rule is popularly known as the Gibbs phase rule all over the world. Here, in the article, we will be discussing the derivation of phase rule.

Gibbs Phase Rule

Gibbs phase rule states that if the equilibrium in a heterogeneous system is not affected by gravity or by electrical and magnetic forces, the number of degree of freedom is given by the equation

F=C-P+2

Where C is the number of chemical components

P is the number of phases

Basically, it describes the mathematical relationship for determining the stability of phases present in the material at equilibrium condition.

In the next section, let us look at the phase rule derivation.

Phase Rule Derivation

The Gibb's phase rule on the basis of the thermodynamic rule can be derived as follows:

First, let us consider a heterogeneous system consisting of P_n number of phases and C_n number of components in equilibrium. Let us assume that the passage of a component from one phase to another doesn't involve any chemical reaction. When the system is in equilibrium, it can be described by the following parameters:

- Temperature
- Pressure
- The composition of each phase

a. The total number of variables required to specify the state of the system is:

- Pressure: same for all phases
- Temperature: same for all phases
- Concentration

The independent concentration variables for one phase with respect to the C components are C – 1. Therefore, the independent concentration variables for P phases with respect to C components are P (C – 1).

Total number of variables = P (C – 1) + 2 (1)

b. The total number of equilibria:

The various phases present in the system can only remain in equilibrium when the chemical potential (μ) of each of the component is the same in all phases, i.e.

$\mu_1, P_1 =$	$\mu_1, P_2 =$	$\mu_1, P_3 =$	…	=	μ_1, P
$\mu_2, P_1 =$	$\mu_2, P_2 =$	$\mu_2, P_3 =$	…	=	μ_2, P
:	:	:			:
:	:	:			:
:	:	:			:
$\mu_C, P_1 =$	$\mu_C, P_2 =$	$\mu_C, P_3 =$	…	=	μ_C, P

The number of equilibria for each P phases for each component is P – 1.

For C components, the number of equilibria for P phases is P (C – 1).

Hence, the total number of equilibria involved is E = C (P – 1). (2)

Equating eq (1) and (2), we get

$F = [P(C-1) + 2 - C] - [C(P-1)]$

$F = [CP - P + 2 - CP + C]$

$F = C - P + 2$

The obtained formula is the Gibbs phase rule.

THERMODYNAMICS

The word thermodynamics implies flow of heat. Thermodynamics is **the study of the relations between heat, work, temperature, and energy**. The laws of thermodynamics describe how the energy in a system changes.

The term **thermodynamics** is derived from Greek word, **`Thermos'** meaning heat and **`dynamics'** meaning flow. Thermodynamics deals with the inter-relationship between heat and work.

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation.

Chemical thermodynamics is the study of the interrelation of heat and work with chemical reactions.

Different Branches of Thermodynamics

Thermodynamics is classified into the following four branches:

- **Classical Thermodynamics**
- **Statistical Thermodynamics**
- **Chemical Thermodynamics**
- **Equilibrium Thermodynamics**

Classical Thermodynamics

In classical thermodynamics, the behaviour of matter is analyzed with a macroscopic approach. Units such as temperature and pressure are taken into consideration, which helps the individuals calculate other properties and predict the characteristics of the matter undergoing the process.

Statistical Thermodynamics

In statistical thermodynamics, every molecule is under the spotlight, i.e. the properties of every molecule and how they interact are taken into consideration to characterize the behaviour of a group of molecules.

Chemical Thermodynamics

Chemical thermodynamics is the study of how work and heat relate to each other in chemical reactions and changes of states.

Equilibrium Thermodynamics

Equilibrium thermodynamics is the study of transformations of energy and matter as they approach the state of equilibrium.

Laws of Thermodynamics

There are four laws of thermodynamics and are given below:

- **Zeroth law of thermodynamics**
- **First law of thermodynamics**
- **Second law of thermodynamics**
- **Third law of thermodynamics**

Zeroth Law of Thermodynamics

The Zeroth law of thermodynamics states that if two bodies are individually in equilibrium with a separate third body, then the first two bodies are also in thermal equilibrium with each other.
This means that if system A is in thermal equilibrium with system C and system B is also in equilibrium with system C, then system A and B are also in thermal equilibrium.

First Law of Thermodynamics

First law of thermodynamics, also known as the law of conservation of energy, states that energy can neither be created nor destroyed, but it can be changed from one form to another.

Second Law of Thermodynamics

The second law of thermodynamics says that the entropy of any isolated system always increases.

Third Law of Thermodynamics

Third law of thermodynamics states that the entropy of a system approaches a constant value as the temperature approaches absolute zero.

Macroscopic system and its properties: If as system contains a large number of chemical species such as atoms, ions, and molecules, it is called macroscopic system.

Extensive properties: These properties depend upon the quantity of matter contained in the system. Examples are; mass, volume, heat capacity, internal energy, enthalpy, entropy, Gibb's free energy.

Intensive properties: These properties depend only upon the amount of the substance present in the system, for example, temperature, refractive index, density, surface tension, specific heat, freezing point, and boiling point.

Endothermic process is a process where heat is absorbed from the surroundings.

Exothermic process is a process where heat is released to the surroundings.

The System and the Surroundings

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.

The universe = the system + the surroundings

Types of the System

We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System

In an open system, there is exchange of energy and matter between system and surroundings.

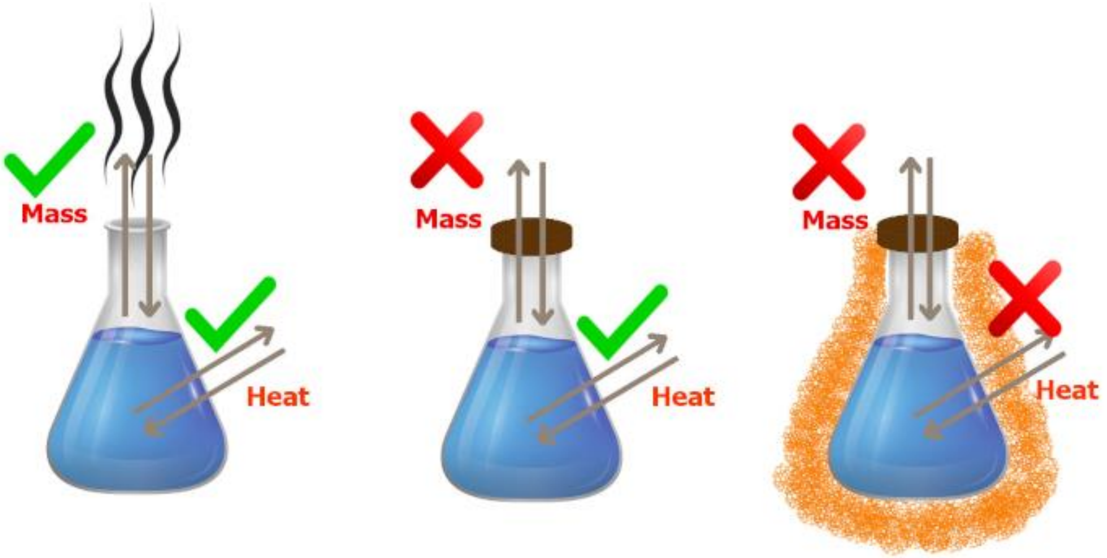
2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.

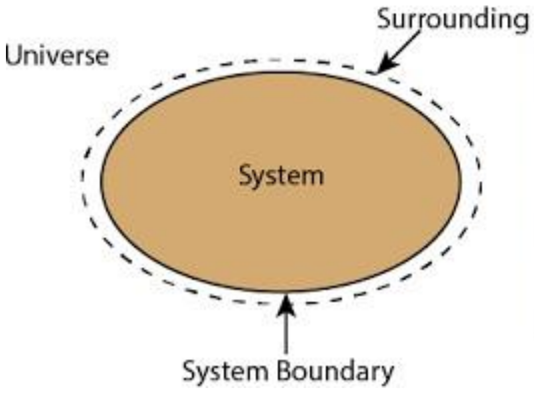
3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings.

Thermodynamic System



Open system	**Closed system**	**Isolated system**
Mass transfer (yes)	Mass transfer (yes)	Mass transfer (No)
Heat transfer (yes)	Heat transfer (No)	Heat transfer (No)



The Four Types of Thermodynamic Processes

The four types of thermodynamic process are isobaric, isochoric, isothermal and adiabatic.

- Isobaric process in which the pressure (P) is kept constant ($\Delta P = 0$).
- Isochoric process in which the volume (V) is kept constant ($\Delta V = 0$).
- Isothermal process in which the temperature (T) is kept constant ($\Delta T = 0$).
- Adiabatic process in which the heat transfer is zero ($Q=0$).

Concepts of Partial molar properties

1. Partial molar properties are defined as the properties which are the quantities change with number of moles.
2. Several extensive properties like volume, free energy, enthalpy, entropy depends on number of mole.

Partial molar volume and its significance

Eg 1) 100ml H_2O + 10ml H_2O = 110ml volume.

Eg 2) 10,000 ml MeOH + 18 ml H_2O = 10,018 ml actual volume but experimental volume is 10,014 ml.

In eg (1) there are no molecular interactions because both are a water molecule that’s why volume is not changed.

In eg (2) actual volume is 10,018 ml but experimentally it gives 10,014 ml only because methanol and water both are different molecules. So some molecular interactions are there that’s why gives 10,014 ml.

This change in volume in binary system is called Partial molar volume.

- G. N. Lewis introduces a new property X which is defined as function of temperature, pressure and number of moles.
- $X = f\,(T, P \text{ and } n_1, n_2)$

Taking partial differentiation on both sides

$$dx = \left(\frac{\partial x}{\partial T}\right)_{P,\, n1,n2,\, \ldots ni} dT + \left(\frac{\partial x}{\partial P}\right)_{T,\, n1,\, n2\ldots ni} dP + \left(\frac{\partial x}{\partial n1}\right)_{T,P,\, n2,n3\ldots ni} dn_1 + \left(\frac{\partial x}{\partial n2}\right)_{T,P,n1,n3,\ldots ni} dn_2$$

We know that $(\frac{\partial x}{\partial n1})_{T, P, n2, n3..,ni} = X_1$ and $(\frac{\partial x}{\partial n2})_{T, P, n1} = X_2$

Then

$$dx = (\frac{\partial x}{\partial T})_{P, n1,n2, ...ni}\ dT + (\frac{\partial x}{\partial P})_{T, n1, n2...ni}\ dP + X_1\ dn_1 + X_2\ dn_2$$

At constant temperature and pressure, i.e. dT= 0 and dP= 0

Then $dX= X_1\ dn_1 + X_2\ dn_2$

Integration on both sides

$$\int dx = \int X1\ dn1 + \int X2\ dn2$$

$$\int dx = X_1 \int dn1 + X_2 \int dn2$$

$$X = X_1\, n_1 + X_2\, n_2$$

The above equation represents the partial molar properties of binary system.

If the system having I components then the above equation changes to

$$X = X_1\, n_1 + X_2\, n_2 + X_3\, n_3 + X_4\, n_4 + ... + X_i\, n_i$$

<u>Significance of Partial molar properties:</u>

1. Partial molar properties always measures for binary system only.
2. The sum of products of number of moles and partial molar property equal to thermodynamic property.

Partial molar volume $V = V_1\, n_1 + V_2\, n_2$

Partial molar energy $E = E_1 n_1 + E_2\, n_2$

Partial molar Gibbs free energy $G = G_1 n_1 + G_2 n_2$.

<u>Determination of Partial molar properties:</u>

Partial molar properties are determined by 3 methods.

1. Graphical method
2. Intercept method
3. Apparent molar volume method

1. Graphical method:

According to definition of partial molar properties

$$\left(\frac{\partial x}{\partial ni}\right) = X_i \quad (I = 1, 2, 3, \ldots i)$$

For binary system $X = X_1 n_1 + X_2 n_2$

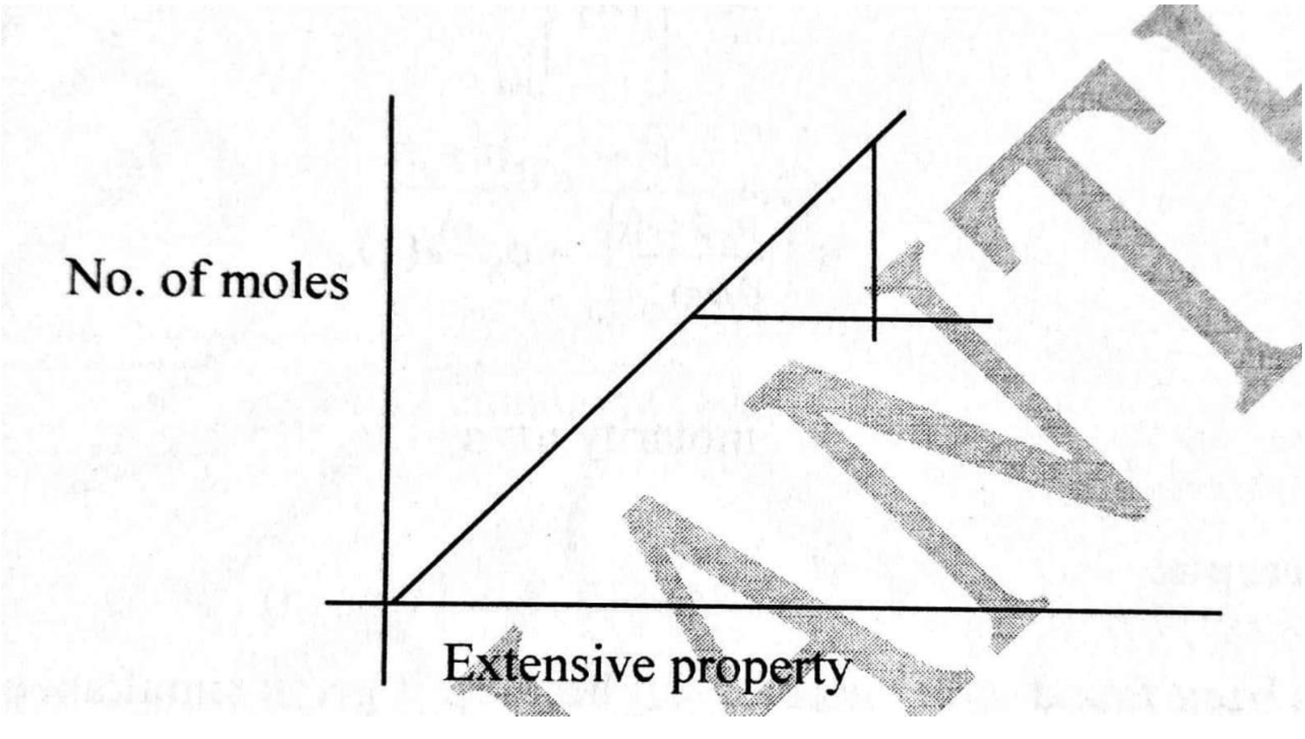
Where x = any extensive property

n_1, n_2 = number of moles of components 1 & 2

X_1, X_2 = partial molar properties of components 1 & 2

For the experimental determination of X_1, take differentiation of X w.r.t. to n_1

- $dx/dn_1 = X_1\, dn_1/ dn_1 + X_2\, dn_2/dn_1$
- $dx/dn1 = X_1 + 0$,
- this equation in the form of $y = mx + c$



Limitation: This method is not of much use as the exact slope cannot be determined.

2. Intercept method:

The method of intercept is more useful because we can measure the partial molar quantities of both components in a binary system.

- This method gives more accurate values of partial molar quantities.
- For this method a new property, mean molar property of solution (x). This is definded as extensive property of solution divided by total number of moles in a system.

Mathematically it is represented as $x = X / n_1 + n_2$

$$x\,(n_1 + n_2) = X$$

Differentiating w.r.t. to n_2 at constant n_1

$[\frac{d}{dn2}\left(x\,(n1 + n2)\right)]_{n1} = [dx/dn_2]_{n1}$ [we know d/dx (uv) = u dv/dx + v du/dx]

$x\,\frac{d}{dn2}(n1 + n2) + (n1 + n2)\frac{dx}{dn2} = [dx/dn_2]_{n1}$

$x\,(0 + 1) + (n1 + n2)\frac{dx}{dn2} = [dx/dn_2]_{n1}$

$x + (n1 + n2)\frac{dx}{dn2} = X_2$ --------------------- (1)

Mole fraction of component 1 is $N_1 = n_1/ n1 + n2$ ---------- (2)

Take differentiation on both sides w.r.t. to n_2 at constant n_1

$(dN_1/dn_2)_{n1} = d/dn_2\,(n_1/ (n_1 + n_2))_{n1}$

$= n_1\,d/dn_2\,[(n_1+n_2)^{-1}]_{n1}$ [since $\frac{d}{dx}X^n = n\,x^{n-1}$]

$= n_1\,[-1/ (n_1 + n_2)^2]_{n1}$

$[dN_1/dn_2]_{n1} = [- n_1/(n_1 + n_2).\ 1/ (n_1 + n_2)]_{n1}$ -------------- (3)

substitude eq (2) in eq (3), we get

$[dN_1/dn_2]_{n1} = [-N_1.\ 1/ (n_1 + n_2)]_{n1}$

$[n_1 + n_2/ dn_2]_{n1} = [- N_1 / dN_1]_{n1}$

Take differentiation with x

$[dx/dn_2 (n_1+n_2)]_{n1} = [-N_1\, dx/dN_1]_{n1}$ -----------------(4)

Substitute eq (4) in eq (1), we get

- $x + [-N_1\, dx/dN_1]_{n1} = X_2$
- $x - N_1 [dx/dN_1]_{n1} = X_2$

$x = X_2 + N_1 [dx/dN_1]_{n1}$

3. Apparent molar volume method:

- Suppose X be the value of any extensive property for a mixing of n_1 moles of component 1 and n_2 moles of component 2.
- X_1 is the value of property per mole of pure component 1.then the apparent molar value can be represented by ϕ_x of component 2.

Mathematically it can be represented as

- $x = n_1X_1 + n_2X_2$
- $x = n_1X_1 + n_2\phi_X$
- $x - n_1X_1 = n_2\phi_X$
- differentiating w.r.t to n_2
- $\frac{d}{dn2}(x - n_1X_1) = \frac{d}{dn2}(n_2\, \phi_X)$
- $\frac{dx}{dn2} - X_1 \frac{dn1}{dn2} = n_2 \frac{d\emptyset x}{dn2} + \phi_x \frac{dn2}{dn2}$
- $\frac{dx}{dn2} - 0 = n_2 \frac{d\emptyset x}{dn2} + \phi_x$
- $\frac{dx}{dn2} = m \frac{d\emptyset x}{dm} + \phi_x$
- $\frac{dx}{dn2} = \frac{d}{dm}(\phi_x\, m)$
- $X_2 = \frac{d}{dm}(\phi_x\, m)$
- $X_2\, dm = d\,(\phi_x\, m)$
- Integration on both sides with suitable limits
- $\int_0^m x2\, dm = \int_0^m d\,(\phi x\, m)$
- $\int_0^m x2\, dm = \phi_x\, m$
- $\frac{1}{m}\int_0^m x2\, dm = \phi_x$

Chemical Potential:

1. The amount of change in free energy is known as chemical potential.

2. It is denoted by μ i.e. $\frac{\partial G}{\partial ni}$ = G_i = μ_i
3. Chemical potential is also known as partial molar free energy.
4. Chemical potential is an intensive property.
5. According to definition of partial molar property

$$G = f(T, P, n_1, n_2)$$

Differentiating on both sides

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\, n1,\, n2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\, n1,\, n2} dP + \left(\frac{\partial G}{\partial n1}\right)_{T,\, P,\, n2} dn_1 + \left(\frac{\partial G}{\partial n2}\right)_{T,\, P,\, n1} dn_2$$

We know that $\left(\frac{\partial G}{\partial n1}\right)_{T,\, P,\, n2} = G_1 = \mu_1$

$\left(\frac{\partial G}{\partial n2}\right)_{T,\, P,\, n1} = G_2 = \mu_2$ then we get

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\, n1,\, n2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\, n1,\, n2} dP + \mu_1\, dn_1 + \mu_2\, dn_2$$

At constant temperature and pressure, dT=0 and dP =0 then we get

$dG = \mu_1\, dn_1 + \mu_2\, dn_2$ ---------for binary system

$dG = \mu_1\, dn_1 + \mu_2\, dn_2 +$ -------------- $+ \mu_i\, dn_i$ -------for I component system

This is the mathematical representation of chemical potential.

Variation chemical potential with Temperature:

According to 2nd law of thermodynamics

$$dG = VdP - SdT$$

At constant pressure (dP = 0)

$$dG = - SdT$$

Differentiating w.r.t. to temperature

$$\frac{\partial G}{\partial T} = - S\, \frac{\partial T}{\partial T}$$

$$\frac{\partial G}{\partial T} = - S$$

Differentiating w.r.t. to n_i

$Ə^2G/ ƏTƏn_i = - S_i$ ------------- (1)

According to definition of chemical potential

$\frac{\partial G}{\partial ni}$ = μ_i

Differentiating w.r.t. to temperature

$Ə^2G/ ƏTƏn_i = \frac{\partial \mu i}{\partial T}$ --------- (2)

Compare eq (1) and eq(2), we get

$\frac{\partial \mu i}{\partial T} = -S_i$

Where S_i = partial molar entropy of i components.

Variation chemical potential with Pressure:

According to 2nd law of thermodynamics

dG = VdP – SdT

At constant temparature (dT = 0)

dG = VdP

Differentiating w.r.t. to pressure

$$\frac{\partial G}{\partial P} = V\frac{\partial P}{\partial P}$$

$$\frac{\partial G}{\partial P} = V$$

Differentiating w.r.t. to n_i

$$\frac{\partial 2G}{\partial P\partial ni} = \frac{\partial V}{\partial ni}$$

$\frac{\partial 2G}{\partial P\partial ni} = V_i$ --------- (1)

According to definition of chemical potential

$\frac{\partial G}{\partial ni}$ = μ_i

Differentiating w.r.t. to pressure

$\frac{\partial 2G}{\partial P \partial ni} = \frac{\partial \mu i}{\partial P}$ ------- (2)

Compare eq(1) and eq(2), we get

$\frac{\partial \mu i}{\partial P} = V_i$

Where V_i = partial molar volume of i components.

<u>Gibbs – Duhem equation and its significance:</u>

Gibbs – Duhem equation describes the relationship b/w changes in chemical potential for component in a thermodynamic system.

According to definition of partial molar property

$$G = f(T, P, n_1, n_2)$$

Differentiating on both sides

$dG = (\frac{\partial G}{\partial T})_{P, n1, n2}\, dT + (\frac{\partial G}{\partial P})_{T, n1, n2}\, dP + (\frac{\partial G}{\partial n1})_{T, P, n2}\, dn_1 + (\frac{\partial G}{\partial n2})_{T, P, n1}\, dn_2$

We know that $(\frac{\partial G}{\partial n1})_{T, P, n2} = G_1 = \mu_1$

$(\frac{\partial G}{\partial n2})_{T, P, n1} = G_2 = \mu_2$ then we get

$dG = (\frac{\partial G}{\partial T})_{P, n1, n2}\, dT + (\frac{\partial G}{\partial P})_{T, n1, n2}\, dP + \mu_1\, dn_1 + \mu_2\, dn_2$

At constant temperature and pressure, dT=0 and dP =0 then we get

$dG = \mu_1\, dn_1 + \mu_2\, dn_2$ ---------for binary system

$dG = \mu_1\, dn_1 + \mu_2\, dn_2 +$ -------------- $+ \mu_i\, dn_i$ -------for I component system ------(1)

Integration on both sides

$\int dG = \int \mu 1\, dn1 + \int \mu 2\, dn2 +$ ------------ $+ \int \mu i\, dni$

$\int dG = \mu_1 \int dn1 + \mu_2 \int dn2 +$ ------------ $+ \mu_i \int dni$

$G = \mu_1 n_1 + \mu_2 n_2 +$ --------- $+ \mu_i n_i$

Take differentiation on both sides

$$dG = (\mu_1\, dn_1 + \mu_2\, dn_2 + \text{-------------} + \mu_i\, dn_i) + (n_1\, d\mu_1 + n_2\, d\mu_2 + \text{-----} + n_i\, d\mu_i) \text{ ----(2)}$$

Compare eq(1) and eq(2), we get

$$(\mu_1\, dn_1 + \mu_2\, dn_2 + \text{--} + \mu_i\, dn_i) = (\mu_1\, dn_1 + \mu_2\, dn_2 + \text{--} + \mu_i\, dn_i) + (n_1\, d\mu_1 + n_2\, d\mu_2 + \text{-} + n_i\, d\mu_i)$$

$$0 = n_1\, d\mu_1 + n_2\, d\mu_2 + \text{-----} + n_i\, d\mu_i$$

$$0 = \sum_0^i ni\ d\mu i$$

This is the Gibbs - Duhem equation.

Significance:

- Gibbs – Duhem equation is helpful in calculating the partial molar quantities of binary system.
- Gibbs – Duhem equation cannot be used for small thermodynamic system.
- Ti is also helpful in calculating the partial vapour pressure of a system.

SOLUTIONS

Solution is defined as homogeneous mixture of two or more components.

- In a solution the component which is having large proportion is called **solvent**.
- In a solution the component which is having small proportion is called **solute**.

Ideal solutions: a solution of two or more substances is said to be ideal, if it obeys Raoults law at all temperatures and concentrations.

- Ex: benzene + toluene
- n-hexane + n-heptane
- Chlorobenzene and Bromobenzene
- Ethyl Bromide and Ethyl Iodide

Non ideal solutions: a solution of two or more substances is said to be non ideal, if it does not obeys Raoults law at all temperatures and concentrations.

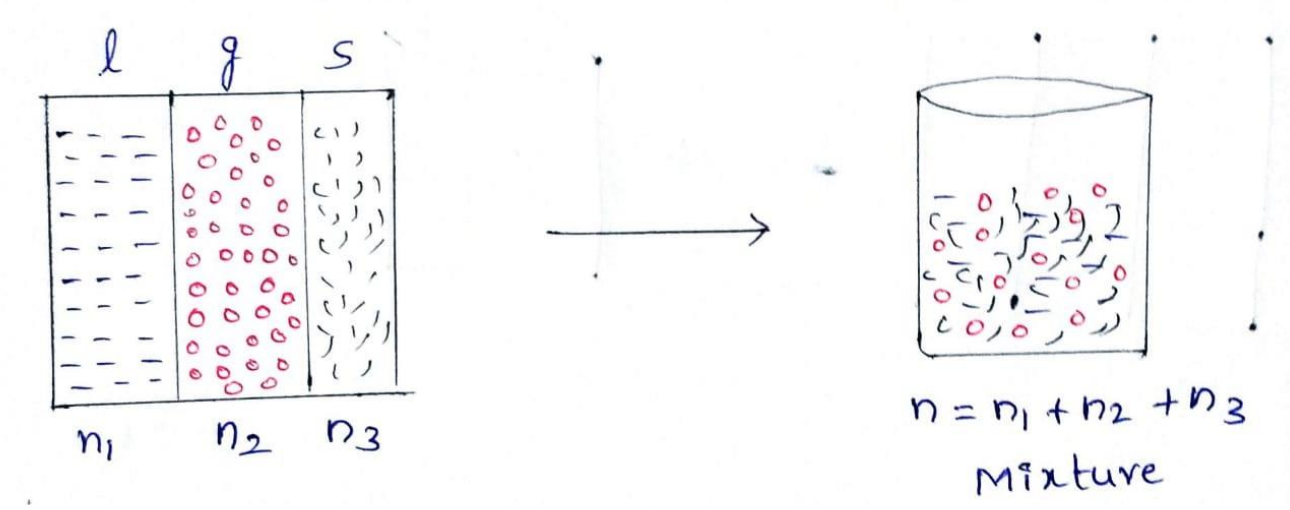
- Ex: water + ethanol
- Chloroform and Benzene (negative deviation from raoults law)
- Acetone and Benzene (positive deviation from raoults law)

Thermodynamic properties of ideal solutions mixing quantities:

When two or more substances are mixed there occurs a change in measurable properties of components always takes place spontaneously.

1. Free Energy Mixing of Ideal Gases:

The formation of mixture from the pure components always takes place spontaneously.



Let us consider a vessel with three compartments and each compartment contains pure substance.

For the pure substance free energies are written as

- $n_1\mu_1 = G_1$
- $n_2\mu_2 = G_2$
- $n_3\mu_3 = G_3$

Where n_1, n_2, n_3 = Number of moles of components 1, 2, 3.

μ_1, μ_2, μ_3 = chemical potentials of components 1, 2, 3.

For initial free energy is $G_{initial} = G_1 + G_2 + G_3$

$G_{initial} = n_1\mu_1 \text{ (Pure)} + n_2\mu_2 \text{ (Pure)} + n_3\mu_3 \text{ (Pure)}$

$G_{final} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3$

Change in free energy for mixing

$\Delta G_{mixing} = G_{final} - G_{initial}$

$\Delta G_{mixing} = (n_1\mu_1 + n_2\mu_2 + n_3\mu_3) – (n_1\mu_1 \text{ (Pure)} + n_2\mu_2 \text{ (Pure)} + n_3\mu_3 \text{ (Pure)})$

$\Delta G_{mixing} = n_1 (\mu_1 - \mu_1 \text{ pure}) + n_2 (\mu_2 - \mu_2 \text{ pure}) + n_3 (\mu_3 - \mu_3 \text{ pure})$ -------- (1)

We know that $\mu_i = \mu_i^0 + RT \ln X_i$

$\mu_i - \mu_i^0 = RT \ln X_i$

$\mu_1 - \mu_1^0 = RT \ln X_1$

$\mu_2 - \mu_2^0 = RT \ln X_2$

$\mu_3 - \mu_3^0 = RT \ln X_3$

Where $\mu_1^0, \mu_2^0, \mu_3^0$ = chemical potentials of pure components.

Substitute the above values in eq(1), we get

$\Delta G_{mixing} = n_1 (RT \ln X_1) + n_2 (RT \ln X_2) + n_3 (RT \ln X_3)$

$\Delta G_{mixing} = RT [n_1 \ln X_1 + n_2 \ln X_2 + n_3 \ln X_3]$ ---------- (2)

According to definition of mole fraction $x_i = \frac{ni}{N}$

$n_i = x_i N$

- $n_1 = x_1 N$
- $n_2 = x_2 N$
- $n_3 = x_3 N$

Substitute the above values in eq(2), we get

$\Delta G_{mixing} = RT [x_1 N \ln X_1 + x_2 N \ln X_2 + x_3 N \ln X_3]$
$\Delta G_{mixing} = NRT [x_1 \ln X_1 + x_2 \ln X_2 + x_3 \ln X_3]$
$\Delta G_{mixing} = NRT [\sum_0^i xi \ln xi]$

2. Entropy mixing of ideal gases:

We know that $\Delta G_m = G_f - G_i$

According to second law of thermodynamics $dG = VdP – SdT$

At constant pressure dP=0

Then dG = - SdT

Differentiating w.r.t. to temperature

$\frac{\partial G}{\partial T}$ = - S $\frac{\partial T}{\partial T}$

$\frac{\partial G}{\partial T}$ = - S ------- (1)

$\frac{\partial G1}{\partial T}$ = - S_1 ------ (2) Initial

$\frac{\partial G2}{\partial T}$ = - S_2 ---- (3) Final

(3) – (2) $\frac{\partial G2}{\partial T} - \frac{\partial G1}{\partial T}$ = - S_2 + S_1

$\frac{\partial}{\partial T}$ (G_2-G_1) = - (S_2-S_1)

$\frac{\partial}{\partial T}$ (ΔG) = - ΔS

For mixing $\frac{\partial}{\partial T}$($\Delta G_{mix}$) = -$\Delta S_{mix}$

We know that ΔG_{mix} = NRT [$\sum_0^i xi \ln xi$]

$\frac{\partial}{\partial T}$ NRT [$\sum_0^i xi \ln xi$] = -ΔS_{mix}

NR $\sum_0^i xi \ln xi$ = -ΔS_{mix}

ΔS_{mix} = - NR $\sum_0^i xi \ln xi$

This above equation represents the entropy mixing of ideal gases.

3. Enthalpy mixing of ideal gases:

We know that ΔG = ΔH - TΔS

For mixing ΔG_m = ΔH_m - TΔS_m

ΔH_m = ΔG_m + TΔS_m

$$\Delta H_m = NRT\,[\,\sum_0^i xi \ln xi] - NRT\,[\,\sum_0^i xi \ln xi] = 0.$$

❁⁑*Vapor – Pressure Raoults Law

Lowering of vapor pressure: The difference between vapor pressure of pure solvent (P_0) and vapor pressure solution (P_s) is called lowering of vapor pressure.

Vapor pressure of pure solvent = P_0

Vapor pressure of solution = P_s

Lowering of vapor pressure = $P_0 - P_s$

Relative Lowering of vapor pressure: The ratio between lowering of vapor pressure ($P_0 - P_s$) and vapor pressure of pure solvent (P_0) is called relative lowering of vapor pressure.

Relative Lowering of vapor pressure = $\frac{P0 - Ps}{P0}$

Statement: The relative lowering of vapor pressure of a solution is equal to mole fraction of Non volatile solute is called Raoults Law.

Mathematically Raoults law can be represented by

$$\frac{P0 - Ps}{P0} = X_2$$

Where P_0 = Vapor pressure of pure solvent

P_s = Vapor pressure of solution

X_2 = Mole fraction of Non volatile solute

Proof: By the definition of chemical potential $\mu_i = \mu_i^0 + RT \ln X_i$

Chemical potential of solution phase $\mu_1(liq) = \mu_1^0\,(liq) + RT \ln X_1$ ------ (1)

Chemical potential of vapor phase $\mu_1(g) = \mu_1^0\,(g) + RT \ln P_s$ ------ (2)

At equilibrium chemical potential of solution phase and vapor phase must be equal.

$\mu_1(liq) = \mu_1(g)$

$\mu_1^0\,(liq) + RT \ln X_1 = \mu_1^0\,(g) + RT \ln P_s$ $\quad \because X_1 + X_2 = 1 \rightarrow X_1 = 1 - X_2$

μ_1^0 (liq) + RT ln (1 – X_2) = μ_1^0 (g) + RT ln P_s -------- (3)

When X_2 = 0 and P = P_0

Then μ_1^0 (liq) + RT ln (1 – 0) = μ_1^0 (g) + RT ln P_0

μ_1^0 (liq) + RT ln (1) = μ_1^0 (g) + RT ln P_0

μ_1^0 (liq) + 0 = μ_1^0 (g) + RT ln P_0

μ_1^0 (liq) = μ_1^0 (g) + RT ln P_0 -------- (4)

(3) - (4) μ_1^0 (liq) + RT ln (1 – X_2) - μ_1^0 (liq) = μ_1^0 (g) + RT ln P_s - μ_1^0 (g) + RT ln P_0

RT ln (1 – X_2) = RT ln P_s - RT ln P_0

RT ln (1 – X_2) = RT (ln P_s - ln P_0)

ln (1 – X_2) = ln P_s - ln P_0

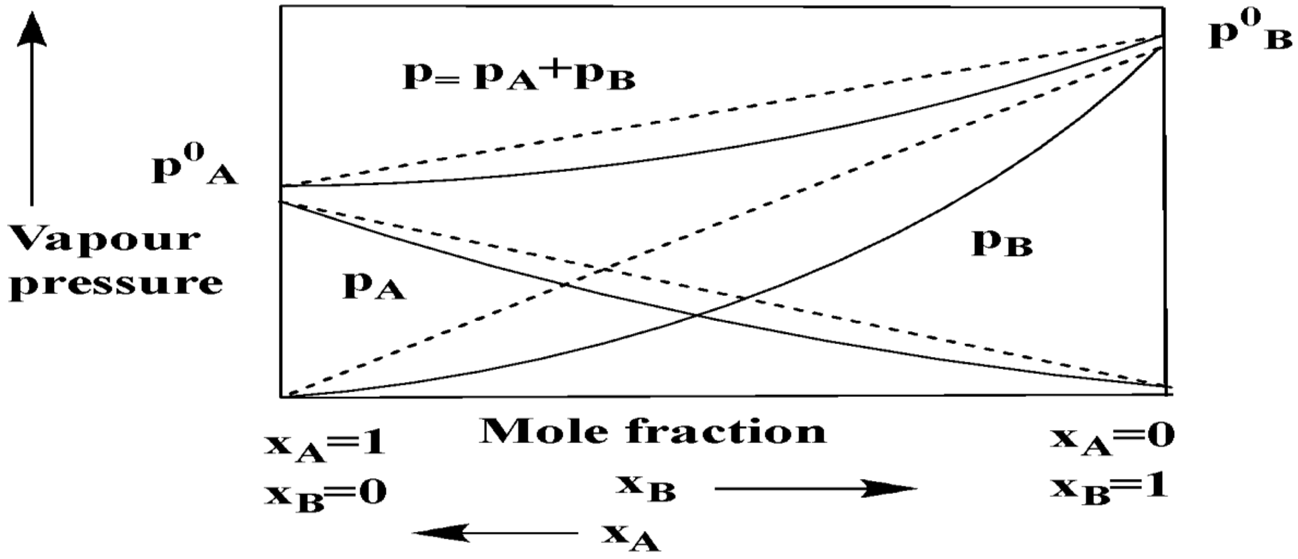
ln (1 – X_2) = ln $(\frac{Ps}{Po})$

$1 - X_2 = \frac{Ps}{P0}$

$1- \frac{Ps}{P0} = X_2$

$\frac{P0 - Ps}{P0} = X2$

Graphical Representation:



⁑⁎❁⁎Vapor-Pressure Henrys Law

The solubility of a gas in a liquid is directly proportional to pressure of the gas. It is called Henrys law.

(OR)

The mass of gas dissolved in a given liquid at constant temperature is directly proportional to pressure of the gas it is called Henrys law.

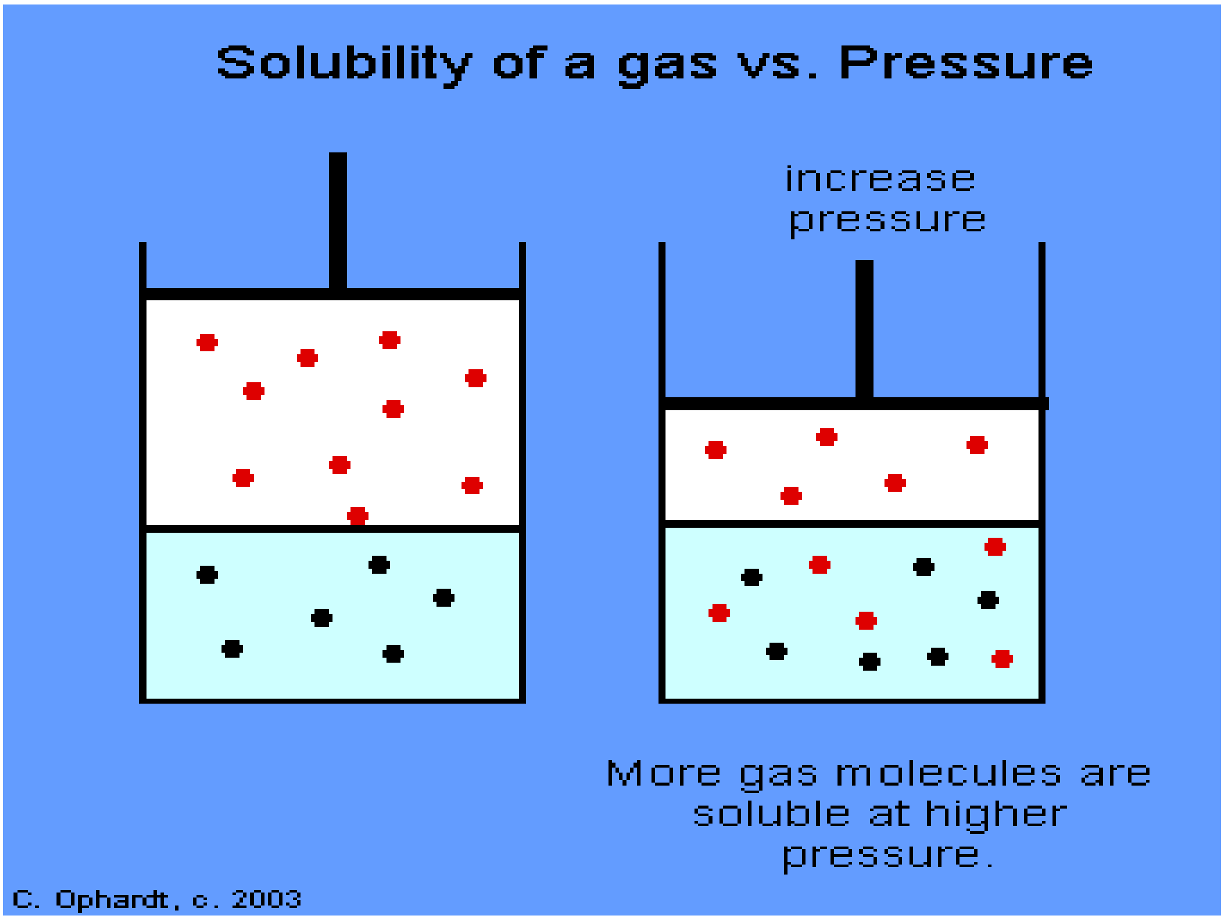
$$M \alpha P$$

$$M=KP$$

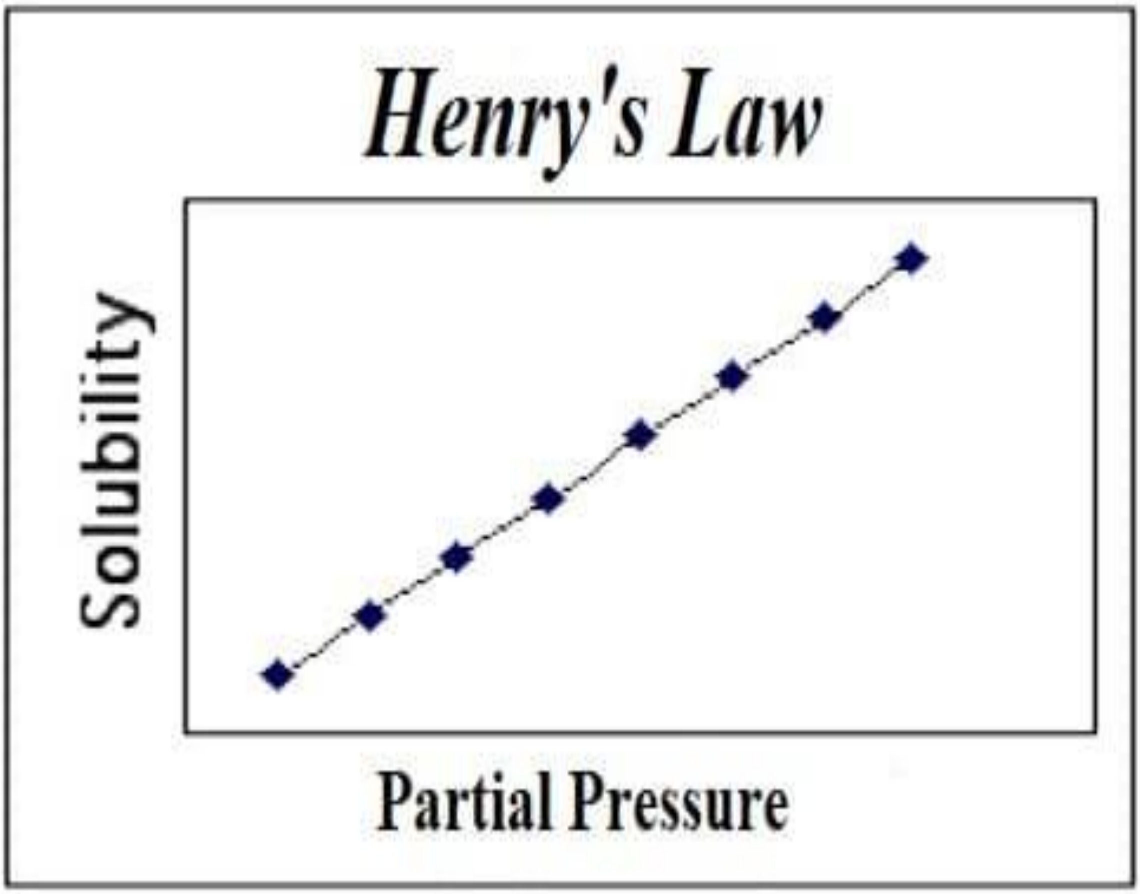
Where K= Henrys constant

M = mass of the gas

P = pressure of the gas



If Henrys law is valid, graph is drawn between solubility of gas v/s pressure of the gas at constant temperature should be a straight line.



Limitations:

→This law is valid for the following conditions.

1. Temperature should be constant throughout the experiment.

2. Pressure is not too low.

3. Gas is not highly soluble.

4. The gas does not disassociate in solvent.

Ex (1): Henrys law is valid for the solubility of HCl and NH_3 in Benzene because both gases are sparingly soluble.

Ex (2): Henrys law is not valid for the solubility of HCl and NH_3 in water because both gases are highly soluble in nature.

Non-ideal solutions

Concept of Fugacity

Fugacity and Fugacity coefficient:

We know that dG = VdP - SdT

At constant Temperature dG = VdP ---------- (1)

For ideal gas PV = nRT

For 1 mole of ideal gas PV = RT

$$V = \frac{RT}{P} \quad \text{--------- (2)}$$

From equations (1) and (2) $dG = \frac{RT}{P}\ dP$

Integrate w.r.t. to Pressure with suitable limits

$$dG = RT\ \int_{P1}^{P2} dP/P \quad \text{---------- (3)}$$

This equation is not applicable to incase of gases in order to remove this difficulty Lewis introduced a new function fugacity (f).

→Fugacity does not depend on the nature of the gas.

→Fugacity is not a physical property.

⁂ P = f

$$dG = RT\ \int_{f1}^{f2} df/f$$

$$dG = RT\ lnf$$

Significance of fugacity (or) fugacity coefficient:

In general the fugacity of real gas is related to its pressure by an equation

Fugacity α P

$$f \alpha\ p$$

$$f = \emptyset p$$

$$\frac{f}{p} = \emptyset$$

Where $\emptyset = fugacity\ coefficient$

<u>Determination of Fugacity:</u>

Fugacity is determined by the following methods

1. Graphical method

2. Approximation calculation method

1. Graphical method:

We know that fugacity of real gas dG = RT ln f -------- (1)

From ideal gas equation dG = VdP - SdT

At constant Temperature dG = VdP ---------- (2)

From equations (1) and (2) RT ln f = VdP -------- (3)

In case of real gases a new function (α) is defined as

$$\alpha = \frac{RT}{P} - V$$

Where α = constant over a range of pressure which are not too high

$$V = \frac{RT}{P} - \alpha \quad \text{------- (4)}$$

Substitute eq (4) in eq (3) $RT \ln f = (\frac{RT}{P} - \alpha)\ dP$

$$RT \ln f = \frac{RT}{P} dP - \alpha\ dP$$

Integrate w.r.t to Pressure $RT \ln f = RT\ \int_0^P \frac{dP}{P} - \int_0^P \alpha\ dP$

$$RT \ln f = RT\ [\int_0^P \frac{dP}{P} - \frac{1}{RT} \int_0^P \alpha\ dP]$$

$$\ln f = \ln P - \frac{1}{RT}\int_0^P \alpha \, dP$$

$$\ln f - \ln P = -\frac{1}{RT}\int_0^P \alpha \, dP$$

$$\ln \frac{f}{p} = -\frac{1}{RT}\int_0^P \alpha \, dP$$

To know the value of fugacity we should know the value of $\int_0^P \alpha \, dP$.

→A graph is drawn between $\frac{\alpha}{RT}$ v/s P.

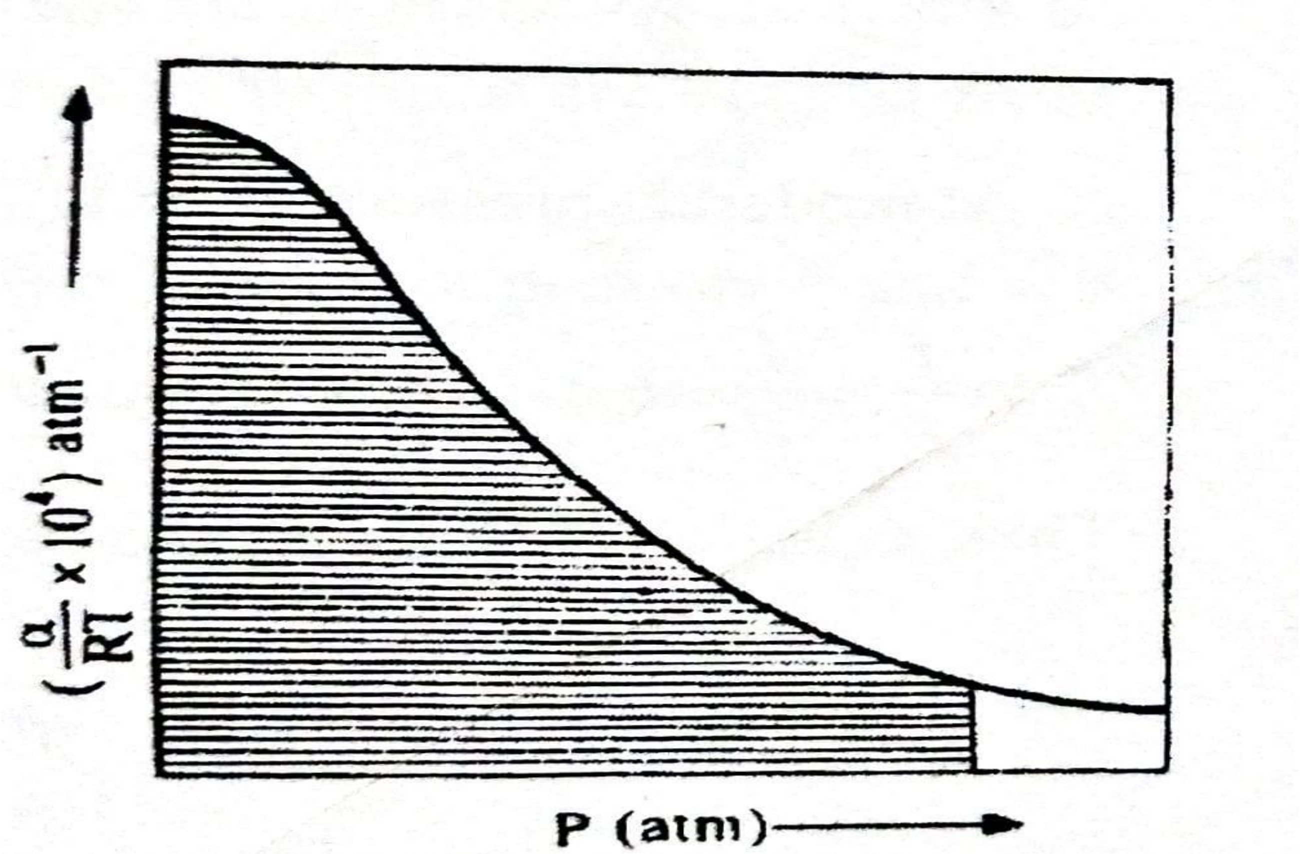


Fig. 1

The area under the curve gives the value of $\int_0^P \alpha \, dP$.

From this value we can calculate the fugacity.

2. Approximation Calculation method:

According to the definition of fugacity

$$\ln\frac{f}{P} = -\frac{1}{RT}\int_0^P \alpha\, dP$$

→α is a constant over a range of pressure which is not too high.

$$\ln\frac{f}{P} = -\frac{\alpha}{RT}\int_0^P dP$$

$$\ln\frac{f}{P} = -\frac{\alpha}{RT}P \text{ ----- (1)}$$

For moderate pressure $\frac{f}{P} = 1$ ∵ when X→ 1

$\ln\frac{f}{P} = \frac{f}{P} - 1$ ------ (2) ln X = X-1

Compare eq(1) and eq(2) $\frac{f}{P} - 1 = -\frac{\alpha P}{RT}$ -------- (3)

We know that $\alpha = \frac{RT}{P} - V$ --------- (4)

Substitute eq(4) in eq(3) $\frac{f}{P} - 1 = -\frac{\frac{RT}{P} - V}{RT}\, P$

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

$$\frac{f}{P} - 1 = -\frac{RT}{RT} + \frac{PV}{RT}$$

$$\frac{f}{P} - 1 = -1 + \frac{PV}{RT}$$

$$\frac{f}{P} = \frac{PV}{RT}$$

$$f = P^2V/RT$$

From this we can calculate the accurate value of fugacity.

Activity and Activity Coefficient:

Activity term is used to replace concentration term in non ideal solutions.

For ideal solution $\mu_i = \mu_i^0 + RT \ln X_i$ ---------- (1)

μ_i = chemical potential of ith component for ideal gas

X_i = mole fraction of ith component for ideal solution

For Non ideal solution $\mu_i = \mu_i^0 + RT \ln a_i$ --------- (2)

μ_i = chemical potential of ith component for non ideal solution

a_i = activity of ith component for non ideal solution

Compare eq (1) and eq (2) $a_i \alpha x_i$

$$a_i = \gamma x_i$$

Where γ = activity coefficient

For ideal solutions $\gamma = 1$

$1 = \frac{ai}{xi}$

$\rightarrow a_i = x_i$

For non ideal solutions $\gamma < 1$ or $\gamma > 1$.

Determination of activity coefficient

1. Determination of activity coefficient from vapor pressure measurements:

I. Activity of solvent:

P_1 = let the vapor pressure of solvent

P_1^0 = vapor pressure of pure solvent

Suppose the vapor pressures are not too high know pressure is replaced by fugacity

$P_1/P_1^0 = f_1/f_1^0 = \gamma$

Hence the activity of solvent in a solution can be easily determined by knowing the values of P_1 & P_1^0.

II. Activity of solute:

If the solute is volatile its activity may be calculated as similar to activity of solvent.

If the solute is Non volatile activity of solute is calculated by the following procedure.

Activity = activity X Pressure

→ $a = \gamma P$

→ $a \alpha P$

From this equation we can calculate the activity of solute from vapor pressure measurements.

2. by using Gibbs-Duhem equation:

This method is more accurate method to determine the activity of solution.

For binary compounds $n_1 \, d\mu_1 + n_2 \, d\mu_2 = 0$ -------- (1)

Where n_1, n_2 = number of moles of components 1 & 2.

μ_1, μ_2 = chemical potential of components 1 & 2.

According to chemical potential $\mu_1 = \mu_1^0 + RT \ln a_1$

$\mu_2 = \mu_2^0 + RT \ln a_2$

Where a_1, a_2 are activities of two components.

Differentiating w.r.t. to a

→$d\mu_1 = 0 + RT \, d \ln a_1$ and $d\mu_2 = 0 + RT \, d \ln a_2$

→ $d\mu_1 = RT \, d \ln a_1$ and $d\mu_2 = RT \, d \ln a_2$ ----------- (2)

Substitute eq (2) in eq (1)

→$n_1 (RT d\ln a_1) + n_2 (RT d\ln a_2) = 0$

→$RT (n_1 d\ln a_1 + n_2 d\ln a_2) = 0$

→ $n_1 d\ln a_1 + n_2 d\ln a_2 = 0$

→ $n_1 d\ln a_1 = - n_2 d\ln a_2$

→$\frac{n1}{n2} = -\frac{dlna2}{dlna1}$

→$\frac{n1}{n2} = -\frac{lna2}{lna1}$

CHEMICAL EQUILIBRIUM

⁎ What is Chemical Equilibrium and write the characteristics of chemical equilibrium?

In a chemical reaction chemical equilibrium is the state in which concentrations of reactants and products must be equal.

Ex: $aA + bB \leftrightarrow cC + dD$

Where a, b, c, d are staichometry coefficients.

A, B are reactants and C, D are products.

$$rate\ of\ reaction = \frac{products}{reactants}$$

Rate of reaction = $[C]^c\ [D]^d / [A]^a\ [B]^b$

Characteristics of chemical equilibrium:

→Chemical equilibrium is also known as dynamic equilibrium.

→Chemical equilibrium is represented as K_c.

→Chemical equilibrium is formed only in closed vessel.

→At chemical equilibrium catalyst is not affected.

→At chemical equilibrium ΔG^0, $\Delta S = 0$.

❀⁂ Effect of Temperature on equilibrium constant – Van't Hoff equation

Vant hoff equation is the combination of Gibbs – Helmholtz equation and Vant hoff isotherm equation.

We know that by the definition of free energy G = H – TS

When a small change is considered ΔG = ΔH - TΔS -------- (1)

We know that dG = VdP – SdT

At constant Pressure dP = 0

Then dG = - SdT

Differentiating w.r.t. to Temperature $\left(\frac{dG}{dT}\right) = -s\frac{dT}{dT}$

$$\left(\frac{dG}{dT}\right) = -s$$

Initial state $\frac{dG1}{dT} = -S1$ ----- (2)

Final state $\frac{dG2}{dT} = -S2$ ----- (3)

Eq (2) – Eq (3)

$$\frac{dG2}{dT} - \frac{dG1}{dT} = -S2 - (-S1)$$

$$\frac{d}{dT}(G2 - G1) = -(S2 - S1)$$

$\frac{d}{dT}(\Delta G) = -\Delta S$ ------ (4)

Substitute eq (4) in eq (1)

$$\Delta G = \Delta H - T(-\frac{d}{dT}\Delta G)$$

$$\Delta G = \Delta H + T\ \frac{d}{dT}\ \Delta G$$

This is known as Gibbs Helmholtz equation.

According to Vant Hoff isotherm equation

$\rightarrow \Delta G = -RT\ln K$

$\rightarrow \ln K = -\frac{1}{R}\left(\frac{\Delta G}{T}\right)$

Differentiating w.r.t. to Temperature

$\rightarrow \frac{d}{dT} lnK = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta G}{T}\right)$ ------- (5)

We know that $\Delta G = \Delta H - T\Delta S$

Dividing with T

$\rightarrow \frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$

Differentiating w.r.t. to Temperature

$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = -\Delta H/T^2 + 0$ -------- (6)

Substitute eq (6) in eq (5)

$\rightarrow \frac{d}{dT} lnK = -\frac{1}{R}(-\Delta H/T^2)$

$$\boxed{\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (4)}$$

→Equation 4 is known as differential form of van’t Hoff equation.

→On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2.

$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta H^\circ}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$[\ln K]_{K_1}^{K_2} = \frac{\Delta H^\circ}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

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

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{T_2-T_1}{T_2T_1}\right]$$

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\left[\frac{T_2-T_1}{T_2T_1}\right] \quad \ldots\ldots\ldots\ldots (5)$$

Equation 5 is known as integrated form of van’t Hoff equation.

Phase equilibrium – Derivation of Phase rule from the concept of Chemical Potential

The phase rule describes the possible number of degrees of freedom in an enclosed system at equilibrium, in terms of the number of separate phases and the number of chemical constituents in the system. It was deduced by J.W Gibbs in the 1870s. Today, the phase rule is popularly known as the Gibbs phase rule all over the world. Here, in the article, we will be discussing the derivation of phase rule.

Gibbs Phase Rule

Gibbs phase rule states that if the equilibrium in a heterogeneous system is not affected by gravity or by electrical and magnetic forces, the number of degree of freedom is given by the equation

F=C-P+2

Where C is the number of chemical components

P is the number of phases

Basically, it describes the mathematical relationship for determining the stability of phases present in the material at equilibrium condition.

In the next section, let us look at the phase rule derivation.

Phase Rule Derivation

The Gibb's phase rule on the basis of the thermodynamic rule can be derived as follows:

First, let us consider a heterogeneous system consisting of P_n number of phases and C_n number of components in equilibrium. Let us assume that the passage of a component from one phase to another doesn't involve any chemical reaction. When the system is in equilibrium, it can be described by the following parameters:

- Temperature
- Pressure
- The composition of each phase

a. The total number of variables required to specify the state of the system is:

- Pressure: same for all phases
- Temperature: same for all phases
- Concentration

The independent concentration variables for one phase with respect to the C components are C – 1. Therefore, the independent concentration variables for P phases with respect to C components are P (C – 1).

Total number of variables = P (C – 1) + 2 (1)

b. The total number of equilibria:

The various phases present in the system can only remain in equilibrium when the chemical potential (μ) of each of the component is the same in all phases, i.e.

μ_1, P_1 =	μ_1, P_2 =	μ_1, P_3 =	…	=	μ_1, P
μ_2, P_1 =	μ_2, P_2 =	μ_2, P_3 =	…	=	μ_2, P
:	:	:			:
:	:	:			:
:	:	:			:
μ_C, P_1 =	μ_C, P_2 =	μ_C, P_3 =	…	=	μ_C, P

The number of equilibria for each P phases for each component is P – 1.

For C components, the number of equilibria for P phases is P (C – 1).

Hence, the total number of equilibria involved is E = C (P – 1). (2)

Equating eq (1) and (2), we get

$F= [P (C-1) +2-C] -[C (P-1)]$

$F= [CP-P+2-CP+C]$

$F=C-P+2$

The obtained formula is the Gibbs phase rule.

UNIT - III

CHEMICAL KINETICS

CHEMICAL KINETICS

→Chemical Kinetics is a branch of Physical Chemistry which deals with the rate of chemical reaction and the influence of various factors such as Concentration, Temperature, Catalyst etc and the reaction rates is called Chemical kinetics.

→The word Kinetics is derived from Greek word "Kinematics" means moment.

DEFINITIONS:

Chemical kinetics: It is a branch in physical chemistry which deals with the study of rate of a chemical reaction, the factor affecting their rates and the mechanism by which a chemical reaction occurs.

Rate of reaction: It is defined as the change in concentration of the reactant or product per unit time.

Average rate: It is defined as the change in concentration of a reactant or product divided by the time interval over which the change occurs.

Instantaneous rate: It is defined as the rate of a reaction at a specific instant.

Rate law: It is defined as an experimentally determined equation that expresses the rate ofchemical reaction in terms of molar concentration of the reactants.

Order of a reaction: It is the sum of the exponents to which the concentration terms in the rate law are raised.

Molecularity of a reaction: It is defined as the number of reacting species (atoms, ions or molecules) involved in an elementary reaction.

Zero order reactions: The chemical reaction in which the rate of the reaction is independent of the concentration of the reactants and remains constant throughout thecourse of the reaction are called zero order reactions.

First order reaction: The reactions in which the rate of reaction depends on the concentration of only one reactant are called first order reactions.

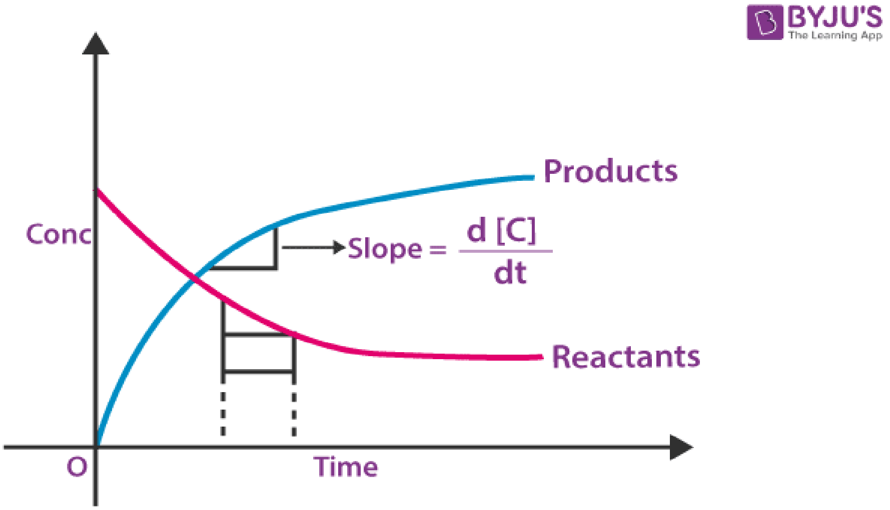
Pseudo first order reactions or Pseudo unimolecular reactions: The chemical reactions that have higher order true rate law but are found to behave as first order called pseudo molecular or pseudo first order reaction.

Half life period: The time required for a chemical reaction to reduce the original concentration of the reactant to half of its initial value is called half life period.

Rate of Formations and Disappearances

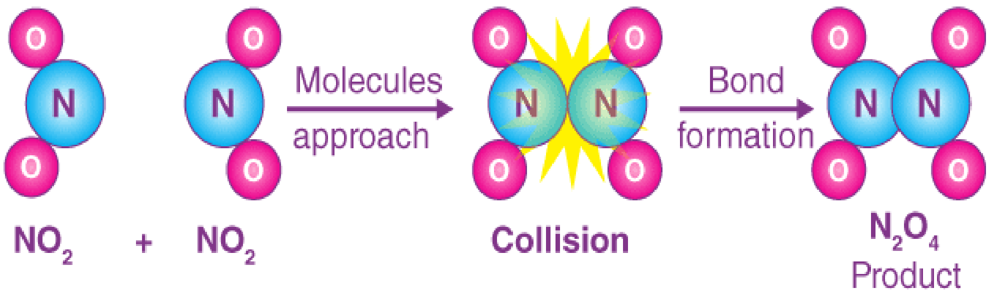
In any chemical reaction, as the reaction proceeds, the amount of reactants decreases, whereas the amount of products increases. One has to understand that the rate of the overall reaction depends on the rate at which reactants are consumed or the rate at which the products are formed.

If a graph is plotted between the concentration of reactants and products and time, rate of formation of products and rate of disappearance of reactants can be easily calculated from the slope of curves for products and reactants. The overall rate of the reaction may or may not be equal to the rate of formations and disappearances.

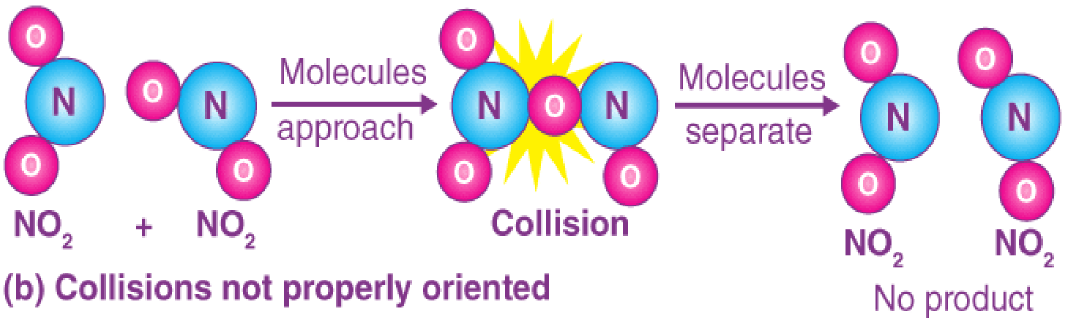


1. Write a brief note on Collision Theory?

- This theory was first proposed by Max Trautz and William Lewis.
- This theory explains about how a chemical reaction occurs and why different reactions give different products.
- It is applicable to gaseous molecules only.
- A chemical reaction occurs only collisions are happens between the reactant molecules.
- During the collisions molecule must be properly oriented.



(a) Properly oriented collisions form products



(b) Collisions not properly oriented

→All collisions are not activated collisions.

→A collision which may lead the product formation is called activated collisions.

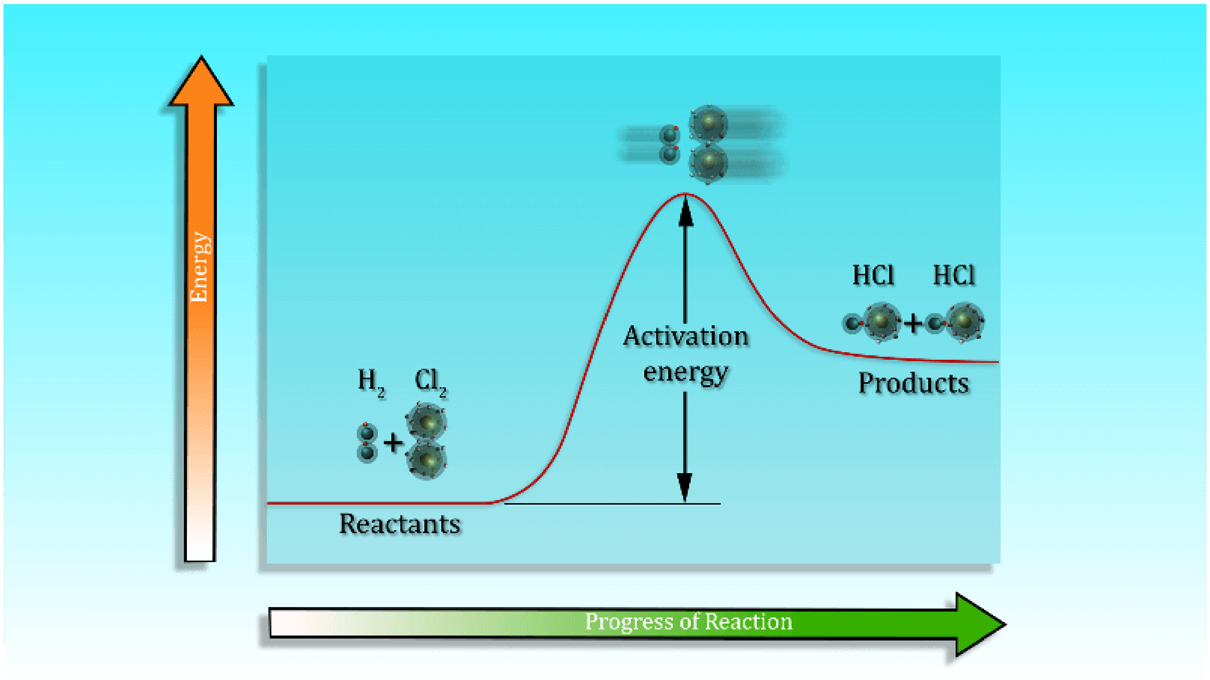
→A collision which may not lead the product formation is called inactivated collisions.

→Activation energy is the minimum energy required to cause the collisions between the reactant molecules.

→Activation energy is denoted as E_a.

→Activation energy is equal to threshold energy minus average energy.

$E_a = E_T - E_{avg}$



→The rate of reaction is directly proportional to the rate of reactant collisions.

$$rate\ of\ reaction = \frac{collisions}{time}$$

→According to Lewis theory rate of reaction between two identical molecules is given by

$A + A \rightarrow P$

Rate α $Z_{AA}\ e^{-Ea / RT}$

Where $Z_{AA} = \mu N_A^2/2\ \ d^2 \sqrt{8\pi KT/\mu}$

N_A = number of A molecules

d = average distance between A & A

μ = reduced mass

→According to Lewis theory rate of reaction between two different molecules is given by

$A + B \rightarrow P$

Rate $\alpha\ Z_{AB}\ e^{-Ea / RT}$

Where $Z_{AB} = N_A\ N_B\ d^2 \sqrt{8\pi KT/\mu}$

Z_{AB} = collision factor

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

N_A = number of A molecules

N_B = number of B molecules

d = distance between A and B

μ = reduced mass

Rate = $K^1\ Z_{AB}\ e^{-Ea / RT}$

$K = A\ e^{-Ea / RT}$

Where $A = K^1\ Z_{AB}$ = Arrhenius factor

→ The collision theory of equation applicable to two different reactions.

Rate of first reaction $K_1 = A\ e^{-Ea / RT1}$ ------ (1)

Rate of second reaction $K_2 = A\ e^{-Ea / RT2}$ ------- (2)

Apply ln for equations (1) & (2)

$\ln K_1 = \ln (A\ e^{-Ea / RT1})$

$\ln K_1 = \ln A + \ln e^{-Ea / RT1}$

$\ln K_1 = \ln A - \frac{Ea}{RT1}$ ------------ (3)

$\ln K_2 = \ln (A\ e^{-Ea / RT2})$

$\ln K_2 = \ln A + \ln e^{-Ea/RT2}$

$\ln K_2 = \ln A - \frac{Ea}{RT2}$ -------- (4)

Then eq (4) – eq (3)

$\ln K_2 - \ln K_1 = \ln A - \frac{Ea}{RT2} - \ln A + \frac{Ea}{RT1}$

$$ln\frac{K2}{K1} = \frac{Ea}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

$$log\frac{K2}{K1} = \frac{Ea}{2.303\,R}\left(\frac{T2 - T1}{T1\,T2}\right)$$

The above equation is known as integrated form of collision theory of reaction rates.

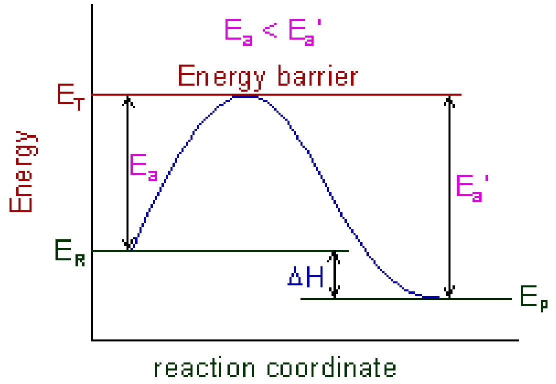
Limitations:

1. This theory is applicable to simple gaseous reactions only.

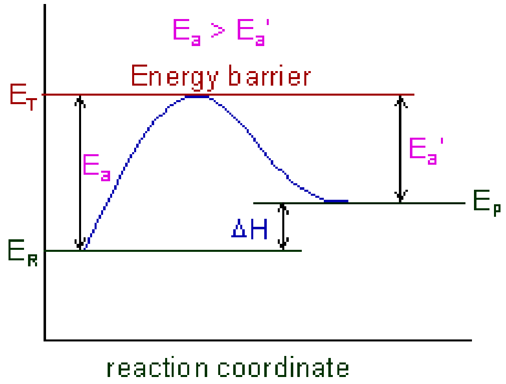
2. In this theory only kinetic energy is considered while vibration and rotational energies as ignored.

3. This theory does not explain bond cleavage and bond formation involved in a chemical reaction.

4. This theory does not explain steric factor which arises from bulky substituent.



Graph for exothermic reaction



Graph for endothermic reaction

2. Explain about Transition State Theory?

(OR)

Write a brief note on Activated Complex Theory?

(OR)

Explain about Absolute Rate Theory?

→This theory was proposed by "Henry Eyring".

→ This theory is also called as absolute rate theory.

→ According to transition state theory the reactants are not directly converted into products.

→ According to transition state theory

Reactant ↔ activated complex → products

→ Reactant molecules react with each other to form activated complex. This is also known as transition state.

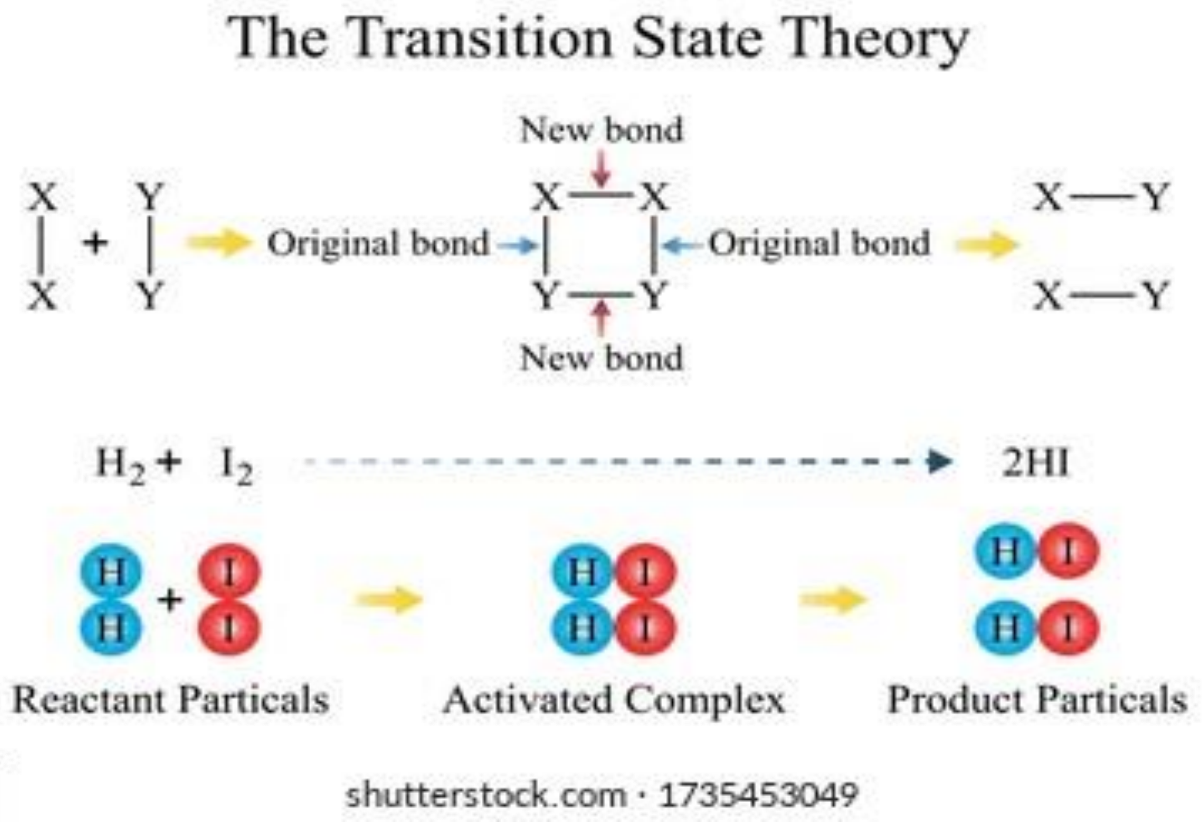
→ The life time of transition state is 10^{-5} to 10^{-8} sec.

→ The transition state always equilibrium with reactant molecules.

→ The transition state decomposes to products.

→ The difference between threshold energy and average energy of a molecule is called activation energy.

$E_a = E_T - E_{avg}$


The Transition State Theory

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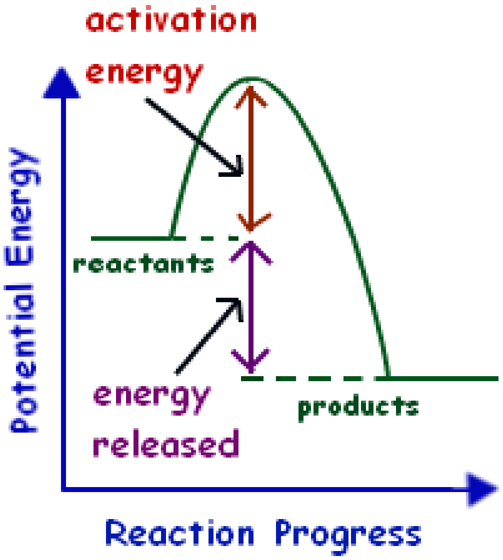
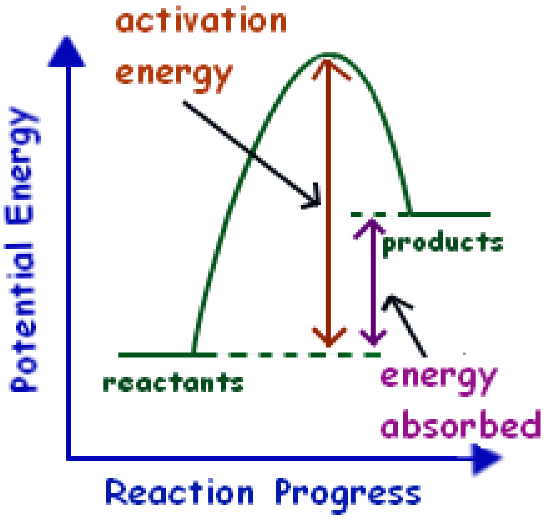
→ This theory may be illustrated by the potential energy surface diagrams.



Exothermic reaction



Endothermic reaction

→ Let us consider a bimolecular reaction between A & B

$A + B \rightleftharpoons [X]^* \rightarrow P$

Equilibrium constant $K^* = \frac{[X]*}{[A][B]}$

$[X]^* = K^* [A] [B]$ ------- (1)

→The rate of reaction is number of activated complexes which posses through the potential barrier in a unit time.

→ Rate of reaction = concentration of activated complexes X frequency

$\frac{dx}{dt} = [X]^* \vartheta$ $[\because \vartheta = \frac{KT}{h}]$

$\frac{dx}{dt} = [X]^* \frac{KT}{h}$ -------- (2)

Substitute eq (1) in eq (2), we get

$\frac{dx}{dt} = K^* [A] [B] \frac{KT}{h}$ ---------- (3)

For the conversion of reactants into products

$A + B \rightarrow P$

$\frac{dx}{dt} = K1\, [A][B]$ ------------- (4)

Compare eq (3) and eq (4)

$K1\, [A][B] = K^* [A] [B] \frac{KT}{h}$

$K1 = K^* \frac{KT}{h}$

$K1 = \exp\left(\frac{-\Delta G0}{RT}\right) \frac{KT}{h}$

Reaction Rate Constant

Activation Energy

Boltzmann Constant

Gibbs Energy of Activation

$$k = Ae^{\frac{-E_a}{RT}} \quad \Rightarrow \quad k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

Pre-exponential Factor

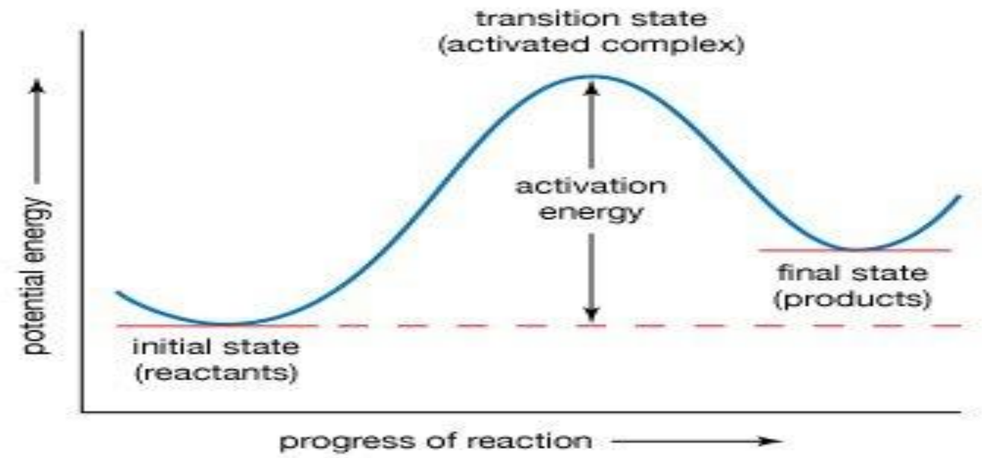
Absolute Temperature (in Kelvin)

Universal Gas Constant

Plank Constant

Arrhenius Equation

Eyring Equation



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Effect of ionic strength Debye – Huckel theory:

→ Ionic strength was first introduced by G.N.Lewies and RANBELL.

→ Ionic strength used to measure the activity of ion as well as concentration of ion.

→ It is defined as half of the sum of the square of the ionic charge which is multiplied by concentration of its ion.

→ It is denoted by I (or) µ.

$$\mu = \frac{1}{2}\sum_{1}^{n} c_i z_i^2$$

Where Z_i = charge of ion

C_i = concentration of ion

→ Ionic strength of the solution always depends on activity of the solution.

→ Activity of ion depends on concentration and activity coefficient.

$a = c\,\gamma$

Where γ = activity coefficient

→ In strong electrodes produced ions are very strong. Then it is impossible to determine ionic strength accurately.

→ In weak electrodes produced ions are weak. Then it is possible to determine the ionic strength accurately.

→ Ionic strength mainly classified into two types

1. Primary Salt Effect
2. Secondary Salt Effect.

3. Write a note on Primary Salt effect?

(OR)

Explain the effect of ionic strength on the rate constant?

(OR)

Derive Bronsted – Bjeerum equation?

→ Primary salt effect was introduced by “Bronsted” later it was modified by “Bjeerum” which is simpler than Bronsted.

→Primary salt effect, it has been observed that **the rate of a reaction can be altered by the presence of non-reacting or inert ionic species in the solution**. This effect is profound when the reaction takes place between ions, even at low concentrations.

→ According to Bjeerum reacting ions first form activated complex which is equilibrium with the reactants and then activated complex decomposes to give the products.

→ The rate of reaction determined by concentration of activated complex.

$$A^{Z_A} + B^{Z_B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[AB^{Z_{AB}}\right]^{*} \xrightarrow{k_3} \text{Products}$$

Where K_1 = rate constant for forward reaction

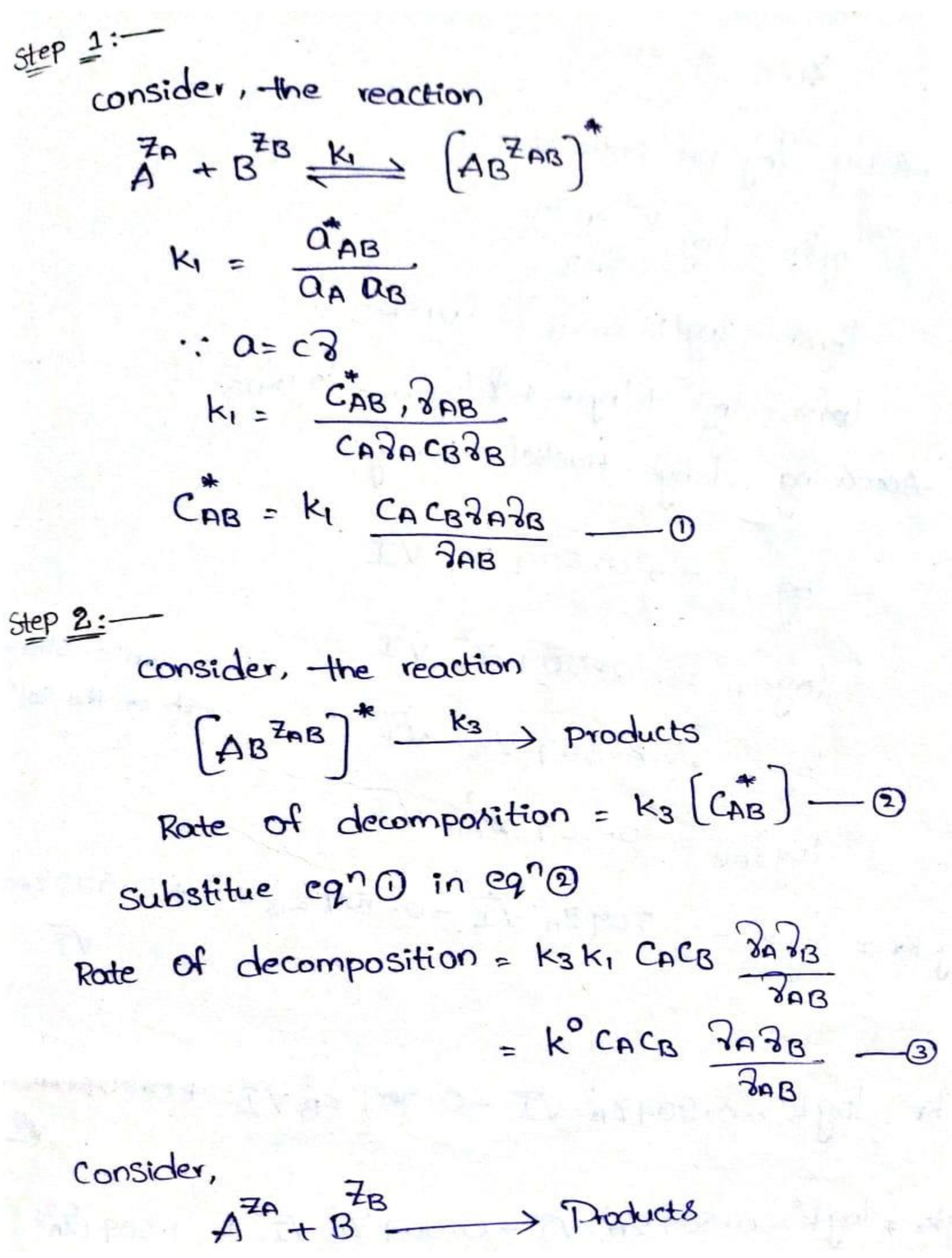
K_2 = rate constant for backward reaction

K_3 = rate constant for decomposition

Z_A = charge of ion A

Z_B = charge of ion B

Z_{AB} = charge of activated complex



Step 1:—

consider, the reaction

$$A^{Z_A} + B^{Z_B} \overset{k_1}{\rightleftharpoons} \left[AB^{Z_{AB}}\right]^*$$

$$K_1 = \frac{a^*_{AB}}{a_A\, a_B}$$

$\because a = c\gamma$

$$k_1 = \frac{C^*_{AB}, \gamma_{AB}}{C_A\gamma_A C_B\gamma_B}$$

$$C^*_{AB} = k_1 \frac{C_A C_B \gamma_A \gamma_B}{\gamma_{AB}} \quad \text{——} ①$$

Step 2:—

consider, the reaction

$$\left[AB^{Z_{AB}}\right]^* \xrightarrow{k_3} \text{Products}$$

$$\text{Rate of decomposition} = k_3 \left[C^*_{AB}\right] \quad \text{——} ②$$

Substitue eqⁿ ① in eqⁿ ②

$$\text{Rate of decomposition} = k_3 k_1\, C_A C_B \frac{\gamma_A \gamma_B}{\gamma_{AB}}$$

$$= k^o\, C_A C_B \frac{\gamma_A \gamma_B}{\gamma_{AB}} \quad \text{——} ③$$

Consider,

$$A^{Z_A} + B^{Z_B} \longrightarrow \text{Products}$$

Rate of reaction = $K_r\, C_A\, C_B$ ------------ (4)

At equilibrium, rate of formation = rate of decomposition i.e, (4) = (3)

$K_r\ C_A\ C_B = K^0\ C_A\ C_B\ \frac{\gamma A\ \gamma B}{\gamma AB}$

$K_r = K^0\ \frac{\gamma A\ \gamma B}{\gamma AB}$

Apply “log” on both sides

$\log K_r = \log K^0\ \frac{\gamma A\ \gamma B}{\gamma AB}$

$\log K_r = \log (K^0\ \gamma_A\ \gamma_B) – \log \gamma_{AB}$

$\log K_r = \log K^0 + \log \gamma_A + \log \gamma_B - \log \gamma_{AB}$ ---------- (5)

According to Debye – Huckel theory

$\log \gamma_i = - 0.509\ Z_i^2 \sqrt{I}$ Similarly

$\log \gamma_A = - 0.509\ Z_A^2 \sqrt{I}$

$\log \gamma_B = - 0.509\ Z_B^2 \sqrt{I}$

$\log \gamma_{AB} = - 0.509\ Z_{AB}^2 \sqrt{I}$

The above values are substituted in eq (5), we get

$\log K_r = \log K^0 – 0.509\ Z_A^2 \sqrt{I} - 0.509\ Z_B^2 \sqrt{I} + 0.509\ Z_{AB}^2 \sqrt{I}$

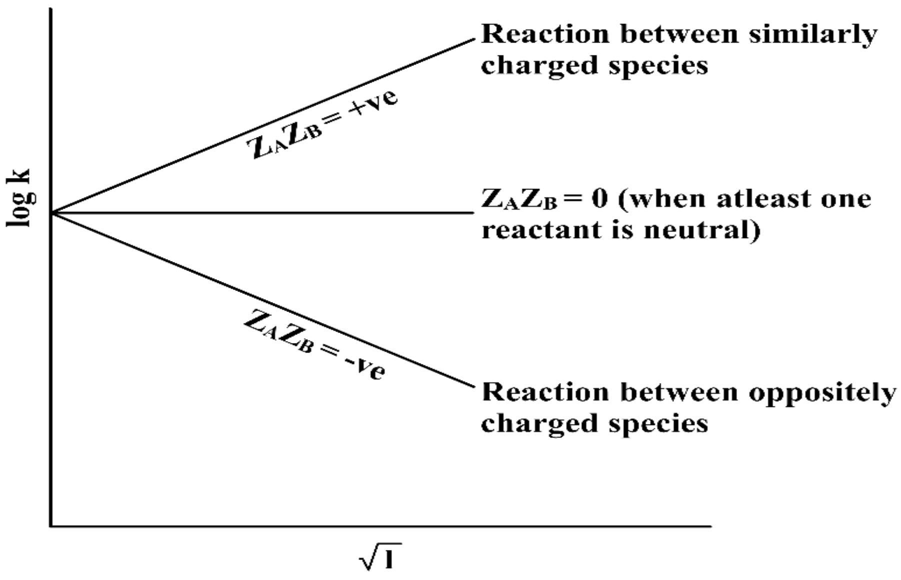
$\log K_r = \log K^0 – 0.509\ Z_A^2 \sqrt{I} - 0.509\ Z_B^2 \sqrt{I} + 0.509\ (Z_A + Z_B)^2 \sqrt{I}$

$\log K_r = \log K^0 – 0.509\ Z_A^2 \sqrt{I} - 0.509\ Z_B^2 \sqrt{I} + 0.509\ (Z_A^2 + Z_B^2 + 2\ Z_AZ_B) \sqrt{I}$

$\log K_r = \log K^0 – 0.509\ Z_A^2 \sqrt{I} - 0.509\ Z_B^2 \sqrt{I} + 0.509\ Z_A^2 \sqrt{I} + 0.509\ Z_B^2 \sqrt{I} + 2\ (0.509)\ (Z_AZ_B) \sqrt{I}$

$\log K_r = \log K^0 + 1.1018\ Z_AZ_B \sqrt{I}$

This equation is known as Brownsted – Bjeerum equation.



4. Explain about Secondary Salt effect?

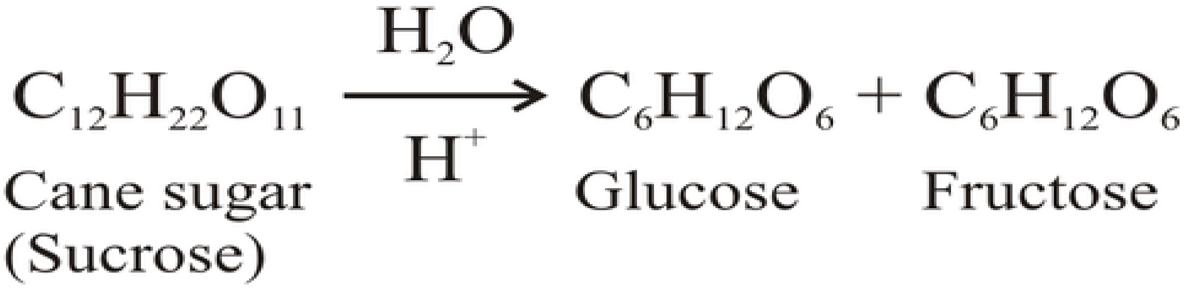
(OR)

Explain the effect of ionic strength on rate of reaction?

→ The actual change in concentration of reacting ion resulting from addition of an electrolyte is called Secondary salt effect.

→ The secondary salt effect is involved in catalytic reactions.

→ Let us consider the hydrolysis of cane sugar which is catalysed by a weak acid



$$\underset{\text{Cane sugar (Sucrose)}}{C_{12}H_{22}O_{11}} \xrightarrow[H^+]{H_2O} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

In the above reaction rate of reaction is directly proportional to concentration of H^+ ions only.

Rate of reaction α $[H^+]$

Rate of reaction = K_R $[H^+]$ --------- (1)

Catalyst comes from disassociation of weak acid

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

= acid dissociation constant

$K_a = a_{H^+}\, a_{A^-} / a_{HA}$

We know that, activity = concentration X activity coefficient

⁂ $a = c\ \gamma$

$$K_a = \frac{[H+]\gamma H+[A-]\gamma A-}{[HA]\gamma HA}$$

$$[H^+] = \frac{Ka\ [HA]\ \gamma HA}{[A-]\ \gamma H+\ \gamma\ A-}$$

$$[H^+] = K_a \frac{[HA]}{[A-]} \frac{\gamma HA}{\gamma H+\ \gamma\ A-}$$

$$[H^+] = K^1 \frac{\gamma HA}{\gamma H+\ \gamma\ A-} \text{ ----------- (2)}$$

Substitute eq (2) in eq (1), we get

$$K = K_R\ K^1 \frac{\gamma HA}{\gamma H+\ \gamma\ A-}$$

$$K = K_0 \frac{\gamma HA}{\gamma H+\ \gamma\ A-}$$

Apply “log” on both sides

$$\log K = \log K_0 \frac{\gamma HA}{\gamma H+\ \gamma\ A-}$$

$\log K = \log K_0 + \log \frac{\gamma HA}{\gamma H + \gamma A-}$

$\log K = \log K_0 + \log \gamma_{HA} - \log (\gamma_H^+ \gamma_A^-)$

$\log K = \log K_0 + \log \gamma_{HA} - \log \gamma_H^+ - \log \gamma_A^-$ -------- (3)

According to Debye – Huckel theory

$\log \gamma_i = -0.509 Z_i^2 \sqrt{I}$ Similarly

$\log \gamma_{HA} = -0.509 Z_{HA}^2 \sqrt{I}$

$\log \gamma_H^+ = -0.509 Z_{H+}^2 \sqrt{I}$

$\log \gamma_A^- = -0.509 Z_{A-}^2 \sqrt{I}$

Substitute the above values in eq (3), we get

$\log K = \log K_0 - 0.509 Z_{HA}^2 \sqrt{I} + 0.509 Z_{H+}^2 \sqrt{I} + 0.509 Z_{A-}^2 \sqrt{I}$

$\log K = \log K_0 - 0.509 (Z_H^+ - Z_A^-)^2 \sqrt{I} + 0.509 Z_{H+}^2 \sqrt{I} + 0.509 Z_{A-}^2 \sqrt{I}$

$\log K = \log K_0 - 0.509(Z_{H+}^2 + Z_{A-}^2 - 2 Z_H^+ Z_A^-) \sqrt{I} + 0.509 Z_{H+}^2 \sqrt{I} + 0.509 Z_{A-}^2 \sqrt{I}$

$\log K = \log K_0 - 0.509 Z_{H+}^2 \sqrt{I} - 0.509 Z_{A-}^2 \sqrt{I} + 1.018 Z_H^+ Z_A^- \sqrt{I} + 0.509 Z_{H+}^2 \sqrt{I} + 0.509 Z_{A-}^2 \sqrt{I}$

$\log K = \log K_0 + 1.018 Z_H^+ Z_A^- \sqrt{I}$

5. Explain the effect of dielectric constant on rate of reaction?

(OR)

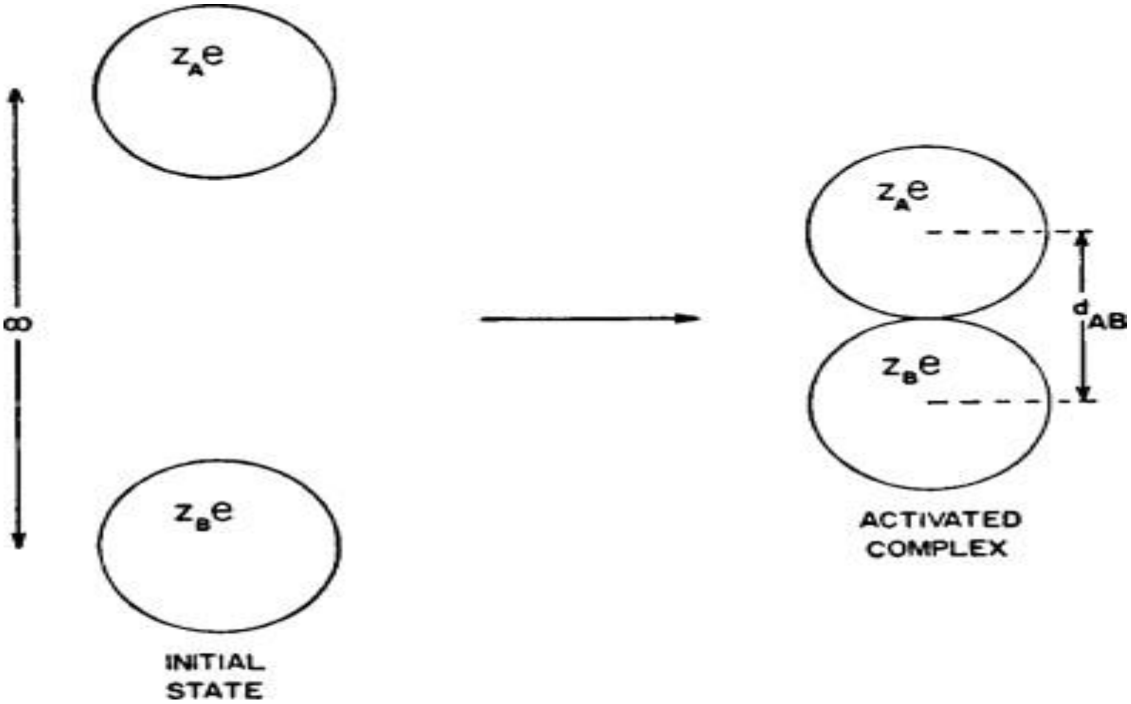
Explain the effect of solvent on rate of reaction?

→ According to collision theory the reactions takes place in gas phase does not involve the electro static interactions.

→ But in case of ionic reactions effected by electro static interactions.

→ Let us consider an ionic reaction between two ions A and B with radius r_A and r_B in a solution.

→ Suppose the two ions are initially at infinite distance. When the two ions are touch each other to form activated complex.



→ The work done to bring the two ions together from infinite distance to small distance (d_{AB}) is given by

$$W = \frac{ZA\, e\, X\, ZB\, e}{\varepsilon\, dAB}$$

$$W = \frac{ZA\, ZB}{\varepsilon\, dAB}\, e^2 \text{ ---------------- } (1)$$

Where Z_A = charge of the ion A

Z_B = charge of the ion B

e = elemental charge

Ɛ = dielectric constant

→ If the signs of two ions are same then the work is positive.

→ If the signs of two ions are different then the work is negative.

→ In this case work is equal to free energy activation which contributes both the electrostatic term and non electrostatic term.

$$\Delta G^{*} = \Delta G^{*}_{n.e.s} + \Delta G^{*}_{e.s}$$

$$\Delta G^{*} = \Delta G^{*}_{n.e.s} + \frac{ZA\,ZB}{\varepsilon\, dAB}\, e^{2} \text{ ------------ (2)}$$

→ According to transition state theory rate constant K is given by

$$K = \frac{KB\ T}{h}\, e^{\frac{-\Delta G*}{RT}} \text{ --------- (3)}$$

Substitute eq(2) in eq(3)

$$K = \frac{KB\ T}{h}\, e^{\frac{-(\Delta G*n.e.s + \frac{ZA\,ZB}{\varepsilon\, dAB} e2)}{RT}}$$

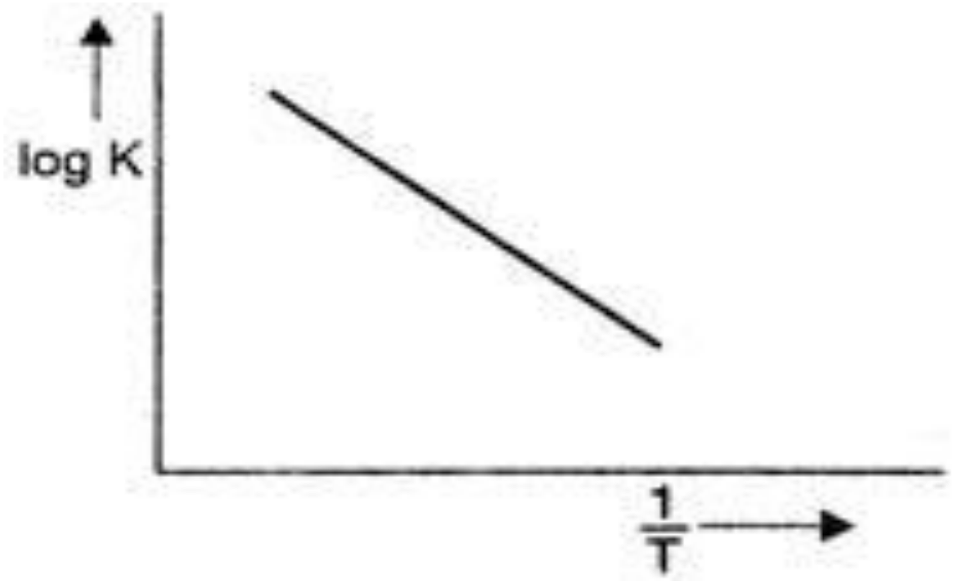
$$K = \frac{KB\ T}{h}\, e^{\frac{-\Delta G*n.e.s}{RT}}\, e^{-\frac{ZA\,ZB}{\varepsilon\, dABRT} e2}$$

Taking "log" on both sides

$$\log K = \log \frac{KB\ T}{h} + \log e^{\frac{-\Delta G*n.e.s}{RT}} + \log e^{-\frac{ZA\,ZB}{\varepsilon\, dABRT} e2}$$

$$\log K = \log K_0 - \frac{ZA\,ZB\ e2}{\varepsilon dAB\ RT} \qquad \text{Where } \log K_0 = \log \frac{KB\ T}{h} + \log e^{\frac{-\Delta G*n.e.s}{RT}}$$

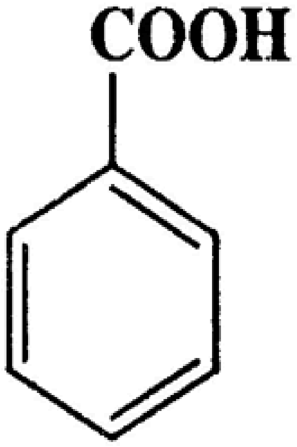
→ A graph is drawn between log K and $\frac{1}{\varepsilon}$ gives a straight line with negative slope.

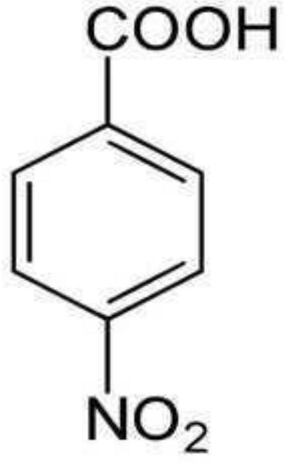


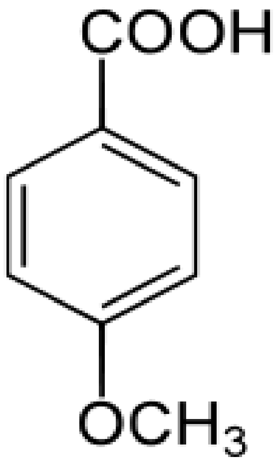
Effect of Substituent:

6. Write a note on Hammett equation?

- The equilibrium constants and rate constants of organic reactions are strongly affected by substitutes present on organic molecules.
- In 1937 Hammett measures the rate constants and equilibrium constants of Meta and para substituted aromatic compounds.
- Consider benzoic acid, para nitro benzoic acid and para methoxy benzoic acid.







- Here in para nitro benzoic acid -NO_2 group is electron withdrawing group.
- Here in para methoxy benzoic acid -OCH_3 group is electron donating group.
- The stability order of these compounds is EWG > H > EDG.

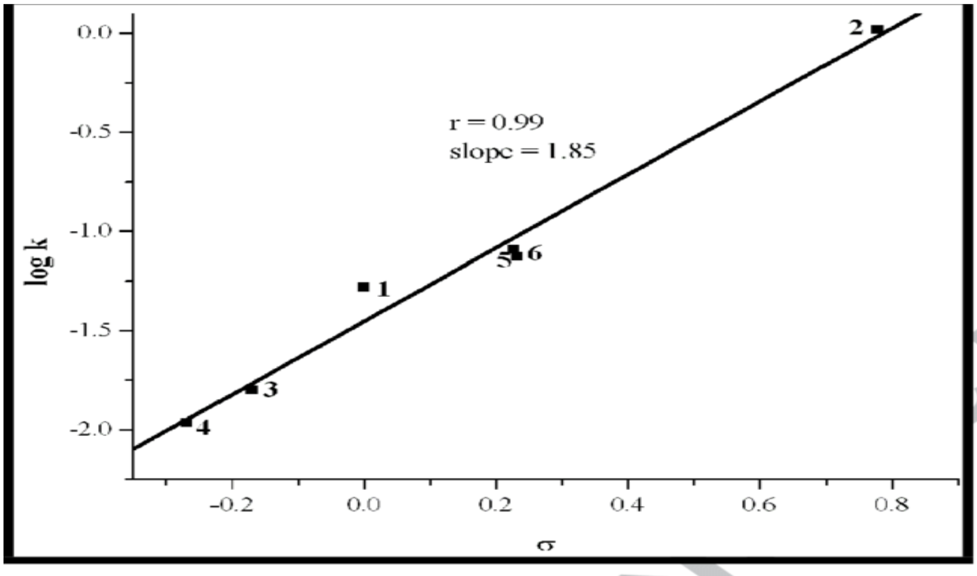
I.e, Para nitro benzoic acid > Benzoic acid > Para moethoxy benzoic acid.

- The reactivity order of these compounds is EDG > H > EWG.

I.e, Para methoxy benzoic acid > Benzoic acid > Para nitro benzoic acid.

- If any electron withdrawing group is present at para position σ value will be positive.
- If any electron donating group is present at para position σ value will be negative.
- A graph is drawn between log K v/s σ gives a straight line.

Linear graph for Meta and para substituted compounds.



- From the above graph Hammett concluded that in case of Meta and para substituted aromatic compounds follows the following equation.

$\log K = \log K_0 + \sigma \rho$

$\log K - \log K_0 = \sigma \rho$

$$\log \frac{K}{K_o} = \sigma \rho$$

Where K = dissociation constant with substituent

K_0 = dissociation constant without substituent

σ = substituent constant

P = reaction constant

Substituent	σ	ρ	$\log \frac{K}{K_o} = \sigma \rho$
EWG	+Ve	+Ve	+Ve
EDG	-Ve	+Ve	-Ve

Limitations:

1. Hammett does not explain rate constants of Ortho substituted aromatic compounds.
2. He does not explain the steric effect.

7. Write a note on Taft equation?

- Taft equation is applicable for ortho substituted aromatic compounds.
- Taft equation is also applicable to aliphatic compounds. Because steric factor play an important role in aliphatic compounds for rate of the reaction.
- Taft considers the polar effect and steric effect.
- Taft equation is represented as

$$\log (K/K_0) = \sigma^* \ \rho^* + S.E$$

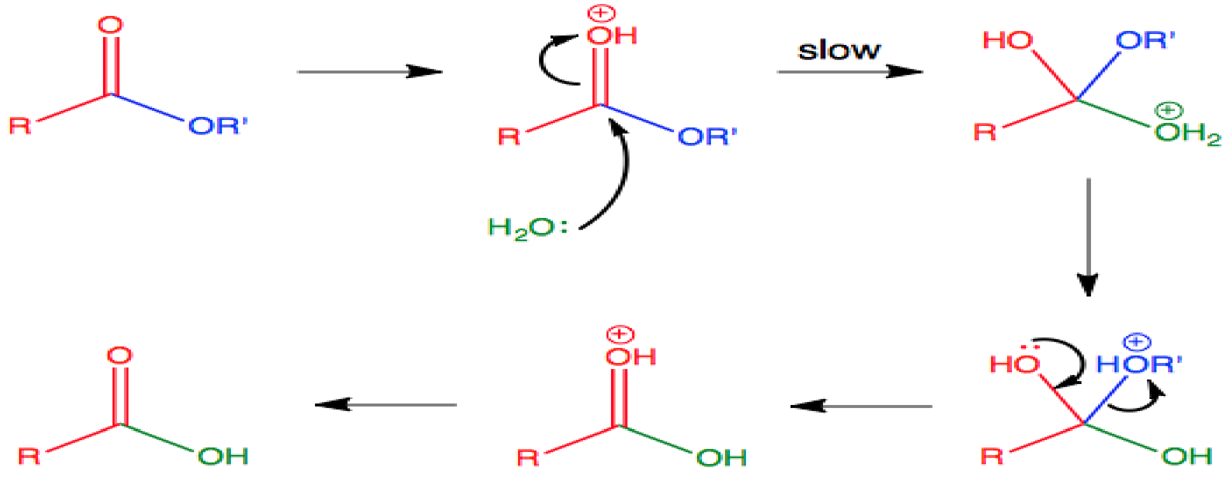
Where K = dissociation constant with substituent

K_0 = dissociation constant without substituent

σ^* = substituent constant and ρ^* = reaction constant

- This is explaining on the basis of reference reaction I.e., hydrolysis of ester.

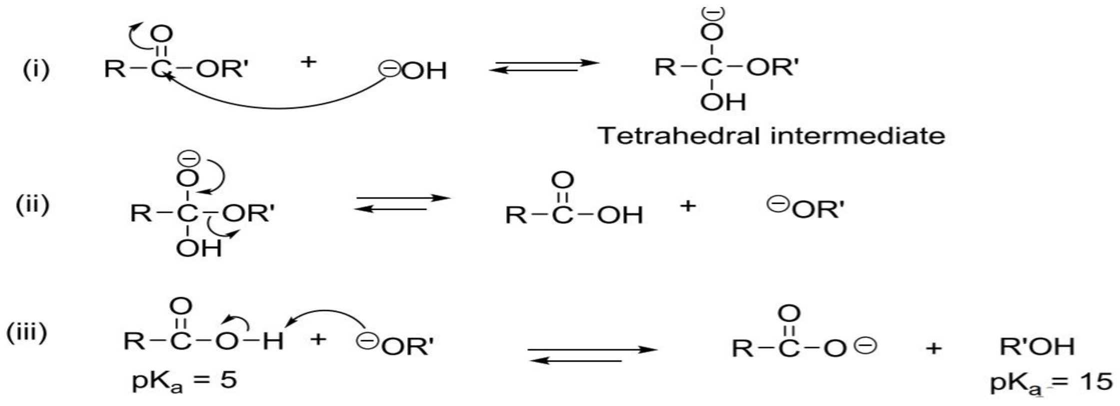
Acid catalyzed hydrolysis of ester:



in this case S.E = 0 and ρ^* = 0, it was determined experimentally.

Base catalyzed hydrolysis of ester:

In this case S.E = 0 and ρ^* = 2.5, it was determined experimentally.



- For acid hydrolysis of ester $\rho^* = 0$, then

$\log (K/K_0) = \sigma^* \; \rho^* + S.E$

$\log (K/K_0) = \sigma^* \; (0) + S.E$

$\log (K/K_0)_A = S.E$ --------- (1)

- For base hydrolysis of ester $\rho^* = 2.5$, then

$\log (K/K_0)_B = \sigma^* \; \rho^* + S.E$

$\log (K/K_0)_B = \sigma^* \; (2.5) + S.E$ ----------- (2)

Eq(2) - Eq(1), we get

$\log (K/K_0)_B - \log (K/K_0)_A = \sigma^* \; (2.5) + S.E - S.E$

$\log (K/K_0)_B - \log (K/K_0)_A = \sigma^* \; (2.5)$

$$\sigma^* = \frac{1}{2.48}\left[\log\left(\frac{k}{k_0}\right)_B - \log\left(\frac{k}{k_0}\right)_A\right]$$

The value of substituent constant can be determined by the above equation.

8. Show that Hammett equation and Taft equations are linear free energy relationship (LFER)?

- Hammett equation is a linear free energy relationship these can be demonstrated as follows.
- Consider dissociation constant of substituted benzoic acid

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

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

$\log K = \frac{-\Delta G0}{2.303\ RT}$ ----------- (1)

- Dissociation constant for unsubstituted benzoic acid

$\Delta G_0{}^0 = - RT \ln K_0$

$\Delta G_0{}^0 = - 2.303\ RT \log K_0$

$\log K_0 = \frac{-\Delta G0}{2.303\ RT}$ ----------- (2)

- According to Hammett equation we may write that

$\log K - \log K_0 = \sigma \rho$ -------- (3)

Substitute eq (1) & eq (2) in eq (3), we get

$$\frac{-\Delta G0}{2.303\ RT} + \frac{\Delta G0}{2.303\ RT} = \sigma \rho$$

$$-\Delta G^0 + \Delta G_0{}^0 = 2.303\ RT\ \sigma \rho$$

$$\Delta G_0{}^0 = 2.303\ RT\ \sigma \rho + \Delta G^0$$

9. Explain about Fast Reactions?

- Reactions which go to equilibrium in a few seconds are known as fast reactions.
- This reaction even proceeded in less time cannot be kinetically studied by conventional methods.
- The main reason for inability is “initial time cannot be determined accurately”.
- Fast reactions are studied by two methods.

1. Flow method
2. Relaxation method

1. Flow method:

- Flow method is also known as “mix and shake method”.
- In which reactants are mixed with in a fraction of seconds.
- It was first introduced by “Rough ton” and “Hastridge” used to measure the half time in the range from 10^{-1} to 10^{-13} sec.
- First reaction studied by using this method was the reaction between Fe^{+3} and CNS^{-1} . the rate of reaction is given by

$K = K_0 [Fe^{+3}] [CNS^{-1}] [1+ a/H^+]$

Where a = empirical constant

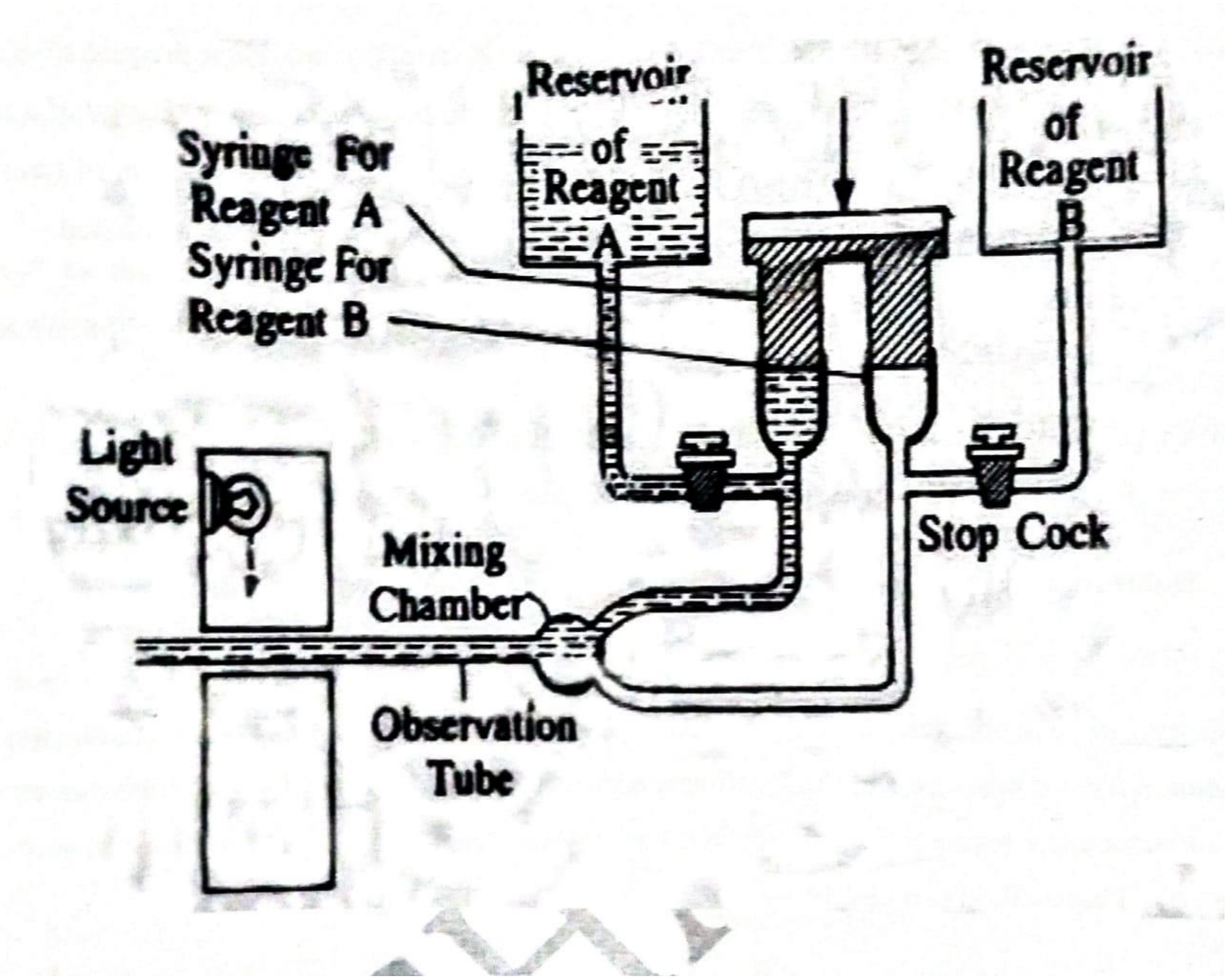
- Flow methods are of two types

  A. Rapid flow method

  B. Stopped flow method

A. Rapid flow method:

- The reactants are mixed as they flow together in a mixing chamber.
- The reaction continues as the thoroughly mixing solutions flow through the outlet tube and observe the composition at different position along the outlet tube is equal to the observation of reactant measures at different times after mixing.
- Disadvantage: It requires large volume of reactant solution.



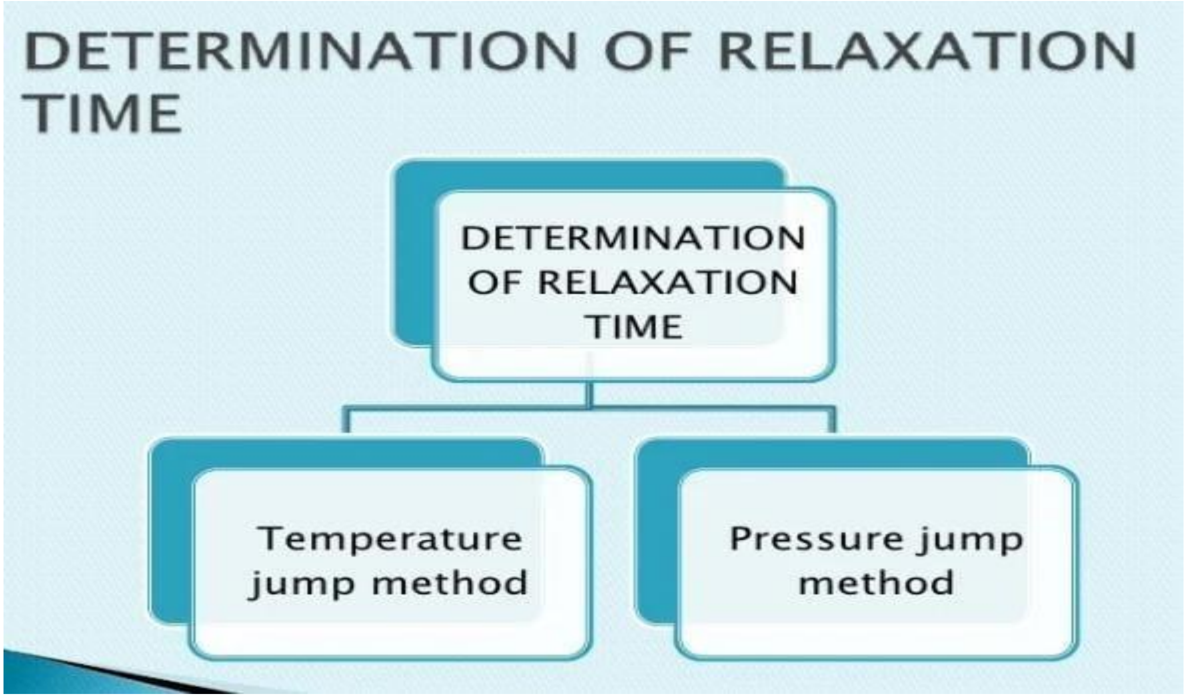
B. Stopped flow method:

- The two solutions are mixed very rapidly by injecting them into a mixing chamber.
- Beyond the mixing chamber the observation cell is fitted with a stopping syringe. When a required volume has been injected.
- Advantage: it requires small volume of the sample.

2. Relaxation method:

- In a relaxation method equilibrium is formed by a rapid change in one of the possible external parameter like temperature and pressure.
- The equilibrium process is then followed by spectrophotometric (or) conductophotometric methods.

- This method can be used for reaction having half time between 10^{-14} to 10^{-7} sec.
- This method can also be used for reversible fast reactions,
- In this method we can determine relaxation time



DETERMINATION OF RELAXATION TIME

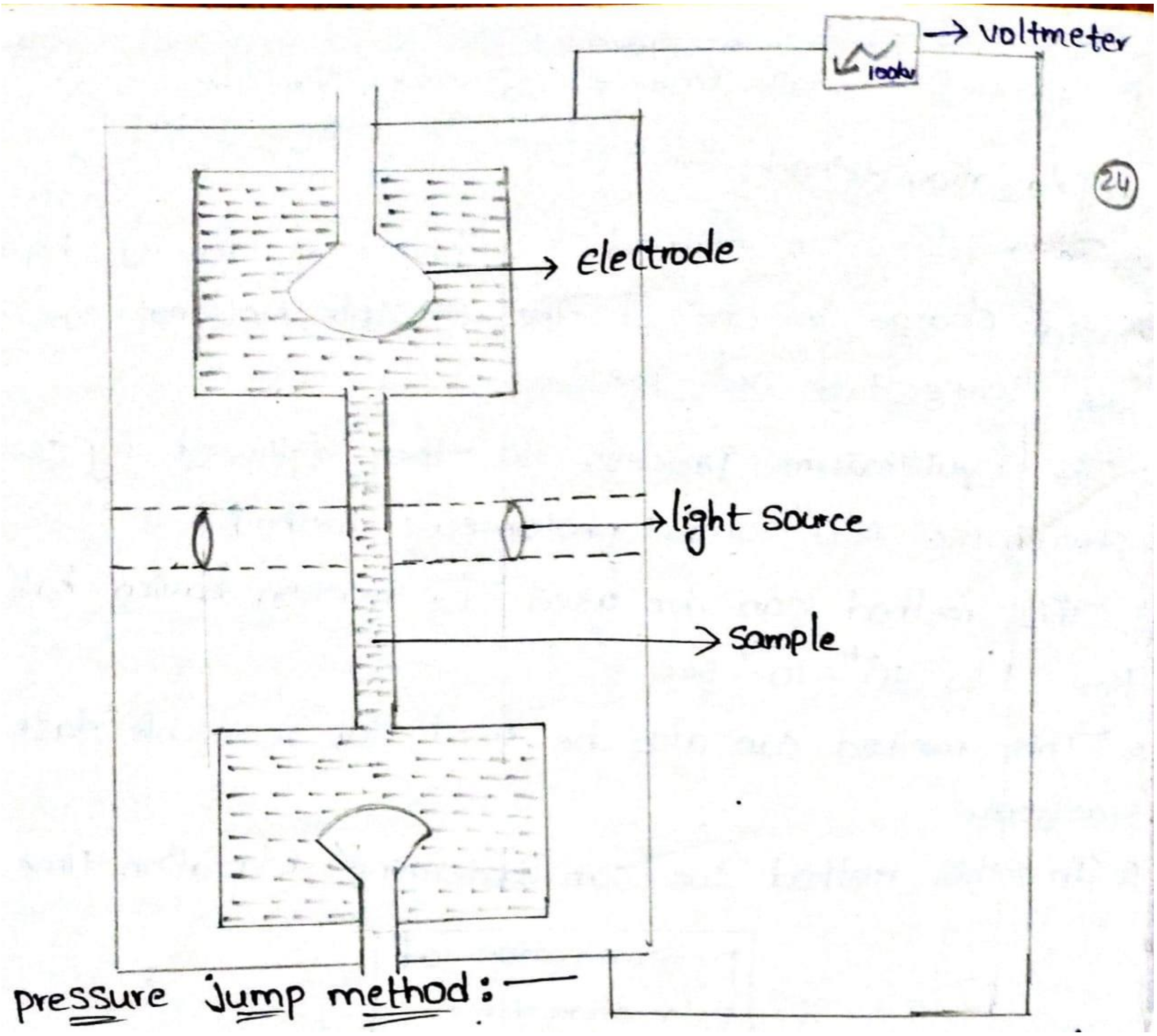
DETERMINATION OF RELAXATION TIME

Temperature jump method

Pressure jump method

Temperature jump method:

- In temperature jump method a temperature change of several degrees (=10^0 c) in 10^{-6} sec is created by a discharge of high voltage. Consider 100kv through a small quantity of sample.
- The relaxation time is depends on concentration followed by absorption spectroscopy.
- Apparatus required in temperature jump method as shown below

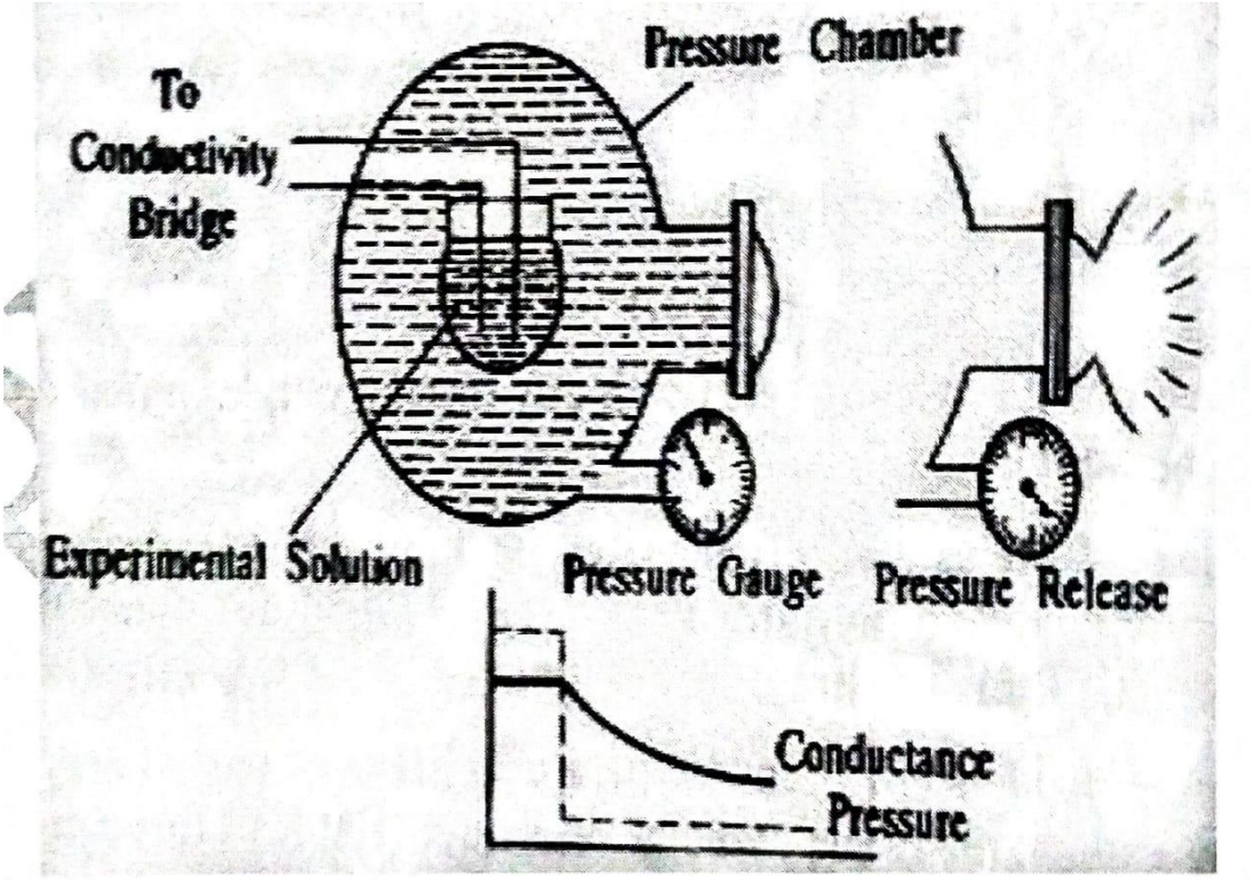


Pressure jump method:

- It involves a sudden and rapid change of pressure to displace the equilibrium.
- The sensitivity of a sample to pressure depends on the change in volume and is represented by the following equation.

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V}{RT}$$

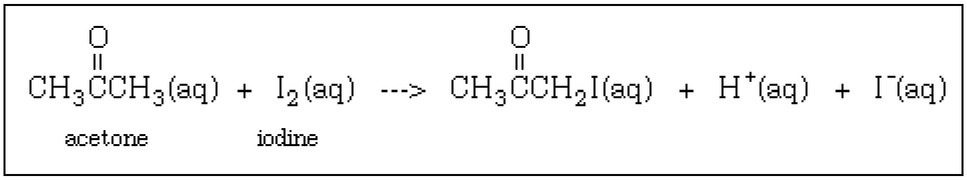
- The sample is placed in a flexible cell which is contained in a pressure chamber a pressure of above 65 atm.



10. General and Specific Acid - Base Catalysis?

General acid catalysis: The reactions which are catalysed by the substance which is having loss of protons is called general acid catalysis.

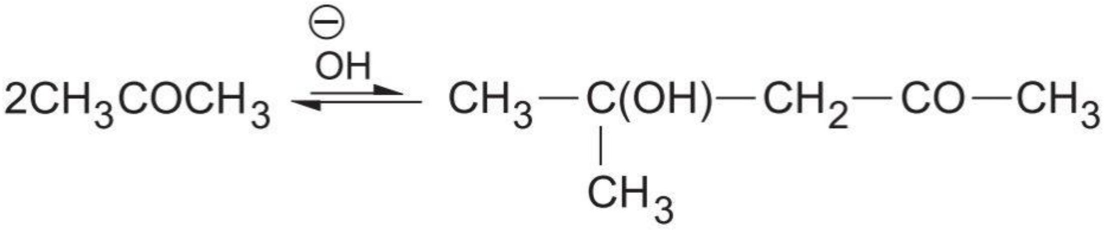
Example: Iodation of acetone



$$\underset{\text{acetone}}{CH_3\overset{\overset{O}{\|}}{C}CH_3(aq)} + \underset{\text{iodine}}{I_2(aq)} \text{ ---> } CH_3\overset{\overset{O}{\|}}{C}CH_2I(aq) + H^+(aq) + I^-(aq)$$

General Base catalysis: The reactions which are catalysed by the substance which is having gain of proton is called general base catalysis.

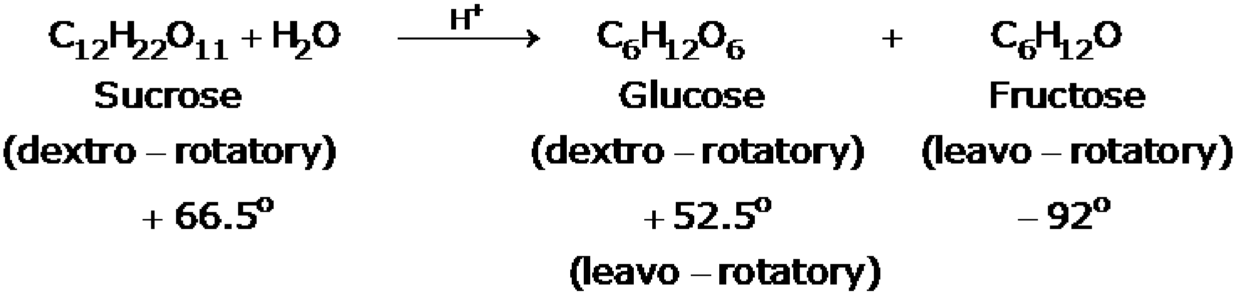
Example: condensation of acetone



$$2CH_3COCH_3 \underset{}{\overset{\overset{\ominus}{OH}}{\rightleftharpoons}} CH_3-\underset{\underset{CH_3}{|}}{C(OH)}-CH_2-CO-CH_3$$

Specific Acid catalysis: The reactions which are catalysed by H^+ ions only are called specific acid catalysis.

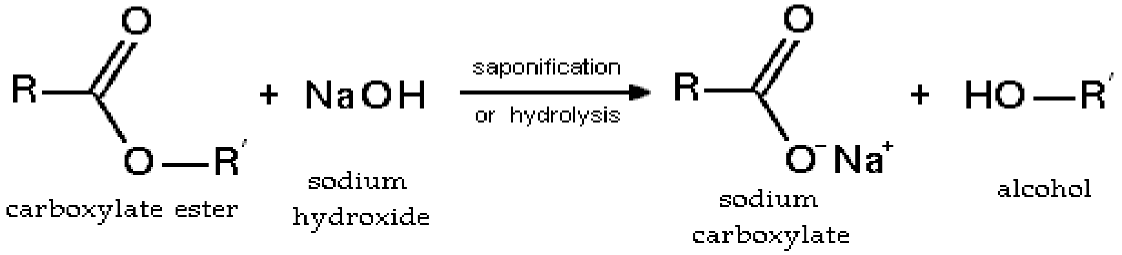
Example: Inversion of cane sugar



$$\begin{array}{cccc} C_{12}H_{22}O_{11} + H_2O & \xrightarrow{H^+} C_6H_{12}O_6 & + & C_6H_{12}O \\ \text{Sucrose} & \text{Glucose} & & \text{Fructose} \\ \text{(dextro – rotatory)} & \text{(dextro – rotatory)} & & \text{(leavo – rotatory)} \\ +66.5^o & +52.5^o & & -92^o \\ & \text{(leavo – rotatory)} & & \end{array}$$

Specific Base catalysis: The reactions which are catalysed by OH^- ions only are called specific base catalysis.

Example: Base catalysed hydrolysis of ester.



Protolytic and Prototrophic Mechanisms for Acid – Base catalysis:

Protolytic Mechanism:

- We know that in acid – base catalysis the transfer of proton from acid to substrate in the first step.
- In the second step transfer of proton to base from the protonated substrate.

  Step – I: $S + HA \leftrightarrow SH^+ + A^-$

  Step – II: $SH^+ + H_2O \rightarrow$ Products

- Rate of formation is products is given by

  $\frac{dP}{dT} = K_2\,[SH^+]\,[H_2O]$

  $\frac{dP}{dT} = K_2\,[SH^+]$ --------- (1)

- According to steady state approximation theory

  Rate of formation = rate of decomposition

  $K_1\,[S]\,[HA] = K_{-1}\,[SH^+]\,[A^-] + K_2\,[SH^+]\,[H_2O]$ $\because [H_2O] = 1$

  $K_1\,[S]\,[HA] = K_{-1}\,[SH^+]\,[A^-] + K_2\,[SH^+]$

  $K_1\,[S]\,[HA] = [SH^+]\,\{K_{-1}\,[A^-] + K_2\}$

  $\frac{K1\,[S][HA]}{K\,1\,[A\,]+K2} = [SH^+]$ --------- (2)

Substitute eq (2) in eq (1), we get

$\frac{dP}{dT}$ = $K_2\, \frac{K1\ [S][HA]}{K\ 1\ [A\ ]+K2}$

Prototrophic Mechanism:

Step – I: $S + HA \leftrightarrow SH^+ + A^-$

Step – II: $SH^+ + A^- \rightarrow$ Products

According to steady state approximation theory

Rate of formation = rate of decomposition

$K_1\ [S]\ [HA] = K_{-1}\ [SH^+]\ [A^-] + K_2\ [SH^+]\ [A^-]$

$K_1\ [S]\ [HA] = [SH^+]\ [A^-]\ (K_{-1} + K_2)$

$[SH^+] = \frac{K1\ [S][HA]}{[A\ ][K\ 1+K2]}$ ------ (1)

Rate of formation of products is given by

$\frac{dP}{dT} = K_2\ [SH^+]\ [A^-]$ ---------- (2)

Substitute eq(1) in eq(2), we get

$\frac{dP}{dT} = K_2\, \frac{K1\ [S][HA]}{[A\ ][K\ 1+K2]}\ [A^-]$

$\frac{dP}{dT} = K_2\, \frac{K1\ [S][HA]}{[K\ 1+K2]}$

11. Predict the rate constants of Parallel reactions, Opposing reactions and Consecutive reactions?

- Only few reactions are straight forward in nature

  I.e. first order reactions

  Second order reactions

  Third order reactions

- Other reactions are complicated because several reactions which takes place simultaneously along the main reactions. Such reactions are known as simultaneous reactions.

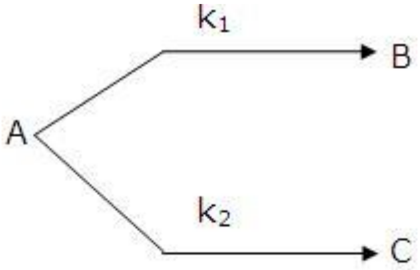
- Simultaneous reactions are divided into three types

   1. Side chain reactions (or) Parallel reactions
   2. Opposing reactions (or) Reversible reactions
   3. Consecutive reactions

1. Side chain reactions (or) Parallel reactions:

- When a reactant A undergoes two (or) more reactions at the same time it is in the case of side reactions.

- Let us consider the following reactions



(10%) side reaction

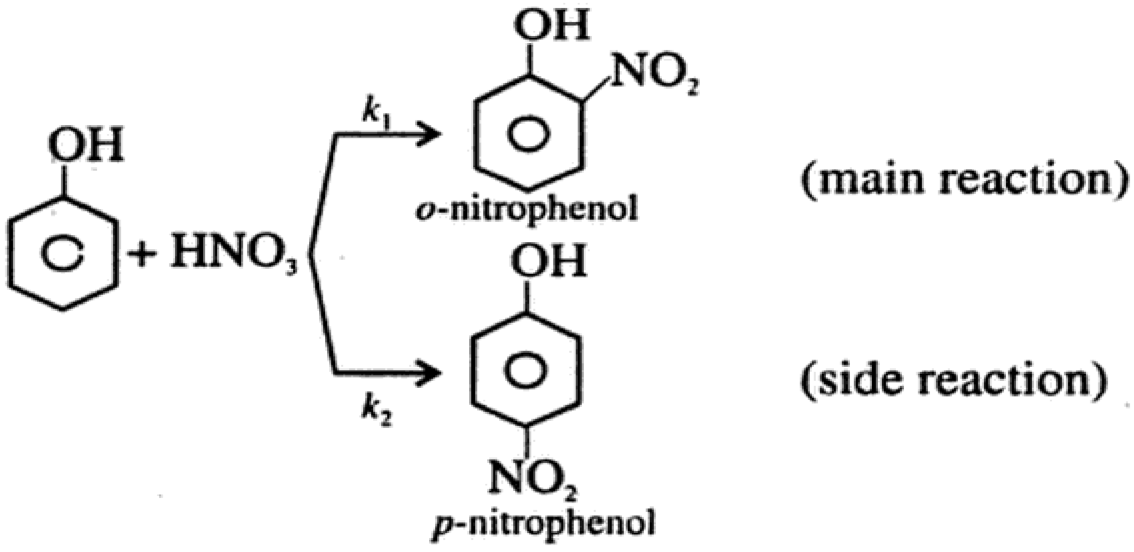
- Where A is the reactant which undergoes reactions I & II to form the products B & C.

- The reaction I (90%) is known as main reaction.

- The reaction II (10%) is known as side reaction.

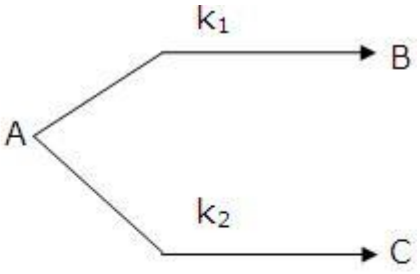
- Example

Nitration of phenol



Mathematical treatment of Parallel reaction:

Let us consider the following parallel reaction



A --------------------→ B + C

T= 0 (a) 0 + 0

T= t (a – x) x + x

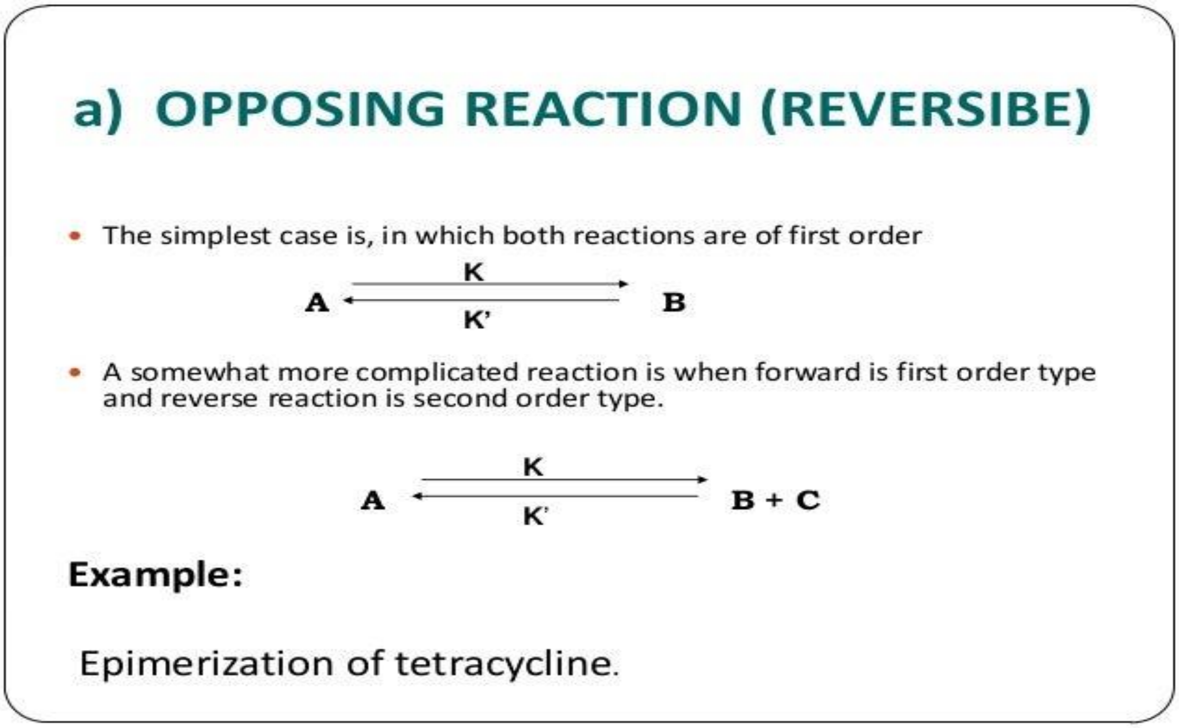
- Suppose “a” is the initial concentration of reactant “A”.
- Let “x” moles of “A” decomposed to form partly “B” and “C”.
- If y and z are the amounts of “B” and “C” at time “t”.
- The rate of disappearance of A = $\frac{-dx}{dt}$

- The rate of formation of B = $\frac{+dy}{dt}$
- The rate of formation of C = $\frac{+dz}{dt}$
- The rate of formation of B&C together = $\frac{+dx}{dt}$
- The net rate $\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}$ ------------ (1)
- $\frac{dy}{dt}$ = K_1 (a – x) ----------- (2)
- $\frac{dz}{dt}$ = K_2 (a – x) ----------- (3)
- Substitute eq(2) & eq(3) in eq(1), we get
- $\frac{dx}{dt}$ = K_1 (a – x) + K_2 (a – x)
- $\frac{dx}{dt}$ = (a – x) ($K_1 + K_2$) $\because$ [$K_1 + K_2 = K$]
- $\frac{dx}{dt}$ = (a – x) K
- $\frac{dx}{a-x}$ = K dt
- Integration on both sides
- $\int \frac{1}{a-x}\, dx = K \int dt$
- - ln (a – x) = K t + C ---------- (3)
- Apply initial conditions t = 0 & x = 0, then
- - ln (a – 0) = K (0) + C
- - ln a = C ---------- (4)
- Substitute eq(4) in eq(3), we get
- - ln (a – x) = K t – ln a

- $\ln a - \ln (a - x) = K t$
- $\ln \left(\frac{a}{a-x}\right) = K t$
- $K = \frac{1}{t} \ln \left(\frac{a}{a-x}\right)$
- $K = \frac{2.303}{t} \log \left(\frac{a}{a-x}\right)$

2. **Opposing Reactions (or) Reversible Reactions:**

- There are certain reactions in which the products of chemical reaction react with each other to form original reaction. Such reactions are called Opposing reactions (or) Reversible reactions.
- In Opposing reactions, the net rate of reaction will be affected by both forward and backward reactions.
- Example



a) OPPOSING REACTION (REVERSIBE)

- The simplest case is, in which both reactions are of first order

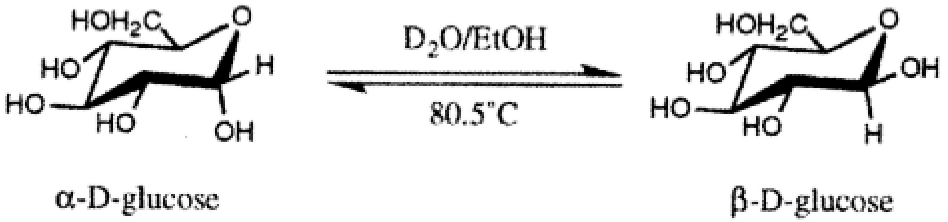
$$A \underset{K'}{\overset{K}{\rightleftharpoons}} B$$

- A somewhat more complicated reaction is when forward is first order type and reverse reaction is second order type.

$$A \underset{K'}{\overset{K}{\rightleftharpoons}} B + C$$

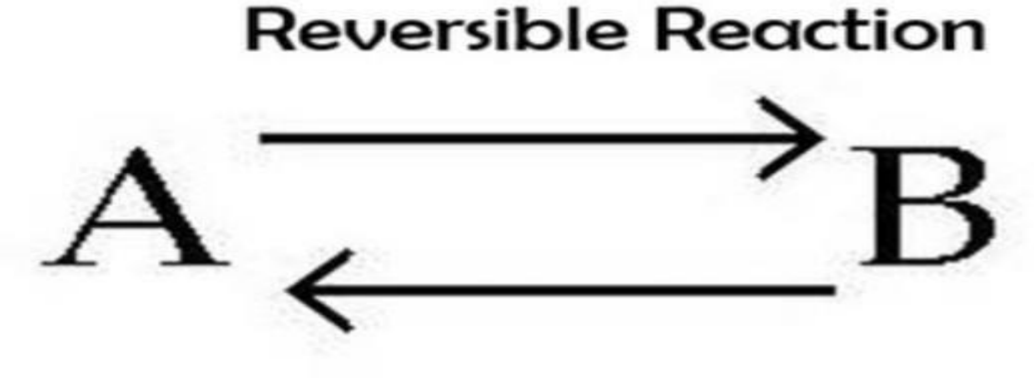
Example:

Epimerization of tetracycline.



Mathematical treatment of Opposing Reactions:

Let us consider the following reaction



- Suppose both forward and backward reactions are first order.
- Where K_1 & K_2 are rate constants for forward reaction and backward reaction.
- A -------------→ B
- T = 0 (a) 0
- T = t (a – x) x
- Suppose "a" is the initial concentration of reactant "A" after time "t" "x" moles of A decomposed to form B.
- The rate of forward reaction = K_1 (a – x) -------- (1)

- The rate of backward reaction = K_2 x ------------ (2)
- The net rate of reaction is rate of forward reaction minus rate of backward reaction.
- $\frac{dx}{dt}$ = K_1 (a – x) – K_2 x ------------ (3)
- At equilibrium net rate of reaction ($\frac{dx}{dt}$) is zero.
- 0 = K_1 (a – x_e) – K_2 x_e
- K_2 x_e = K_1 (a – x_e)
- $K2 = \frac{K1\ (a-Xe)}{Xe}$ --------- (4)
- Substitute eq(4) in eq(3), we get
- $\frac{dx}{dt}$ = K_1 (a – x) – K_2 $\frac{K1\ (a-Xe)}{Xe}$
- $$\frac{dx}{dt} = \frac{K1\ (a-X)Xe - K1\ (a-Xe)X}{Xe}$$
- $$\frac{dx}{dt} = \frac{K1\ a\ Xe - K1\ X\ Xe\ - K1\ aX + K1\ X\ Xe}{Xe}$$
- $$\frac{Xe}{Xe-X}\ dx = K1\ a\ dt$$
- Integration both sides
- $$\int \frac{1}{Xe-X}\ dx = \frac{K1\ a}{Xe} \int dt$$
- - ln (X_e – X) = $\frac{K1\ a}{Xe}$ t + C ----------- (5)
- Apply initial conditions t = 0 & x = 0
- - ln (X_e – 0) = $\frac{K1\ a}{Xe}$ (0) + C

- $- \ln X_e = C$ ---------- (6)
- Substitute eq(6) in eq(5), we get
- $- \ln (X_e – X) = \frac{K1\ a}{Xe}\ t – \ln X_e$
- $\ln X_e - \ln (X_e – X) = \frac{K1\ a}{Xe}\ t$
- $\ln(\frac{Xe}{Xe-X}) = \frac{K1\ a\ t}{Xe}$
- $K_1 = \frac{Xe}{a\ t} \ln (\frac{Xe}{Xe-X})$
- $K_1 = \frac{2.303\ Xe}{a\ t} \log (\frac{Xe}{Xe-X})$

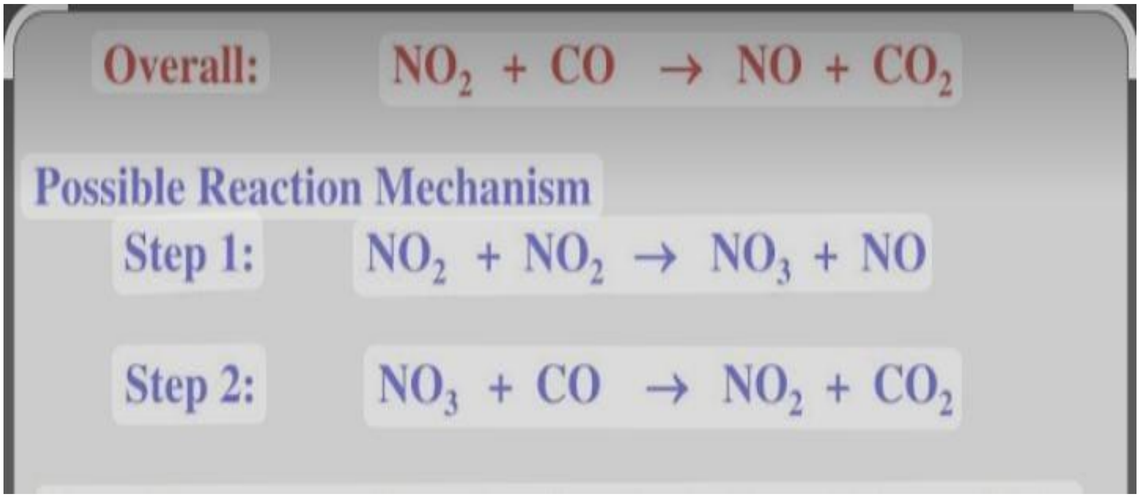
2. Consecutive reactions:

The reactions in which the reactant forms an intermediate and the intermediate forms the product in one or many subsequent reactions are called consecutive reactions.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

A= reactant, B= intermediate, C= product. Initially only the reactant A will be present. As the reaction starts, A produces an intermediate B is formed, it produces the product C through K2, Rate Constant. After the completion of reaction only 'C' is present and concentrations of A and B will be zero.

Example



Overall: $NO_2 + CO \rightarrow NO + CO_2$

Possible Reaction Mechanism

Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

Mathematical treatment of consecutive reactions:

Let us consider the following reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Suppose "a" is the initial concentration of A and x, y, z are the concentrations of A, B, C respectively. Then

$a = x + y + z$ ----------- (1)

the rate of disappearance is $\frac{-dx}{dt} = K_1\, x$

$\frac{-dx}{x} = K_1\, dt$

Integration on both sides

$-\int \frac{dx}{x} = K_1 \int dt$

$-\ln x = K_1\, t + C$ ----------- (2)

Apply initial conditions x = a & t = 0

$-\ln a = K_1\, (0) + C$

$-\ln a = C$ -------- (3)

Substitute eq(3) in eq(2), we get

$-\ln x = K_1 t - \ln a$

$\ln a - \ln x = K_1 t$

$\ln(\frac{a}{x}) = K_1 t$

$K_1 = \frac{1}{t} \ln(\frac{a}{x})$

$K_1 = \frac{2.303}{t} \log(\frac{a}{x})$

12. **Explain about Skarbal Diagram?**

(OR)

Explain the effect of P^H on reaction rate?

- We known that in acid catalysed reaction rate of reaction is depend on concentration of H^+ ions only.
- Rate of reaction α $[H^+]$

  $K_r = K_0 [H^+]$

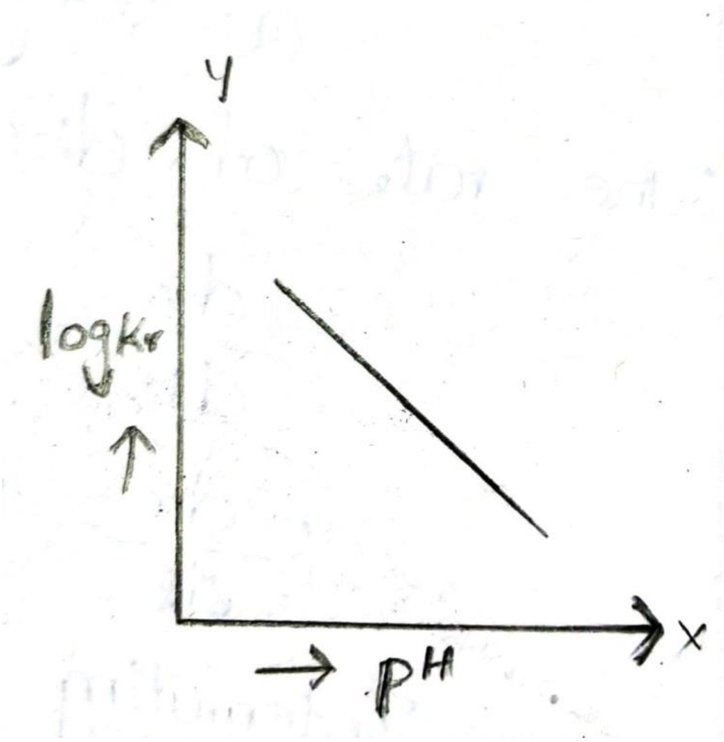
  Taking "log" on both sides

  $\log K_r = \log \{K_0 [H^+]\}$

  $\log K_r = \log K_0 + \log [H^+]$

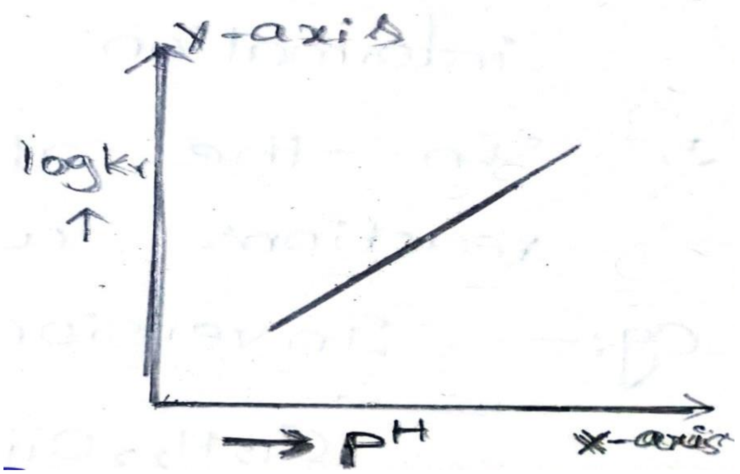
  We know that $P^H = -\log [H^+]$

  $\log K_r = \log K_0 - P^H$

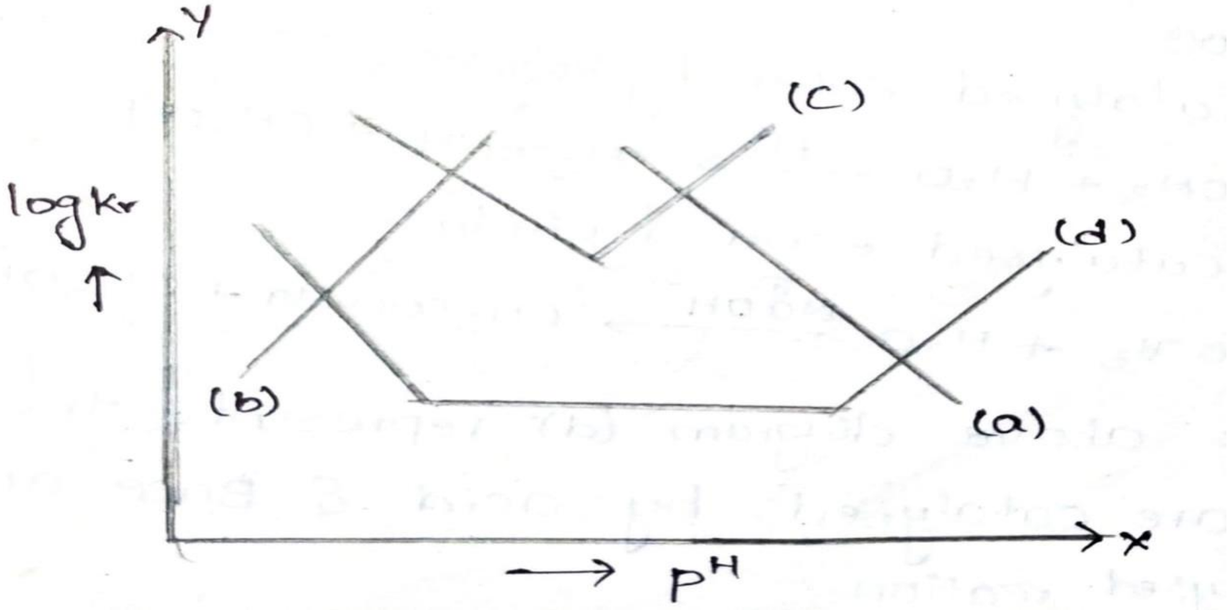


- We know that in base catalysed reactions rate of reaction is depends on concentration of OH^- ions only.
- Rate of reaction α $[OH^-]$
- $K_r = K_0 [OH^-]$
- Taking “log” on both sides
- $\log K_r = \log \{K_0 [OH^-]\}$
- $\log K_r = \log K_0 + \log [OH^-]$ ------ (1)
- from the ionic product of water
- we know that $K_W = [H^+] [OH^-]$
- $\frac{Kw}{[H+]} = [OH^-]$ -------------- (2)
- Substitute eq(2) in eq(1), we get
- $\log K_r = \log K_0 + \log (\frac{Kw}{[H+]})$

- $\log K_r = \log K_0 + \log K_W - \log [H^+]$
- we know that $P^H = - \log [H^+]$
- $\log K_r = \log K_0 + \log K_W + P^H$

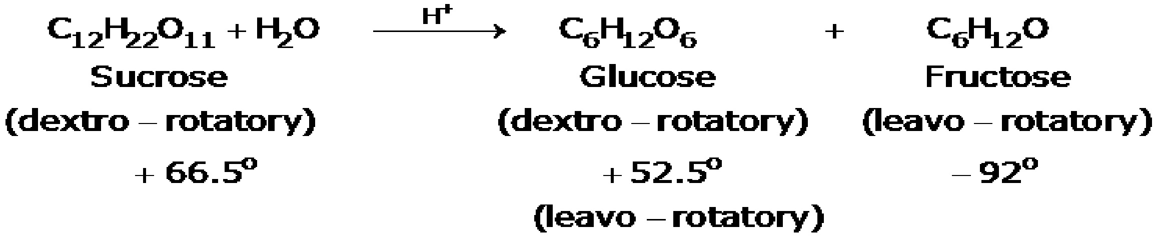


- Skarbal plotted a graph between $\log K_r$ V/S P^H for number of reactions of acid catalyzed reaction, base catalyzed reaction, both acid – base catalyzed reactions and un catalyzed reactions.
- Skarbal diagram gives the information above acid catalyzed reactions, base catalyzed reactions, both catalyzed reactions and uncatalyzed reactions.



- From the above graph the following information can be obtained.
- In the above diagram (a) represents the reactions which are catalyzed by H^+ ions only.

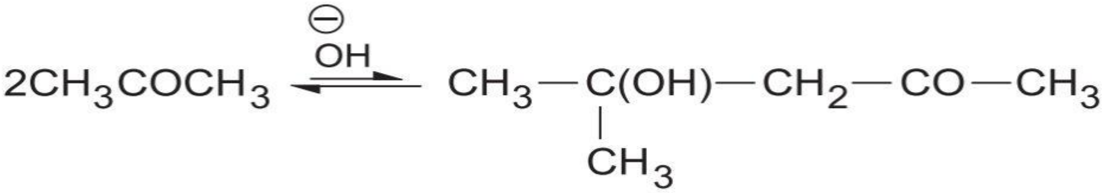
Example: inversion of cane sugar



$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O$$

- In the above diagram (b) represents the reactions which are catalyzed by OH^- ions only.

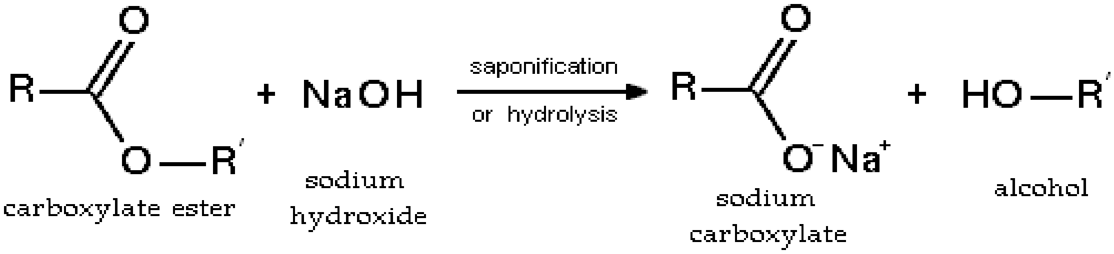
Example: condensation of acetone

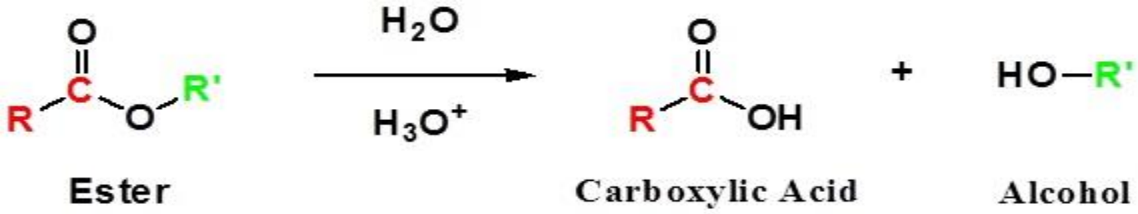


$$2CH_3COCH_3 \overset{\ominus}{\underset{}{\overset{OH}{\rightleftharpoons}}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C(OH)}}-CH_2-CO-CH_3$$

- In the above diagram (c) represents the reactions which are catalyzed by both H^+ & OH^- ions.

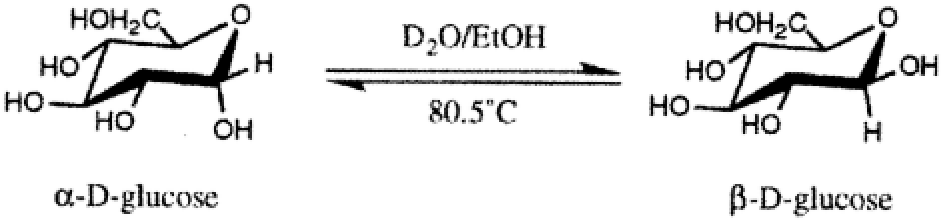
Example: Hydrolysis of ester





- In the above diagram (d) represents the reactions which are catalyzed by acid, base and uncatalyzed reactions.

Example: muta rotation of α – D glucose to β – D glucose



MICELLES AND MACROMOLECULES

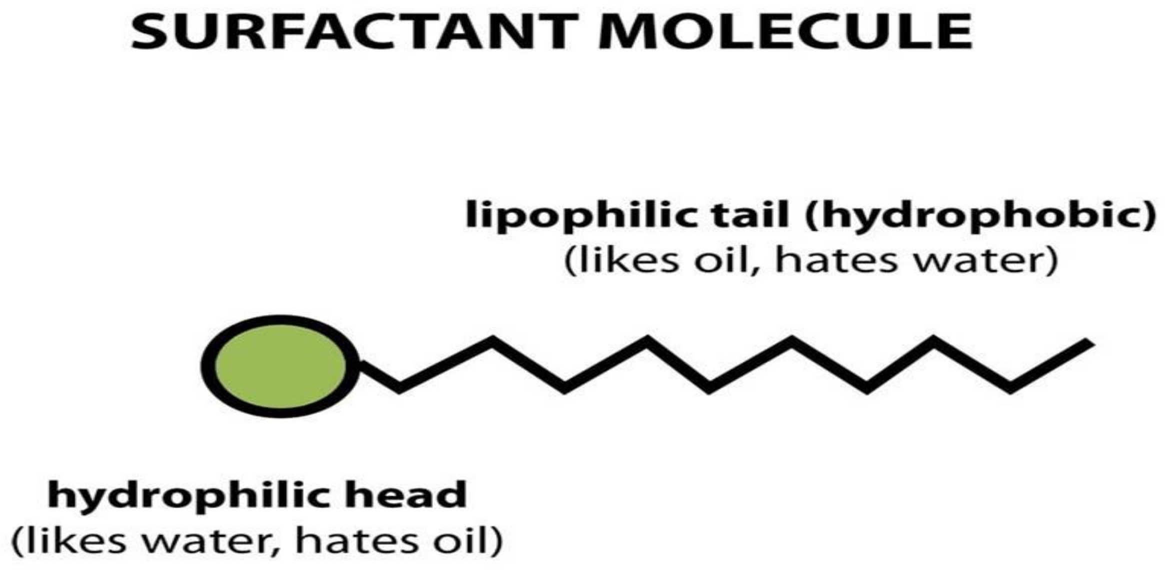
MICELLES

⁂ 1. What are Surfactants and explain their classification?

Surfactants:

→Surfactant word comes from the Surface active agents.

→Surfactants are usually organic compounds having amphiphilic nature, i.e. it containing both hydrophobic and hydrophilic groups.



→Surfactants may act as detergents, wetting agents, emulsifiers and foaming agents.

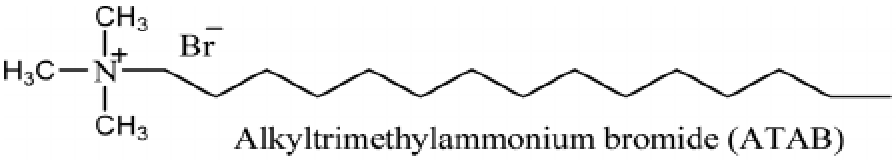
→Surfactants added to a liquid reduces its surface tension.

→Surface active agents are classified into four types

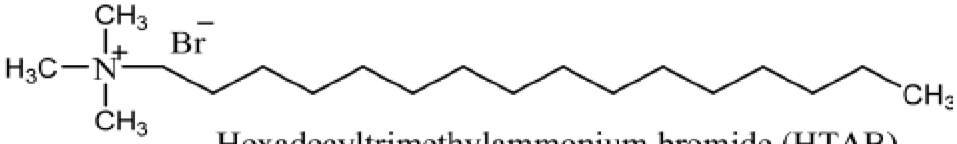
1. Cationic Surfactants
2. Anionic Surfactants
3. Amphoteric Surfactants
4. Non ionic Surfactants

1. Cationic Surfactants: Cationic surfactants those which disassociates in water to form positively charged ions.

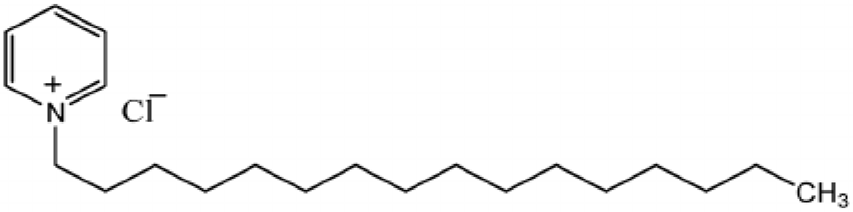
Examples are



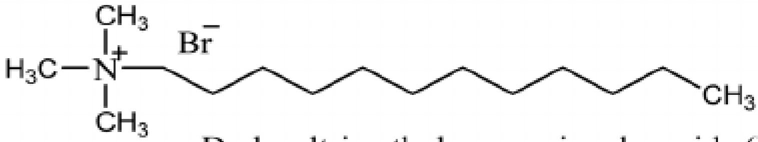
Alkyltrimethylammonium bromide (ATAB)



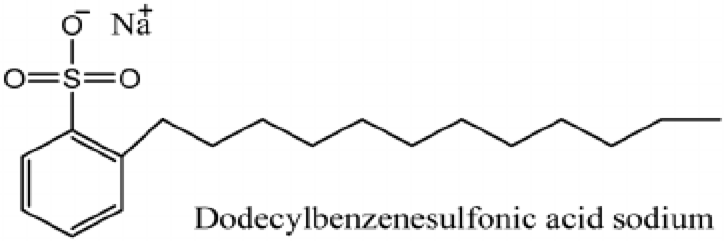
Hexadecyltrimethylammonium bromide (HTAB)



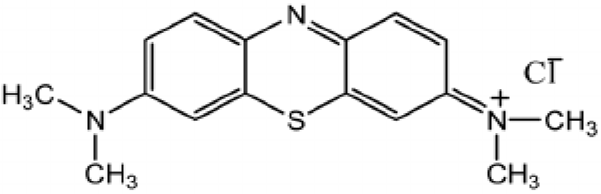
Cetylpyridinium chloride (CPC)



Dodecyltrimethyl ammonium bromide (DTAB)



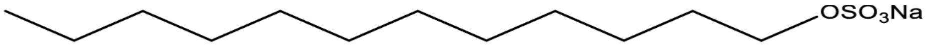
Dodecylbenzenesulfonic acid sodium salt (DBS)



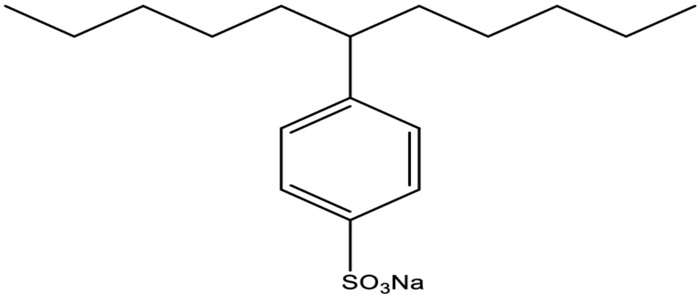
Methylene Blue (MB)

2. Anionic Surfactants: Anionic surfactants those which disassociates in water to form negatively charged ions.

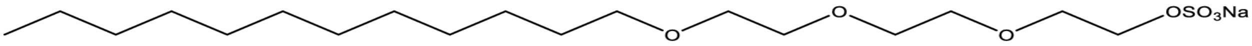
Examples are



Alkyl sulfate



Alkylbenzene sulfonate

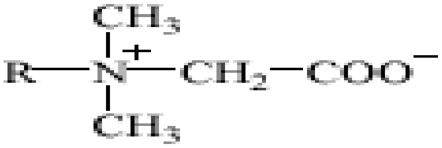


Alkyl ether sulfate

3. Amphoteric Surfactants: Amphoteric surfactants those which disassociates in water to form both negatively charged ions and positively charged ions.

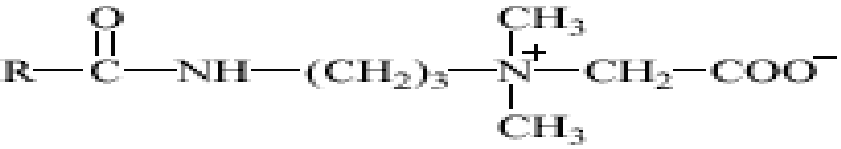
Examples are

Alkyl betaine



$$R-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_2-COO^-$$

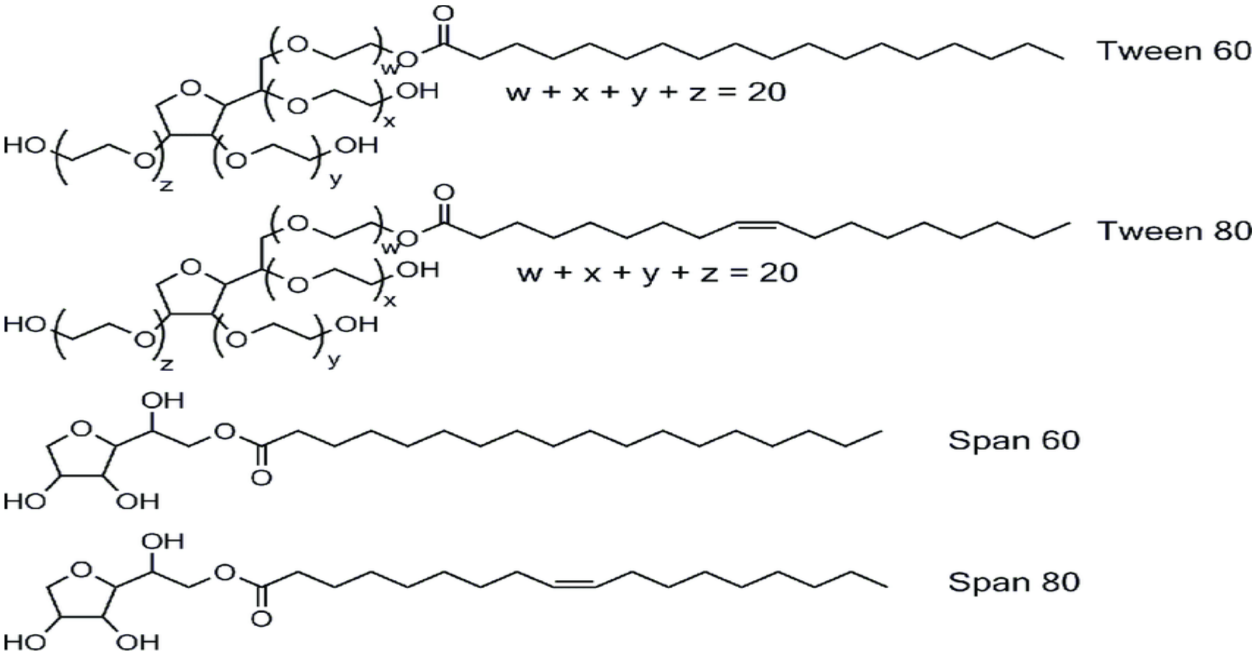
Alkylamidopropyl betaine

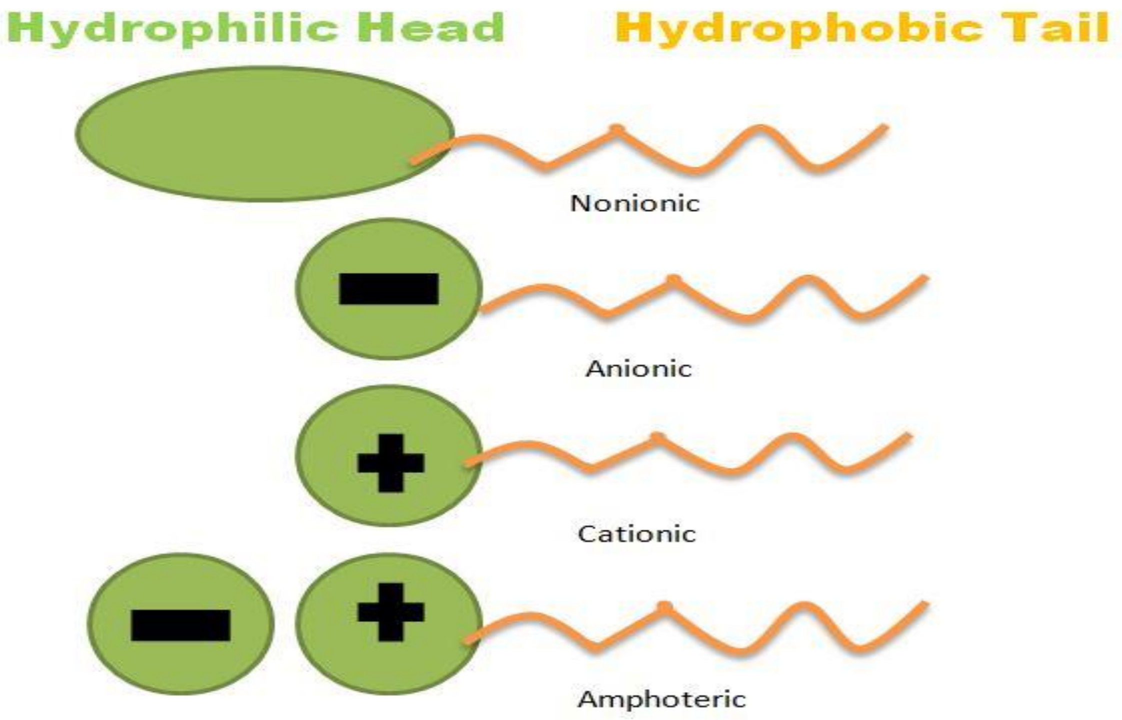


$$R-\overset{O}{\overset{||}{C}}-NH-(CH_2)_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_2-COO^-$$

4. Non ionic Surfactants: Non ionic surfactants are those which do not disassociate in water.

Examples are fatty alcohols, glycosides etc.



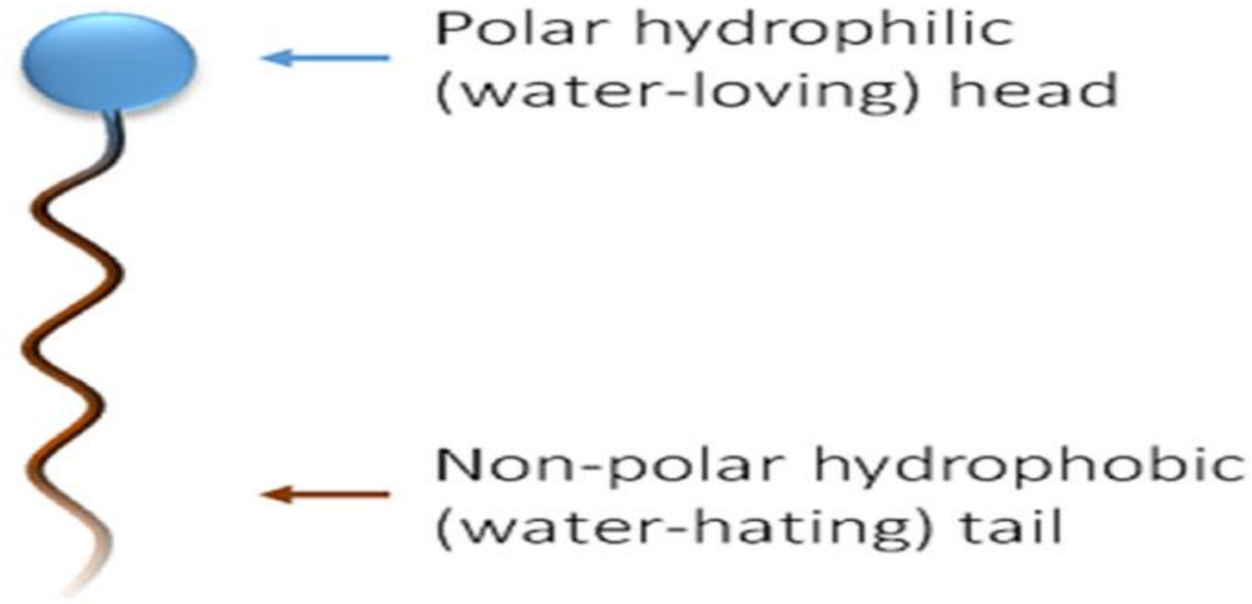


2. Explain Micellization?

→Micellization process may be defined as cleaning action of soaps and detergents.

→This process explains about how to surfactant molecules remove the dust particles from clothes and other materials.

→Surfactant molecules having diphilic nature, i.e. it having polar end (hydrophilic end) and non polar end (hydrophobic end). It can be represented as



→When dust cloth dipped in water and adds some surfactant initially surfactant molecules are oriented to dust molecules and then further to form micelle. The dust is removing in the form of micelle.

→This process is called as Micellization Process.

The process of micellization shown by the following

Most of the dirt is oily in nature and oil does not dissolve in water. The molecule of soap constitutes sodium or potassium salts of long-chain carboxylic acids. In the case of soaps, the carbon chain dissolves in oil and the ionic end dissolves in water. Thus, the soap molecules form structures called micelles. In micelles, one end is towards the oil droplet and the other end which is the ionic face outside. Therefore, it forms an emulsion in water and helps in dissolving the dirt when we wash our clothes.

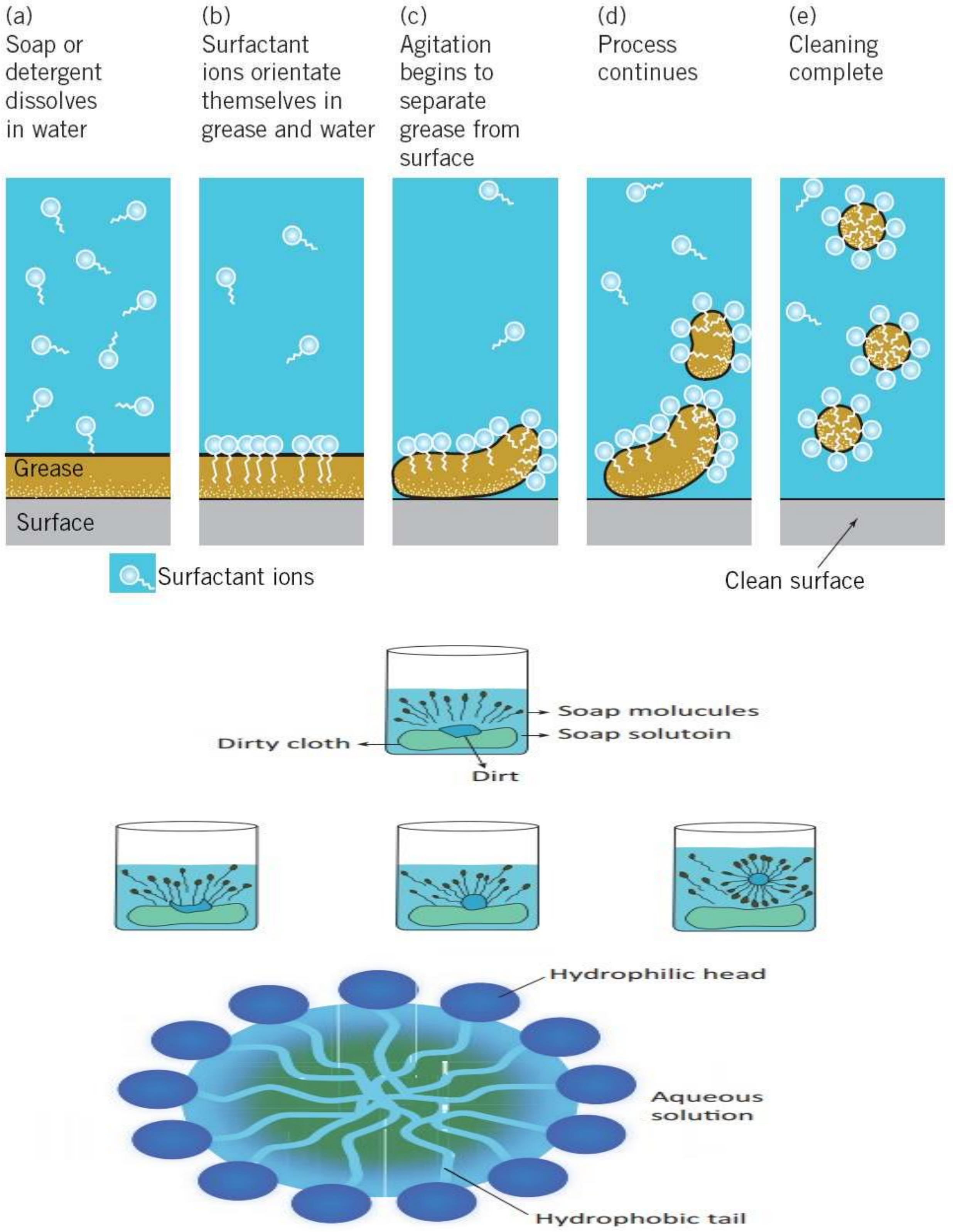


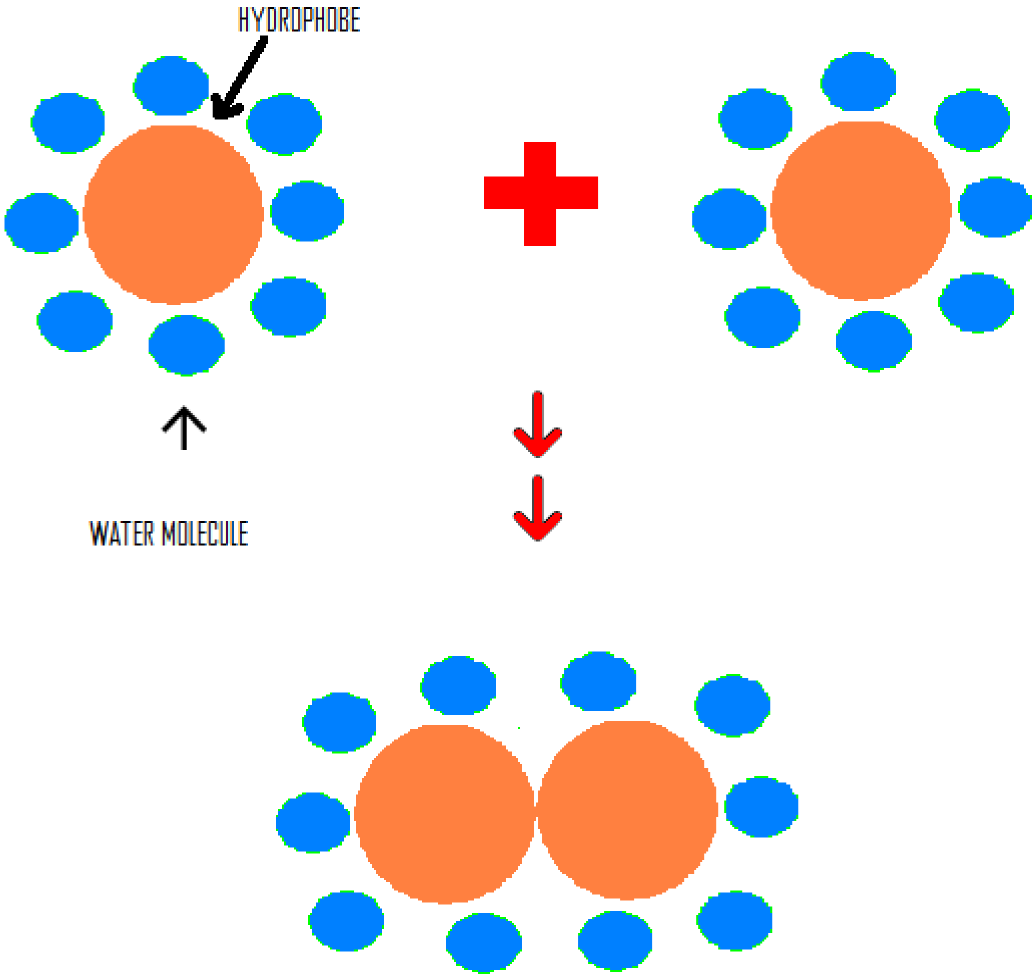
Figure 11.3 Cleansing action of soap

3. Explain Hydrophobic Interaction?

→Hydrophobic interactions describe the relations between water and **hydrophobes** (low water-soluble molecules).

→ Hydrophobes are nonpolar molecules and usually have a long chain of carbons that do not interact with water molecules. The mixing of fat and water is a good example of this particular interaction.

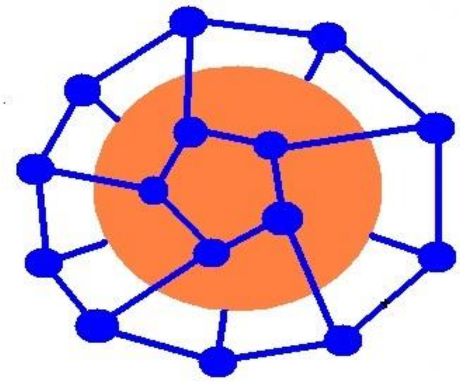
→American chemist **Walter Kauzmann** discovered that nonpolar substances like fat molecules tend to clump up together rather than distributing itself in a water medium, because this allow the fat molecules to have minimal contact with water.



→The image above indicates that when the hydrophobes come together, they will have less contact with water. They interact with a total of 16 water molecules before they come together and only 10 atoms after they interact.

Thermodynamics of Hydrophobic Interactions

When a hydrophobe is dropped in an aqueous medium, hydrogen bonds between water molecules will be broken to make room for the hydrophobe; however, water molecules do not react with hydrophobe. This is considered an endothermic reaction, because when bonds are broken heat is put into the system. Water molecules that are distorted by the presence of the hydrophobe will make new hydrogen bonds and form an ice-like cage structure called a *clathrate* cage around the hydrophobe. This orientation makes the system (hydrophobe) more structured with a decrease of the total entropy of the system; therefore $\Delta S<0$.



The change in enthalpy (ΔH) of the system can be negative, zero, or positive because the new hydrogen bonds can partially, completely, or over compensate for the hydrogen bonds broken by the entrance of the hydrophobe. The change in enthalpy, however, is insignificant in determining the spontaneity of the reaction (mixing of hydrophobic molecules and water) because the change in entropy (ΔS) is large.

According to the Gibbs Energy formula

(1) $\Delta G=\Delta H-T\Delta S$

With a small unknown value of ΔH and a large negative value of ΔS, the value of ΔG will turn out to be positive. A positive ΔG indicates that the mixing of the hydrophobe and water molecules is not spontaneous.

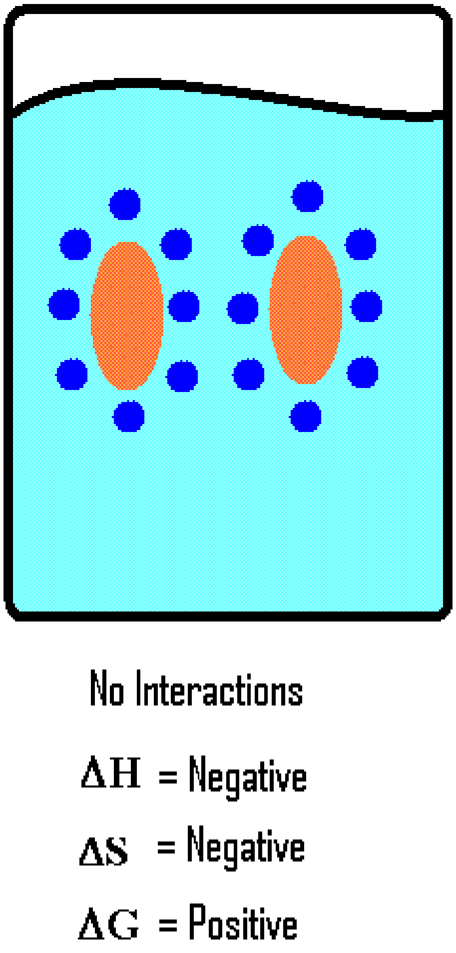
Formation of Hydrophobic Interactions

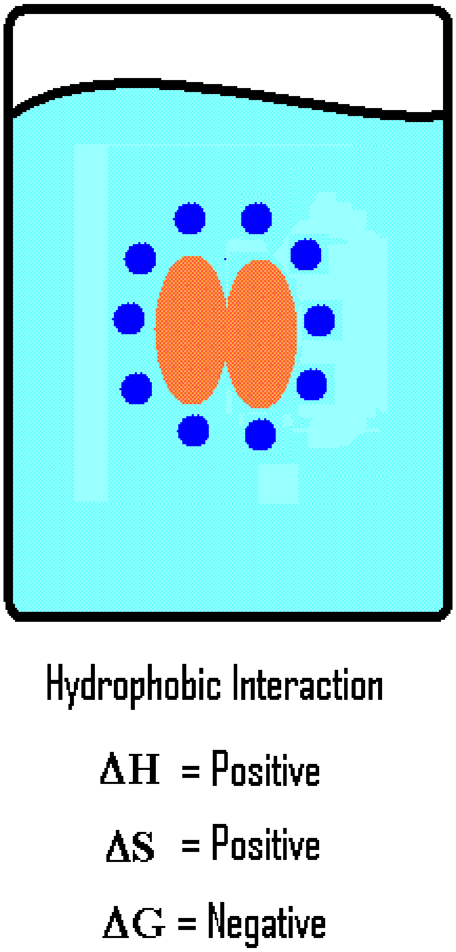
The mixing hydrophobes and water molecules are not spontaneous; however, hydrophobic interactions between hydrophobes are spontaneous. When hydropobes come together and interact with each other, enthalpy increases (ΔH is positive) because some of hydrogen bonds that form the clathrate cage will be broken. Tearing down a portion of the clathrate cage will cause the entropy to increase (ΔS is positive), since forming it decreases the entropy.

According to the Equation 11

- ΔH = small positive value
- ΔS = large positive value

Result: ΔG is negative and hence hydrophobic interactions are spontaneous.





4. What is Critical Micellar Concentration (CMC) and explain the factors affecting the CMC?

→The lowest concentration at which micelle first appears is called Critical Micellar Concentration (CMC).

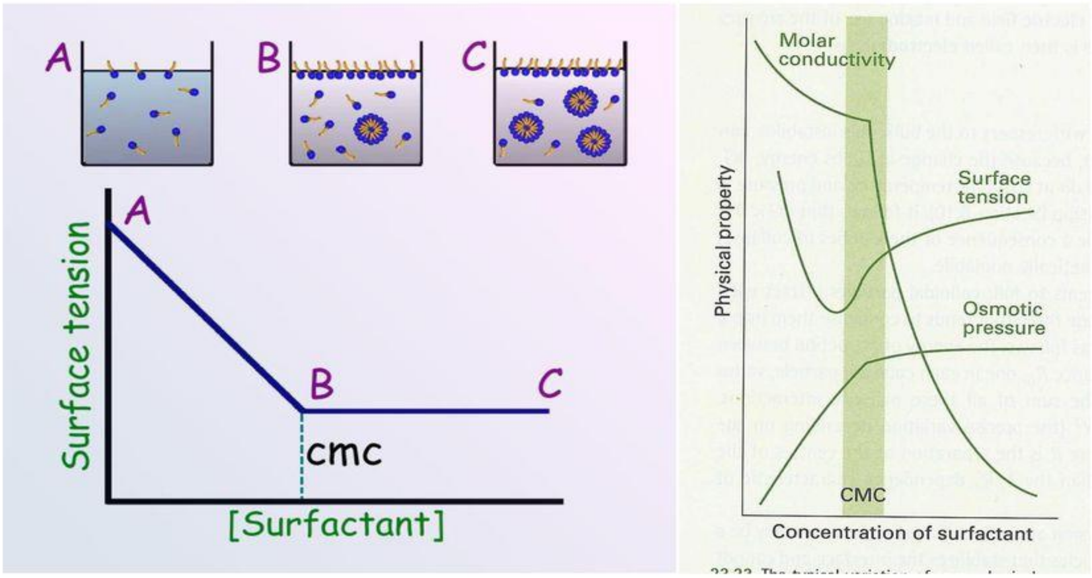
→CMC is an important characteristic of surfactant.

→Before reaching the CMC, Surface tension changes with concentration of surfactant.

→After reaching the CMC, Surface tension does not change but Concentration will be change.

→The Critical micellar concentration is the point at which surfactant molecules combined together in a liquid to form groups are known as micelles.

CMC determination



CMC = critical micelle concentration

Factors affecting critical micelle concentration:

1. Size and structure of hydrophobic group: An increase in the hydro-carbon chain length causes a logarithmic decrease in the CMC.

2. Nature of hydrophilic group: An increase in hydrophilicity increases the CMC.

3. Addition of electrolytes: Addition of electrolytes, such as salt, to solutions of ionic surfactants decreases the CMC.

4. Effect of temperature: Size of micelles increases and CMC decreases with increasing temperature.

5. Alcohol: Addition of alcohol to an aqueous solution, thus increasing the CMC.

5. Explain Thermodynamics of Micellization?

→The Surfactant CMC plays a factor in Gibbs free energy of Micellization.

→There are two general approaches

1. Phase Separation Model
2. Mass Action Model

1. Phase Separation Model: Consider an anionic surfactant in which "n" number of surfactant "S" and "n" number of counter ions M^+ combine together to form micelle.

The Chemical Potential of micelle is $\mu^0_{mic} = \mu_1^0 + RT\ln a_1$ ---------- (1)

Where μ^0_{mic} = Standard chemical potential of micelle

μ_1^0 = Standard chemical potential of surfactant monomer

a = activity of surfactant

According to definition of activity $a_1 = f_1 x_1$ ---------- (2)

Where f_1= activity coefficient

X_1= mole fraction

Substitute eq (2) in eq (1), we get

$\mu_m{}^0 = \mu_1{}^0 + RT\ln f_1x_1$

Here f_1 taken as unity then $f_1=1$.

$\mu_m{}^0 = \mu_1{}^0 + RT\ln x_1$

The CMC may be identified with x_1, we get

$\mu_m{}^0 = \mu_1{}^0 + RT\ln [CMC]$

ΔG should be calculated using the CMC expressed as a mole fraction.

2. Mass Action Model: This model assumes dissociation – association equilibrium between surfactant and micelle. Thus equilibrium constant can be calculated.

→ For non ionic surfactants where change effects are absent.

→The equilibrium simply represented as

$$N = \frac{Vmic}{\vartheta} = \frac{\frac{4}{3}\ \pi R3}{\vartheta}$$

In this case equilibrium constant K_m is given by $K_m = [S_n]/[S^n]$ ----- (1)

The standard free energy is $\Delta G_{mic}{}^0 = RT\ln [K_m]$ ----- (2)

Substitute eq (2) in eq (1), we get $\Delta G_{mic}{}^0 = RT\ln[\frac{Sn}{S^n}]$

$$\Delta G_{mic}{}^0 = RT\ln[(S_n) – (S^n)]$$

6. Explain Solubilization Process?

→It can be defined as the preparation of thermodynamically stable isotropic solution of a substance normally insoluble (or) very slightly soluble in a given solvent.

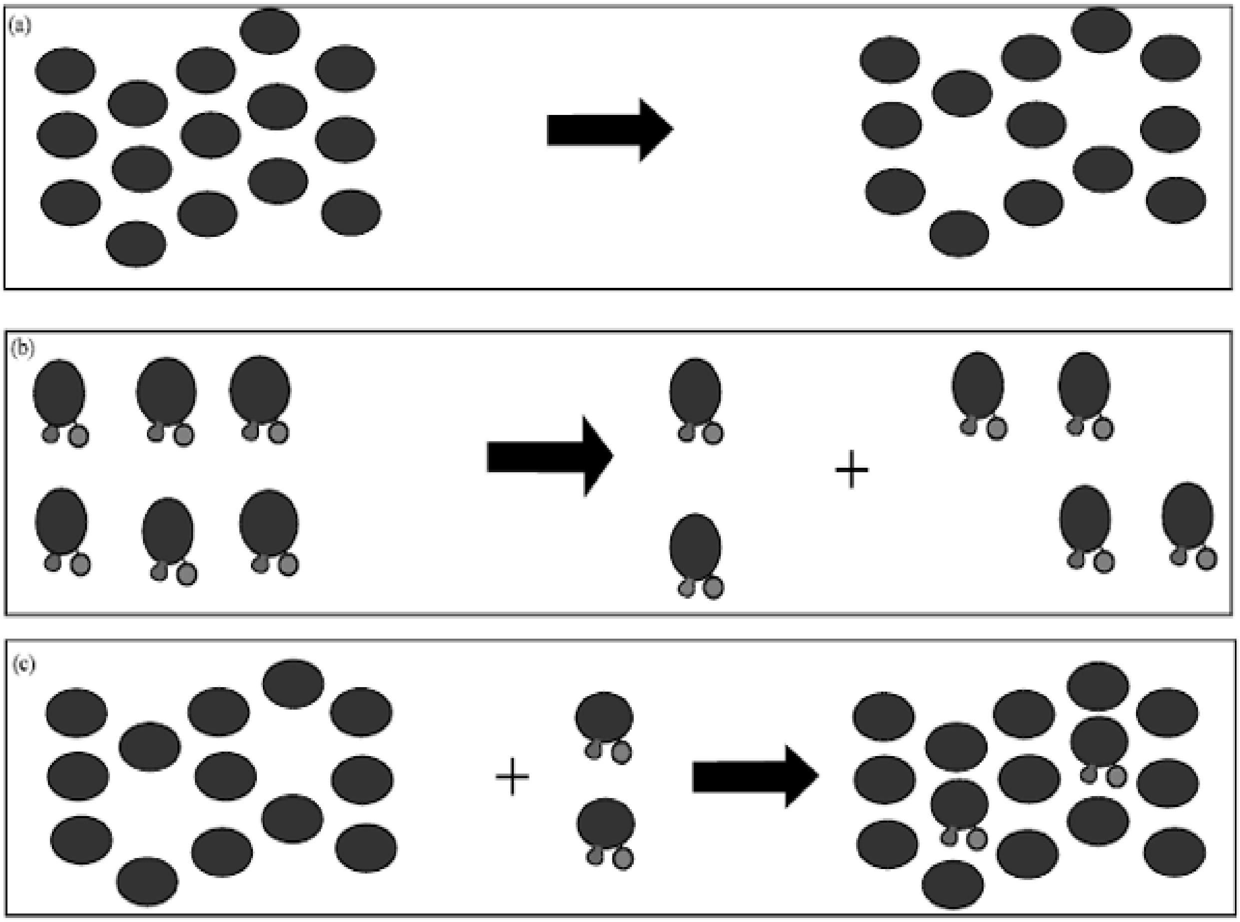
→The process of solubilization involves the breaking of intra molecular bonds in the solute. The separation of molecules of the solvent provides a space in the solvent for the interaction between solvent and solute.

Mechanism:

a). Breaking of solvent – solvent intra molecular bonds to provides space in the solvent.

b). Breaking of solute – solute intra molecular bonds.

c). Transfer of solute into solvent for the formation of solute – solvent inter molecular forces.



FACTORS AFFECTING SOLUBILIZATION

The solubility depends on the nature and composition of solvent medium, the physical form of the solid as well as temperature and pressure of system. Consider a lot of factor which affects the solubility like:

1. Nature of solvent & solute: The amount of solute that dissolves depends on the type of solute used.

2. Temperature:

→In Endothermic process solubility increases, temperature will also increases.

→In exothermic process solubility decreases, temperature will increases.

3. Pressure:

→For solids and liquids pressure will not affected.

→For gases solutes pressure increases, solubility also increases.

4. Particle Size: Size of the particle increases, solubility decreases.

5. Polarity: Polarity of the solute and solvent molecules will affect the solubility.

Advantages:

→These are thermodynamically stable.

→Require Minimum energy.

→Easy of manufacturing.

→Improve the efficacy of drug.

Disadvantages:

→Use of large concentration of surfactant & co-surfactant causes various health problems.

→The surfactant must be non toxic for using pharmaceutical applications.

MACROMOLECULES

(POLYMERS)

1. Define Polymer and explain the classification of polymers?

→The word polymer is derived from Greek "Poly" = Many and "mers" = parts.

→Thus, polymer means composed of many parts (or) many units.

→Polymer is a large molecule formed by the combination of small molecules through the covalent bonds.

Examples are Polyethylene, PVC etc.

Classification of Polymers:

Polymers are classified into several types.

1. Based on Source: Based on source polymers are classified into 3 types.

A) Natural Polymers

B) Semi Synthetic Polymers

C) Synthetic Polymers

A) Natural Polymers: These polymers made from natural sources (plants & animals).

Examples are Proteins, Rubbers, Nucleic acids, silk etc.

B) Semi Synthetic Polymers: These polymers made from naturally occurring polymers by carrying out some chemical modifications.

Example: Cellulose + $(CH_3CO)_2O$ -----------→ Cellulose diacetate

C) Synthetic Polymers: These polymers are prepared in laboratory.

→Synthetic polymers are also known as "Man Made Polymers".

Examples are Nylon 6, 6, PVC, Teflon etc.

2. Based on Structure: Based on structure polymers are classified into 3 types.

A) Linear Polymers

B) Branched Polymers

C) Cross linked Polymers

A) Linear Polymers: In this type of polymers monomer units are attached by the straight chains.

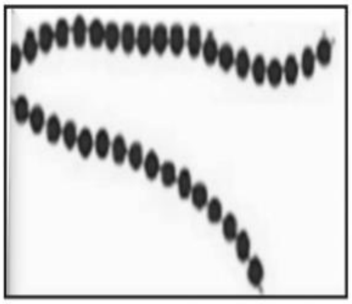
Example: PVC.

B) Branched Polymers: In this type of polymers monomer units are attached to side chain of the main chain.

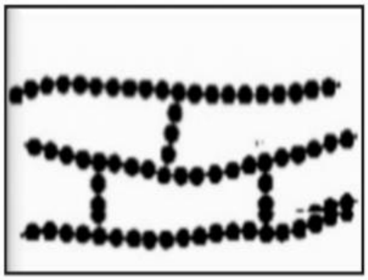
Example: Low density Polythene.

C) Cross linked Polymers: In this type of polymers monomer units are cross linked to each other.

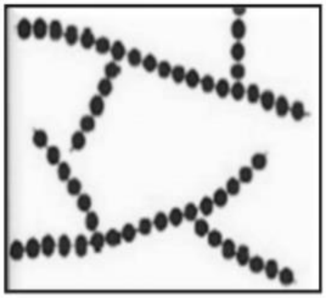
Example: Bakelite.



Linear polymers



Cross-linked chain polymers



Branched chain polymers

3. Based on Molecular Forces: Based on molecular forces polymers are classified into 4 types.

A) Fibers

B) Elastomers

C) Thermo plastic polymers

D) Thermo setting polymers

A) Fibers: If polymers are drawn into long filaments then they are called fibers.

They have high tensile strength, strong hydrogen bonding, tough.

Example: Nylon-6, 6.

B) Elastomers: These are rubber like polymers which shows good strength and elongation.

These polymer chains are hold by weakest attractive forces.

Example: Natural rubber, synthetic rubber.

C) Thermo plastic polymers: These are softening on heating, shifted on cooling are called Thermo plastic polymers.

Example: Polyethylene and PVC.

D) Thermo setting polymers: These are changing their shape on heating and do not retain their original shape on cooling are called Thermo setting polymers.

Example: Bakelite.

4. Based on Carbon atom: Based on carbon atom polymers are 2 types.

A) Organic Polymers

B) Inorganic Polymers

A) Organic Polymers: These are the polymers back bone chain is made up of carbon atoms.

Example: Nylon, Diamond, PVC, Graphite.

B) Inorganic Polymers: These are the polymers back bone carbon chain is does not make up of carbon atoms.

Example: Silicon, Glass, Rubber.

5**. Based on Mode of Polymerization:** Based on mode of polymerization polymers are mainly 2 types.

A) Addition Polymerization

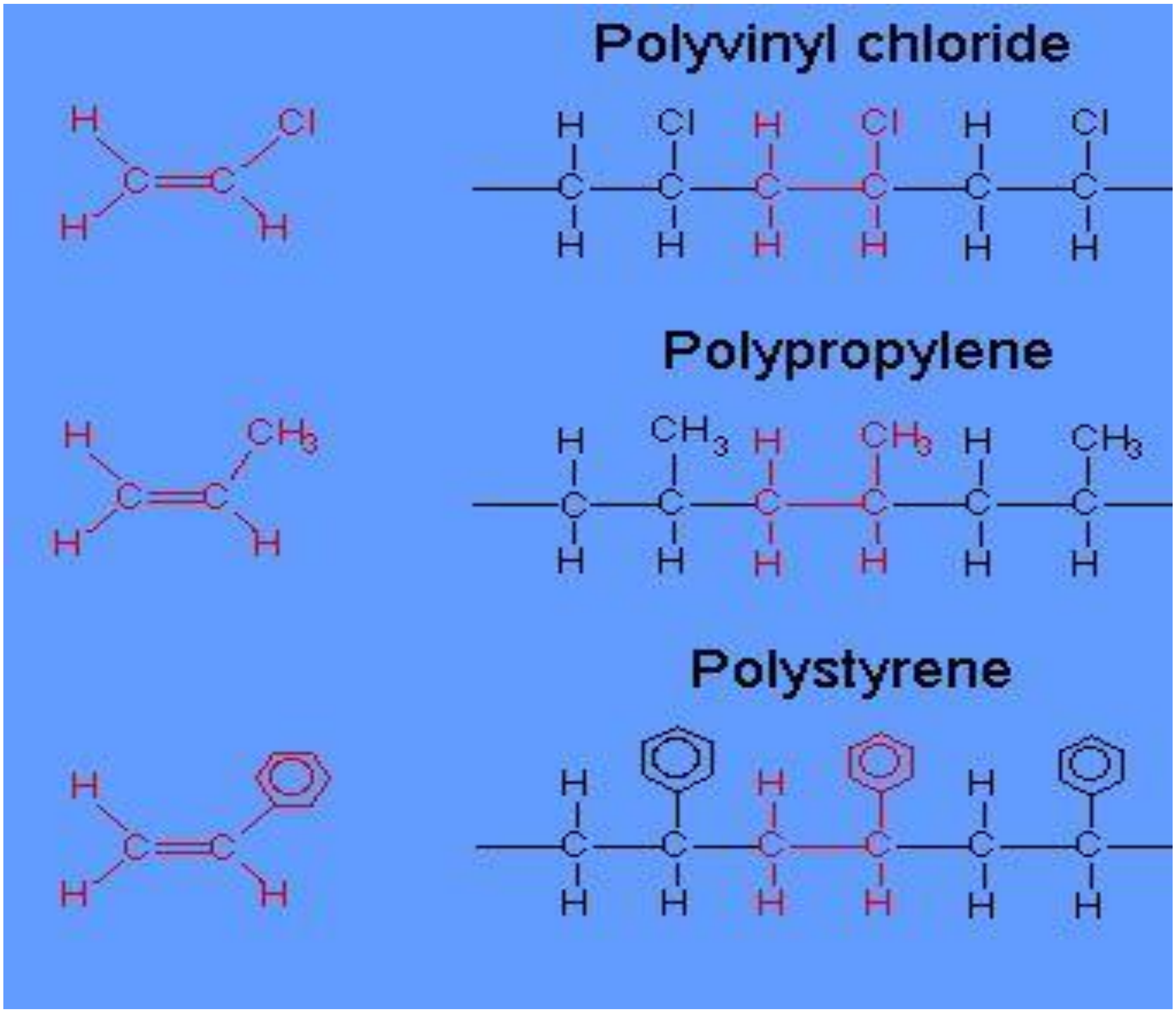
B) Condensation Polymerization

A) Addition Polymerization: When monomers are added to form polymers without elimination of any by product.

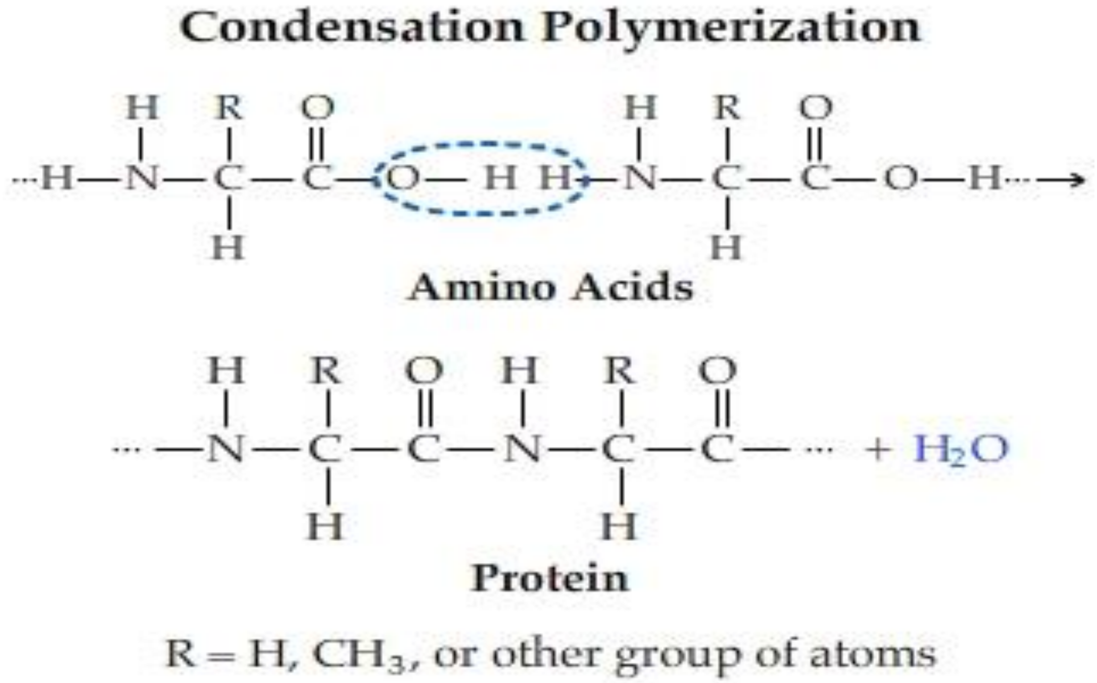
→The polymer formed is an exact multiple of the original monomer units.

→Monomers containing double bonds can undergo this polymerization.

Examples are PVC, Polypropylene, and Polystyrene etc.



B) Condensation Polymerization: When monomers are added to form polymer with the elimination of small molecules like water, ammonia.



R = H, CH_3, or other group of atoms

2. Write a note on Electrical conducting Polymers?

→Electrical conducting polymers are organic polymers which conduct electricity due to delocalization of π electrons.

→Conjugated polymers are semi conductors while doped polymers are conductors.

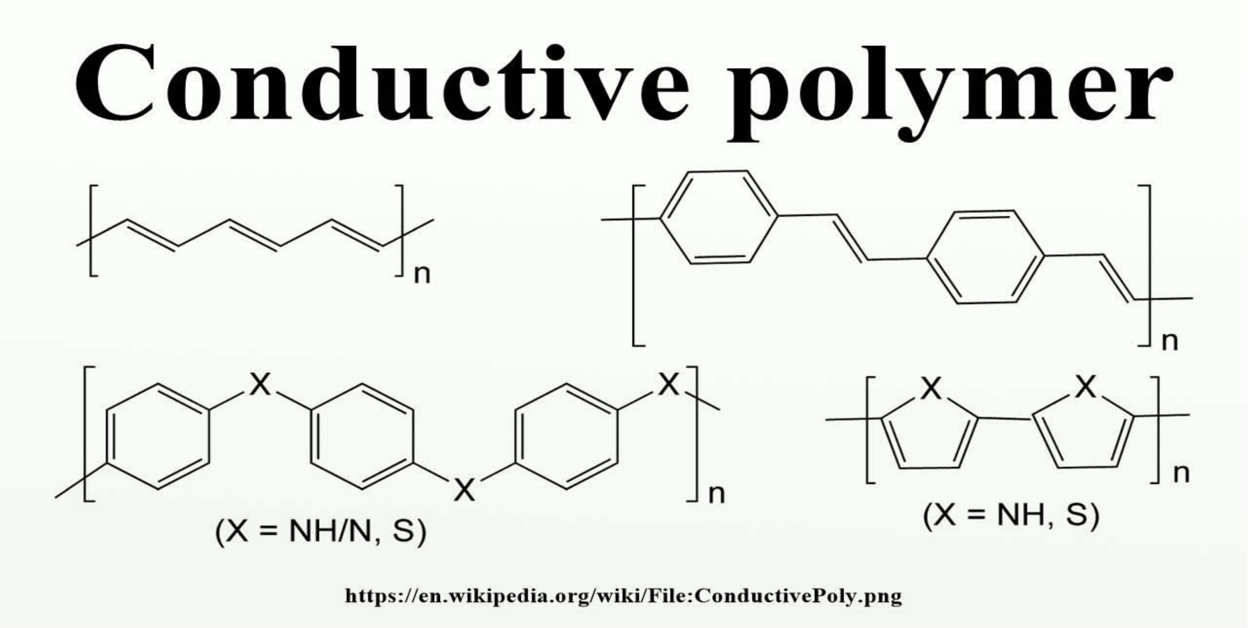
Conditions: There are two main conditions.

→The first condition is polymer consists of alternating single and double bonds.

→The second condition is process of doping.

Example: $(CH_2)_n + x\,Na \xrightarrow{\hspace{2cm}} (CH_2)_n^- (Na)_x^+$

→First electrical conducting polymer is poly acetalene.



https://en.wikipedia.org/wiki/File:ConductivePoly.png

Applications:

1. Used in an anti static substance in photographic films.

2. Used in compact capacitors.

3. Used in solar cells and transistors.

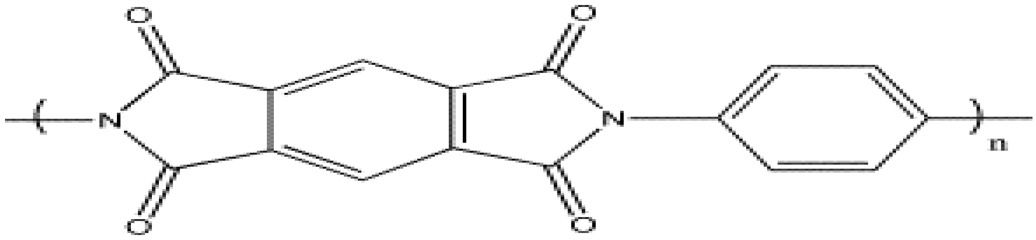
4. Used in light emitting diodes.

3. Write a note on Fire Resistant Polymers?

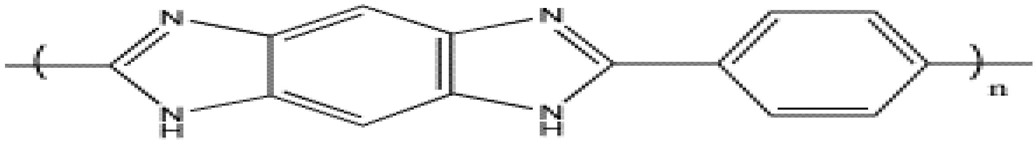
→Fire resistant polymers are resistant to degradation at high temperatures.

→Most of the fire resistant polymers made of aromatic cyclic ring (or) hetero cyclic rings.

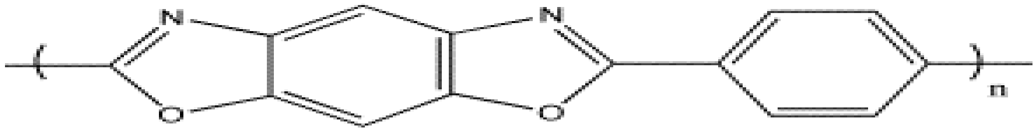
→Fire resistant polymer is made from non flammable fabrics and materials.



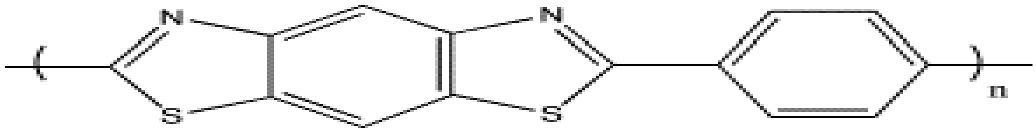
polyimide



polybenzimidazole



polybenzoxazole



polybenzthiazole

Applications:

1. These are used in Airplanes, Military boats.

4. Write a note on Liquid Crystal Polymers?

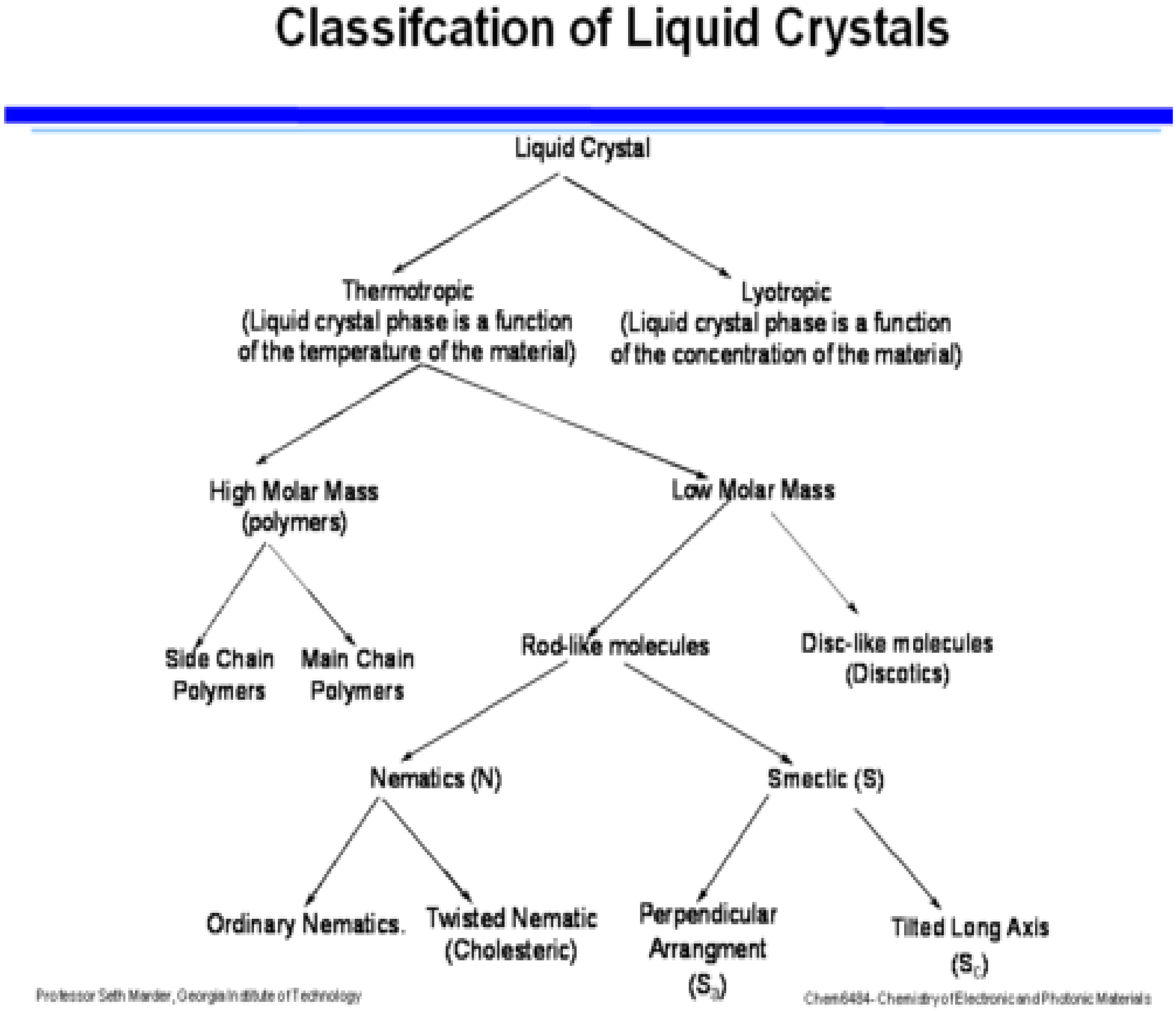
→Liquid crystal polymers are special type of thermo plastic polymers.

→Liquid crystal polymers are a class of aromatic polymers.

→Liquid crystal polymers are fire resistant polymers.

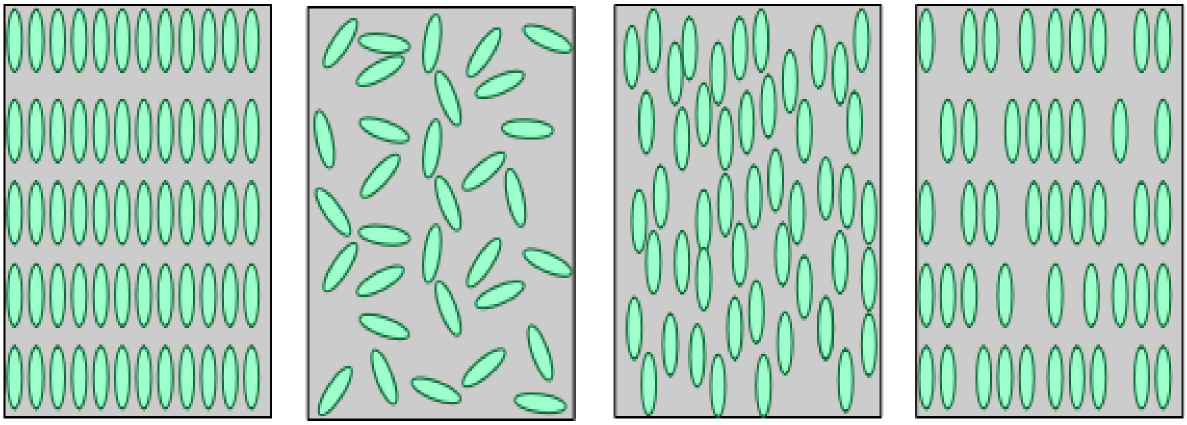
→Liquid crystal polymers are two types

1. Thermo tropic
2. Lyo tropic



Professor Seth Marder, Georgia Institute of Technology

Chem6484- Chemistry of Electronic and Photonic Materials



Solid phase: orientation and periodicity

Liquid phase: no orientation or periodicity

Nematic phase: orientation, no periodicity

Smectic phase: orientation with some periodicity

6. Explain about the Molecular weight of polymers?

→Molecular weight is an important property of any molecule.

→It is particularly important for macro molecules like protein, starch, nucleic acid.

→Now, we know that macro molecules composed of monomers.

→For macro molecules it is possible only take in terms of average molecular weights.

→There are two types of average molecular weights.

1. Number – average molecular weight [M_n]
2. Weight – average molecular weight [M_w]

1. Number – average molecular weight [M_n]:

It is defined as the weight of the sample of a macro molecule divided by the total number of molecules.

→It is denoted as M_n.

→ $M_n = \frac{Weight\ of\ polymer}{n}$

Polymer consists of n_1 molecules of molecular weight M_1 and n_2 molecules of molecular weight M_2 and so on, then

$$M_n = \frac{n1M1+n2M2+n3M3+ ----}{n1+n2+n3+ -----}$$

number average molecular weight ($\overline{M}_n$)

$$\overline{M}_n = \frac{\Sigma\ N_i\ \overline{M}_i}{\Sigma N_i}$$

Example: A polymer sample containing 3 molecules of molecular weight 5, 6 molecules of molecular weight 7, 8 molecules of molecular weight 10. Then find M_n ?

$$M_n = \frac{3X5 + 6X7 + 8X10}{3+6+8} = \frac{137}{17} = 8.0588$$

2. Weight – average molecular weight [M_W]:

It is defined as molecular mass of each species multiply with mass of that species and dividing the total with mass of all species.

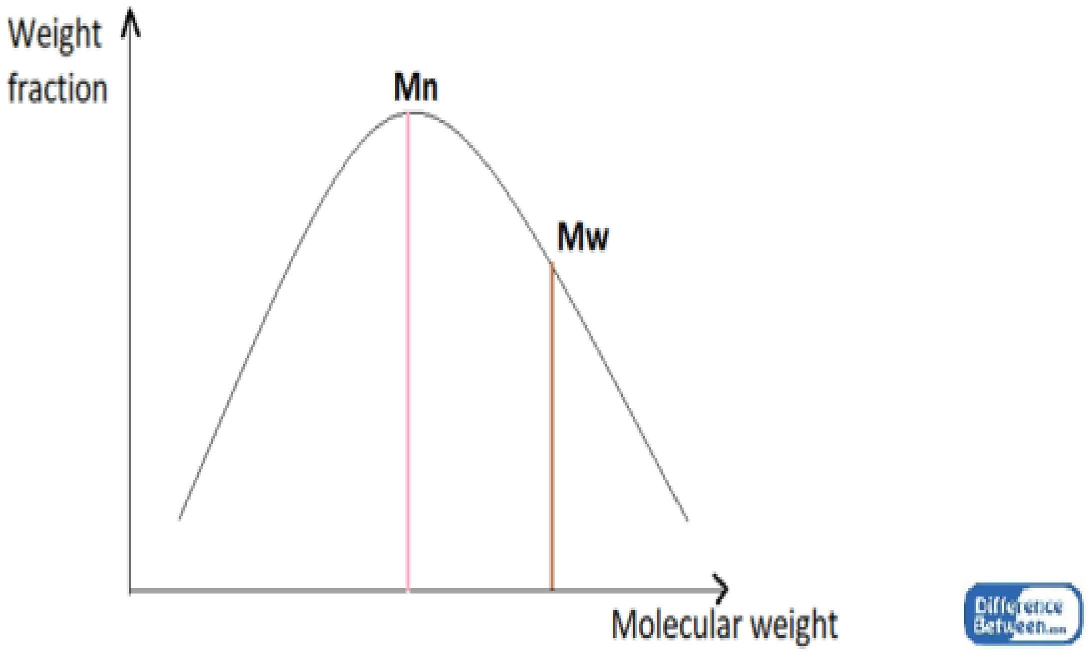
$M_w = n_1M_1^2 + n_2M_2^2 + n^3M_3^2$ + --- / $n_1M_1 + n_2M_2 + n_3M_3$ + ---

$$\overline{M_w} = \frac{\sum_{i=1}^{N} N_i M_i^{\,2}}{\sum_{i=1}^{N} N_i\, M_i} = \frac{\sum_{i=1}^{N} w_i M_i}{\sum_{i=1}^{N} w_i} = \sum_{i=1}^{N} w_i M_i$$

Example: A polymer sample containing 3 molecules of molecular weight 5, 6 molecules of molecular weight 7, 8 molecules of molecular weight 10. Then find M_w?

$M_w = 3x5^2 + 6x7^2 + 8x10^2 / 3x5 + 6x7 + 8x10$

$$M_w = \frac{1169}{137} = 8.53$$


Weight fraction
Mn
Mw
Molecular weight
Difference Between.com

Molecular Weight Determination

1. Explain molecular weight determination by using End Group analysis?

The end group analysis is a chemical method used for calculating the M_n. Polymer sample contains reactive functional groups at one end (or) both ends of the molecule.

$M_n = \frac{functionality}{functional\ group\ equivalent}$

Functionality:

1. Functionality is the number of reactive functional groups present in the polymer.

Example: 1. Carboxyl – Terminated Polybutadiene (CTPB)

2. Hydroxyl – Terminated Polybutadiene (HTPB)

2. Functionality of CTPB, HTPB is 2, means each molecule posses two reactive functional groups.

3. Apart from hydroxyl and carboxyl groups several end groups such as aldehyde, ester, amines are also be present.

Functional group equivalent:

1. Chemical methods are employed to find out total number of functional groups present in a given rate of polymer.

2. It is expressed as functional group equivalent for 100 grams.

$$\frac{F.G.E}{100g}$$

Chemical Method:

The Carboxyl value of CTPB is determined by dissolving a known quantity of polymer in a mixture of ethanol and toluene (1:3) and titrating against alk.KOH.

From titrate value $\frac{carboxyl\ equivalent}{100g} = \frac{VN}{10W}$

Where V = Volume of KOH

N = Normality of KOH

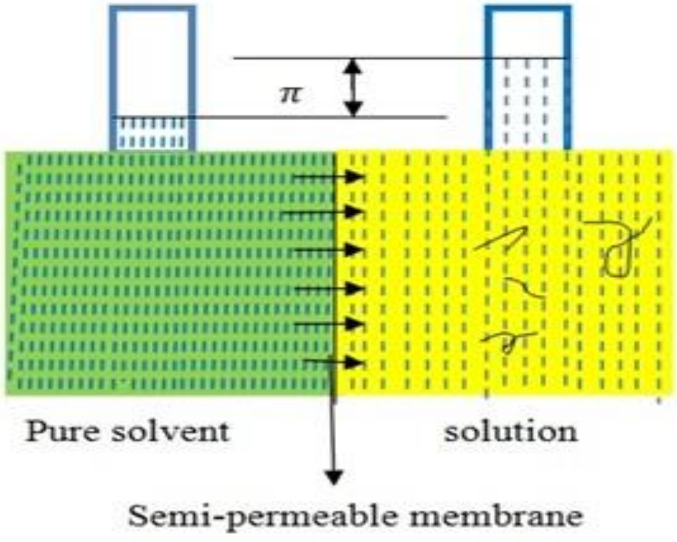
W = weight of sample

2. Write about the molecular weight determination by using Osmometry?

→This method is depends upon the principle of Osmosis.

→Membarane Osmometry is a widely using technique to determine the M_n of polymers.

→The migration of solvent molecules into solution is called Osmosis.



→If the solution is very dilute the osmotic pressure is given by vantt Hoff equation.

$\pi V = nRT$

$$\pi = \frac{n}{V} RT$$

Where π = Osmotic pressure

n = molar concentration of polymer

$$n = \frac{weight}{molecular\ weight} = \frac{W}{M}$$

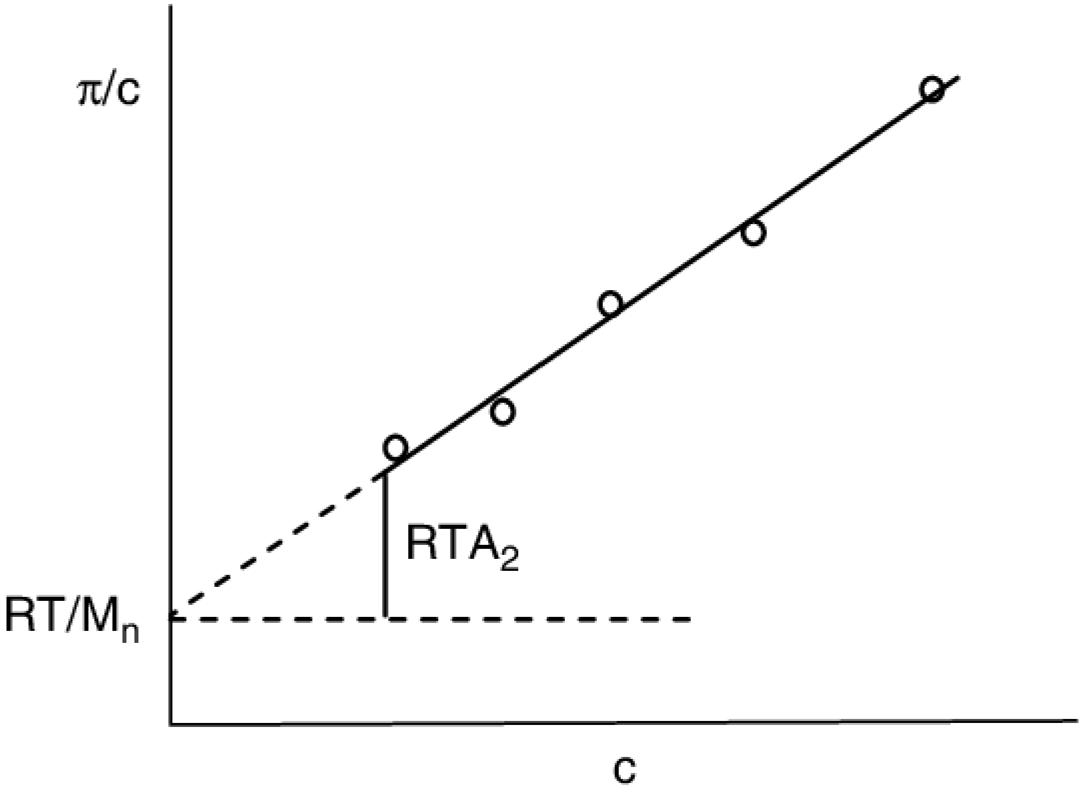
$$\pi = \frac{W}{M}\frac{RT}{V}$$

$$\pi = C\ \frac{RT}{V}$$

$$\frac{\pi}{C} = \frac{RT}{V}$$

Where C = concentration of polymer solution in gram / liter.

A graph is drawn between $\frac{\pi}{c}$ v/s C gives a straight line.



→This method is more convenient method to determine the molecular weight of polymer in between 50,000 – 1, 00,000.

→Osmotic pressure obtained by osmometric device in which the solvent and solution of polymer separated by membrane. The solvent molecules pass through membrane into the polymer solution until the equilibrium is adjusted between solutions.

→The difference in heights of polymer solution and solvent is known as Osmotic pressure.

3. Explain molecular weight determination of polymer by using Viscometer method?

1. This is a more convenient method for the determination of molecular weight of polymer.

2. In this method we determine the molecular weight of polymers in terms of viscosity average molecular weight.

3. The viscosity of polymer solution depends on nature of the polymer solution.

4. The viscosity of polymer solution is very high compared to pure solvent.

5. Viscosity is a temperature dependent so all measurements done at constant temperature.

6. In this method we prepare different concentrations of polymer solutions and measure the viscosity at each concentration of polymer solution.

7. If "η" is the viscosity of the polymer solution

η_0 is the viscosity of the pure solvent.

Then Relative Viscosity = $\frac{\eta}{\eta_0} = \frac{t}{t_0} = \eta_r$

8. If C is the concentration of polymer solution then the specific viscosity of solution is

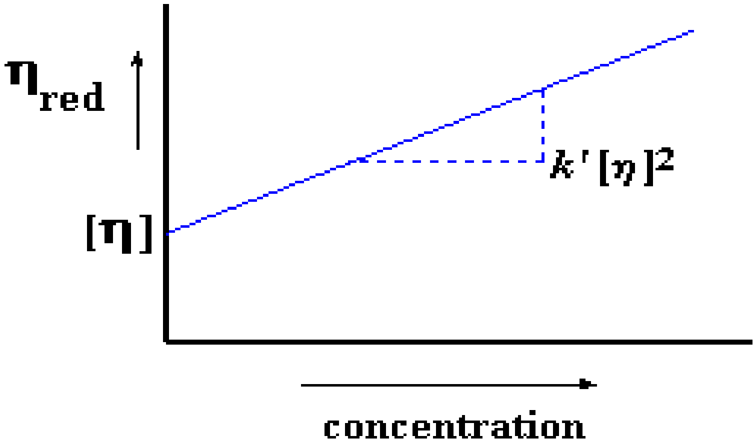
Specific Viscosity = $\frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_r - 1 = \eta_{sp}$

9. If C is the concentration of polymer solution then the reduced viscosity of polymer solution.

Reduced viscosity = η_{sp} / c

10. A graph is drawn between η_{sp} / c v/s C gives a straight line with intercept η_i.

Where η_i = Intrinsic viscosity



A plot of reduced viscosity vs. concentration.
We call the *y*-intercept $[\eta]$, or the intrinsic viscosity.
The slope is related to $[\eta]$, it's equal to $k'[\eta]^2$.

11. There is a relation between intrinsic viscosity and molecular weight of polymer by Mark – Howunic equation

$\eta_i = K M^a$

Taking logarithm on both sides

$\rightarrow \log \eta_i = \log K M^a$

$\rightarrow \log \eta_i = \log K + \log M^a$

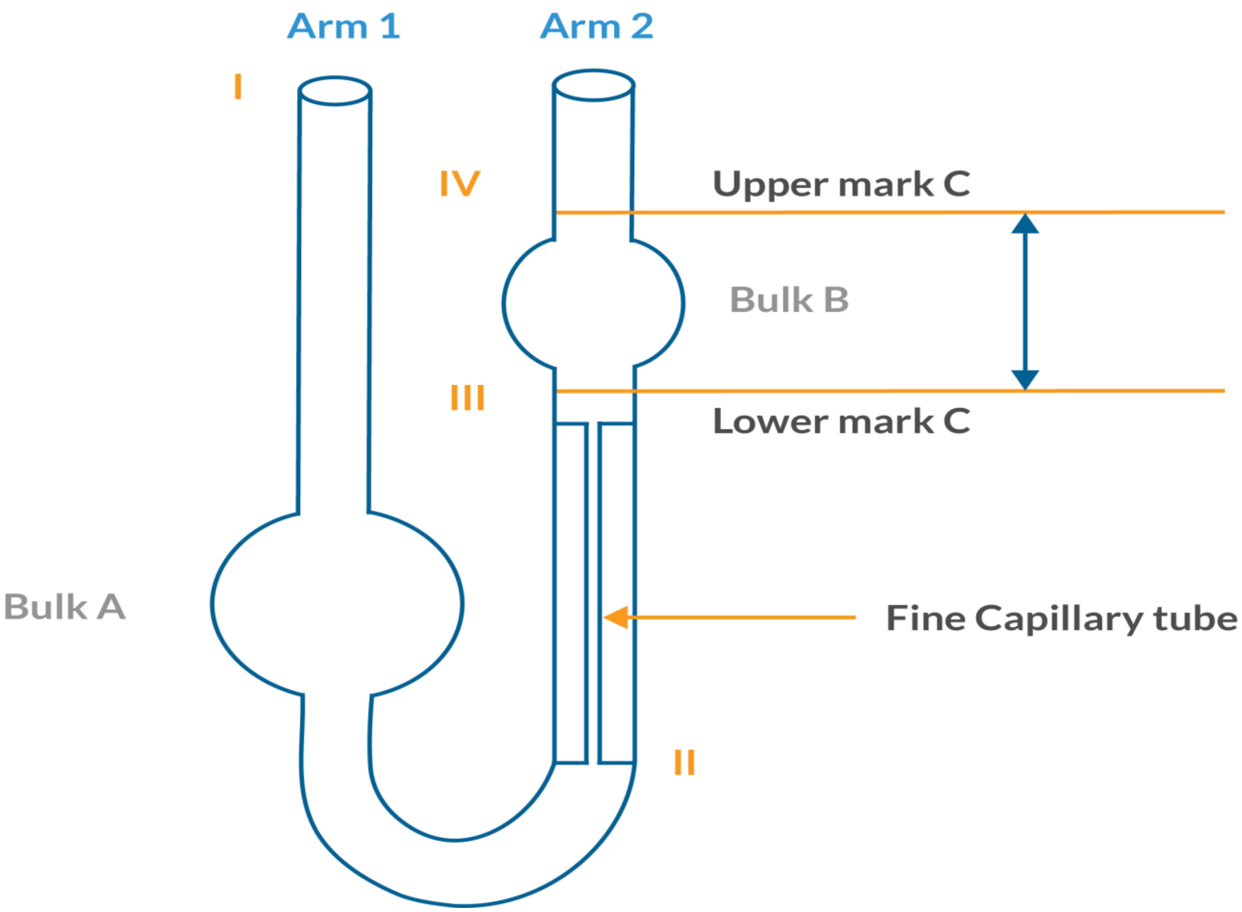
$\rightarrow \log \eta_i = \log K + a \log M$

$\rightarrow \log \eta_i - \log K = a \log M$

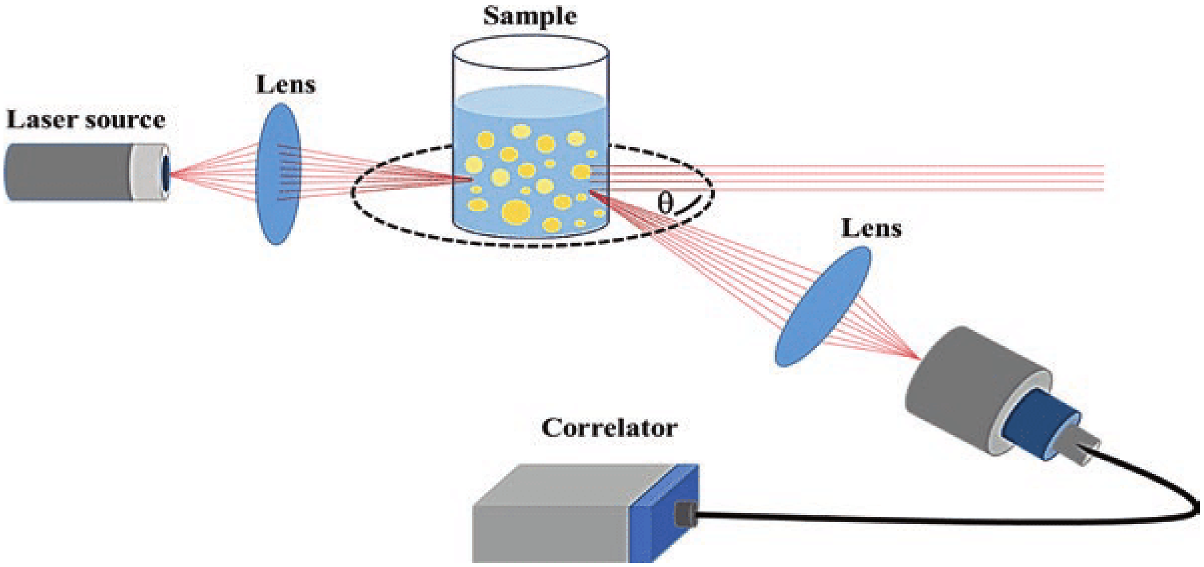
$\rightarrow \log \eta_i - \log K / a = \log M$

Where K & a are constants.

From this equation we can calculate the molecular weight by viscometer.



4. Explain molecular weight determination of polymer by using Light scattering method?



→This method is used to determine the molecular weight of polymers in terms of weight average molecular weight (M_W).

→Due to big size molecules in solution turbidity is produced.

→The light rays passing through the polymer solution due to turbidity.

→Incase of proteins are higher polymers turbidity is small.

→Turbidity increases with increase in concentration as well as molecular weight.

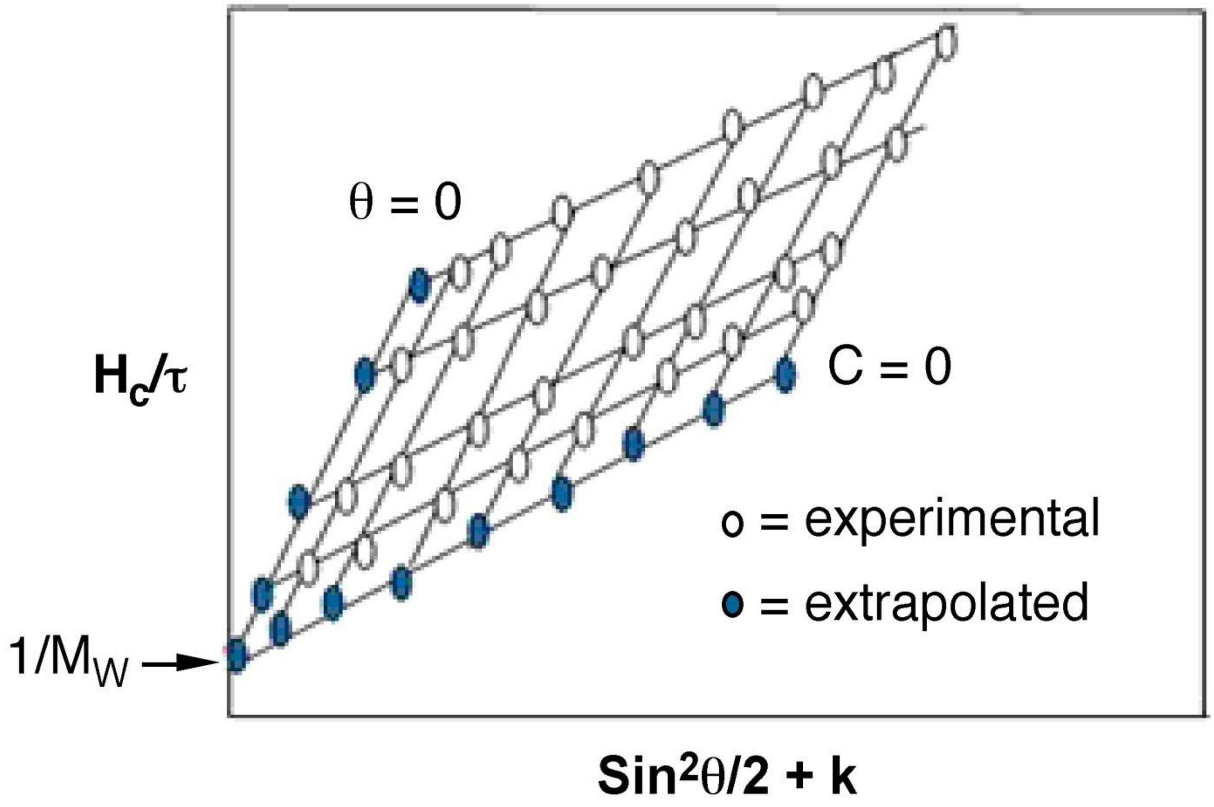
→There is a relation between turbidity and molecular weight given by Debye

$$\frac{HC}{T} = \frac{1}{M} + 2BC$$

Where B = second viral coefficient

H = constant

→A graph is drawn between $\frac{HC}{T}$ v/s C gives a straight line with intercept ($\frac{1}{M}$).



→This curve was plotted by Zimm”s. so this is called Zimm”s curve.

→From the intercept value we get the molecular weight of polymer.

→This method gives wrong results at above 10, 00,000.

5. Explain molecular weight determination of polymer by using Ultra – Centrifuge method?

(OR)

Explain molecular weight determination of polymer by using Sedimentation method?

→The centrifuge force applies for the polymer solution is very high.

→ These high centrifugal forces are called ultra centrifuge force.

→Polymer solution is subjected to ultra centrifuge then it wills sediment down.

→The rate of sedimentation directly proportional to size of the polymer molecules.

→By using this principal there are two different methods for the determination of molecular weight of polymer.

1. Sedimentation – Velocity method
2. Sedimentation – Equilibrium method

<u>1. Sedimentation – Velocity method:</u>

→In this method all polymer molecules are subjected to different – different centrifuge forces.

→The polymer molecule sediment down on the basis of molecular weight of polymer.

→The rate of sedimentation of polymer molecules at distance “x” from the centre is given by

$$\frac{dx}{dT} f = \omega^2 x [1 - \vartheta_d] M$$

Where d = density of solvent

ϑ = partial molar volume of polymer

ω = angular velocity

f = fraction of force

$\frac{dx}{dT}$ = rate of sedimentation

X = distance from the centre

$$\frac{dx}{dT}\,\frac{1}{\omega 2x} = \left[\frac{1-\ \vartheta d}{f}\right]M$$

$$S = \left[\frac{1-\vartheta d}{f}\right]M$$

$$M = \frac{Sf}{1-\vartheta d}$$

2. Sedimentation – Equilibrium method:

→In this method all polymer molecules are subjected to same amount of centrifuge forces.

→In this method two layers are formed, in the upper layer concentration is low and in the lower layer concentration is high.

→Then the molecular weight of polymer can be calculated by using

$$M = \frac{2RT\ ln\frac{C2}{C1}}{\omega\ (1-\ \vartheta d)(x2-x1)(x2+x1)}$$

Where C_1, C_2 are concentrations of two layers from the distance x_1 and x_2.