SOLUTIONS :

A **solution** is defined as a homogeneous mixture of two or more substance having uniform properties throughout.

A **two- component (or binary**) systems consisting of a solute and solvent. The solute is present in small proportion whereas solvent is in large proposition.

Types of solutions

i. Solid-in-Liquid solutions e.g. NaCl in water
ii. Liquid-in-Liquid solutions e.g. ethanol in water
iii. Gas-in-Liquid solutions e.g. Oxygen in water

Solutions of liquid in liquid

The solubility of liquid in another liquid is determined by molecular structure of solute and solvent following like dissolves like principle.
Hence two substance having similar molecular structures and similar intermolecular forces are soluble in each other.

Raoult's law:

The law states that partial vapour pressure of a component in a liquid-liquid mixture is directly proportional to the mole fraction of that component.
Thus for a solution of two liquids A & B,

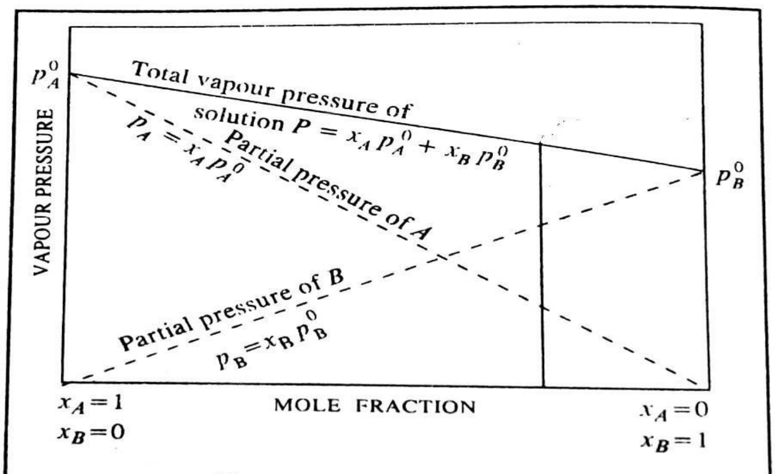
$$p_A \propto \chi_A \quad \Longrightarrow \quad P_A^o\,\chi_A$$
$$p_B \propto \chi_B \quad \Longrightarrow \quad P_B^o\,\chi_B$$

Thus, total vapour pressure

$$P = P_A^o\,\chi_A + P_B^o\,\chi_B$$

$$P = P_A^o + \chi_B(P_B^o - P_A^o)$$

A solution is said to be ideal if it **obeys Raoult's law** exactly at all concentration and all temperatures is known **as ideal solution.**

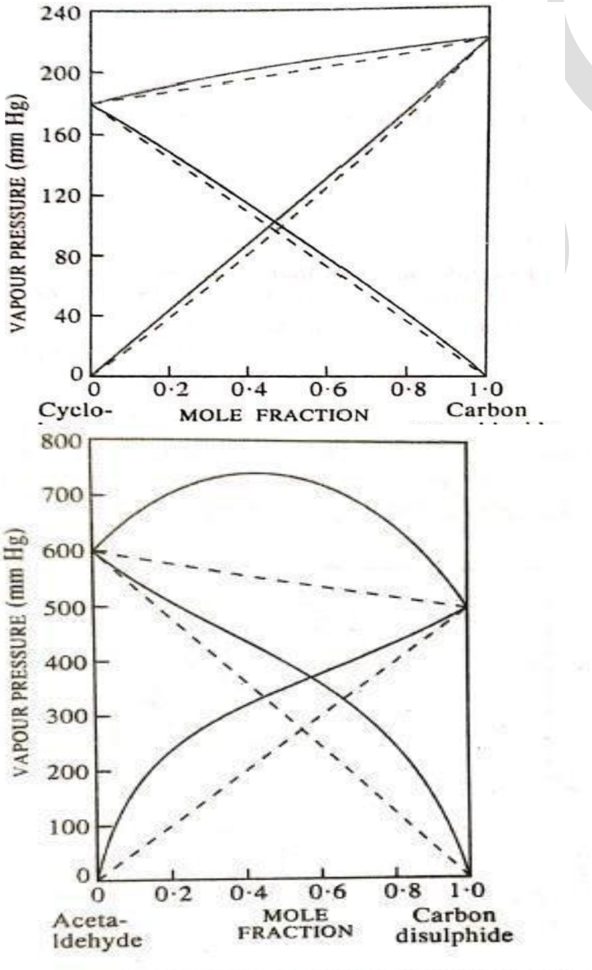


Vapour pressures of ideal solutions.

Vapour pressure of Non-ideal or Real solutions

- The vapour pressure of an ideal solution is given by Raoult's law.

  But some of the solutions whose **vapour pressure deviated (+Ve or –Ve) from ideal behaviour** in vapour phase or in solution; such solutions are called **Non-ideal or real solutions.**
- The non-ideal solutions are of three types



Positive deviations from ideal behaviour.
The dotted lines represent ideal behaviour.

Type-I

This type of solution shows **small positive deviations** from ideal behaviour,

The vapour pressure of this solution is slightly greater than that predicted by Raoult's law.

The total vapour pressure curve **remains** within the vapour pressure of each pure components.

e.g. : Cyclohexane - CCl_4 solution.

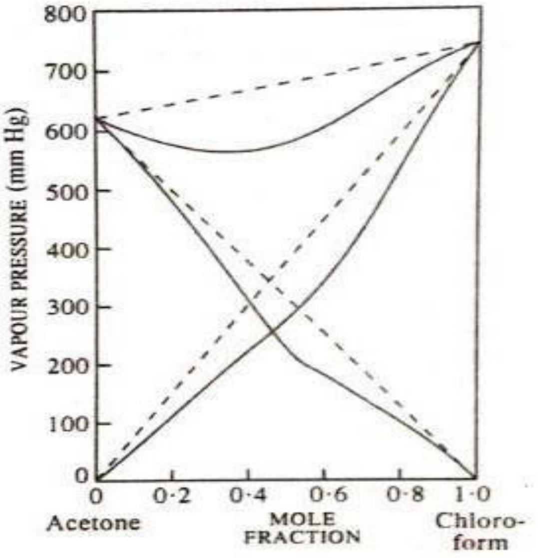
Type-II

This type of solution, shows **large positive deviations** from ideal behaviour.

The vapour pressure of solution is greater than that predicted by Raoult's law.

The total vapour pressure curve raise to **a maximum** which is above the vapour pressure of each pure components,

e.g. : (i) $CH_3CHO – CS_2$. ii) $H_2O – CH_3CH_2CH_2\text{-}OH$
(iii) $CH_3CH_2\text{-}OH – CHCl_3$



Negative deviations from ideal behaviour.
The dotted lines represent ideal behaviour.

Type-III

This solution shows **large negative deviations** from ideal behaviour.

Here the vapour pressure of solution is less than that predicted by Raoult's law.

The total vapour pressure curve dips to **a minimum** which is below the vapour pressure of each pure components,

e.g. : (i) $CH_3COCH_3 – CHCl_3$ (ii) $H_2O – H_2SO_4$

(iii) $H_2O – HNO_3$

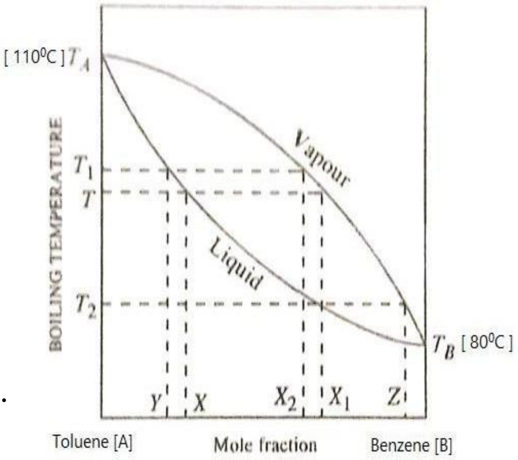
Fractional distillation of Binary liquid solutions :

It is explained by boiling temperature-composition curve of liquid and vapour phase diagram

The solutions are of three types, since having different boiling point; behave differently on distillation at constant pressure.

Solution of type-I [Ideal liquid mixture]

e.g. : Toluene - Benzene



Boiling temperature—composition curves for liquid and vapour phases in binary solutions of Type 1

The boiling temperature-composition diagram is shown in figure.

Suppose a solution of **A (Toluene) and B (Benzene)** of composition X is heated, the solution boills at temperature T. At this temperature the vapour is coming out that will have the composition X_1 (say).

The X_1 contains more amount of **B** (**benzene, lower boiling)** than X. At this time the residual liquid will contain more amount of **A (toluene, higher boiling)** that composition denoted as Y.

The Y composition boils at higher temperature T_1 and the vapour is coming out. Again it has **B (benzene)** in riche amount that is represented by X_2

The composition of residual liquid will again enriched with **A (toluene)**.The temperature of this composition will again have to be raised before it can boil.

By repeating this process, at one stage (at T_2 and its composition Z) it is possible to separate pure **A(benzene) and B (toluene).**

But it is a **tedious process.** However this can be achieved using suitable fractionating column.

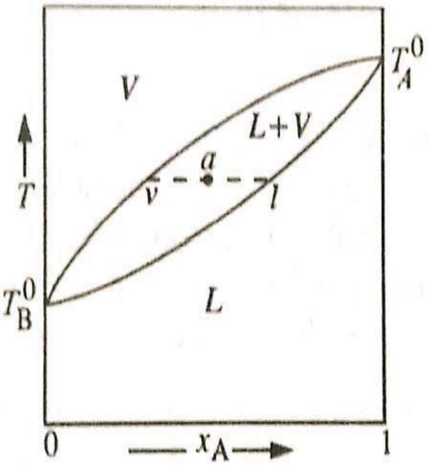
The Lever Rule and Fractional Distillation :

Consider a boiling temperature-composition curve of components A and B.

We assumed that B is more volatile than A that says, Boiling point (T_B^o) of pure B less than that of A (T_A^o).

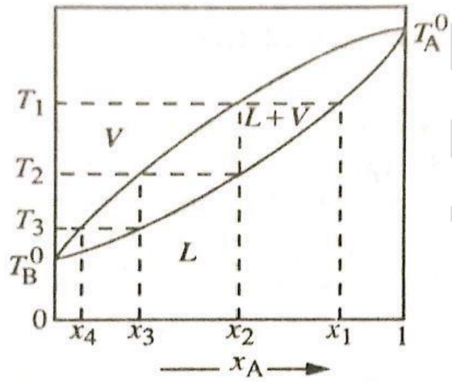
In this case, the composition of the liquid and vapour phases can be determined with help of lever rule.

We take any point 'a' in two-phase [liquid-vapour (L+V) region]. Drawing a horizontal line, **called tileline,** passing through the point 'a' and it meets the liquid equilibrium (liquid + Vapour) curve at 'l' and vapour equilibrium (liquid + Vapour) curve at 'v'. Then according to the **Lever rule,** ratio of amount of liquid phase to vapour phase is equal to the ration of the lengths av and al.



Lever rule in liquid ⇌ vapour equilibrium

$$\frac{n_L}{n_V} = \frac{length\ av}{length\ al}$$



Theoretical plates in fractional distillation

The lever rule explains the principle of fractional distillation of two liquids.

If liquid composition x_1 is heated to temperature T_1, the vapour contains more B and the corresponding composition is x_2.

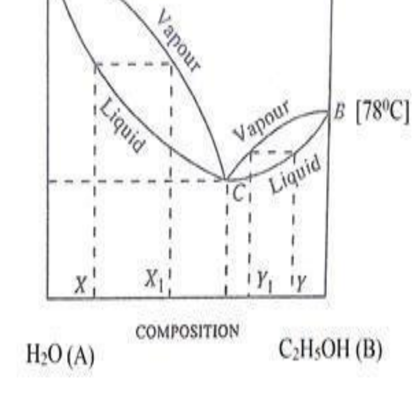
On cooling the vapour to temperature T_2, the liquid phase obtained a composition x_2

When the vapour is further cooled to temperature T_3, the liquid phase richer in B. Proceeding this way we can get pure liquid B when it meet the boiling point (T^0).

<u>Solution of Type-II : Non-ideal liquid mixture with minimum boiling point :</u>

e.g. : Water–Alcohol system

The Boiling temperature-composition curve meet at point C **with minimum boiling point**. In that point liquid and vapour phase have the same composition.



The liquid mixture boils at a constant temperature (at point C behave like a pure chemical compound) and distilled over completely at the same temperature without change in composition. It is called **constant boiling mixture or Azeotropic mixture.**

Let us consider distillation of mixture of composition X, the first fraction collected have the composition X_1, it will be richer in Azeotropic mixture and the composition of residual liquid shift towards A. By repeated distillation it is possible to separate pure A(water) from Azeotropic mixture but never pure alcohol.

When the composition Y is distilled the vapour contain more amount of Azeotropic mixture have composition Y_1. The residual liquid contains more amount of alcohol and shift towards B. By repeated distillation it is possible to separate pure alcohol but never pure water.

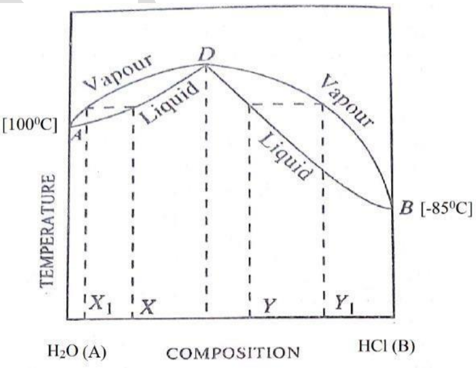
In water-Ethanol system Azeotropic mixture boiling at **78.13^0C** and the composition has **95.67% ethanol.**

Solution of Type - III : Non-ideal liquid mixture with maximum boiling point :

e.g.: Water – HCl system

The temperature composition curve is obtained at point D with maximum boiling point and is denoted as **Azeotropic mixture.**

Let us consider a mixture of composition X. The first fraction distillate have the composition X_1. It will be rich in **A** and the composition of residual liquid shifts towards D. By repeated distillation it is possible to separate pure A (water) from Azeotropic mixture, but never pure B(HCl).



When the composition Y is distilled, the vapour contains more amount of B with azeotropic mixture having composition Y_1,and the distillate shift towards B. The residual liquid contains more amount of A(**water)** and shifts towards D. By repeated distillation it is possible to separate pure B(**HCl) from Azeotropic mixture** but never pure A(**water).**

In water-HCl system Azeotropic mixture boils at **108.5^0C** and the composition has **20.24 % HCl.**

Distillation of immiscible liquids : Steam Distillation :

Principle :

In immiscible liquids, the addition of one liquid to the other does not alter the properties of either liquid and each liquid exerts its own vapour pressure.

Hence, the total vapour pressure of the mixture will be the sum of the vapour pressure of pure liquids at same temperature.

$$P = p_A^o + p_B^o$$

Where p_A^o and p_B^o are the vapour pressure of pure liquids A & B respectively.

Any liquid-liquid mixture will boil at a particular temperature when its total vapour pressure become equal to the prevailing pressure (1atm) at the temperature

$$p_A^o + p_B^o = atmospheric\ pressure$$

This temperature will be lower than the normal boiling point of either liquids in mixture.
The mole amount of each component in vapour phase is propositional to its vapour pressure.

If n_A and n_B are the mole amounts of the components A & B at the boiling point, then

$$\frac{n_A}{n_B} = \frac{p_A^o}{p_B^o} \qquad \text{-------} \quad \text{(i)}$$

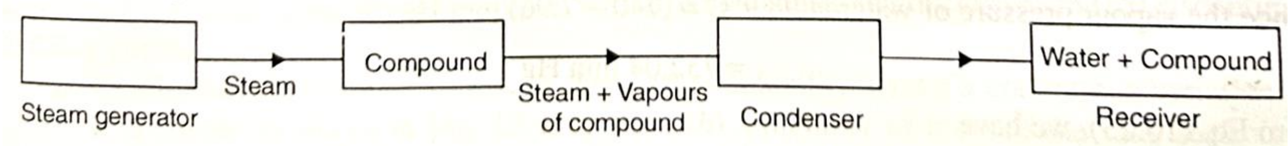
If w_A and w_B are the masses and M_A and M_B are the molar masses of A and B respectively, then

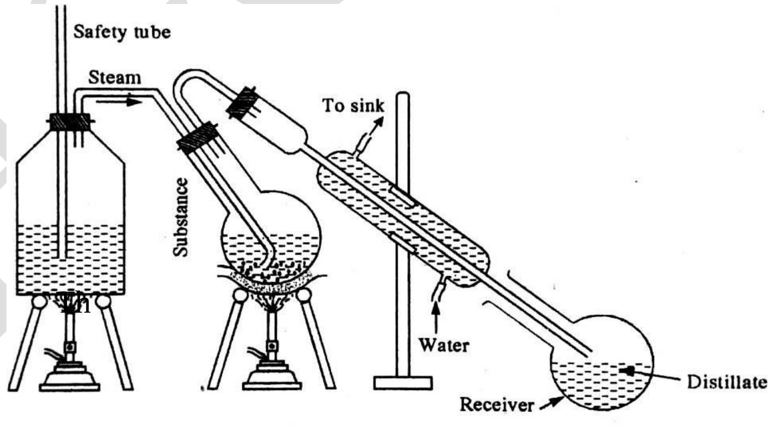
$$\frac{w_A}{w_B} = \frac{n_A\, M_A}{n_B\, M_B} \qquad \text{-------} \quad \text{(ii)}$$

$$\therefore \text{ Equations (i) \& (ii)} \Longrightarrow \frac{w_A}{w_B} = \frac{p_A^o\, M_A}{p_B^o\, M_B} \quad \text{-------} \quad \text{(iii)}$$

So the mass of a liquid in the distillate will be proportional to the product of its vapour pressure and molar mass.

Also the ratio of masses of liquid components is equal to the ratio of product of their vapour pressures and molar masses.
A mixture of immiscible liquids begins to boil when sum of their vapour pressure is equal to atmospheric pressure. When a liquid material to be distilled has a high boiling point, and decomposition might occur if direct distillation is employed, the process of steam distillation may be used. Here the solubility of steam in the liquid must be very low. Steam is passed directly into the liquid.





Steam distillation.

Applications of steam distillation technique :

1. It is used to purify high temperature sensitive organic compounds having high boiling points and immiscible in water. **e.g. : Aniline**, its normal B.P is **180^{0}C**. But it is made to boil and distils over at lower temperature by passing stream through it.
2. Iodobenzene can be purified by this technique. It has b.p. 180^{o}C. It is also immiscible in water. On passing steam through it, the distillation takes place at 98^{o}C.

At 98^{o}C $p^o_{H_2O} = 712\ mm\ Hg$ and $p^o_{iodobenzene} = 48\ mm\ Hg$.

$\therefore$ Total vapour pressure $P = (712 + 48) mm\ Hg = 760\ mm\ Hg$

$\therefore$ The mass ratio of iodobenzene to water $\frac{W_{iodobenzene}}{W_{H_2O}} = \frac{48 \times 204}{712 \times 18} \simeq \frac{7}{9}$

i.e. For each 7+9=16g of distillate 7g iodobenzene is separated.

Though vapour pressure of iodobenzene is much lower, it's high molar mass $(204\ g\ mol^{-1})$ counterbalances so as to make the relative yield appreciably large.

Partially miscible liquids:

The partially miscible liquids are completely miscible at above or below temperature, **is called critical solution temperature (CST)** or **consolute temperature.**

In liquid pairs, two phases having dissimilar composition in equilibrium at a given temperature **is called conjugate phases**

If the partial miscibility increases at increasing temperature, the liquid pairs become completely miscible, **is called Upper critical solution temperature (UCST)**

e.g. : i) Phenol-Water, ii) Aniline-Water,
iii) Aniline- Hexane, iv) Cyclohexane-Methanol.

If the partial miscibility increases at lower temperature, the liquid pairs become completely miscible, **is called Lower critical solution temperature (LCST).**

e.g.: i) $(C_2H_5)_2NH$-H_2O, ii) $(C_2H_5)_3N$-H_2O

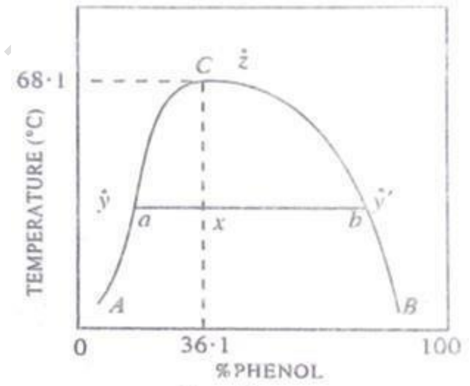
Those in which the partial miscibility increases on both raising as well as lowering the temperature in certain ranges, the liquid pairs become completely miscible.

e.g.: i)H_2O–nicotine ii) H_2O–β Picoline systems.

Those in which complete miscibility cannot be obtained.

e.g.: Ether -Water

Phenol-Water System:



Phenol–water system

Phenol-water system is a partially miscible to form a conjugate solution (have different composition in liquid pairs) at ordinary temperature.

The conjugate solution come to miscible (homogeneous phase) completely at **68.1^{0}C** denoted as critical solution temperature (CST).

Phase diagram of phenol-water system is shown in the figure.

In phase diagram, at ordinary temperature of **30^{0}C,** the composition of conjugate solution indicated by $a$is aqueous layer and $b$is phenol layer.

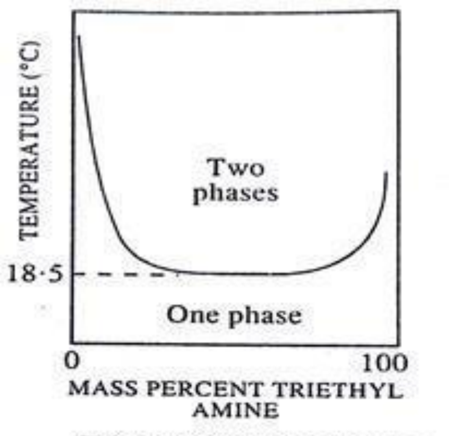
The mixture of solution (water and phenol) i denoted by point x. the curve AC is said y while CB curve is y'

At *y* it will be an unsaturated solution of phenol in water and at *y′* will be unsaturated solution of water in phenol.

Further addition of phenol to *y* or water to *y′* will result separation of two layers.

The point z represent consolute temperature or critical solution temperature (CST), in that point further addition of phenol to water or water to phenol will not formed two layers.

Triethylamine-Water system:



Triethylamine–water system.

In this partially miscible system, mutual solubility increase with decrease temperature

So that it has **lower consolute temperature (LCST)**

The mutual solubility of two liquids are plotted graphically shown in figure.

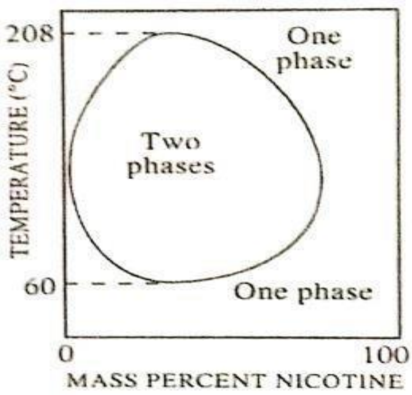
The consolute temperature is **18.5^{0}C,** above this temperature, the liquid give two different layers but below this temperature, they are completely miscible in all proportions.

Nicotine–Water System:

It shows both upper and lower consolute temperature of 208^{0}C and 60.8^{0}C respectively.

Between these two temperatures, mixture of water and nicotine separate into two liquid layers.

It is partially miscible in this two liquid layers.



Nicotine–water system.

Nernst Distribution Law :

When a solute distribute itself between two immiscible solvent in contact with each other at constant temperature, the solute get distributed between the two solvents at a constant ratio irrespective of total amount of solute and irrespective of the any other molecular species which may be present.

Conditions for Nernst Distribution Law :

1. Temperature must be constant
2. Substance dissolves in both the immiscible solvents in the same form i.e. the distributing substance must not dissociate or associate in either of the solvents.
3. No chemical reaction takes place between the solute and either of the solvents.
4. Concentration of the solute is low.

The ration of the concentrations in the two solvents is called the ***partion coefficient*** or ***distribution coefficient*** **(K_D) .**

For example :

When **iodine** is added to a mixture of water and CCl_4, it distributes such a way in equilibrium, the ratio of concentration of iodine in two solvent is constant at constant temperature.

$$K_D = \frac{[I_2]_{H_2O}}{[I_2]_{CCl_4}} = \frac{c_{H_2O}}{c_{CCl_4}}$$

Limitations of Nernst distribution Law :

This law is valid only at following conditions

1. At constant temperature
2. The solution should be dilute
3. The two solvents must be immiscible
4. Similar molecular species must be exist in two solvents.

Thermodynamic derivation of the Nernst Distribution Law :

Suppose a solute X is present in two immiscible solvents A and B in contact with each other. Now suppose that the chemical potential of solute in solvent A is μ_1 and in solvent B is μ_2. When two phases are in equilibrium, their chemical potentials too will be equal to one another. So that,

$\mu_1 = \mu_2$ …………(1)

Since $\mu = \mu^o + RT \ln a$ …………..(2)

Where, μ^o is the chemical potential of the pure state and a is the activity.

Therefore, $\mu_1 = \mu_1^o + RT \ln a_1$ for Phase 1 …………..(3)

And $\mu_2 = \mu_2^o + RT \ln a_2$ for Phase 2 ………….(4)

Hence, $\mu_1^o + RT \ln a_1 = \mu_2^o + RT \ln a_2$

Or, $\mu_2^o - \mu_1^o = RT \ln \frac{a_1}{a_2}$ …………..(5)

Since R is a gas constant. At constant temperature, the standard chemical potentials μ_1^o and μ_2^o are also constant. And hence,

$\frac{a_1}{a_2} = constant\ (at\ constant\ temperature)$ ………(6)

Since the solutions are dilute, they behave ideally and hence Henry's law is obeyed in each phase, according to which activity is proportional to mole fraction.

$\frac{a_1}{a_2} = \frac{k_1\chi_1}{k_2\chi_2} = constant\ (at\ constant\ temperature)$ …….(7)

Where χ_1 and χ_2 are the mole fractions of the solute in the two phases and k_1 and k_2 are the Henry's law constants for the solute in the two phases.

$\frac{\chi_1}{\chi_2} = constant\ (at\ constant\ temperature)$ ………(8)

Since the solutions are dilute, the ratio of the mole fractions is almost the same as the ratio of the concentrations. Hence,

$\frac{\chi_1}{\chi_2} = \frac{c_1}{c_2} = constant\ (at\ constant\ temperature)$ ………(9)

Thus, if a substance is present in two phases in contact with each other, then, at equilibrium,

$\frac{c_1}{c_2} = constant\ (at\ constant\ temperature) = K_D$ ……..(10)

This is the Nernst Distribution Law.

_____X_____