# MARUDHAR KESARI JAIN COLLEGE FOR WOMEN (AUTONOMOUS) VANIYAMBADI PG Department of Chemistry III B.Sc. Chemistry- semester- V

**E-Notes** 

# COURSENAME: PHYSICALCHEMISTRY-I

#### CODE:FCH53

# **UNIT-I SOLUTIONS**

Solutions of liquids in liquids -Ideal Solution and Raoult's law - Vapour pressure of ideal solutions. Vapour Pressure-Composition and Temperature-Composition Curves of Ideal and Non-ideal Solutions. Thermodynamics of Solutions.Gibbs-DuhemMargules equation - Vapour pressure of Non-ideal solutions - Fractional distillation of Binary liquid solutions - Lever rule- Azeotropic mixtures - Partially miscible liquids.CST and effect of impurity on CST. Phenol - Water, Triethylamine - Water and Nicotine - Water systems - Immiscible Liquids- Steam Distillation. Nernst distribution law - Definition - Thermodynamic derivation - Applications.

Learning Objective: To impart knowledge about the Solutions, Phase Rule and its Applications

**Learning Outcome:**Explain the Thermodynamics of ideal and Non-ideal solutions, Nernst distribution law and its applications.

# **SOLUTIONS:**

solution is defined by IUPAC as "A liquid or solid phase containing more than one substance, when for convenience one substance, which is called the solvent, is treated differently from the other substances, which are called solutes.

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

The substance of which the solution is made are called its **components.** So solutions are generally **two-component** (**or binary**) systems consisting of a solute and solvent. The solute is present in small proportion whereas solvent is in large proposition.

A solution may exist in gaseous state, liquid state or solid state, hence the types of solutions are

- i. Solid-in-Liquid solutions
- ii. Liquid-in-Liquid solutions
- iii. Gas-in-Liquid solutions

# Solutions of liquid in liquid

- i. The solution contain two liquid (binary liquid) solution which are volatile.
- ii. The solubility of liquid in another liquid is determined by molecular structure of solute and solvent. Thus in liquid solution the molecules are very close together.
- iii. If the solute molecules have large intermolecular force on one another, it forming a separate phase from that of the solvent.
- iv. Similarly, if the solvent molecules attract one another strongly and have no affinity for the solute molecules, it form a separate phase.
- v. In formation of solution, the general rule is that like dissolves like. Hence two substance having similar molecular structures and similar intermolecular forces are soluble in each other.
- vi. In general, polar substance dissolves polar substances and nonpolar substances dissolved nonpolar substances.

# **Raoult's law:**

The **French chemist Raoult** proposed "a quantitative relationship between partial vapour pressure and the mole fraction of component in solution" is known as **Raoult's law** 

This law states that "the partial pressure of any volatile component (liquid) of

Let us consider binary solution contain volatile liquid component A & B whose moles  $n_A$  and  $n_B$ , If  $p_A$  and  $p_B$  are their partial pressure, then

According to the Raoult's law,

Where  $x_A$  and  $x_B$  are mole fraction of the component A & B

$$x_A = \frac{\mathbf{n}_A}{(\mathbf{n}_A + \mathbf{n}_B)} x_B = \frac{\mathbf{n}_B}{(\mathbf{n}_A + \mathbf{n}_B)}$$

 $p^0_A$  and  $p^0_B$  are vapour pressure of pure component A & B respectively

If the vapour behaves like ideal gas, According to **Dalton's law of partial pressure**, the total vapour pressure P is given by sum of partial pressure of individual component.

 $P = p_A + p_B$ 

Sub equ(1) in (2)

$$P = x_A p_A^0 + x_B p_B^0 \dots 3$$

In general, Raoult's law may be denoted as

$$\mathbf{p}_i = x_i \, \mathbf{p}_i^0$$

And total pressure may be written as

$$\mathbf{P} = \boldsymbol{\Sigma} \mathbf{p}_{i}$$

The Raoult's law give us a definition of an ideal solutions.

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 pressure of ideal solution:

From total vapour pressure of Raoult's law equation

$$P = x_A p_A^0 + x_B p_B^0$$
(1)

Where P is total vapour pressure of solution

 $x_A$  and  $x_B$  are mole fraction of liquid component A & B in solution and

 $p_A^0$  and  $p_B^0$  are vapour pressure of purecomponent A & B We know that  $x_A + x_B = 1$  (or)  $x_A = 1-x_B$ 

Sub  $x_A$  value in Equ<sup>(1)</sup>

$$P = (1 - x_B) p_A^0 + x_B p_B^0$$

$$P = p_A^0 + x_B (p_B^0 - p_A^0)....(2)$$

The above equation give straight-line equation form y = mx + c

The plot of P (total vapour pressure) versus  $x_B$  (mole fraction) will give a straight line with slope =  $(p_B^0 - p_A^0)$  and y-axis intercept =  $p_A^0$ 



# Activity of a component in an ideal solution

But

Consider a binary solution contains component A and B forming an ideal solution,

According to Raoult's law, the partial vapour pressure of component A is given by

$$p_A = x_A p_A^0$$
 (or)  $p_A'_0 = x_A$ .....(1)

Since vapour pressure of liquid component of solution at ordinary temperature are low (less than 1atm), the fugacity (f) may be taken as equal to pressure,

$$p_{A} / p_{A}^{0} = \frac{f_{A}}{f_{A}} = x_{A} ....(2)$$

$$\frac{f_{A}}{f_{A}} = a_{A}$$

Where  $f_A$  is the fugacity of component A

f<sub>A</sub><sup>0</sup>is the fugacity of pure component A

 $a_A$  is activity of component A in solution.

Hence  $x_A = a_A$ 

An ideal solution is defined as **the activity of each component** is equal to its **mole fraction** under all conditions of temperature, pressure and concentration.

In general, the activity and mole fraction is given by

 $a_i = x_i$ 

#### **Gibbs-Duhem-Margules Equation:**

Let us consider, a **binary solution** contain A & B componentsin equilibrium with their vapour at constant temperature and pressure.

If  $n_A$  and  $n_B$  are number of moles of component A & B respectively.

According to Gibbs-Duhem equation,

 $n_A d\mu_A + n_B d\mu_B = 0....$ 

Where  $\mu_A$  and  $\mu_B$  are the chemical potential of A & B components respectively

On dividing Equ(1) by  $n_A + n_B$  we get

$$\frac{n_A}{n_A+n_B}d\mu_A + \frac{n_B}{n_A+n_B}d\mu_B = 0$$

Where  $x_A$  and  $x_B$  are mole fraction of A & Bcomponents

In thermodynamically, the chemical potential  $(\mu)$  of any constituent of a liquid mixture is

 $\mu_i = \mu_i^0 + RT \ln f_i \dots 3$ 

Where  $\mu_i^0$  is constant for the substance at constant temperature

 $f_i$  is fugacity of the given constituent in the liquid or in the vapour Phase at equilibrium,

On differentiating Equ<sup>3</sup> at constant temperature, we get

 $d\mu_i = RT \ d \ In \ f_i \ \dots \ (4)$ 

Substitute Equ(4) in (2), we get

$$x_{\rm A}RTd \ln f_A + x_{\rm B}RTd \ln f_B = 0 \dots (5)$$

Dividing Equ(5) by  $dx_A$  and  $dx_B$  we get

 $\frac{x_A RTd \ln f_A}{dx_A} + \frac{x_B RTd \ln f_B}{dx_B} = 0 \dots (6)$ 

If  $x_A + x_B = 1 \Rightarrow x_A = 1 - x_B$ 

Hence  $dx_A = -dx_B$ 

Therefore Equ<sup>6</sup> become

 $\frac{d\ln}{dx_A/x_A} - \frac{\ln f_B}{dx_B/x_B} = 0 \text{ (or)} \quad \frac{d\ln f_A}{d\ln x_A} - \frac{d\ln f_B}{d\ln x_B} = 0 \text{ (or)} \quad \frac{d\ln f_A}{d\ln x_A} = \frac{d\ln f_B}{d\ln x_B}$ (7)

#### This equation is valid whether the vapour pressure behaves ideally or non-ideally.

If the vapour behaves as an ideal gas, the fugacity ( $f_i = f_A$  and  $f_B$ ) can be replaced by vapour pressure

So that the Equ(7) becomes

 $\frac{d \ln p_A}{d \ln x_A} = \frac{d \ln p_B}{d \ln x_B}.$ (8)

#### The Equ<sup>(8)</sup> is known as the **Gibbs-Duhem-Margules equation**

This equation relates the composition of mixture in liquid phase with the partial vapour pressures in the gas phase.

#### Ideal solutions and the Gibbs-Duhem-Margules Equation:

For an ideal solution, according to Raoult's law

For component A

Logarithms on both sides and differentiating, we get

 $d \ln p_A = d \ln x_A \qquad \text{(or)}$   $\frac{d \ln p_A}{d \ln x_A} = 1 \qquad (2)$ 

From Gibbs-Duhem-Margules Equation

For component B

$\frac{d \ln p_B}{d} = 1 \dots$	
$d \ln x_B$	
Integrating Equ <sup>(3)</sup> we get,	
$\ln p_B = \ln x_B + \ln k \dots$	
Where $\ln k$ is integration constant	
Taking antilogEqu(4), we get	

$$p_B = k x_B$$

From above expression component A & B obeys Raoult's law.

#### THERMODYNAMICS OF IDEAL SOLUTIONS

# Gibbs free energy change of mixing $(\Delta G_{mix})$ for an ideal solution

Let  $n_A$  moles of a liquid A and  $n_B$  moles of liquid B form a solution

According to **thermodynamics**, the free energy (G) of the solution at a given temperature and pressure is given by

Where  $G_A$  and  $\overline{G}_B$  are partial molar free energies (chemical potentials) of the component A & B respectively.

If  $G_A^0$  and  $G_B^0$  are the **free energies** of per mole of the pure component A & B respectively, then, change in free energy of mixing ( $\Delta G_{mix}$ ) is

 $\Delta G_{mix} = (Free energy of solution) - {Sum of free energies of the pure components}$ 

$$\Delta G_{\text{mix}} = G - (n_A G_A^0 + n_B G_B^0) \dots (2)$$

Sub Equ(1) in (2), we get

$$\Delta G_{\text{mix}} = (n_A G_A + n_B G_B) - (n_A G_A^0 + n_B G_B^0)$$
  
=  $(G_A - G^0)_A + n_B (\bar{G}_B - G^0)_B$ .....(3)

Where  $(G_A - G_A^0)$  and  $(G_B - G_B^0)$  are changes in partial molar free energies of components A & B respectively on mixing.

#### Fromthermodynamic equation

Where  $\mu_i$  is chemical potential of component *i* 

 $\mu_i^0$  is standard chemical potential of same substance

 $a_i$  is activity of component

Since chemical potential has same quantity as the partial molar free energy,

The above Equ(4) may be written as

(For component A) $G_A = G_A^0 + RT \ln a_A$ 

 $\bar{G}_A - G_A^0 = RT \ln a_A.$ 

(For component B)

$$G_B = G_B^0 + RT \ln a_B$$

$$G_B - G_B^0 = RT \ln a_B \tag{6}$$

Sub Equ<sup>(5)</sup> and <sup>(6)</sup> in <sup>(3)</sup>

 $\Delta G_{\text{mix}} = n_A RT \ln a_A + n_B RT \ln a_B \dots (7)$ 

If the solution is ideal, the activity of each component should be equal to its mole fraction

 $(a_A = x_A \text{ and } a_B = x_B)$ 

Hence, free energy of mixing of an ideal solution becomes

 $\Delta G_{\rm mix} = n_A RT \ln x_A + n_B RT \ln x_B \dots$ 

If there are more than two component in solution, the above equation becomes

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B + n_C RT \ln x_C + \dots \dots$$

 $= \operatorname{RT} \Sigma n_i \ln x_i \dots 9$ 

Dividing Equ<sup>(8)</sup> both sides by  $n_A + n_B$ , we get

$$\frac{\Delta G_{mix}}{n_A + n_B} = \frac{n_A}{n_A + \eta_B} \operatorname{RTln} x_A + \frac{n_B}{n_A + n_B} \operatorname{RTln} x_B$$

 $= x_A RT \ln x_A + x_B RT \ln x_B \dots (10)$ 

If  $n_A + n_B = 1$ , then Equ (10) becomes

$$\Delta \mathbf{G}_{\mathrm{mix}} = \mathbf{RT}(\mathbf{x}_A \ \ln \mathbf{x}_A + \mathbf{x}_B \ \ln \mathbf{x}_B)....(1)$$

If there are more than two component in solution, then Equ(1) becomes

$$\Delta G_{\text{mix}} = \text{RT}(x_A \ln x_A + x_B \ln x_B + x_C \ln x_C + \dots)$$

 $= \operatorname{RT} \Sigma x_i \ln x_i \dots (12)$ 

Since  $x_i$  always less then unity,  $\Delta G_{mix}$  is always a negative quantity.

#### Vapour pressure of Non-ideal or Real solutions

- The vapour pressure of a 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 three types, they are



# Type-I

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

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

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

Eg: Cyclohexane - CCl<sub>4</sub>

# Type-II

1. In this solution, shows **large positive deviations** from ideal behaviour,

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

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



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

**Eg:** (i)  $CH_3CHO - CS_2(ii) H_2O - CH_3CH_2CH_2-OH$ (iii)  $CH_3CH_2-OH - CHCl_3$ 

# Type-III

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

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

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

**Eg:** (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

Eg: Toluene-Benzene

1. The Boiling temperature-composition diagram is shown in figure.

2.Suppose a solution**A** (**Toluene**) of composition X is heated, the solution bills at temp T. at this

<u>temp</u> the vapour is coming out that will have the composition  $X_1$ 

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

4. The Y composition boils at higher temp  $T_1$  and the vapour is coming out, now again it has**B** (**benzene**) in riche amount that is represented by  $X_2$ 

5. The composition of residual liquid will again enriched with **A** (toluene). The <u>temp</u> of this composition will again have to be raised before it can boil.

- By repeating this process, at one stage (at T<sub>2</sub> and its composition Z) it is possible to separate pure A(benzene) and B (toluene).
- 7. But it is a **tedious process** however this can be achieved using suitable fractionating column.

#### Solution of Type-II

#### [Non-ideal liquid mixture with minimum boiling point]





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

2. 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, is called constant boiling mixture orAzeotropic mixture.

Let us consider distillation of mixture of composition X, the first fraction collected have the composition  $X_1$ , it will be richer inAzeotropic mixture and the composition of residual liquid shift towards A.By repeated distillation it is possible to separate pure 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<sup>o</sup>C** and the composition has **95.67** % ethanol.

#### Solution of Type-III

#### [Non-ideal liquid mixture with maximum boiling point]





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

Let's mixture of composition X is to be distilled it's first fraction of composition is  $X_1$ , it will be rich

inAand the composition of residual liquid shift towards D. By repeateddistillation it is possible to separate pure waterfromAzeotropic mixture but never pure HCl.

When the composition Y is distilled, the vapour contain more amount of B with azeotropic mixture havecomposition  $Y_1$ , distillate shift towards B and the residual liquid contains more amount of waterand shiftstowards D. By repeateddistillation it is possible to separate pure HCl from Azeotropic mixture but never pure water.

In water-HCl system Azeotropic mixture boiling at 108.5<sup>o</sup>C and the composition has 20.24 % HCl

# Lever Rule and Fractional Distillation

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



We assumed that B is more volatile than A that says, Boiling point  $(T^0_B)$  of pure B less than that of A  $(T^0_A)$ 

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]. Draw a horizontal line **called tile line** passing through

Lever rule in liquid <u>avapour equilibrium</u>

a' and it meet the liquid equilibrium (liquid + Vapour) curve

at (l) and vapour equilibrium (liquid + Vapour) curve at v.

The ration of amount of liquid phase to vapour phase is given by

$$\frac{n_{liquid}}{n_{vapour}} = \frac{\text{length av}}{\text{length al}}$$

This is called **the Lever rule.** 



Theoretical plates in fractional distillation

The lever rule explain the principle of fractional distillation of two liquids (shown in figure)

If liquid composition  $x_1$  is heated to temperature  $T_1$ . The vapour contains riche of B that 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  $(T_B^0)$ .

#### **Distillation of Immiscible liquids:**

- 1. 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.
- 2. Hence, the total vapour pressure of the mixture will be the sum of the vapour pressure of pure liquids at same temperature.

$$P = p_A^0 + p_B^0$$

Where  $p_A^0$  and  $p_B^0$  are the vapour pressure of pure liquids A & B respectively.

3. Any system will boiled when its total vapour pressure become equal to the prevailing pressure (1atm) at the temperature

$$p_A^0 + p_B^0$$
 = atmospheric pressure

- 4. This temperature will be lower than the normal boiling point of either liquids in mixture.
- 5. The number of moles of each component in vapour phase is propositional to its vapour pressure.

If n<sub>A</sub> and n<sub>B</sub> are the number of moles of the component A & B at boiling point,

Then

$$\frac{\underline{n}_A}{n_B} = \frac{\underline{p}_A^0}{p_B^0}.....1$$

if  $w_A$  and  $w_B$  are the actual masses and

 $M_A$  and  $M_B$  are the molar masses, then Equ: 1 can be written as

$$\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B}$$
$$\frac{w_A}{w_B} = \frac{p_A^0 M_A}{p_B^0 M_B}......2$$

So the mass of the liquids in distillate will be in the ration of their vapour pressures and molar masses.

#### **Function of fractional distillation:**

- 1. The mass of liquid is equal to the ratio of their vapour pressures and molar masses, this principle is used in distillation process.
- It is used to purify organic compounds having high boiling point and must be immiscible in water. Eg: Aniline, its normal B.P is 180°C. But it is made to boil and distil over at lower temperature by passing stream through it.



liquid that is to be distilled is placed in the round-bottomed flask, clamped at angle to prevent the solution splashed into the condenser.

- 4. The distillation flash is heated at sand bath to avoid too much condensation of water into it.
- 5. The vapour of the organic compound mixed with steam and condensed in the receiver.
- 6. In this BP of liquid is  $98.5^{\circ}$ C which is lower than the BP of either water or aniline.

$$\frac{w_A}{w_B} = \frac{p_A^0 M_A}{p_B^0 M_B}$$

 $W_A$  and  $W_B$  are mass of water and aniline respectively

 $p_A^0$  and  $p_B^0$  are vapour pressure of water and aniline 717 and 43 torr respectively

 $M_A$  and  $M_B$  are molar mass of water and aniline 18 and 93 gmol<sup>-1</sup> respectively

 $\frac{\text{Mass of water}}{\text{Mass of aniline}} = \frac{18 \text{ gmol} - 1 \times 717 \text{ torr}}{93 \text{ gmol} - 1 \times 43 \text{ torr}} = 3.23$ 

# Partially miscible liquids:

- 1. The partially miscible liquids are completely miscible at above or below temperature, is calledcritical solution temperature (CST) or consolute temperature.
- 2. In liquid pairs, two phases having dissimilar composition in equilibrium at a given temperature is called conjugate phases
- **3.** If the partial miscibility increases at increasing temperature, the liquid pairs become completely miscible, **is called Upper critical solution temperature (UCST)**

<b>Eg:</b> i)	Phenol - Water,	ii) Aniline-Water,
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iii) Aniline - Hexane, iv) Cyclohexane - Methanol.

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

**Eg:** i)  $(C_2H_5)_2NH - H_2O$ , ii)  $(C_2H_5)_3N - H_2O$ 

5. 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.

**Eg:** i)  $H_2O$  – nicotine ii)  $H_2O - \beta$  Picoline systems.

6. Those in which complete miscibility cannot be obtained.

Eg: Ether - Water

#### **Phenol-Water System:**



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

2) The conjugate solution come to

miscible(homogeneous phase) completely at **68.1**<sup>o</sup>Cdenoted as critical solution temperature (CST).

3) Phase diagram of phenol-water system is shown figure.

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

5) The mixture of solution (water and phenol) idenoted 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.

- 6) Further addition of phenol to y or water to y' will result separation of two layers.
- The point z represent consolute temperature (CST), in that point further addition of phenol to water or water to phenol will not formed two layers.

### **Triethylamine-Water system:**



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

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

3) The mutual solubility of two liquid are plotted graphically shown in fig.

4) The consolute temperature is **18.5<sup>o</sup>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  $208^{\circ}$ C and  $60.8^{\circ}$ C respectively.

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

It is partially miscible in this two liquid layer.

# **Nernst Distribution Law:**

When a solute distribute itself between two immiscible solvent in contact with each other, 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.

## For example:

When **iodine** is added to water and CCl<sub>4</sub>, it distribute such a way in equilibrium, the ratio of concentration of iodine in two solvent is constant at constant temperature.

$$\frac{[I_2]_{H_2}}{[I_2]_{CCl_4}} = K D$$

# Where $K_D$ is distribution coefficient or partition coefficient.

# 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 solvent must be immiscible
- 4. Similar molecular species must be exist in two solvents.

# Thermodynamic derivation:

Suppose a solute *x*, is present in two immiscible solvent A & B in contact with each other, let  $\mu_A$  and  $\mu_B$  are chemical potential of the solute in solvent A & B respectively

At equilibrium  $\mu_A = \mu_B$   $\mu_A = \mu_A^0 + RT \ln a_A$ .....for solvent A  $\mu_B = \mu_B^0 + RT \ln a_B$ .....for solvent B  $\mu_A^0 + RT \ln a_A = \mu_B^0 + RT \ln a_B$  $RT \ln \frac{a_A}{a_B} = \mu_B^0 - \mu_A^0$ 

At constant temperature  $\mu^0_A$  and  $\mu^0_B$  are constant

$$\frac{a_A}{a_B} = \text{constant}$$

For dilute solution the activity may be replace by concentration

$$\frac{C_A}{C_B} = \mathbf{K}_{\mathrm{D}}$$

This is the Nernst distribution law.

# Case: 1

Association of the solute in one of the solvent:



Let X represent the molecular formula of the solute it remains in solvent-I (phase-I). in which concentration is C.

Suppose it is largely associated to give the molecule  $X_n$  in phase II. The associated molecule will exists in equilibrium with single molecule as shown in figure.

Association in one of the phases.

Let  $C_2$  be the total concentration of the solution in phase

Applying **the law of chemical equilibrium** between the associated and single molecule in the second phase.

$$X_{n} \longrightarrow nX$$

$$K = \frac{[X]^{n}}{[X_{n}]}$$

$$[X]^{n} = K \times [X_{n}]$$

$$[X] = n\sqrt{K \times [X_{n}]}$$

$$[X] = constant . n\sqrt{[X_{n}]}$$

If the solute exist largely as associated molecule, which is generally true except at very high dilution. The concentration of the associated molecule.  $[X_n]$  may be taken as equal to  $C_2$ 

$$[X_n] = C_2$$

$$[X] = constant \times {^n}\sqrt{C_2}$$

Since the distribution law is valid only for concentration of similar molecular species in two phases.

$$\frac{C_1}{[X]} = \text{constant}$$

Sub [X] value in above Equ

$$\frac{C_1}{constant \times \sqrt[n]{C_2}} = constant = K_D$$

X Conc. $c_1$	Phase 1 no dissociation
$X \rightleftharpoons A + B$ $c_2(1-\alpha) \leftarrow c_2\alpha + c_2\alpha$ $c_2\alpha + c_2\alpha$ $c_2\alpha + c_2\alpha$ $c_2\alpha + c_2\alpha$	Phase II dissociation

Dissociation of the solute in one of the solven

Dissociation in one of the phases.

Consider a solute x which dissolves in phase I without any change to give species A & B,

- 1. Let  $C_1$  is a concentration of the solute in phase I and  $C_2$  is the total concentration of the solute in phase-II.
- 2. If  $\alpha$  is the degree of dissociation of the solute in phase-II then at equilibrium in phase-II is

$$X \implies A + B$$

$$C_2(1-\alpha) \qquad C_2\alpha \quad C_2\alpha$$

In this case the ratio of the concentration of the undissociated species in the two solvent will be constant

$$\frac{C_1}{C_2(1-\alpha_1)} = KD$$

Similarly if the solute dissociate in both the solvents

$$\frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)} = K_D$$

Where  $\alpha_1$  and  $\alpha_2$  are the degree of dissociation of the solute in phase-I and phaseII

# Case: 3

Solute enter into chemical combination with one of the solvents:



Combination with the solvent.

When solute enter into chemical combination, there is no change in general equation of Nernst distribution law.

Consider a solute x in phase-I does not undergo chemical change,

Let  $C_1$  is concentration of solute in phase-I and  $C_2$  is total concentration of solute in phase-II,

If the solute enter into chemical combination with phase-II to form complex molecules

 $\begin{array}{c} X + nS \implies X, nS \\ C_2 (1 - \alpha) \qquad C_2 \alpha \end{array}$ 

Concentration of uncombined solute molecules =  $C_2(1 - \alpha)$ 

Concentration of the complex molecules formed =  $C_2 \alpha$ 

Applying law of chemical equilibrium

$$\frac{C_2 \alpha}{C_2 (1-\alpha)} = K$$

$$\frac{C_2 \alpha}{C_2 (1-\alpha)} = constant.....(1)$$

The distribution law is valid only for concentration of single molecule of solute in both phase

$$\frac{C_1}{C_2(1-\alpha)} = constant \dots (2)$$

Dividing Equ. (2) by (1)

$$\frac{C_1}{C_2\alpha} = constant.....(3)$$

Where  $\alpha$  is fraction of solute that combine with solvent (phase-II), is constant at a given temperature. So the above Equ. (3) become

The combination of solute with one of the solvents does not change in

fundamental equation of the distribution law but it changing in partition coefficient value.

# **Application of Nernst distribution Law:**

# **I)** Solvent Extraction:

- Let V ml of a solution containing W gram of solute be repeatedly extracted with v ml of another solvent which is immiscible with first.
- 2. Let  $w_1$  be the mass of solute that remains unextracted at end of the first operation.

$$\frac{\frac{w_1}{V}}{\frac{w-w_1}{v}} = K_D$$

On rearranging

$$w_1 = W\left[\frac{K_D}{K_D V + v}\right]$$

Similarly at the end of the second extracted. The solute which remains unextracted.

$$w_2 = w_1 \left[ \frac{K_D V}{K_D V + v} \right]$$

On substituting value of w<sub>1</sub>

$$w_{2} = W \left[ \frac{K_{D} V}{K_{D} V + v} \right] \left[ \frac{K_{D} V}{K_{D} V + v} \right]$$
$$w_{2} = W \left[ \frac{K_{D} V}{K_{D} V + v} \right]^{2}$$

In general the amount that remains unextracted at the end of n<sup>th</sup> operation is

$$w_n = W \left[ \frac{K_D V}{K_D V + \nu} \right]^n$$

- 3. In order to make  $w_n$  as small as possible for a given value of K<sub>D</sub>. *n*Should be as large as possible. But  $n \times v$  is equal to the total volume of extracting solvent that is constant. Therefore it is better to give n as large, v as small.
- 4. The efficiency of extraction increases by increasing the number of extraction using only small amount of the extracting solvent each time.

#### **II)** Determination of hydrolysis constant:

- 1. When one of the product of hydrolysing salt is soluble in an immiscible solvent like benzene.
- The salt and other components are not soluble on heating, then K<sub>D</sub> value can be used to calculate the hydrolysis constant.
- 3. For example: Aniline hydrochloride undergoes hydrolysis as follows

$$C_6H_5NH_2.HC1 \xrightarrow{H_2O} C_6H_5NH_2.HC1 + H_2O \xrightarrow{C_6H_6} C_6H_5NH_2 + HC1$$

#### Aqueous solution

- 4. It gives aqueous solution is shaken with benzene, aniline gets distributed between water and benzene. But the salt and acid are insoluble in benzene.
- 5. Let x is be the initial concentration of the salt and y be the concentration of aniline in benzene layer.
- 6. If K<sub>D</sub> is distribution coefficient of aniline between water and benzene.

$$K_{D} = \frac{C_{water}}{C_{benzene}}$$

$$C_{water} = K_{D} \times C_{benzene}$$

$$C_{water} = K_{D} \times y$$

7. The concentration of HCl in water must be equal to the concentration of aniline in water and benzene.

$$[HCl] = K_D. y + y$$

8. The concentration of the un-hydrolysed salt

$$[C_{6}H_{5}NH_{2} . HCl] = x (K_{D}. y + y)$$

$$K_{H} = \frac{[C_{6}H_{5}NH_{2}][HCl]}{[C_{6}H_{5}NH_{2}.HCl]}$$

$$K_{H} = \frac{[K_{D}.y] \times [K_{D}.y + y]}{[x - (K_{D}.y + y)]}$$

#### **III)** To determinate association of the solute:

$$\frac{C_1}{constant \times \sqrt[n]{C_2}} = constant = K_{D}$$

#### IV) To determinate dissociation of the solute:

$$\frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)} = K_D$$

Practice Questions 1.Derive thermodynamics of ideal gases 2.Explain completly missible liquids

3.Derive Gibbs Duhum Equation 4.Explain Raoutls law 5.Derive Nernst Equation.

Reference Books

1.Principles of Physical Chemistry - B. R. Puri, Sharma and Madan S. Pathania 2.Text Book of Physical Chemistry - P. L. Soni, O. P. Dharmarha and U. N Dash

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Web resources: 1.http://openlibrary.org/ 2.http://www.aad.org/