

SOLUTIONS

A solution is a homogeneous mixture of two or more components whose composition may be varied within certain limits.

In a solution the dissolved component, which is generally in smaller proportions is called solute, the dissolving medium which is generally in larger proportions is called solvent.

Thus a solution is a binary mixture of a solute in the solvent.

Based on the amount of solute present in a given volume of solvent, solutions are of three types.

- (i) A Solution which dissolves some more solute at a given temperature is called an unsaturated solution.
- (ii) The solution which cannot dissolve any more solute at a given temperature is called a saturated solution and is the most stable solution. In this solution an equilibrium exists between the dissolved solute and undissolved solute.
- (iii) A solution which has an excess of solute than actually required for its saturated solution is called a supersaturated solution and is a highly unstable solution.

Types of solutions:

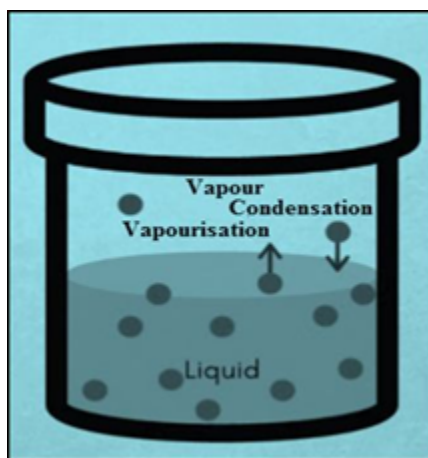
Depending on the physical state of the solute and the solvent, we have nine types of solutions as shown in table

Solute	Solvent	Examples
Gas	Gas	Air
Gas	Liquid	Soda water (CO ₂ in water) (aerated water)
Gas	Solid	H ₂ in Palladium metal
Liquid	Gas	Moisture in air
Liquid	Liquid	Ethyl alcohol in water
Liquid	Solid	Hg in gold, Jellies
Solid	Gas	Camphor in air
Solid	Liquid	Salt or sugar in water
Solid	Solid	Alloys like brass (Zinc in copper)

Among these solutions gas in liquid, liquid in liquid and solid in liquid are much significant. In this chapter we shall discuss liquid in liquid type of solutions only.

Vapour pressure of liquid

In a closed vessel the molecules steadily accumulate in the space above the liquid. This process is called evaporation. As the number of molecules increases, then the molecules show a tendency to return to the liquid phase which is called condensation as shown in the fig.



At each temperature a condition of equilibrium exists when the number of molecules leaving the liquid to enter the space above is equal to the number of molecules returning to the liquid at a given time.

Thus the vapour pressure of the liquid at a given temperature is defined as the pressure exerted by the vapour on the surface of the liquid, when the vapour and liquid are in the equilibrium state. Vapour pressure is the characteristic property of a liquid. It increases with increase in temperature.

Liquid-Liquid Binary Mixtures

Based on the miscibility of one liquid in other liquid, liquid-liquid binary mixtures can be classified into three types.

1. Completely miscible liquid-liquid binary mixtures
2. Partially miscible liquid-liquid binary mixtures and
3. Completely immiscible liquid-liquid binary mixtures.

1. Completely miscible liquid-liquid binary mixtures:

The binary mixtures in which one liquid is completely miscible with the other liquid in all proportions are called completely miscible liquid-liquid binary mixtures.

eg: ethyl alcohol + water

2. Partially miscible liquid-liquid binary mixtures:

The binary mixtures in which one liquid is partially miscible with the other liquid are called partially miscible liquid-liquid binary mixtures.

eg: phenol + water; ether + water; aniline + water; carbon disulphide + methanol

3. Completely immiscible liquid-liquid binary mixtures:

The binary mixtures in which one liquid is completely immiscible with the other liquid are called completely immiscible liquid-liquid binary mixtures.

eg: carbon disulphide + water

The Ideal Solutions-Raoult's law:

A solution is said to be an ideal solution if the molecules in the solution attract one another with equal force irrespective of their nature. This means that if we have an ideal solution of B in A, then the forces between A and A, B and B and A and B should be the same.

Therefore, in an ideal solution

(i) the total volume of the solution = Volume of A + Volume of B.

$$\text{i.e., } \Delta V(\text{mixing}) = 0$$

(ii) No heat is evolved or absorbed on mixing the components.

$$\text{i.e., } \Delta H(\text{mixing}) = 0$$

Ideal solutions obey Raoult's law.

Raoult's law applied to Ideal solutions

According to Raoult's law, the partial pressure of any volatile constituent of a solution at a given temperature is equal to the product of the vapour pressure of the pure constituent and its mole fraction in the solution. For example, in an ideal solution of B in A at room temperature T

$$P_B = P_B^0 \cdot X_B.$$

where P_B = Partial pressure of B in solution,

$$P_B^0 = \text{Vapour pressure of pure B}$$

X_B = Mole fraction of B.

Similarly

$$P_A = P_A^0 \cdot X_A.$$

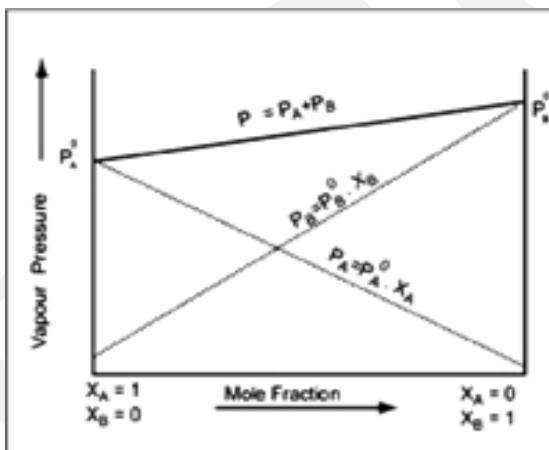
Total pressure P of the vapour according to Dalton's law of partial pressures is

$$P = P_A + P_B$$

$$P = P_A^0 \cdot X_A + P_B^0 \cdot X_B.$$

$$P = P_A^0(1 - X_B) + P_B^0 \cdot X_B. \quad \{\text{since } X_A + X_B = 1\}$$

If a mixture of two liquids A and B behaves ideally, then according to the equations $P_A = X_A P_A^0$ and $P_B = X_B P_B^0$, the plot of the partial pressures of each constituent A and B and the total pressure P against its respective mole fractions in the liquid phase is a straight line as shown in figure



But only a limited number of mixtures obey Raoult's law over a wide range of concentrations. Some examples of ideal solutions are:

1. Ethylene dibromide and propylene dibromide mixture at 358K.
2. Benzene and ethylene dichloride mixture at 323K.
3. n-hexane and n-heptane mixture at 303K.

1. Non-Ideal solution with Positive Deviation:

Consider a solution formed by mixing the two liquids A and B.

If the interactions of A-B are weaker than those of A-A or B-B, then the molecules A and B have more tendency to escape from the mixture. i.e. solution than that of pure liquids. This results in the increase of total vapour pressure of the solution than the

corresponding vapour pressure of the ideal mixture. Such solutions are non-ideal solutions with positive deviation. For that solution we can write

$$P_A > . X_A$$

$$\text{And } P_B > . X_B$$

$$\text{and } P > P_A + P_B \text{ or } P > . X_A + . X_B$$

Examples:

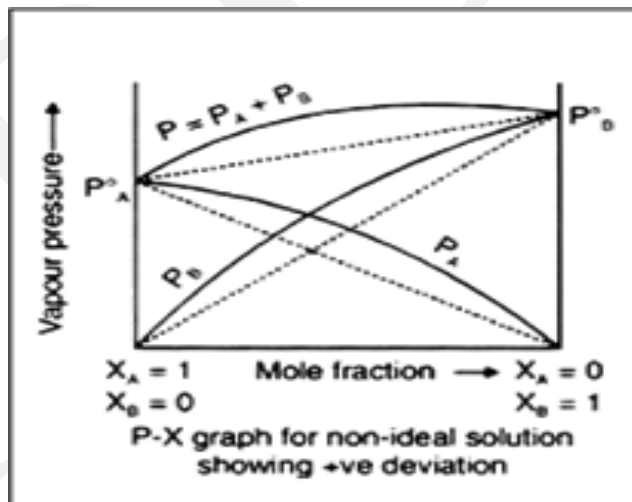
Ethyl alcohol and water, acetone and ethyl alcohol, acetone and carbon disulphide, carbon tetrachloride and Toluene etc.

For these solutions

$$\Delta H_{\text{mix}} = + Ve$$

$$\Delta V_{\text{mix}} = + Ve$$

The figure for vapour pressure-mole fraction curve for non-ideal solution with positive deviation is shown in figure in which the dotted lines indicate the ideal behavior. The practical curves obtained for the non-ideal solution here are above the ideal values. So there is positive deviation from ideal behavior.



2. Non-Ideal solution with Positive Deviation:

If a mixture of two liquids A and B is considered in which A-B interactions are stronger than those of A-A and B-B then the vaporization of the molecules of A and B from the mixture or solution would be less and so the total pressure of the mixture becomes lesser than the corresponding vapour pressures for an ideal solution. As a result, it leads to the formation of a non-ideal solution with negative deviation. For this type of solutions we have

$$P_A < . X_A$$

$$P_B < . X_B$$

$$\text{and } P < P_A + P_B \text{ or } P < . X_A + . X_B$$

Examples:

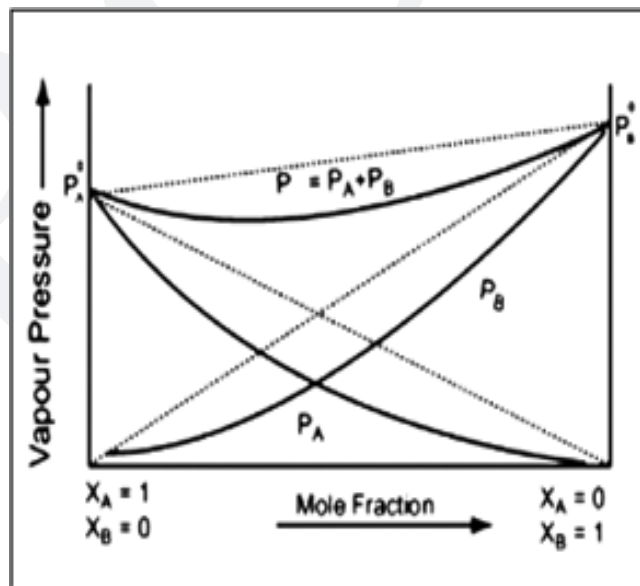
Water and sulphuric acid, acetone and chloroform, ether and chloroform, benzene and chloroform, water and nitric acid, water and perchloric acid etc.

For these solutions

$$\Delta H_{\text{mix}} = - \text{Ve}$$

$$\Delta V_{\text{mix}} = - \text{Ve}$$

The diagram normally obtained for such types of non-ideal solutions with negative deviation is as shown in figure. The dotted lines in the vapour pressure-mole fraction curves shown indicate the ideal behavior. All the practical curves obtained are found to be below the ideal curves. So there is negative deviation from ideal behavior or Raoult's law.



Azeotropic Mixtures or constant boiling mixtures:

Azeotropic mixture is defined as a mixture of two or more liquids of definite composition which boils at a constant temperature and distills over completely at the same temperature without any change in composition.

Azeotropic mixture although boils at a constant temperature (at constant pressure), they are not regarded as compounds.

It may be noted that the boiling points as well as the composition of the azeotropic mixture (azeotropes) change with pressure.

Azeotropic mix- tures are of two types namely:

- (i) Maximum boiling point azeotropic mixtures and
- (ii) Minimum boiling point azeotropic mixtures.

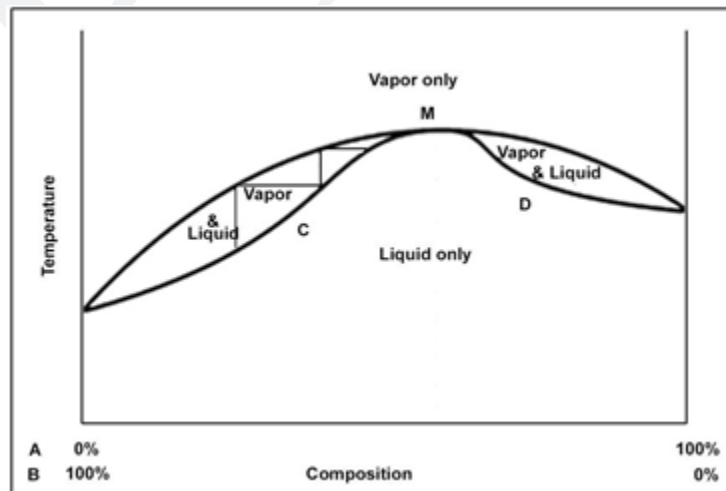
(i). Maximum boiling point azeotropic mixtures

Solutions of the type which distill unchanged at a constant temperature and show a maximum boiling point are called maximum boiling point azeotropic mixture.

The best known example of this type is presented by hydrochloric acid and water which forms a constant boiling mixture at 110 °C and containing 20.24% of the acid.

The maximum boiling point of this mixture is higher than that of pure water (100 °C) and hydrochloric acid (80 °C).

If a mixture of any composition is distilled either hydrochloric acid or water will passover, the composition will move to the point of minimum vapour pressure (Maximum boiling point) when it distills without any change in composition as shown in figure.



For example if a mixture of composition C i.e., any point between M and 100% A is distilled, the vapour will be containing more of A than the original mixture and the residue is enriched in B.

The boiling point of the mixture rises. As the process is continued the residue will approach the composition M. By taking the fractions from the mixture and by a series of re-distillations we can eventually get a distillate of pure A and a residue of azeotropic mixture M. Similarly we can separate a mixture of composition D into a pure component B and the constant boiling mixture M. Thus, the fractional distillation of maximum boiling point azeotropes give a distillate of azeotropic mixture, M and a residue of pure component B.

The examples for maximum boiling point azeotropic mixtures are shown in table along with constant boiling points and composition of azeotropes at 1 atm. Pressure.

<u>Component A</u>	<u>Boiling point (°C)</u>	<u>Component B</u>	<u>Boiling point (°C)</u>	<u>Constant B.P of Azeotrope (°C)</u>	<u>Composition (weight % of B)</u>
Water	100	HCl	80	110	20.24
Water	100	HNO ₃	86	120.5	68
Water	100	HCOOH	100.7	107.1	77.5

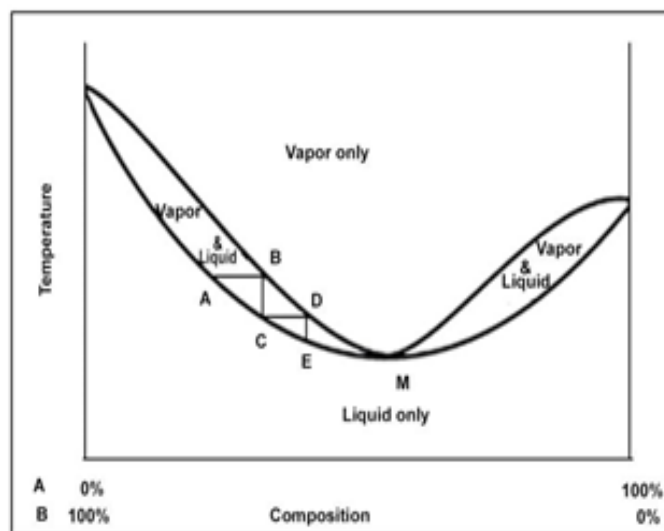
(ii). Minimum boiling point azeotropic mixtures

Solutions of this type, which distilled unchanged at constant temperature and show a minimum boiling point are called minimum boiling point azeotropic mixture.

The best known example for this type is ethyl alcohol and water, which forms a constant boiling mixture at 78.2°C and containing 4.4% of water and 95.6% of ethyl alcohol. This temperature is lower than that of water (100 °C) and ethyl alcohol (78.3 °C).

The boiling point composition diagram for this type of azeotropic mixture is shown in figure.

The upper curve represents the vapour curve and the lower curve shows the liquid curve. The two curves meet at a point M which represents the composition of the liquid mixture, with minimum boiling point. The liquid and the vapour in equilibrium will have the same composition at this temperature. The liquid represented by this point M boils at constant temperature i.e.; distills over completely without change in composition. Such a system in which the composition of the distill is unchanged is called azeotropic mixture.



The examples for minimum boiling point azeotropic mixtures are shown in table along with constant boiling points and composition of azeotropes at 1 atm. Pressure.

<u>Component A</u>	<u>Boiling point (°C)</u>	<u>Component B</u>	<u>Boiling point (°C)</u>	<u>Constant B.P of Azeotrope (°C)</u>	<u>Composition (weight % of B)</u>
Water	100	Ethanol	78.3	78.2	4.4
Water	100	Propanol	98.2	87.7	28.3
Water	100	Pyridine	115.5	92.6	43

2. Partially Miscible Liquid Mixtures

These are the binary liquid mixtures, in which two liquids are partially miscible with each other. A large number of liquids are known which dissolve in one another only to a limited extent such as ether and water.

Ether dissolves about 1.2% water and water dissolves about 6.5% ether.

Since their mutual solubilities are limited, they are only partially miscible.

When equal volumes of ether and water are shaken together, two layers are formed namely

- (i) one larger is of the saturated solution of ether in water
- (ii) the other layer is of the saturated solution of water in ether.

These two solutions in equilibrium with each other are referred to as conjugate solutions.

Other examples: phenol-water, aniline- water etc.

CRITICAL SOLUTION TEMPERATURE:

The two layers in a partially miscible binary liquid mixture attain the same composition with the raise in temperature. This means that the mutual solubility of the two components increase with the increase in temperature. The two layers become identical in composition and become completely miscible and the two layers become one single layer only at a particular temperature called the **critical solution temperature (CST)** or the **consolute temperature**.

Above this temperature the two partially miscible liquids become miscible in all proportions and the composition outside this curve will consist of one liquid layer only. Thus critical solution temperature is defined as the temperature at which partially miscible liquids become completely miscible in all proportions.

The partially miscible systems on the basis of their critical solution temperature can be classified into three types:

(a) Systems with upper critical solution temperature(UCST).

Ex.: Phenol-Water system, aniline-water system, aniline-hexane system, methanol-carbon disulphide system.

(b) Systems with lower critical solution temperature(LCST).

Ex.: Triethylamine-water system.

(c) System with both upper and lower critical solution temperatures(UCST & LCST).

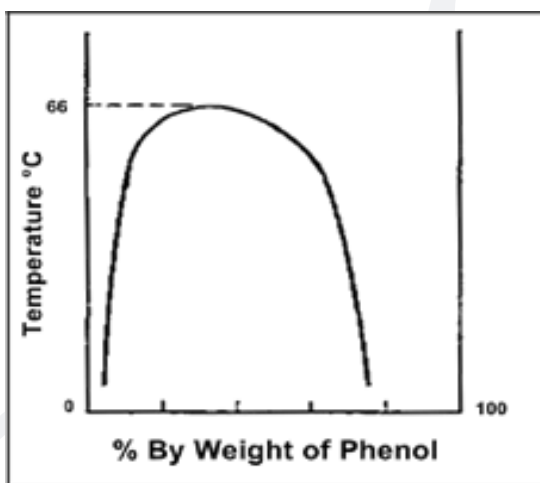
Ex.: Nicotine-water system.

1.Systems with Upper Critical Solution Temperature-

Phenol-Water system:

- ❖ Consider two liquids: phenol and water. The two liquids are partially miscible in each other.
- ❖ When a little phenol is added to water at room temperature, it will dissolve completely. This means that phenol and water form a miscible system when phenol is present in low percentage.

- ❖ But if addition of phenol is continued, then it is observed that dissolution of phenol in water stops beyond a particular point by the formation of two visible liquid layers.
- ❖ One of these layers is a saturated solution of phenol in water and the other one is the saturated solution of water in phenol.
- ❖ These two liquid systems are in equilibrium with each other and are called conjugate solutions.
- ❖ The effect of temperature on the mutual solubility of these type mixtures of conjugate solutions is of special interest.
- ❖ The effect of temperatures on the mutual solubility of phenol-water system can be easily understood from the graph shown in figure



- ❖ The curve shown in the figure represents the miscibility of phenol and water with temperature.
- ❖ The left hand side of the parabolic curve represents one of the conjugate solutions which indicate the percentage of phenol dissolved in water at various temperatures.
- ❖ The solubility of phenol increases with temperature. The right hand side of the curve shows the other conjugate solution layer that gives the percentage of water in phenol. The solubility of water in phenol also increases with increase of temperature.
- ❖ The two solution curves meet at the maximum on the temperature-composition curve of the system.
- ❖ This point here corresponds to temperature 66 °C and composition of phenol as 33%. Thus at a certain maximum temperature, the two conjugate solutions merge and become identical and only one layer results.

- ❖ The temperature at which the two conjugate solutions or layers merge into one another to form one layer is called the critical solution temperature (CST) or Upper Critical Solution Temperature (UCST).
- ❖ This is characteristic of a particular system and is influenced very much by the presence of impurities.
- ❖ At any temperature above the critical solution temperature, phenol and water are miscible in all proportions.
- ❖ Outside the curve there is complete homogeneity of the system i.e., one layer only.

Effect of impurity on Consolute Temperature

If an impurity is added to the partially miscible liquid mixture, then the mutual solubilities of the component liquids in the mixture are affected.

The mutual solubilities of the liquids also depend on the nature and quantity of the added impurity.

If the added impurity is soluble in only one of the two liquids, then mutual solubilities of the two liquids decrease and the added impurity raises the consolute temperature.

If potassium chloride is added to the phenol-water system, then its consolute temperature rises considerably. This is because KCl is soluble in water but not in phenol.

Similarly, when an organic substance like naphthalene is added as an impurity to the phenol-water system, here also the consolute temperature is increased. In this case the rise in consolute temperature is because of the solubility of naphthalene in phenol but not in water.

3. Completely Immiscible Liquid Mixtures

- ❖ There are a number of pairs of liquids which do not exhibit any mutual solubility either at room temperature or higher or lower than the room temperature.
- ❖ Such pairs of liquid mixtures are called completely immiscible liquid mixtures.
- ❖ In these liquid mixtures each liquid behaves independently of the other.
- ❖ Hence the properties of each liquid will be unaffected by the presence of the other.
eg: CS₂-H₂O, CCl₄-H₂O, H₂O-Hg etc.

Nernst Distribution Law:

Nernst carried out a large number of experiments to study the distribution of many solutes between suitable immiscible solvents. He generalized his observations in the form of a law known as Nernst distribution law or Nernst partition law.

According to this law, “at constant temperature the dissolved solute distributes itself between the two immiscible solvents in contact with each other, in such a way that at equilibrium, the ratio of concentration of the solute in the two solvents is constant.”

However, the following conditions are to be followed for the validity of the distribution law,

- (i) The solute should dissolve in both the solvents in the same form i.e., the substance should not undergo dissociation or association in either of the solvents.
- (ii) There should be no chemical combination between the solute and either of the solvents and
- (iii) The solution should be dilute.

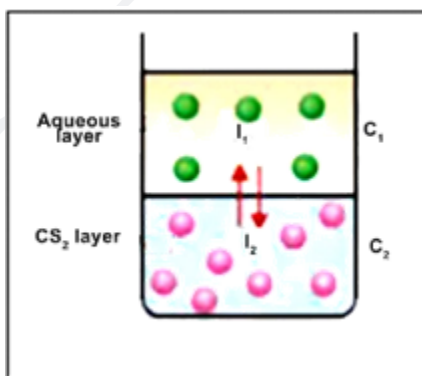
If C_1 and C_2 are the concentrations of the solute at a given temperature in the two immiscible solvents 1 and 2 of binary system, then according to Nernst Distribution law, we have,

$$C_1/C_2 = K \text{ (Constant)}$$

where K is called the distribution or partition coefficient of the solute between the two solvent.

It is independent of the total amount of solute distribution in the two immiscible solvents.

Let us consider the distribution of iodine (solute) in the two immiscible solvents water and carbon disulphide. When iodine solution in CS_2 is shaken for a long time with water, then iodine distributes itself between water and CS_2 .



This experiment is repeated with different amounts of iodine with time and it is observed that the ratio of its concentration in the two solvents remains constant at a given temperature.

$$\therefore K = \frac{\text{Concentration of } I_2 \text{ in } CS_2 \text{ layer}}{\text{Conc. of } I_2 \text{ in water layer}}$$
$$K = \frac{C_1}{C_2}$$

(i) Modified form of distribution law for the dissociation of solute in one of the solvents

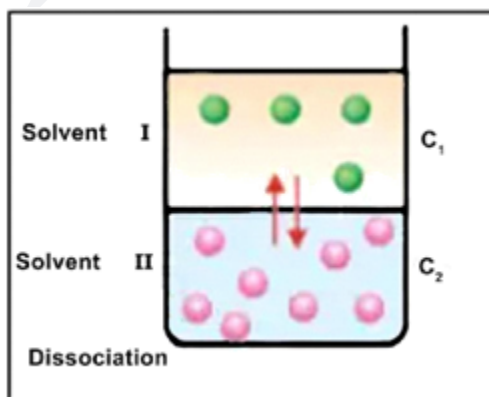
The Nernst distribution law discussed above holds good in cases where the solute exists as simple molecules in the two solvents. However, this is not true for all the solutes.

If there is any dissociation of the solute in one of the solvents, then the distribution law is to be modified as follows:

Let us consider a case where the solute is undergoing dissociation in solvent II and no dissociation in solvent I.

Let C_1 and C_2 be the total concentration of the solute (X) in solvent I and II respectively.

If α is the degree of dissociation of the solute in solvent II, then the total concentration of the undissociated solute in solvent II would be $C_2(1 - \alpha)$ as shown in the figure.



Applying the Nernst distribution law, the ratio of concentration of solute having

$$K = \frac{c_1}{c_2(1-\alpha)}$$

same molecular mass is given by

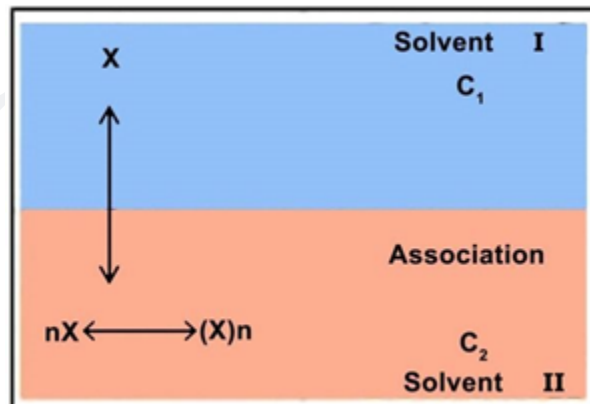
Suppose, we have a case in which the solute is dissociated in solvent I with α as degree of dissociation and the solute remains undissociated in solvent II, then the partition coefficient is given by

$$K = \frac{c_1(1-\alpha)}{c_2}$$

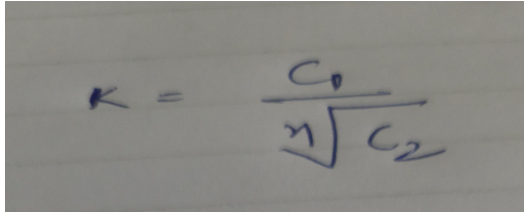
(i) Modified form of distribution law for the association of solute in one of the solvents

Consider a solute (X) which distributes in the two immiscible solvents. Suppose in solvent I it remains as such without any molecular change as shown in the figure. and let its concentration in this solvent I as C_1 .

Suppose the solute X undergoes molecular association ($nX \rightleftharpoons X_n$) in the solvent II and let its concentration here be C_2 .



Then the modified form of distribution law is given as


$$K = \frac{C_1}{\gamma \sqrt{C_2}}$$

PRGGC

$$C_2 = \frac{0.84 \times 1000}{50}$$

$$C_2 = 16.8 \text{ g/L}$$

partition coefficient of X between water and ether

$$= \frac{C_1}{C_2} = \frac{4.16}{16.8} = 0.25$$

Applications of Distribution Law :-

- 1) Calculation of solubility of a solute in a solvent.
- 2) Distribution Indicator
- 3) Determination of extent of association or dissociation of a solute in a solvent.
- 4) Study of chemical equilibrium involving formation of complex ions
- 5) In the process of extraction
- 6) In the determination of degree of hydrolysis.

1) Calculation of solubility of a solute in a solvent :-

When a solute is shaken with two immiscible solvents in contact with each other, at equilibrium both the solvents are saturated with the solute.

\therefore The conc at equilibrium solubility of solute in both solvents. So, the distribution law can be written as

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K$$

Where $C_1 = S_1 \Rightarrow$ solubility of solute in solvent - 1

$C_2 = S_2 \Rightarrow$ solubility of solute in solvent - 2

2) Distribution Indicator :-

certain solvents can appreciably dissolve even the small amount of solute present in some other solvent. when such a solvent is shaken with a dilute solution

of the solute in some other solvent then most of the solute gets distributed into this solvent.

Hence, it acts as an indicator for the presence of even a small amount of the ~~molecular~~ solute.

I_2 in water \rightarrow colourless

$I_2 \rightarrow$ soluble in $CS_2 \rightarrow$ bright violet

$$\frac{CS_2}{H_2O} = 400 \quad [\because CS_2 \text{ is carbondisulphide}]$$

3) Determination of extent of association or dissociation of a solute in a solvent:-

\rightarrow In the distribution experiment, if the ratio of conc of solute in both the solvents i.e., $\frac{c_1}{c_2} = \text{constant}$, then the solute behave normally in both the solvents.

\rightarrow If solute undergoes association in one of the solvents i.e., $nX \rightleftharpoons X_n$, (having conc c_2 in it).

Then we know that distribution law get modifies as

$$\frac{c_1}{n\sqrt{c_2}} = K$$

From the value of n the molecular mass of the solute in this solvent can be calculated by multiplying the actual molecular mass by n .

\rightarrow The value of n can be calculated by two ways.

a) By hit & trail method:-

$$c_1 \text{ \& } c_2 \Rightarrow \frac{c_1}{n\sqrt{c_2}} = K$$

where $n = 1, 2, 3, 4, \dots$

Logarithmic method :-

(12) We have equation, $\frac{c_1}{\sqrt[n]{c_2}} = K \Rightarrow \frac{c_1}{(c_2)^{1/n}} = K$

(or) $c_1 = K(c_2)^{1/n}$

Taking log on both sides

$\log c_1 = \log K + \frac{1}{n} \log c_2$

Let we have the experimental values of c_1, c_2 & c_1', c_2'

$\log c_1 = \log K + \frac{1}{n} \log c_2 \rightarrow (1)$

$\log c_1' = \log K + \frac{1}{n} \log c_2' \rightarrow (2)$

Subtracting (2) from (1), we have

$\log c_1 - \log c_1' = \frac{1}{n} (\log c_2 - \log c_2')$

or $n = \frac{\log c_2 - \log c_2'}{\log c_1 - \log c_1'}$

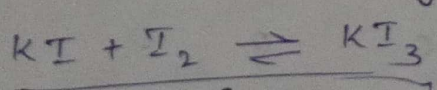
→ If solute undergoes dissociation in one of the solvent in which its concentration is c_2 , then the distribution law is applicable as :-

$\frac{c_1}{c_2(1-\alpha)} = K$

Thus, if the degree of dissociation (α) of solute is known at one concentration, the value of α at any other concentration can be obtained using above equation, since the value of K is constant.

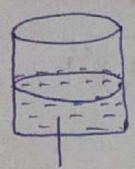
4) In the study of chemical equilibrium involving formation of complex ions :-

Consider a reaction involving formation of complex ions



$K_{eq} = \frac{[KI_3]}{[KI][I_2]}$

5) In the process of extraction:-



Mixture solution
of organic compound
in water.



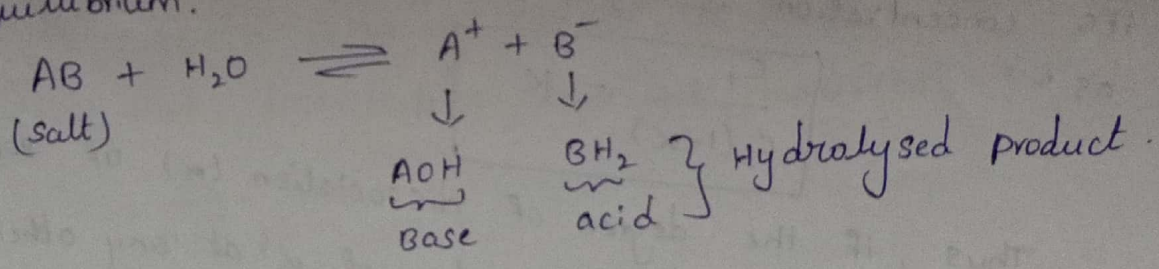
water layer
organic layer
(Extracting solvents)

Conditions:-

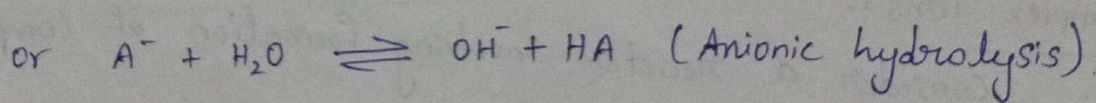
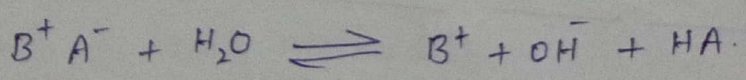
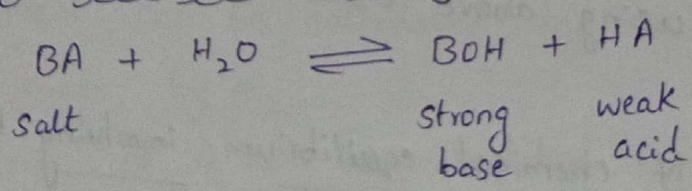
- i) The distribution coefficient of the substance between the extracting solvents and the solvent in which it is already dissolved should be very high in the favour of extracting solvent.
- ii) To recover the maximum amount of substance, the extracting solvent should not be used in one lot, rather it should be used in maximum no. of installments. (This is known as multiple extraction or multistep extraction).

6) In the determination of degree of hydrolysis:-

The degree of hydrolysis of a salt may be defined as the fraction of the total amount of salt which is hydrolysed at the point of equilibrium.



i) salt of weak acid + strong base



Let initial conc

c	0	0
Conc at equilibrium	c(1-h)	ch

hydrolysis constant K_h is given as $K_h = \frac{[OH^-][HA]}{[A^-]}$

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{c(1-h)} = \frac{ch^2}{1-h}$$

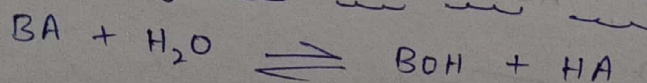
If 'h' is quite small as compared to 1, then $1-h \approx 1$.

$$\therefore K_h \approx ch^2$$

$$\text{or } h^2 = \frac{K_h}{c}$$

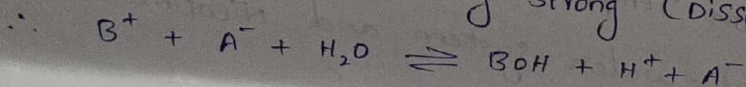
$$\text{or } h = \sqrt{\frac{K_h}{c}}$$

2) salt of strong acid and weak base :-



weak base strong acid

$BA + HA \rightarrow$ being strong (dissociate completely)



or $B^+ + H_2O \rightleftharpoons BOH + H^+$ (cationic hydrolysis)

$$K_h = \frac{[BOH][H^+]}{[B^+]}$$

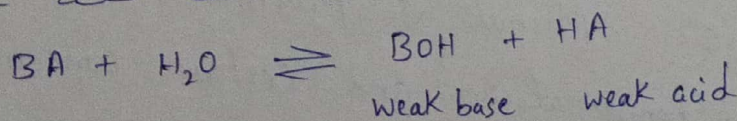
$$= \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{1-h} = K_h$$

At $h \ll 1$ $K_h \approx ch^2$

$$\text{or } h = \sqrt{\frac{K_h}{c}}$$

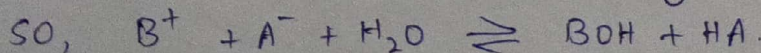
$B^+ + H_2O \rightleftharpoons BOH + H^+$
Initial c 0 0
equilibrium c(1-h) ch ch

3) salt of weak acid and weak base :-

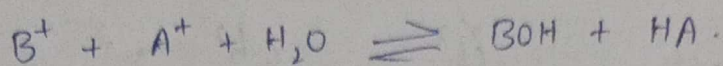


Both weak acid & weak base \rightarrow weakly dissociated.

But salt BA \rightarrow completely dissociated.



It involves both cationic & Anionic hydrolysis at equilibrium.



Initial conc c c 0 0

At equilibrium $c(1-h)$ $c(1-h)$ ch ch

$$\begin{aligned} \therefore K_h &= \frac{[BOH][HA]}{[B^+][A^-]} \\ &= \frac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \frac{h^2}{1-h^2} \end{aligned}$$

In case of the salt, $h \ll 1$ $\therefore (1-h) \approx 1$

$$\begin{aligned} \therefore K_h &\approx h^2 \\ \text{or } h &= \sqrt{K_h} \end{aligned}$$

6) Define critical solution temperature. Explain the critical solution temperature of phenol-water system and nicotine-water system?

critical solution temperature :-

The temperature at which complete miscibility is reached as the temperature is raised or in some cases lowered - used of two liquids that are partially miscible under ordinary conditions are called critical solution temperature (or) consolute temperature.

CST of phenol-water system :- [ROTHMUND in 1898]

The CST or consolute temperature for phenol-water system is 68.5°C . Phenol is partially miscible with water and at certain temperature and certain concentration, one liquid phase will obtain. In this case temperature is increases (\uparrow ing).