

Chapter-1

SOLUTIONS

Introduction

When several non reacting substances are mixed, then there are three possible types of mixtures formed :

- (a) Coarse mixture (Sand + Salt and Sugar + Salt)
- (b) Colloidal dispersion (Gum + water and fine clay + water)
- (c) True Solution (Salt + water)

In the coarse mixture, there exists heterogeneity where as in true solutions there is complete homogeneity, In colloidal dispersions, the heterogeneity is not readily apparent and it is not homogenous.

Distinction between Solute and Solvent

I. Phase Method

Let there be a substance 'A' in solid phase and 'B' in liquid phase then if the phase of the resulting mixture is

- (a) Solid, then Solute = B and Solvent = A.
- (b) Liquid, then Solute = A and Solvent = B

II. Amount Method

According to this method, the substance which is in larger proportion by mass is solvent while the one in lesser proportion is solute.

e.g. a solid mixture of A and B. if $W_A > W_B$ then solute is B and solvent is A.

In the solutions of solids in liquids, where the liquid is usually present in large excess over the solid, there is no ambiguity, here liquid is solvent and solid is solute.

However when we deal with solubility of liquid

e.g. Acetone + water, here the one which is in larger quantity is solvent.

Saturated, Unsaturated And Super Saturated Solutions

Saturated Solution :

A solution which contains as much solute as it can hold at a given temperature is said to be a saturated solution.

Unsaturated Solution :

A solution which contains less amount of solute, than the amount of solute it can hold, then it is called unsaturated solution.

Super Saturated :

A solution which contains more solute than the amount it can hold at a particular temperature is called as super saturated solution.

To Determine State of Solution

To determine the state of solution with respect to saturation, one needs to introduce some dissolving substance, If on adding this, one observes that

- (a) If the substance dissolves, then it is unsaturated.
- (b) If the substance does not dissolve then it is saturated.
- (c) If precipitation takes place then the original solution is supersaturated.

Types of Binary Solutions (Table-1)

S.No.	Solute	Solvent	Example of solution
1.	Solid	Solid	Alloy (Brass)
2.	Liquid	Solid	Hydrated salts Butter
3.	Gas	Solid	H ₂ /Ni adsorption
4.	Solid	Liquid	Sugar in water
5.	Liquid	Liquid	Alcohol in water
6.	Gas	Liquid	Cold drinks
7.	Solid	Gas	Dust, Smoke
8.	Liquid	Gas	Fog
9.	Gas	Gas	Air

Factors Influencing Solubility

The extent to which a substance will dissolve in another varies greatly with the substance, and depends on nature of solute, solvent, temperature, and pressure.

1. The effect of pressure on solubility is small unless gases are involved.
2. The effect of temperature however is very pronounced. The direction in which the solubility of a substance in a solvent, changes with temperature depends on **heat of solution**.

(a) If the **dissolution is exothermic** then the **solubility decreases with increase in temperature**.

(b) If the **dissolution is endothermic** then the **solubility increases with increase in temperature**.

3. In general, the compounds with similar character are more readily soluble in each other. While those with entirely different chemical characteristics will be very much insoluble.

Hence with these two extreme ends, a considerable number of intermediate stages are possible, which we call as mutual solubilities e.g.

(i) When ethyl alcohol and water are mixed, the two dissolve in each other in all proportions and hence there is no saturation limit. Such substances are **completely miscible liquids**.

(ii) When water and mercury are mixed they do not dissolve in each other at all and hence are called **completely immiscible liquids**.

(iii) Between these two extreme pairs we have liquid pairs as ether + water, phenol + water which dissolve in each other to a limited extent only. Liquid pairs of these kinds are called **partially miscible**.

Vapour Pressure of Ideal solution Containing Volatile liquids

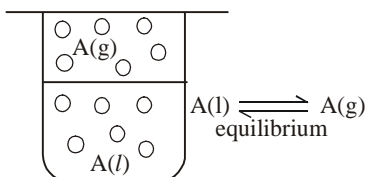
In a liquid, the molecules are always in the state of random motion, due to collision of molecules with each other and with walls of container. This leads to the molecules acquiring certain kinetic energy. The molecules of the liquid which possess high kinetic energy have a tendency to change to vapour state.

The minimum energy which the molecules of a liquid should acquire to transform from liquid state to vapour state is termed as escape energy. **Lesser the escape energy, greater is the volatility of a liquid** from liquid surface.

When a liquid is placed in a closed container then due to evaporation, vapours of liquid are produced which ultimately leads to an equilibrium state due to the tendency of the vapours to convert back to liquid.

Vapour Pressure

The pressure exerted by the vapours of the liquid which are in equilibrium with the liquid phase at the given temperature is called vapour pressure.



The vapour pressure of liquid depends upon

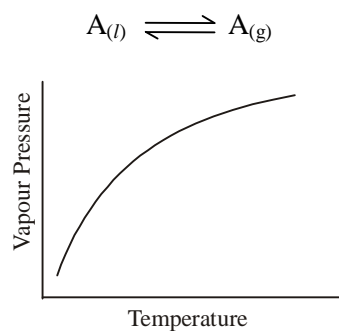
- (i) Nature of the liquid
- (ii) Temperature

(i) Nature of Liquid

When the intermolecular forces of attractions are stronger then the vapour pressure will be low because less number of molecules can leave the liquid

(ii) Temperature

Higher the temperature, greater would be the vapour pressure. This is because when temperature is raised, kinetic energy of the molecules increase and therefore the number of molecules leaving surface of liquid, is large.

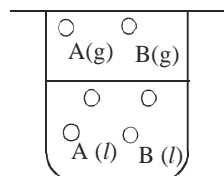


The Clausius Clapeyron equation gives the relationship for vapour pressure of liquid with temperature

i.e.
$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right].$$

Vapour Pressure of Solution

Let two volatile liquids A and B dissolve in each other to form an ideal solution. Then the vapours above the solution will contain the vapours of A and B.



As it has been found convenient to set up an ideal gas, as a criterion of gas behaviour, so it is desirable to define an ideal solution on whose predictable properties we can judge the behaviour of a solutions.

An ideal solution is one in which the activity of each constituent is equal to its mole fraction throughout complete range of concentration.

Hence applying Dalton's law of partial pressure the **vapour pressure** of the **solution** will be

$$P_{\text{vapours}} = P_{\text{solution}} = P_A + P_B = \text{vapour pressure of solution.}$$

Where P_A and P_B are the partial vapour pressures of A and B.

Solution being dilute (Condition for ideality) **Raoult's law can be applied.**

Raoult's law for binary solutions state that "the vapour pressure of any volatile constituent of a binary solution at any given temperature is equal to the product of the vapour pressure of pure constituent and its mole fraction".

$$P_A = P_A^0 \chi_A$$

$$P_B = P_B^0 \chi_B$$

P_A^0 and P_B^0 are vapour pressure of pure A and B respectively

χ_A and χ_B are mole fraction of A and B respectively

Hence

$$P_s = P_A^0 \chi_A + P_B^0 \chi_B$$

Hence,

$$P_s = P_A^0(1 - \chi_B) + P_B^0 \chi_B \quad [\chi_A + \chi_B = 1]$$

$$P_s = P_A^0 + (P_B^0 - P_A^0)\chi_B$$

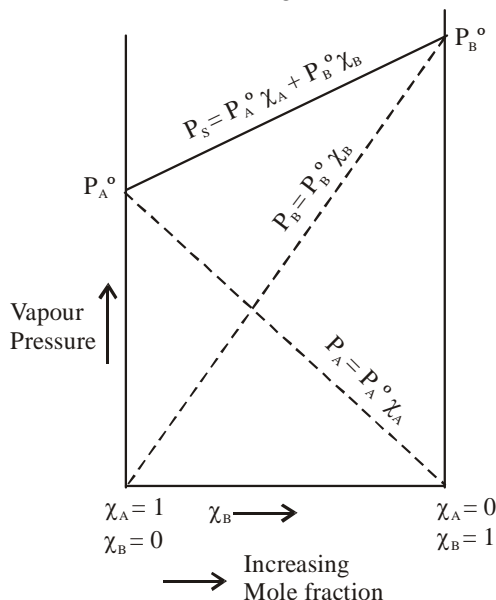
This equation is of the form $y = mx + c$

Where $y = P_s$, $c = P_A^0$, $x = \chi_B$, and $m = (P_B^0 - P_A^0)$

The value of m (slope) may be (+ve) or (-ve)

Depending upon whether $P_B^0 > P_A^0$ ($m = +ve$) or $P_B^0 < P_A^0$ ($m = -ve$)

Hence a plot of a graph of P_s vs χ_B will be a straight line with an intercept on y-axis.



Note: Formation of a true ideal solution is rare and largely exceptional. However a large number of solution are obtained which are found to be nearly ideal.

Vapour Pressures of Actual Liquid Pairs

Ideal Solution

A few binary miscible liquid systems which obey *Raoult's* law throughout the complete range of concentration.

e.g.

- (1) Ethylene dibromide and Propylene dibromide
- (2) Chlorobenzene and Bromobenzene
- (3) Benzene and Ethylene dichloride
- (4) $\text{CCl}_4 + \text{SnCl}_4$
- (5) $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$
- (6) n-Hexane + n-Heptane
- (7) Benzene + Toluene

Such systems are called nearly ideal or ideal solutions.

Such solutions obey *Raoult's* law and comply to the equation $P_s = P_A^0 \cdot \chi_A + P_B^0 \cdot \chi_B$.

To comply to this condition for ideality the two liquids A and B should fulfill the following conditions :

1. The attractive forces between the particles A and B (*i.e.* A–B interactions) should be equal to the attractive forces between A and A (*i.e.* A–A interaction) and between B and B (*i.e.* B–B interaction)
2. Such an interaction can be equal if the structure and polarity are almost same. *e.g.* $\text{CH}_3\text{--OH}$ and $\text{C}_2\text{H}_5\text{--O--H}$.

In such solutions

- (i) $\Delta V_{\text{mix}} = 0$
- (ii) $\Delta S_{\text{mix}} = 0$
- (iii) $\Delta H_{\text{mix}} = 0$.

Because

$$(a) \left[\frac{\partial \Delta G(\text{mix})}{\partial P} \right]_T = \Delta V_{\text{mix}} = 0. \quad (b) \left[\frac{\frac{\partial \Delta G(\text{mix})}{T}}{\partial T} \right]_P = -\frac{\Delta H_{\text{mix}}}{T^2} = 0$$

$$\Rightarrow \Delta H_{\text{max}} = 0$$

Non Ideal Solutions

There are certain liquid pair systems which deviate from the *Raoult's* law to a greater or lesser extent depending upon the nature of the liquids and the temperature.

$$i.e. \quad P_s \neq P_i \Rightarrow P_s \neq P_A^0 \chi_A + P_B^0 - P_A^0 \chi_B$$

Set A

- (i) Ether + Acetone
- (ii) $\text{CCl}_4 + \text{CH}_3\text{OH}$
- (iii) C_6H_6 + acetone
- (iv) $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$
- (v) n-Hexane + Ethyl alcohols

Set B

- (i) $\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$
- (ii) $\text{H}_2\text{O} + \text{HNO}_3$
- (iii) $\text{H}_2\text{O} + \text{HCl}$
- (iv) Chloroform + Acetone
- (v) $\text{CH}_3\text{COOH}_3 + \text{CHCl}_3$

None-Ideal Solution Showing Positive Deviation

Here the **A Sets** of solution show a relationship where the vapour pressure of the solution observed is greater than the vapour pressure of solution under ideal conditions

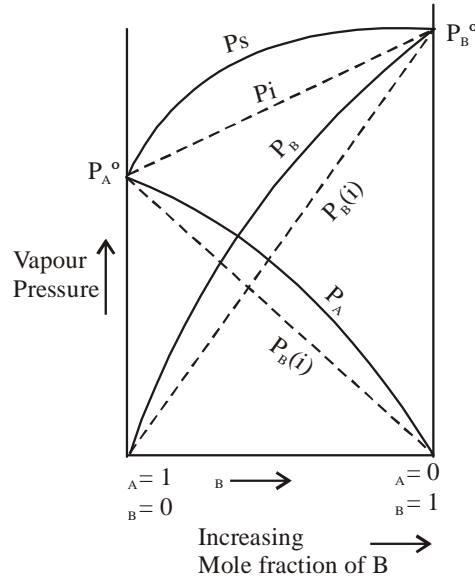
$$i.e. P_s(\text{obs}) > P_s(\text{actual})$$

or

$$P_s > P_i \quad \text{where } P_i = P_A^0 \chi_A + P_B^0 \chi_B$$

$$i.e. P_s > P_A^0 \chi_A + P_B^0 \chi_B$$

Such solutions are said to have +ve deviation from ideality. The graph obtained resembles as given below



The reasons for such a +ve deviations could be linked to the fact that after mixing the interactions between the liquid A and B is less than the interaction between A–A particle and B–B particles

i.e. A–B interactions < A–A interactions and B–B interactions.

This leads to a less escape energy for the molecules of A and B liquids.

As interactions of A–B is weaker the heat energy required for the breakage of A–A and B–B interaction are more than the heat energy evolved during the A–B interaction.

Hence

$$\Delta H_{\text{mix}} = +ve \Rightarrow \Delta H_{\text{mix}} > 0.$$

This also leads to an increase in volume of solution after mixing

$$\Delta V_{\text{mix}} > 0. \quad \Delta V_{\text{mix}} = V_{\text{obs}} - V_{\text{actual}} \quad \Delta S_{\text{mix}} > 0$$

Non-Ideal Solution Showing Negative Deviation

The **B set** of solutions show a relationship where the vapour pressure of solution observed is lesser than the vapour pressure of the solution under ideal conditions *i.e.*

$$P_{s(\text{obs})} < P_{\text{solution (ideal)}}$$

$$P_s < P_i.$$

$$\Rightarrow P_s < P_A^0 \chi_A + P_B^0 \chi_B$$

Here this equation is due to the fact that when interactions increase the escape kinetic energy required, increases, leading to a lowering of vapour pressures such that $P_A < P_A^0 \chi_A$ and $P_B < P_B^0 \chi_B$

Hence the sum

$$P_A + P_B < P_A^0 \chi_A + P_B^0 \chi_B$$

$$\Rightarrow P_s < P_i$$

When the interactions between liquid A particles and liquid B particles increases

A–B interaction > A–A interaction and B–B interactions.

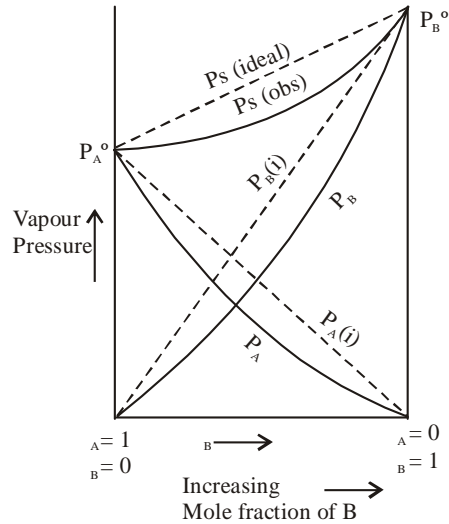
Then the heat energy released when A–B interaction take place will be more than compared to the heat energy required for breaking the A–A interaction or B–B interactions. Hence the net result is

$$\Delta H_{\text{mix}} < 0 \Rightarrow \Delta H_{\text{mix}} = -\text{ve. and also}$$

$$\Delta V_{\text{mix}} < 0 \Rightarrow \Delta V_{\text{mix}} = -\text{ve}$$

$$\Delta S_{\text{mix}} > 0.$$

The graph corresponds to the one given.



Vapour Phase Composition

To obtain the relationship between the composition of solutions and the composition of the vapour above it.

Let γ_A and γ_B be the mole fraction of components A and B in the vapour phase above the liquid solution consisting of χ_A and χ_B mole fractions of A and B respectively in liquid phase.

Then according to gas law

$$\frac{P_B}{P_{(s)}} = \gamma_B \quad \text{and} \quad \frac{P_A}{P_{(s)}} = \gamma_A \quad \left[\frac{P_A}{P_{(s)}} = \frac{n'_A}{n'_A + n'_B} = \gamma_A \right]$$

$$\Rightarrow \frac{P_B^0 \chi_B}{P_{(s)}} = \gamma_B = \frac{P_B^0 \chi_B}{P_A^0 \chi_A + P_B^0 \chi_B} = \text{Vapour phase composition of B}$$

$$\text{and} \quad \frac{P_A^0 \chi_A}{P_{(s)}} = \gamma_A = \frac{P_A^0 \chi_A}{P_A^0 \chi_A + P_B^0 \chi_B} = \text{Vapour phase composition of A.}$$

Generally the distillate composition is the vapour phase composition

Azeotropic and Zeotropic Mixtures

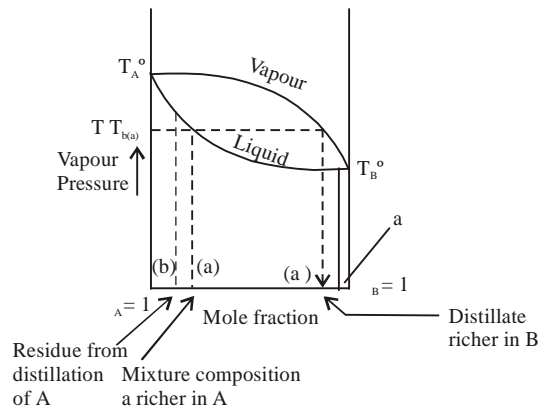
The study of the vapour pressure curves of completely miscible liquid mixture is of great help in separating the constituents of the liquid mixtures by distillation.

Azeotropic mixture are those completely miscible liquid mixtures which distil over unchanged in composition and boils at constant temperature.

The separation by fractional distillation is possible only when the vapour phase has a composition different from that of the boiling mixture.

When a plot of the boiling point temperature versus composition of solution is done then we get.

I For Ideal Solution



$\gamma_A^{n'_A}$	$\gamma_B^{n'_B}$
Vapour Phase	
$\chi_A^{n_A}$	$\chi_B^{n_B}$
Liquid Phase	

Graph for boiling point vs composition for ideal solution

Point 1: Mixture composition (a) taken richer in a component (A)

Point 2: Mixture composition (a) boils at $T_{b(a)}$ temperature

Point 3: Distillate (a) of (a) is the mixture composition richer in component B.

Point 4: 'b' is residue during distillation of mixture composition 'a'.

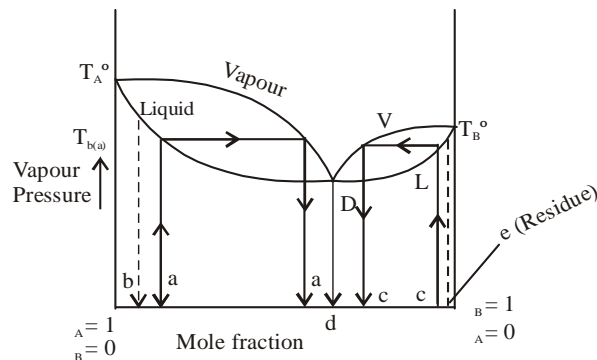
Hence such solution can be successfully solution separated into pure A and pure B

Successive distillation of 'a' give 'a'' and then finally pure B. as distillate.

II For non Ideal Solutions

A) Positive deviation solution or (Minimum boiling azeotropes)

When temperature versus composition graphs are drawn for +ve deviation solution we get



(Graph for boiling point vs to composition for non-ideal solution showing +ve deviation)

Point 1: Here when mixture composition 'a' is boiled, then the distillate (a') becomes more rich in 'B' but, successive distillation of a' will finally lead to compositions ('d') where vapour phase and liquid phase compositions are same. Hence d(D) is a solution which cannot be separated into pure A and B. Hence it is a minimum boiling azeotropic mixture. But the residue 'b' becomes richer in 'A'.

Point 2: When mixture composition 'c' is boiled then distillate is (c') richer in 'A' but successive distillation makes it to composition d(D) *i.e.* minimum boiling azeotropic mixture.

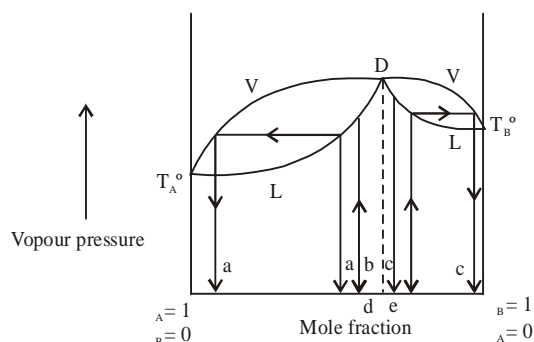
The distillate is 'e' richer in (B) component

Table for Minimum Boiling Azeotropic Mixtures

Component A	B.pt	Component B	B.P.	B. pt of Azeotropic mixture	% of B
H ₂ O	100°C	CHCl ₃	61.2°C	56.12	97%
H ₂ O	100°C	C ₂ H ₅ OH	78.3°	78.13	96%
H ₂ O	100°C	C ₆ H ₆	80.2°C	69.25	91%
H ₂ O	100°C	C ₃ H ₇ OH	97.2°C	87.7	97%
Chloroform	61.2°C	CH ₃ OH	64.7°C	53.43	13.6%

B) Negative Deviation solutions (Maximum Boiling Azeotropic mixture)

When temperature versus composition are drawn for the solutions showing –ve deviation the graph obtained is



(Graph of Boiling point V_s composition for non-ideal solutions –ve deviation)

Point 1: When mixture composition ‘a’ is taken, then on boiling.

- (i) Distillate a’ is obtained which is richer in component A
- (ii) Residue is ‘b’

Successive distillation of ‘b’ leads to azeotropic solution D. (Maximum boiling azeotropic mixture)

- (iii) Successive distillation of a’ will lead to pure (A)

Point 2: When mixture composition c is taken and boiled.

- (i) Distillate is c’ which is richer in component B and successive distillation of distillates lead to solution becoming pure ‘B’
- (ii) The residue of ‘c’ is ‘e’ successive distillation of ‘e’ makes the residue richer in ‘D’ which is maximum boiling azeotropic mixtures.

Table for Maximum Boiling Azeotropic Mixture

A	B.pt of A in °C	B	B.pt of B in °C	B. pt of Azeotropic mix	% of B
HCl	–20	H ₂ O	100	108.5°C	79.96
HNO ₃	86	H ₂ O	100	120.5°C	32
CHCl ₃	61.2	Acetone	56.5	64.7°C	20
CHCl ₃	61.2	CH ₃ COOC ₂ H ₅	57	64.8°C	23

Ratio of Distillate to Residue Compositions

The relative proportions of the two liquids in the distillate can be calculated on the basis that the number of moles of each component present in the vapour phase is proportional to its vapour pressure.

If n'_A and n'_B are the number of moles of the components A and B in the vapour phase, then

$$n'_A/n'_B = p_A^\circ / p_B^\circ \quad (1)$$

If w_A and w_B represent the actual masses of the two components in the distillate and M_A and M_B their respective molecular masses, then Eq. (1) may be written as

$$\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B} = \frac{p_A^\circ M_A}{p_B^\circ M_B} \quad \Rightarrow \quad \boxed{\frac{w_A}{w_B} = \frac{p_A^\circ M_A}{p_B^\circ M_B}}$$

Thus the masses of the liquids in the distillate will be in the ratio of their vapour pressures and molar masses.

Solubility of Gases In Liquids

Gases dissolve in liquids to form true solutions. The degree of solubility depends upon the nature of the gas, nature of the solvent, pressure and temperature. Gases like Nitrogen, Hydrogen and Helium dissolve to a slight extent, while gases like Hydrogen chloride and Ammonia are more soluble. The larger solubility of HCl and Ammonia is accounted by the chemical reaction of these gases with the solvent to form Hydrochloric acid, and Ammonium hydroxide respectively.

Under the same pressure and temperature,

- (a) N_2 , CO_2 are more soluble in CH_3OH than in H_2O .
- (b) H_2S and NH_3 , are more soluble in H_2O than in C_2H_5OH .

From this it is quite right to say that chemical similarity between solute and solvent leads to higher solubility. e.g. Hydrocarbon vapours (non polar) are more soluble in other hydrocarbons (non polar) and other organic solvents than they do in water. HCl vapours (polar) are more soluble in H_2O (polar) than in CS_2 (non polar).

Factors Influencing Solubility of Gases in Liquids

The solubility of gases depends upon :

- (i) Nature of solute or solvent
- (ii) Temperature
- (iii) Pressure (In case of gases)

1. Nature of Gas and Nature of Solvent

The solubility of gas in a given solvent varies considerably with nature of the gas. Generally speaking, the gases which are easily liquified, are more soluble in common solvents.

Thus CO_2 is more soluble than H_2 and O_2 in water or in any other solvent.

The gases which are capable of forming ions in aqueous solutions, are much more soluble in water than in other solvents, e.g. Hydrogen chloride is highly soluble in water but not in Benzene, because HCl dissociates into H^+ & Cl^- ions in water, Similarly NH_3 is highly soluble in H_2O than in Benzene

The solubility of gases is generally expressed in terms of absorption coefficient (a). This is defined as the volume of the gas reduced to STP dissolved by a unit volume of a solvent at the temperature of the experiment and under a pressure of one atmosphere of the gas.

The absorption coefficient of few gases at $20^\circ C$ in different solvents.

	H ₂	N ₂	O ₂	CO ₂
<i>Solvent</i>				
H ₂ O	0.017	0.015	0.028	0.88
C ₂ H ₅ OH	0.080	0.130	0.130	3.00
C ₆ H ₆	0.066	0.104	0.105	—

2. Effects of Temperature

It has been found that under constant pressure the solubility of a gas diminishes with rise in temperature. The absorption coefficient of a few gases at different temperatures are :

Temperature	CO ₂	O ₂	N ₂
0	1.713	0.0484	0.0239
10	1.194	0.0380	0.0196
20	0.878	0.0380	0.0196
30	0.665	0.0260	0.0138
40	0.530	0.0231	0.0118

3. Effects of Pressure on the solubility of gases in liquids

The effect of pressure on the solubility of a given gas at a particular liquid at constant temperature can be obtained by carefully observing the process in reverse direction viz. the gas as a solute which vapourizes to establish a vapour pressure above the solution.

Henry's Law :

It states that at constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas above it.

When several gases are dissolved simultaneously in a solvent, the solubility of each gas from a mixture of gases is directly proportional to the partial pressure of the gas mixture. The proportionality constant will however be different for each gas.

The strict applicability of Henry's law is limited to the lower pressure and at high pressures the law is less applicable.

Generally, higher the temperature and lower the pressure, the more closely is the law obeyed. This law is not valid when the gas reacts with the solvent, or when the dissolved gas ionizes.

Solubility of Partially Miscible Liquids

These are pairs of liquids which dissolve in each other to a limited extent only.

There are four types of such partially miscible liquid-liquid systems.

Case-1: Those in which partial miscibility increases with increase in temperature

e.g. C₆H₅OH + H₂O, C₆H₅NH₂ + H₂O
C₆H₅NH₂ + Hexane, CH₃OH + CS₂
Cyclohexane + CH₃OH

Case-2: Those in which partial miscibility decreases with increase in temperature

e.g. (C₂H₅)₂NH + H₂O, (C₂H₅)₃N + H₂O

Case-3 : Those in which partial miscibility increase both on increasing the temperature as well as decreasing the temperature, in certain ranges

e.g. H₂O + Nicotine, and H₂O + β-Picoline

Case-4: Those in which complete miscibility cannot be attained.

e.g. Ether + H₂O

Nernst Distribution Law

H_3BO_3 is soluble in both water and amyl alcohol. But when a solution of H_3BO_3 in amyl alcohol is shaken with water, it is found that H_3BO_3 distributes itself in such a way that the ratio of the concentration of H_3BO_3 in water and alcohol is a constant at particular temperature.

Similarly Iodine is soluble in H_2O and CCl_4 and the distribution of Iodine in H_2O and CCl_4 remains constant at a particular temperature.

This is also one of the direct consequences of thermodynamic requirement for equilibrium.

Let a substance 'X' be miscible in two immiscible pairs of solvents A and B. Then

$$\frac{a_A}{a_B} = \text{Constant} = K$$

This equation $\frac{a_A}{a_B} = \text{Constant} = K$ is a mathematical representation of Nernst distribution law.

It states that a substance will distribute itself between two solvents until at equilibrium the ratio of the activities of the substances in two layers is a constant at any given temperature.

Assuming the solution to be dilute or when solute behaves ideally the activity becomes equal to concentration C and hence we have

$$K = \frac{C_B}{C_A}$$

where K = distribution or partition coefficient of solute between two solvents.

K depends upon

- (i) Nature of solute
- (ii) Nature of liquids involved.
- (iii) The temperature at which the liquids are maintained.
- (iv) The magnitude depends upon the manner in which the constant is represented C_A/C_B or C_B/C_A .

Colligative Properties of Solution

Solutions of Non Volatile Solute and Volatile Solvent

Colligative Properties

The properties which depend entirely upon the *number of particles of solute* in a given volume of solvent and not on the chemical nature of the solute molecule are defined as Colligative properties.

Here we shall consider four properties of solution containing non volatile solutes.

- (i) Lowering in vapour pressure.
- (ii) Elevation in boiling point
- (iii) Depression in freezing point
- (iv) Osmotic pressure

It is convenient to subdivide the solutions in the

A. Solutions of non electrolytes

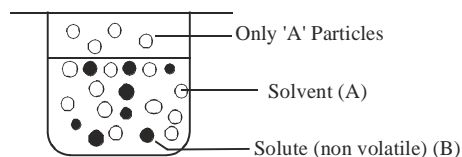
B. Solutions of electrolytes

A. Solutions of Non Electrolyte

Lowering in Vapour pressure

When a non volatile solute is present in the solution, the vapour pressure of the solution will be less than vapour pressure of pure solvent.

Let there be a solution of solute B in solvent A



Since 'B' is non volatile it won't go to the vapour phase hence the vapours above solution will be only due to volatile solvent 'A'. Since

$$P_A \propto P_A^0 \chi_A$$

$\Rightarrow P_A < P_A^0$ so vapour pressure is lowered.

For a binary system $\chi_A + \chi_B = 1$.

Substituting the value of χ_A

$$\Rightarrow P_A = P_A^0 (1 - \chi_B)$$

$$P_A = P_A^0 - P_A^0 \chi_B$$

$$\Rightarrow P_A^0 \chi_B = P_A^0 - P = \Delta P \text{ (Lowering in vapour pressure)}$$

$$\Delta P = P_A^0 \chi_B$$

$$\Rightarrow \Delta P \propto \chi_B$$

\Rightarrow Lowering in vapour pressure is directly proportional to the mole fraction of solute

The relative lowering in vapour pressure is equal to the mole fraction of solute.

$$\frac{\Delta P}{P_A^0} = \chi_B$$

Hence

(a) Lowering in vapour pressure is directly proportional to the mole fraction of solute in the solution.

(b) Relative lowering in vapour pressure is equal to the mole fraction of solute.

1. Calculation of molecular mass of solute (B) in solvent (A)

$$\Delta P = P_A^0 \chi_B = P_A^0 \frac{n_B}{n_A + n_B}$$

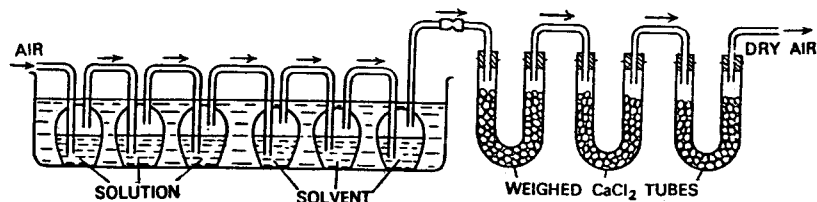
$$= P_A^0 \left[\frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \right]$$

But when the solution is dilute then $\frac{W_B}{M_B} \ll \frac{W_A}{M_A}$ and hence $\frac{W_B}{M_B}$ can be neglected in the denominator

$$\Rightarrow \Delta P = P_A^0 \times \frac{W_B \times M_A}{W_A \times M_B}$$

$$\text{or } M_B = \left[\frac{P^0}{\Delta P} \right] \times \left[\frac{W_B \times M_A}{W_A} \right]$$

2. The relative lowering in vapour pressure is determined by *Ostwald And Walker Method*. In this method a stream of dry air is passed successively through a set of weighed bulbs containing the solution and then through a set of merged bulbs containing pure solvent and finally through weighed U-shaped tubes containing anhydrous CaCl_2 .



- (a) Let the loss in weight of solution bulbs be = w_1 gm.
 (b) Loss in weight of solvent bulbs = w_2 gm
 (c) Loss in weight of solution bulbs (w_1) \propto vapour pressure of solution.
 (d) Loss in weight of solvent bulbs (w_2) \propto vapour pressure of solvent – vapour pressure of solution.
 $\Rightarrow P_s \propto w_1$ and $(P^0 - P_s) \propto w_2$

$$\Rightarrow \frac{P^0 - P_s}{P^0} = \frac{w_2}{w_1 + w_2} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Total loss in weight of solution bulbs and solvent bulbs}} = X_B \text{ i.e. mole}$$

fraction of solute

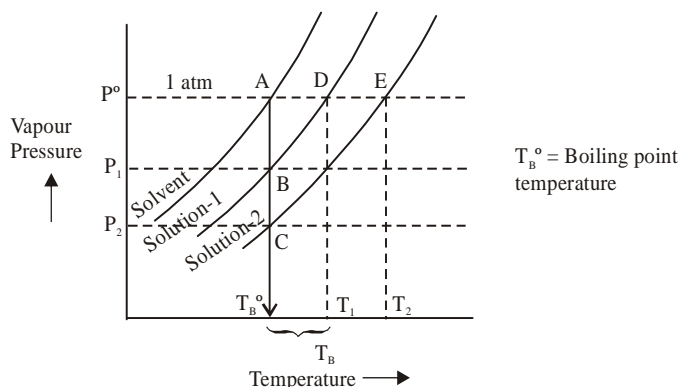
Elevation in Boiling Point

When a liquid is heated then due to rise in temperature the liquid vapourises and the vapour pressure increases. When the vapour pressure of the liquid becomes equal to the atmospheric pressure, the liquid begins to boil. The temperature at which the equilibrium vapour pressure of the liquid becomes equal to the atmospheric pressure is called boiling point.

When a non volatile solute is added to the solvent the vapour pressure of the solvent in the solution decreases. Consequently the solution has to be heated to a higher temperature to have its vapour pressure equal to atmospheric pressure.

Relationship for elevation in Boiling points

Consider the graph of vapour pressure verses temperature in Kelvin scale.



Here Triangle ADB and ACE are similar

Hence

$$\frac{AD}{AE} = \frac{AB}{AC}$$

$$\frac{T_1 - T^0}{T_2 - T^0} = \frac{P^0 - P_1}{P^0 - P_2}$$

$$\Rightarrow T_1 - T^0 \propto P^0 - P_1$$

$$\Rightarrow \Delta T_B \propto \Delta P$$

Also

$$\Delta P \propto \chi_B$$

$$\Rightarrow \Delta T_B \propto \chi_B$$

$$\Delta T_B \propto \frac{n_B}{n_A + n_B}$$

$$\Delta T_B \propto \frac{n_B}{n_A} \text{ [Dilute solutions]}$$

$$\Delta T_B \propto \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\Rightarrow \Delta T_B = K_B \frac{W_B}{M_B \times W_A}$$

When $\frac{W_B}{M_B} = 1$ mole and $W_A =$ mass of solute in kilogram (kg)

$$\Rightarrow \Delta T_B = K_B \times m \quad m = \text{molality of solution} \quad K_B = \text{Ebullioscopic constant}$$

$\Delta T_B \propto K_B$ [when concentration is kept constant]. Hence elevation in boiling point depends upon

K_B *i.e.*, nature of solvent

$$\Delta T_B \propto m \quad \text{[When solvent taken is same]}$$

K_B is defined as the elevation in boiling point of a solvent when 1-gm mole of a non-volatile solute is dissolved in 1000 gm of solvent.

$$K_b = \frac{RT_b^2}{1000 l_v} \quad l_v = \text{latent heat of vapourization per gram of the solvent}$$

$$\text{Also } K_b = \frac{RT_b^2 \times M_0}{1000 \times \Delta H_v} \quad \text{where } M_0 = \text{molecular weight of solvent.}$$

$$\Delta T_B = \frac{K_b W_{\text{solute}}}{M_{\text{solute}} \times W_{\text{solvent}}} \times 1000$$

$$\Delta T_B = \frac{K_b W_B}{M_B \times W_A} \times 1000$$

$W_B = W_{\text{solute}} =$ Mass of solute taken

$M_B = M_{\text{solute}} =$ Molecular weight of solute

$W_A = W_{\text{solvent}} =$ Mass of solvent taken in grams

$$\Rightarrow M_{\text{solute}} = \frac{K_b W_B}{\Delta T_B \times W_A} \times 1000$$

Also $\frac{T_{B(1)}}{\Delta T_{B(2)}} = \frac{K_{B(1)}}{K_{B(2)}}$ when concentration is same but solvent different

$$\frac{\Delta T_{B(1)}}{\Delta T_{B(2)}} = \frac{m_1}{m_2} \quad \text{when solvent is same but concentration different}$$

$$\frac{\Delta T_{B(1)}}{\Delta T_{B(2)}} = \frac{Mo(2)}{Mo(1)} \Rightarrow \Delta T_B \propto \frac{1}{Mo(1)} \quad \text{when solvent same and amount of solute is same}$$

Depression in Freezing Point

When a solvent is cooled, a temperature is eventually reached at which solid begins to separate from the solution. The temperature at which this separation begins is called as freezing point of solvent.

At freezing point liquid and solid are in equilibrium.



At the freezing point, the vapour pressure of liquid and solid will be same.

Addition of a non-volatile solute, decreases the vapour pressure of pure liquid. Therefore for a solid to have the same vapour pressure as the solution, the temperature would lower down. This phenomenon is called depression in freezing point.

Relationship for Depression in Freezing Point.

Here again.

$$\Delta T_f \propto \Delta p \quad \Delta T_f \propto \Delta P$$

$$\Delta p \propto \text{molality} \quad \text{or} \quad \Delta P \propto X_B$$

$$\Delta T_f \propto \text{molality} \quad \Delta T_f \propto X_B$$

$$\Rightarrow \Delta T_f \propto \frac{n_B}{n_A} \quad \text{for dilute solutions}$$

$$\Rightarrow \Delta T_f = K_f \frac{W_B}{M_B W_A} \quad \text{when } W_A \text{ is in kilogram}$$

$$\rightarrow \boxed{\Delta T_f = K_f m}$$

K_f = Molal depression constant

K_f is defined as the depression in freezing point of a solvent when 1-gm mole of a non-volatile solute is dissolved in 1000 gm of solvent. *i.e.*

$$\boxed{K_f = \frac{RT_f^2}{1000l_f}}$$

also

$$\boxed{K_f = \frac{RT_f^2 M_0}{1000\Delta H_f}}$$

where T_f = freezing point

T_f = latent heat of fusion per gram

Also

$$\boxed{\Delta T_f = \frac{RT_f \times w \text{ solute}}{M \text{ solute} \times W \text{ solvent}} \times 1000}$$

Hence molecular weight of solute

$$\boxed{M_{\text{solvent}} = \frac{K_f \times W \text{ solute}}{\Delta T_f \times W \text{ solvent}} \times 1000}$$

Since $\Delta T_f = K_f m \Rightarrow \Delta T_f \propto K_f$ [When concentration is same but different solvents are taken]
 $\Delta T_f \propto m$ [when solvent is same but different concentration are taken]

Osmotic Pressure

Osmosis

1. The phenomenon of osmosis, was first observed by Abbe Nollet, may be defined as a process in which pure solvent molecules pass through a semipermeable membrane from a solution of low concentration to a solution of higher concentration.
 - (a) *Exo-osmosis* is the outward flow of water from a cell containing an aqueous solution through a semipermeable membrane, e.g. grapes in NaCl solution.
 - (b) *Endo-osmosis* is the inward flow of water into a cell containing an aqueous solution through a semipermeable membrane, e.g. grapes in water.
2. The most frequently used semipermeable membrane in laboratory is that of copper ferrocyanide, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ because it is very strong and can withstand very high pressure. Remember that semipermeable membrane of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ does not work in non-aqueous solution because it gets dissolved in non-aqueous solvents. Other synthetic semipermeable membrane is that of calcium phosphate. Natural semipermeable membranes are parchment paper, cell walls, pig's bladder, skin surrounding white of an egg, membrane surrounding RBCs etc.

When a solution (say of sugar) is separated from the pure solvent (water in present case) by means of a semipermeable membrane (a membrane which allows only the solvent molecules but not the solute molecules to pass through it), the pure solvent passes through the membrane and goes to solution (osmosis) till the hydrostatic pressure of the liquid column exactly balances the tendency of water to pass inward through the semipermeable membrane. The hydrostatic pressure set up as a result of osmosis is a measure of the osmotic pressure of the solution. For instance, if the solution of density d rises to height h , then osmotic pressure is expressed as

$$\pi = h \times d \times g, \text{ where } g \text{ is the acceleration due to gravity.}$$

The osmotic pressure may be defined as the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semipermeable membrane.

Osmotic pressure may also be defined in several other ways.

- (i) Osmotic pressure is the excess pressure which must be applied to a given solution in order to increase its vapour pressure until it becomes equal to that of the solution.
- (ii) Osmotic pressure is the negative pressure produced when a solution is separated from the solvent by a semipermeable membrane.
- (iii) Osmotic pressure is the hydrostatic pressure produced when a solution is separated from the solvent by a semipermeable membrane.

Laws of Osmotic Pressure

The different laws of osmotic pressure are

1. Boyle-Van't Hoff law
2. Charles-Van't Hoff law
3. Avogadro-Van't Hoff law
4. Van't Hoff theory of osmotic pressure

1. **Boyle-Van't Hoff Law :**

It state that “temperature remaining constant, the osmotic pressure of dilute solution is directly proportional to molar concentration of solution.

$$\pi \propto c$$

$$\Rightarrow \pi = \text{constant} \times c$$

$$\Rightarrow \frac{\pi}{c} = \text{constant}$$

If n moles of the substance are dissolved in V litres of solution.

$$c = \frac{n}{V}$$

$$\Rightarrow c \propto \frac{1}{V}$$

$$\Rightarrow \pi V = \text{constant [At constant temperature]}$$

2. **Charles-Van't Hoff Law :**

It state that “ for a given concentration of solution, the osmotic pressure of a dilute solution is directly proportional to the temperature.

$$\pi \propto T \Rightarrow \frac{\pi}{T} = \text{constant}$$

3. **Avogadro-Van't Hoff Law :**

“Osmotic pressure of a dilute solution is directly proportional to the number of moles of solute present in the solution”

$$\pi \propto n$$

4. **Van't Hoff Theory of Dilute solution :**

Van't Hoff gave an idea that dilute solution behave like ideal gases and gas laws obeyed by ideal gas are also obeyed by dilute solution .

We know that

$$V \propto \frac{1}{\pi} \quad (\text{Boyle - Van't Hoff Law})$$

$$V \propto T \quad (\text{Charles Van't Hoff law})$$

$$V \propto n \quad (\text{Avogadro - Van't Hoff law})$$

$$\Rightarrow V \propto \frac{n \times T}{\pi}$$

$$\Rightarrow V = \frac{nRT}{\pi} \quad R = \text{solution constant (0.0821 lit atm K}^{-1} \text{ mol}^{-1}\text{)}$$

$$\Rightarrow \pi = \frac{n}{V} RT$$

$$\pi = CRT$$

Hence at a given temperature

$$\pi \propto C$$

Important relations concerning osmotic pressure, P or π

(i) $\pi V = n RT$ or $\pi V = n ST$ or $\pi = \frac{n}{V} ST$ or $\pi = CST$

where π = Osmotic pressure in atmospheres

n = Number of moles of the solute present in V litres of the solution

C = Concentration of the solution in moles per litre

T = Temperature in K

R or S = 0.0821 l atm deg⁻¹ mole⁻¹

$$(ii) \pi V = \frac{w}{M_0} ST \left(\because n = \frac{w}{M_0} \right)$$

$$M_0 = \frac{wST}{\pi V} \quad (M_0 = \text{Molecular weight of solute})$$

where w = Wt. of solute in g dissolved in V l of solution

$$(iii) \pi = h d g$$

where h = Height, d = density, g = Acceleration due to gravity.

(iv) In isotonic solutions, since osmotic pressure, p is equal, their concentration (C) must also be equal, *i.e.*

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}, \quad \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

(v) If a number of solutes are present in the solutions and π_1, π_2, π_3 etc. are their individual osmotic pressures, then

$$\text{Total osmotic pressure} = \pi_1 + \pi_2 + \pi_3 + \dots$$

Reverse osmosis

If a pressure higher than osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semipermeable membrane. Since here the flow of solvent is in the reverse direction to that observed in the usual osmosis, the process is called reverse osmosis. It is used in the desalination of sea water to obtain pure water.

Isotonic Solutions

A pair of solutions having the same osmotic pressure are known as isosmotic or isotonic solutions. If two such solutions are separated by a semipermeable membrane, there will be transference of solvent from one solution to the other. Isosmotic solutions separated by semipermeable membrane are known as isotonic solutions. Isotonic solutions have the same concentration. 0.85% NaCl solutions is found to be isotonic with blood, while 0.9% NaCl solution isotonic with human RBCs. A solution having lower or higher osmotic pressure than the other is to be hypotonic or hypertonic respectively in respect to other solution.

(i) When placed in water or hypotonic solutions, cell swell and burst (hemolysis), Endo-osmosis occurs.

(ii) When placed in hypertonic solutions, the fluid from the plant cells comes out and thus the cells contract in size (plasmolysis). When excess of fertilizers (like urea) are applied, plasmolysis takes place and plants dry up (wilt), Exo-osmosis occurs.

Osmolarity

Osmolarity is the term used by physiologists to discuss the osmotic behaviour solutes which either dissociate or associate in solution. Mathematically,

$$\text{Osmolarity} = \text{Molarity} \times \text{No. of particles produced per formula unit of the solute}$$

B. Solution of Electrolytes

Abnormal Behaviour of Solutions

Since the colligative properties of solutions, viz. lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure, depend solely on the number of solute particles present in solution and not on their nature, colligative properties of the solutes which undergo dissociation

(electrolytes) in solution would be higher than expected for the normal substances (non-electrolytes). For example, one mole of a solute like glucose, cane sugar, urea, etc. when dissolved in 1000 g of water depresses the freezing point of water by 1.86°C. However, solution of one mole of NaCl or BaCl₂ in 1000 g of water depress the freezing point of water by 3.72°C (2 × 1.86) and 5.58°C (3 × 1.86) respectively because each molecule of NaCl and BaCl₂ dissociates to give 2 (Na⁺ & Cl⁻) and three (Ba²⁺ and 2Cl⁻) ions respectively and each ion behaves as a particle in itself. Thus, among the 0.1 M solution of the various substances like cane sugar, NaCl, BaCl₂, Al₂(SO₄)₃, etc. the colligative effect will be maximum in Al₂(SO₄)₃ solution giving 5 ions per molecule.

Similarly, there are certain substances which associate when dissolved in a particular solvent. Hence the molecular weight of such substances as determined with the help of colligative properties will be more than theoretically calculated value from the molecular formula. For example, the observed molecular weight of acetic acid when dissolved in benzene is found to be 118 which is nearly double the value (60) calculated from its molecular formula, CH₃COOH. This is due to the fact that acetic acid, in benzene, does not exist as CH₃COOH but as a dimer, i.e. (CH₃COOH)₂.

Vant'f Hoff Factor, *i*.

To account for the above anomalies, Van't Hoff introduced a factor '*i*' in the Van't Hoff equation ($\pi V = nRT$) of osmotic pressure. The modified equation may thus be written as, $\pi V = i nRT$

The factor '*i*' was defined by the expression

$$i = \frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}}$$

The experimental value of *i* can be obtained by dividing the observed osmotic pressure of the solution under the study with that of the solution of a normal substance (say sucrose) of the same concentration (molarity) as that of the substance under study.

Now since osmotic pressure behaves like other colligative properties, the factor *i* can also be applied to other colligative properties. Thus in general,

$$i = \frac{\text{Actual number of particles}}{\text{No. of particles when no ionisation/association}}$$

$$i = \frac{\text{Observed colligative property (experimental)}}{\text{Normal colligative property (calculated)}}$$

Now since molecular weight of a solute is inversely proportional to the colligative property, the factor *i* may also be defined in the following way

$$i = \frac{\text{Normal molecular wt. (calculated value)}}{\text{Observed molecular wt. (experimental value)}}$$

Evidently for a normal substance (which neither dissociates nor associates in solution), the factor *i* is always unity.

When the Van't Hoff factor is included then the colligative properties get modified as follows

(a) Relative Lowering in Vapour Pressure

$$\frac{P^0 - P_s}{P^0} = i \times X_B$$

$$i = \frac{[(C - C\alpha) + xC\alpha + yC\alpha]}{C}$$

$$\Rightarrow i = \frac{1 - \alpha + x\alpha + y\alpha}{1}$$

$$= 1 + [(x + y) - 1]\alpha$$

Let $x + y = n =$ number of particles formed after dissociation

$$\Rightarrow i = 1 + (n - 1)\alpha$$

$$\alpha = \frac{i - 1}{n - 1}$$

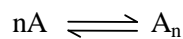
2. Association

Degree of Association : It may be defined as the number of molecules associated over initial concentration

$$\alpha = \frac{\text{Number of moles associated}}{\text{Initial concentration}}$$

$$i = \frac{\text{Total number of moles of particles at equilibrium}}{\text{Initial concentration}}$$

Let n molecules of an electrolyte A undergo association



Let the initial concentration of A = C

The degree of association = α

when $C\alpha$ moles of A associate then $\frac{C\alpha}{n}$ moles of A_n are formed

Number of moles at equilibrium $(C - C\alpha) \rightleftharpoons \frac{C\alpha}{n}$

$$\Rightarrow i = \frac{C - C\alpha + \frac{C\alpha}{n}}{C}$$

If $C = 1$

$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$$

$$i = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$\Rightarrow \alpha = \frac{i - 1}{\frac{1}{n} - 1}$$