## Chapter-02

# Solution

## LECTURE-1

The solution is a homogeneous mixture of two or more substances in the same or different physical phases. The substances forming the solution are called components of the solution. Based on the number of components a solution of two components is called a binary solution.

**Solute and Solvent**

In a binary solution, a solvent is a component which is present in large quantity while the other component is known as solute.

**Classification of Solutions:**

**(A)** The following types of solutions are seen based on the physical state of solute and solvent.

**Types of Solutions**

| **Type of Solution** | **Solute** | **Solvent** | **Common Examples** |
|---|---|---|---|
| *Gaseous Solutions* | *Gas* | *Gas* | *Mixture of oxygen and nitrogen gases* |
| | Liquid | Gas | Chloroform mixed with nitrogen gas |
| | Solid | Gas | Camphor in nitrogen gas |
| *Liquid Solutions* | *Gas* | *Liquid* | *Oxygen dissolved in water* |
| | Liquid | Liquid | Ethanol dissolved in water |
| | Solid | Liquid | Glucose dissolved in water |
| *Solid Solutions* | *Gas* | *Solid* | *Solution of hydrogen in palladium* |
| | Liquid | Solid | Amalgam of mercury with sodium |
| | Solid | Solid | Copper dissolved in gold |

[if the water is used as a solvent, the solution is called aqueous solution and if not, the solution is called a non-aqueous solution.]

**(B)** Depending upon the amount of solute dissolved in a solvent we have the following types of solutions:

**(i) Unsaturated solution** A solution in which more solute can be dissolved without raising the temperature is called an unsaturated solution.

(ii) **Saturated solution** A solution in which no solute can be dissolved further at a given temperature is called a saturated solution.

**(iii) Supersaturated solution** A solution that contains more solute than that would be necessary to saturate it at a given temperature is called a supersaturated solution.

**Solubility:**

The maximum amount of a solute that can be dissolved in a given amount of solvent (generally 100 g) at a given temperature is termed as its solubility at that temperature.

The solubility of a solute in a liquid depends upon the following factors:

(i) Nature of the solute

(ii) Nature of the solvent

(iii) The temperature of the solution
(iv) Pressure (in case of gases)

**Henry's Law:**

The most commonly used form of Henry's law states "the partial pressure (P) of the gas in the vapour phase is proportional to the mole fraction (x) of the gas in the solution" and is expressed as:

$$p = K_H . x$$

Greater the value of $K_H$, the higher the solubility of the gas. The value of $K_H$ decreases with an increase in temperature. Thus, aquatic species are more comfortable in cold water [more dissolved $O_2$] rather than Warm water.

**Applications:**

1. In the manufacture of soft drinks and soda water, $CO_2$ is passed at high pressure to increase its solubility.
2. To minimize the painful effects (bends) accompanying the decompression of deep-sea divers. $O_2$diluted with less soluble. He gas is used as breathing gas.
3. At high altitudes, the partial pressure of $O_2$ is less than that at the ground level. This leads to low concentrations of $O_2$ in the blood of climbers which causes 'anoxia'.

**The concentration of Solutions:**

The concentration of a solution is defined as the relative amount of solute present in a solution. Based on the concentration of solution there are two types of solutions.
(i) Dilute solution
(ii) Concentrated solution

**Methods of Expressing Concentration of Solutions:**

The various expression for the concentrations of solutions can be summarized as

**(i)** **Percentage by weight** (w / w %) :
It is defined as the amount of solute present in 100 g of solution.

w / w % = weight of solute / weight of solution * 100

(ii) **Percentage by volume** (w / V%):

It is defined as the weight 01 solute present in 100 mL of solution.
w / V % = weight of solute / weight of solution * 100
or the volume of solute present in 100 mL of solution.
u / V % = volume of solute / volume of solution * 100

**(iii)** **Mole fraction** (x):

It is defined as the ratio of the number of moles of a component to the total number of moles of all the components. For a binary solution, if the number of moles of A and B is $n_A$ and $n_B$ respectively, the mole fraction of A will b

$$\chi_A = \frac{n_A}{n_A + n_B}$$

$$\chi_B = \frac{n_B}{n_A + n_B} \quad \because \chi_A + \chi_B = 1$$

For a solution containing ‘n’ number of components, we have:

$$x_i = \frac{n_i}{n_1 + n_2 + \dots\dots + n_i} = \frac{n_i}{\sum n_i}$$

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + \dots\dots\dots\dots\dots\dots + x_i = 1$$

(iv) **Molarity** (M) :
It is the number of moles of solute present in 1L($dm^3$) of the solution.
M = number of moles of solute/volume of solution (L)
M = mass of solute (in gram) * 1000 / mol. wt. of solute x volume of solution (in mL)
Molarity varies with temperature due to the change in volume of solution.
[When the molarity of a solution is 1 M, it is called a molar solution. 0.1 M solution is called a decimolar solution while 0.5 M solution is known as semi molar solution]
Molarity = Percent by mass * density * 10 / molecular weight
Dilution law, $M_1 V_1 = M_2 V_2$ (for dilution from volume $V_1$ to $V_2$)
For the reaction between two reactants, $M_1 V_1 / n_1 = M_2 V_2 / n_2$
where $n_1$ and $n_2$ arc stoichiometric coefficient in the balanced equation.
**(v)** Molality **(m)**: It is the number of moles of solute per kilogram of the solvent.
Molality = mass of solute in gram * 1000 / mol. wt. of solute * mass of solvent (in g)
Molality is independent of temperature.
[Whcn solvent used is water, a molar (1 M) solution is more concentrated than a molal (1 M) solution.]

**(vi) Parts per million**: *When a solute is present in* ***trace quantities, it*** is convenient to express concentration in **parts per million (ppm)** and is defined as:

Parts per million =

$$= \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

# LCTURE-2

## Solubility

The solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent. It depends upon the nature of the solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in the solution of a solid or a gas in a liquid.

### The solubility of a Solid in a Liquid

Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and nonpolar solutes in nonpolar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two, or we may say **like dissolves like.**

When a solid solute is added to the solvent, some solute dissolves, and its concentration increases in solution. This process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated from the solution. This process is known as crystallization**. A stage is reached when the two processes occur at the** same rate. Under such conditions, the number of solute particles going into the solution will be equal to the solute particles separating and a state of dynamic equilibrium is reached.

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$

At this stage, the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure.

**saturated solution:** The solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution.**

The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its **solubility**.

Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution. Unsaturated solution:** It *is one in which more solute can be dissolved at* the same temperature.

### Effect of temperature

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by the equation as

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$

This, being dynamic equilibrium, must follow **Le Chateliers Principle. In** general, if in a *nearly saturated solution, the dissolution process is* endothermic ($\Delta_{sol} H > 0$), the solubility should increase with a rise in temperature, and if it is exothermic ($\Delta_{sol} H < 0$) the solubility should decrease. These trends are also observed experimentally.

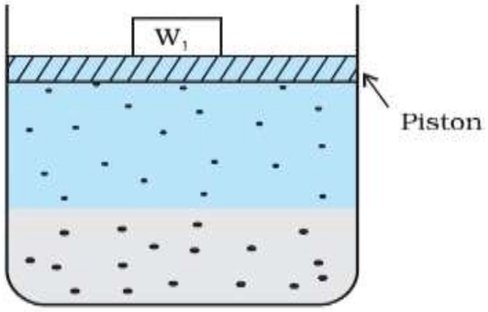
## Effect of pressure

Pressure does not have any significant effect on the solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

## The solubility of a Gas in a Liquid

Many gases dissolve in water. Oxygen dissolves only to a small extent in water. It is this dissolved oxygen that sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. The solubility of gases in liquids is greatly affected by pressure and temperature.

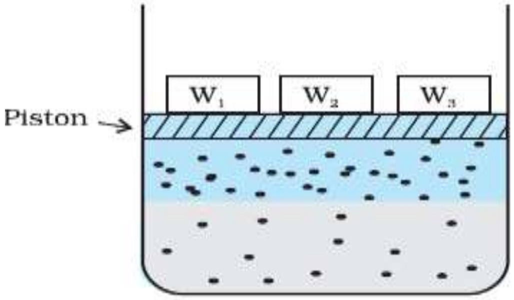
The solubility of gases increases with an increase in pressure. For the solution of gases in a solvent, consider a system as shown.



The lower part is a solution and the upper part is a gaseous system at pressure p and temperature T.

Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions rate of gaseous particles entering and leaving the solution phase is the same.

Now increase the pressure over the solution phase by compressing the gas to a smaller volume as shown in the figure.



This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of the solution to enter it. The solubility of the gas will increase until a new equilibrium is reached increasing the pressure of a gas above the solution and thus its solubility increases.

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as **Henry's law.**

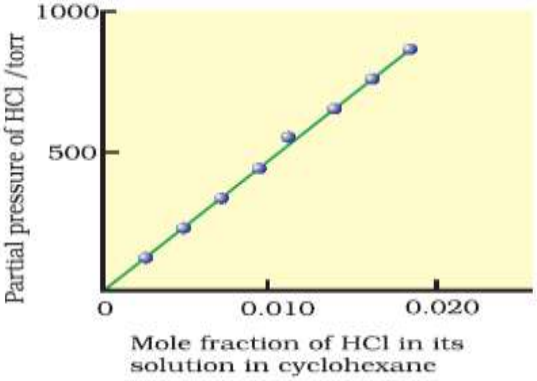
**The law states that** at a constant temperature, **the solubility of a gas in a liquid is directly proportional to the pressure of the gas.**

Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of the partial pressure of the gas. If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the **mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.**

The most commonly used form of Henry's law states that "**the partial pressure of the gas in the vapour phase (*p*) *is* proportional to the mole fraction of the gas (*x*) *in* the solution" and is expressed as:**

$$p = K_H \ x$$

Here *KH is Henry's law constant. If we draw a* graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig.



Different gases have different *KH values at the same* temperature. This suggests that *KH is a* function of the nature of the gas.

The higher the value of *KH at a given pressure, the lower is the solubility* of the gas in the liquid. KH values for both N2 and O2 increase with an increase of temperature indicating that the solubility of gases increases with the decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

Henry's law finds several applications in industry and explains some biological phenomena.

- To increase the solubility of CO2 in soft drinks and soda water, the bottle is sealed under high pressure.

- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in the blood. When the divers come towards the surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as *bends, which are painful and dangerous to live.*

To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen, and 32.1% oxygen).

- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as *anoxia.*

## Effect of Temperature

The solubility of gases in liquids decreases with a rise in temperature. When dissolved, the gas molecules are present in the liquid phase and the process of dissolution can be considered similar to condensation, and heat is evolved in this process.

The dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with an increase in temperature.

# LECTURE-3

**Raoult's Law** The Raoult's law states "For a solution of two volatile liquids, the vapor pressure of each liquid in the solution is less than the respective vapor pressure of the pure liquids and the equilibrium partial vapor pressure of the liquid is directly proportional to its mole fraction. For a solution containing two liquids A and B, the partial vapor pressure of liquid A is

$$p_A \propto \chi_A \quad \text{or} \quad p_A = k\chi_A$$

$$\text{where, } \chi_A = \frac{n_A}{(n_A + n_B)} = \text{mole fraction of liquid } A$$

The proportionality constant is obtained by considering the pure liquid when $\chi_A = 1$ then $k = P^\circ_A$, the vapor pressure of the pure liquid, hence

$$p_A = p_A^\circ \chi_A$$

Similarly, $$p_B = p_B^\circ \chi_B$$

The total vapour pressure of the solution,

$$p_T = p_A + p_B = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$= p_A^\circ + (p_B^\circ - p_A^\circ)\chi_B$$

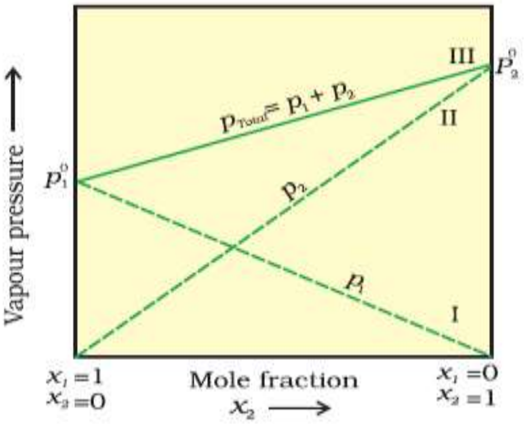
The following conclusions can be drawn from the equation:

(i) Total vapor pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapor pressure over the solution varies linearly with the mole fraction of component 2.

(iii) Depending on the vapor pressures of the pure components 1 and 2, total vapor pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

A plot of $p_1$ or $p_2$ versus the mole fractions $x_1$ and $x_2$ for a solution gives a linear plot as shown in Fig. These lines (I and II) pass through the points and respectively when $x_1$ and $x_2$ equal unity.



The composition of the vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If $y_1$ *and* $y_2$ *are the mole fractions of the* components 1 and 2 respectively in the vapor phase then, using Dalton's law of partial pressures:

$$p_1 = y_1 \; p_{\text{total}}$$
$$p_2 = y_2 \; p_{\text{total}}$$

In general

$$p_i = y_i \; p_{\text{total}}$$

## Raoult's Law as a special case of Henry's Law

According to Raoult's law, the vapor pressure of a volatile component in a given solution is given by $p_i = x_i \, p_i^0$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$$p = K_H \; x.$$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution.

## Vapour Pressure of Solutions of Solids in Liquids

If a non-volatile solute is added to a solvent to give a solution the vapor pressure of the solution is solely from the solvent alone. This vapor pressure of the solution at a given temperature is found to be lower than the vapor pressure of the pure solvent at the same temperature.

In the solution, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced.

Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapor pressure is also reduced.

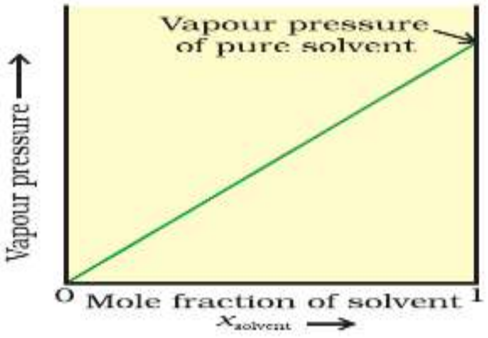
The decrease in the vapor pressure of the solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature.

Raoult's law in its general form can be stated as **for any solution the partial vapor pressure of each volatile component in the solution is directly proportional to its mole fraction.**

In a binary solution, let us denote the solvent by 1 and solute by 2. When the solute is non-volatile, only the solvent molecules are present in the vapour phase and contribute to vapor pressure. Let *p1 be* the vapor pressure of the solvent, *x1 be* its mole fraction, *pi*0 be its vapor pressure in the pure state. Then according to Raoult's law

$$p_1 \propto x_1$$

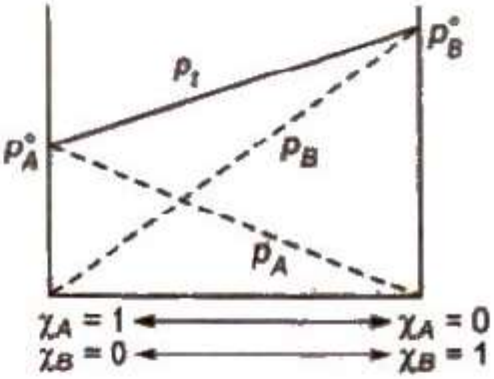
$$\text{and} \quad p_1 = x_1 \; p_1^0$$



## LECTURE-4

**Ideal Solutions:**

Those solutions in which solute-solute (B-B) and solvent-solvent (A-A) interactions are almost similar to solvent-solute (A-B) interactions are called ideal solutions. These solutions satisfy the following conditions :



(i) The solution must obey Raoult's law, i.e.

$$p_A = p_A^\circ \chi_A,\ p_B = p_B^\circ \chi_B$$

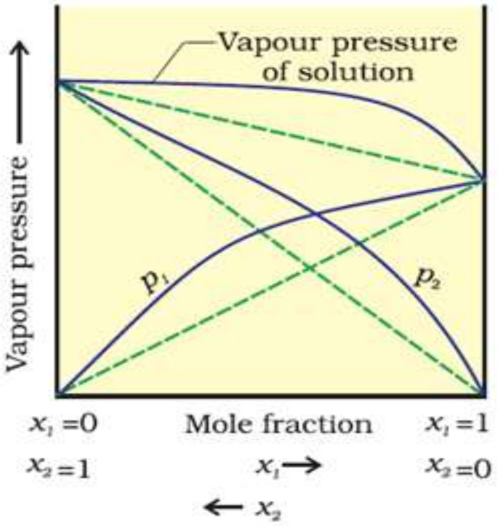
(ii) ΔHmix = 0 (No energy evolved or absorbed)
(iii) ΔVmix = 0 (No expansion or contraction on mixing)
Some solutions behave like nearly ideal solutions, e.g., benzene + toluene. n-hexane + n-heptane, ethyl iodide + ethyl bromide, chlorobenzene + bromobenzene.

**Non-ideal Solutions:**

Those solutions which show deviation from Raoult's law is called a non-ideal solution.
For such solutions,
$\Delta H_{mix} \neq 0$
$\Delta V_{mix} \neq 0$
(a) **Non-ideal solutions showing positive deviation** In such a case, the A – B interactions are weaker than A – A or B – B interactions and the observed vapor pressure of each component and the total vapor pressure are greater than that predicted by Raoult's law. The solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

$$p_A > p_A^\circ \chi_A,\ p_B > p_B^\circ \chi_B$$
$$p_{\text{total}} > p_A^\circ \chi_A + p_B^\circ \chi_B$$

For such solutions

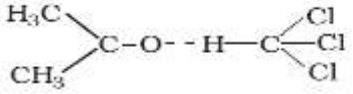


(b) **Non-ideal solution showing negative deviation** In such a case, the A – B interactions are stronger than A – A or B – B interactions, and the observed vapor pressure of each component and the total vapor pressure are lesser than that predicted by Raoult's law.

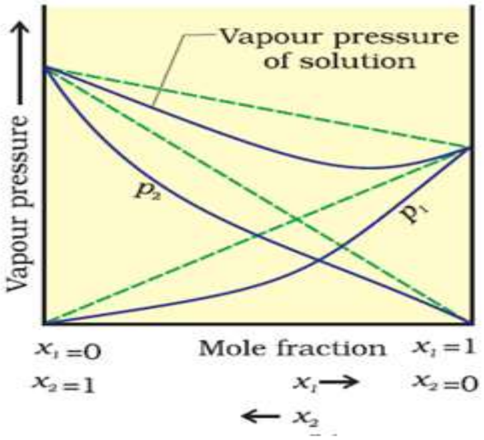
$$p_A < p_A^\circ \chi_A,\ p_B < p_B^\circ \chi_B$$

$$p_{total} < p_A^\circ \chi_A + p_B^\circ \chi_B$$

**Ex:** A mixture of chloroform and acetone forms a solution with a negative deviation from Raoult's law. This is because the chloroform molecule can form a hydrogen bond with the acetone molecule as shown.



This decreases the escaping tendency of molecules for each component and consequently the vapor pressure decreases resulting in a negative deviation from Raoult's law.



## Azeotropes:

Some liquids on mixing, form **azeotropes which are binary mixtures** having the same composition in liquid and vapor phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called **minimum boiling azeotrope and maximum boiling azeotrope. The solutions which show a large positive deviation from** Raoult's law form minimum boiling azeotrope at a specific composition.

For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapor have the same composition, and no further separation occurs.

The solutions that show a large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid, and 32% water by mass, with a boiling point of 393.5 K.

# LECTURE-5

## Colligative Properties and Determination of Molar Mass:

Colligative properties are those properties that depend only upon the number of solute particles in a solution irrespective of their nature.

## Relative Lowering of Vapour Pressure:

It is the ratio of lowering in vapor pressure to the vapor pressure of the pure solvent. The relative lowering in vapor pressure of a solution containing a nonvolatile solute is equal to the mole fraction of solute in the solution.

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \chi_B$$

where, $\frac{p_A^\circ - p_A}{p_A^\circ}$ = relative lowering of vapour pressure

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A + n_B}$$

for dilute solutions, $n_B << n_A$. Hence,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A}$$

or

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{W_B \times M_A}{M_B \times W_A}$$

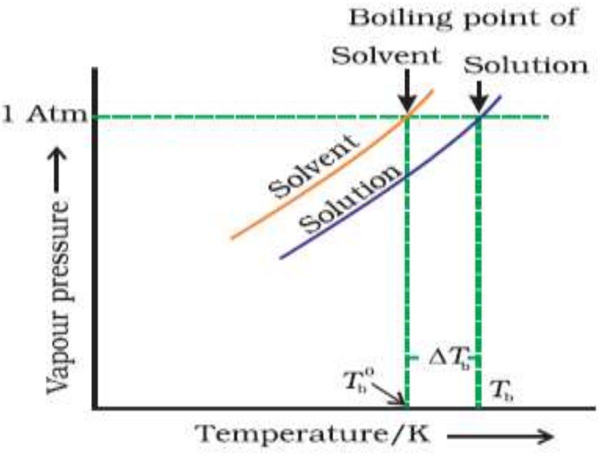
$$M_B = \frac{W_B}{W_A} \times M_A \times \frac{p_A}{(p_A^\circ - p_A)}$$

The above expression is used to find the molecular weight of an unknown solute dissolved in a given solvent. Where $W_B$ and $W_A$ = mass of Solute and solvent respectively. $M_B$ and $M_A$ = molecular weight of solute and solvent respectively.

Ostwald and Walker's method is used to determine the relative lowering of vapor pressure.

**Elevation in Boiling Point** ($\Delta T_b$):

The boiling point of a liquid is the temperature at which its vapor pressure becomes equal to the atmospheric pressure. As the vapor pressure of a solution containing a nonvolatile solute is lower than that of the pure solvent, its boiling point will be higher than that of the pure solvent as shown in the figure. The increase in boiling point is known as elevation in boiling point, $\Delta T_b$



$\Delta T_b = T_b - T^\circ_b$

$\Delta T_b = K_b$ m (where; m = molality)

$K_b$ is molal elevation constant or ebullioscopic constant. The molecular mass of solute can be calculated as

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

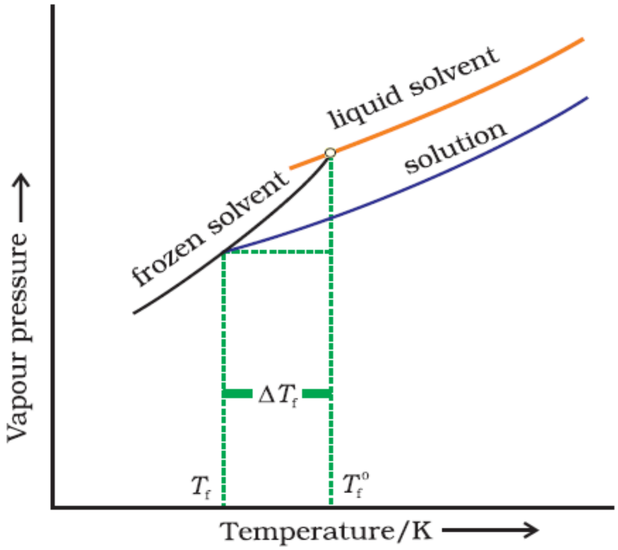
$$M_B = K_b \cdot \frac{W_B}{W_A} \times \frac{1000}{\Delta T_b}$$

where $W_B$ and $W_A$ = mass of solute and solvent respectively.
$K_b$ has units of K / m or K kg mol$^{-1}$, for water, $K_b$ = 0.52 K kg mol$^{-1}$
The boiling point elevation of a solution is determined by
(i) Landsberger's method
(ii) Cottrell's method

## LECTURE-6

**Depression in Freezing Point** ($\Delta T_f$):

The freezing point of a liquid is the temperature at which the vapour pressure of the solvent in its liquid and solid phase become equal. As we know that the vapour pressure of a solution containing non-volatile solute is lower than that of pure solvent, the solid form gets separated at a lower temperature as shown in the figure.



This decrease in the freezing point of a liquid is known as depression in the freezing point.
Depression in freezing point ($\Delta T_f$) = $T^\circ_f - T_f$

$$\Delta T_f = K_f \cdot m = K_f \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

To find molecular mass of solute,

$$M_B = \frac{K_f \cdot W_B \times 1000}{\Delta T_f \cdot W_A}$$

where $K_f$ is molal depression constant or cryoscopic constant.

$K_f$ has units of K / m or K kg $mol^{-1}$.

Ethylene glycol is usually added to water in the radiator to lower its freezing point. It is called an antifreeze solution.

[Common salt (NaCI) and anhydrous CaC12 are used to clear snow on the roads because they depress the freezing point of water. The freezing point depression is determined by the Beckmann method or Rast method.]

Calculations of molal elevation constant ($K_b$) and molal depression constant ($K_f$)

$$K_b = \frac{M_A R(T_b^\circ)^2}{\Delta H_v}, K_f = \frac{M_A \cdot R(T_f^\circ)^2}{\Delta H_f}$$

$T_b^\circ$ = boiling point of solvent

$T_f^\circ$ = freezing point of solvent

$\Delta H_f$ = molar enthalpy of fusion

$\Delta H_v$ = molar enthalpy of vaporisation

**<u>Osmotic Pressure</u>** **(π):**

**Osmosis** is the phenomenon of the spontaneous flow of the solvent molecules through a semipermeable membrane from pure solvent to the solution or from a dilute solution to a concentrated solution. It was first observed by Abbe Nollet.

Some natural semipermeable membranes are animal bladder, cell membrane, etc.

$CU_2[Fe(CN)_6]$is an artificial semipermeable membrane which does not work in non-aqueous solutions as it dissolves in them.

Osmosis maybe

**(i) Exosmosis**:

It is the outward flow of water or solvent from a cell through a semipermeable membrane.

**(ii) Endosmosis**: It is an inward flow of water or solvent from a cell through a semipermeable membrane.

The hydrostatic pressure developed on the solution which just prevents the osmosis of pure solvent into the solution through a semipermeable membrane is called **osmotic pressure.**

$$\text{Osmotic pressure } (\pi) = RCT; \left(C = \frac{n_B}{V} = \frac{W_B}{M_B V}\right)$$

$$M_B = \frac{W_B RT}{\pi V}$$

$$\pi = \frac{dRT}{M_B}; \left(d = \frac{W_B}{V}\right)$$

where, d = density, R = solution constant,
T = temperature, $M_B$ = molar mass of solute
Based on osmotic pressure, -the solution can be

**(i) Hypertonic solution:**

A solution is called hypertonic if its osmotic pressure is higher than that of the solution from which it is separated by a semipermeable membrane. When a plant cell is placed in a hypertonic solution, the fluid from the plant cell comes out and the cell shrinks, this phenomenon is called plasmolysis.

**(ii) Hypotonic solution:**

A solution is called hypotonic if its osmotic pressure is lower than that of the solution from which it is separated by a semipermeable membrane.

**(iii) Isotonic solution:**

Two solutions are called isotonic if they exert the same osmotic pressure. These solutions have the same molar concentration. 0.91% solution of pure NaCl is isotonic with human RBCs. Two solutions are isotonic if they have the same molar concentration, e.g., if x % solution of X is isotonic with y % solution of Y, this means the molar concentration of X = Molar concentration of Y

$$\frac{x}{100} \times \frac{1000}{M_X} = \frac{y \times 1000}{100 \times M_Y} \Rightarrow \frac{x}{M_X} = \frac{y}{M_Y}$$

The osmotic pressure method is the best method for determining the molecular masses of polymers since the observed value of any other colligative property is too small to be measured with reasonable accuracy.

**Reverse osmosis** When the external pressure applied to the solution is more than osmotic pressure, the solvent flows from the solution to the pure solvent, which is called reverse osmosis. The desalination of seawater is done by reverse Osmosis.

## LECTURE-7

### Abnormal Molecular Masses:

In some cases, observed colligative properties deviate from their normal calculated values due to association or dissociation of molecules. As we know,
Colligative property $\propto 1 / M_B$
lienee, higher and lower values of molar mass is observed in case of association and dissociation respectively, e.g., in benzene, acetic acid gets associated, so, its observed molecular mass is 120. Similarly, KCl undergoes dissociation in aqueous solution, so its observed molecular mass is 37.25.
These observed values are corrected by multiplying with van Hoff factor (i).

## Van’t Hoff Factor (i)

It is the ratio of the observed value of colligative property to the calculated value of the colligative property.

i = observed value of the colligative property / calculated value of colligative property

or i = normal molecular mass / observed molecular mass

or i = number of particles after association or dissociation/number of particles initially

So to correct the observed value of molar mass, Van’t Hoff factor (i) must be included in different expressions for colligative properties.

$$\Delta T_b = i\,K_b \cdot m$$
$$\Delta T_f = iK_f \cdot m$$
$$\pi = i\,CRT$$
$$\frac{\Delta p}{p_A^\circ} = ix_B$$

## Degree of Dissociation (α) and van’t Hoff Factor (i):

(i) If one molecule of a substance gets dissociated into n particles or molecules and α is the degree of dissociation then

| | $A \longrightarrow$ | $nP$ |
|---|---|---|
| Initially | 1 mol | 0 |
| At eq. | $1-\alpha$ | $n\alpha$ |

Total number of moles at equilibrium

$$= 1 - \alpha + n\alpha$$

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

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

## Degree of Association (α) and van’t Hoff Factor (i):

If n molecules of a substance ‘A’ associate to form $A_n$ and α are the degree of association then

| | $nA$ | $\longrightarrow$ | $A_n$ |
|---|---|---|---|
| Initially | 1 mol | | 0 |
| At equilibrium | $1 - \alpha$ | | $\frac{\alpha}{n}$ |

**Total number of moles at equilibrium**

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

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

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

van’t Hoff factor (i) > 1 for solutes undergoing dissociation and it is < 1 for solutes undergoing association.