## Solution \& Colligative Properties

## Solution

A homogeneous mixture of two or more pure substances whose composition may be altered within certain limits is termed as solution.

### 1.1 Characteristics of Solution

(i) It is homogeneous in nature, yet retaining the properties of its constituents.
(ii) It is made of two parts i.e. a solute and a solvent.
(iii) The component which has the same physical state in pure form as the solution is called solvent and the other is called solute. Example, in case of solution of sugar and water, sugar is the solute and water is solvent.
(iv) If both the components have same state as the solution, the one component which is in excess is called solvent and the other is called solute. Example, alcohol in water, benzene in toluene etc.

### 1.2 Types of Solution

|  | Solvent |  | Solute |
| :--- | :--- | :--- | :--- |
| 1. | Gas |  | Examples |
| 2. | Gas |  | Mixture of gases, air. |
| 3. | Gas | Liquid | Water vapour In air, mist. |
| 4. | Lquid | Gas | Sublimation of a solid Into a gas, smoke storms. |
| 5. | Lquid |  | Liquid |
| 6. | Mixture of miscible liquids e.g. alcohol in water. |  |  |
| 7. | Lquid | Solid | Salt in water, sugar in water. |

### 1.3 Cause of Miscibility of Liquids

(I) Chemically alike liquids dissolve in one another. e.g. all alkanes are miscible in all proportions with one another because they are non-polar. Similarly polar liquid dissolves in each other; e.g. lower alcohol in water.
(II) Dipole interactions i.e. water and ether, water and phenol.
(III) Molecular size of liquids which are mutually soluble are also approximately same.
2. SOLUBILITY

The maximum amount of a solute that can be dissolved in 100 g of solvent at a given temperature (usually $25^{\circ} \mathrm{C}$ ) is known its solubility at that temperature.

Solubility $=\frac{\text { Amount of substnace dissolved }}{\text { Amount of solvent }} \times 100$
The solubility of a solute in a liquid depends upon the following factors
(a) Nature of the solute i.e. ionic or covalent (polar or non-polar).
(b) Nature of the solvent i.e. polar with high dielectric constant or non-polar.
(c) Temperature - Usually the solubility of the solute increases with increase of temperature (e.g. $\mathrm{KNO}_{3}$, $\mathrm{NH}_{4} \mathrm{Br}$ ) but in some cases increase in solubility is negligible (e.g. NaCl ) and in cases of some salts (e.g. $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and $\mathrm{CeSO}_{4}$ solubility decreases with increase in temperature).
3. Methods of Expressing the Concentration of a Solution

There are many ways of expressing the concentration of a solution. These methods are as follows -
(i) Mass percentage -

It may be defined as the number of parts by mass of solute per hundred parts by mass of solution. For example. a $5 \%$ (by mass) solution of sugar in water means that 100 g of solution contain 5 g of sugar.
(ii) Volume percentage -

It may be difined as the number of parts by volume of solute per hundred parts by volume of solution. For example. a $25 \%$ (by volume) solution of ethyl alcohol means that $100 \mathrm{~cm}^{3}$. of the solution contain $25 \mathrm{~cm}^{3}$ of ethyl alcohol and $75 \mathrm{~cm}^{3}$ of water.
(iii) Normality -

Normality of a solution is defined as the number of gram equivalent of the solute dissolved per litre of the solution. It is represented by N. Mathematically.
Normality $N=\frac{\text { Mass of solute in grams per litre }}{\text { Equivalentmass of the solute }}$
A solution having normality equal to one is called "normal solution". Such a solution contains one gram equivalent of solute per litre of solution. A seminormal solution contains $\frac{1}{2}$ gram equivalent. A decinormal
solution contains $\frac{1}{10}$ gram equivalent and a centinormal solution contains $\frac{1}{100}$ gram equivalent of solute per litre of solution.
or Normality $=\frac{\text { Mass of the solution } \times 1000}{\text { Equivalent mass of the solute } \times \mathrm{V}}$
Where V is the volume in millilitre.
(iv) Molarity (M) -

Molarity of a solution is defined as the number of gm moles of the solute dissolved per litre of the solution. It is represented by capital M. Mathematically.
Molarity $(M)=\frac{\text { Mass of the solution in grams per litre }}{\text { Molecular mass of the solute }}$
A solution having molarity "one" is called molar solution. It may be remembered that both normality as well as molarity of a solution changes with change in temperature.
(v) Molality (m) -

Molality of a solution may be defmed as the number of gm moles of the solute dissolved in $1000 \mathrm{gm}(1 \mathrm{~kg})$ of the solvent. It is represented by small ' $m$ '. Mathematically

Molality $(m)=\frac{\text { Mass of the solution in grams per } \mathrm{kg} \text { of solvent }}{\text { Molecular mass of the solute }}$
A solution containg one mole of solute per 1000 gm of solvent ( 1 kg ) has molality equal to one and is called molal solution. Molality is expressed in units of moles per kilogram ( $\mathrm{mol} \mathrm{kg}^{-1}$ ). The molality of a solution does not change with temperature.
(vi) Mole fraction -

Mole fraction may be defined as the ratio of the number of moles of one component to the total number of moles of all the components (i.e. solute and solvent) present in the solution.
Let us suppose that a solution contains the components $A$ and $B$ and suppose that a gram of $A$ and $b$ gram of $B$ are present in it. Let the molecular masses of $A$ and $B$ are $M_{A}$ and $M_{B}$ respectively.

Then number of moles of $A$ are given by $n_{A}=\frac{a}{M_{A}}$
and number of moles of $B$ are given by $n_{B}=\frac{b}{M_{B}}$
Total number of moles of $A$ and $B=n_{A}+n_{B}$
Mole fraction of $A, X_{A}=\frac{n_{A}}{n_{A}+n_{B}}$
Mole fraction of $B, X_{B}=\frac{n_{b}}{n_{A}+n_{B}}$
Sum of mole fractions of all components is always one.

$$
\text { i.e. } X_{A}+X_{B}=\frac{n_{A}}{n_{A}+n_{B}}+\frac{n_{B}}{n_{A}+n_{B}}=1
$$

So if mole fraction of one component of a binary solution is known say $X_{B}$. then the mole fraction of $X_{A}=1-X_{B}$.
It may be noted that the mole fraction is always independent of the temperature.
(vii) Mole percent -

Mole percent is the number of moles of a component in 100 mole of the solute and solvent.
Mole percent $=$ Mole fraction x 100
Example. for a solution containing 8 moles $\mathrm{NH}_{3}$ and 12 moles of $\mathrm{H}_{2} \mathrm{O}$.
Mole fraction of $\mathrm{NH}_{3}, \mathrm{X}_{\mathrm{NH}_{3}}=\frac{8 \text { mole }}{12 \text { moles }+8 \text { moles }}=\frac{2}{5}$
Mole percent of $\mathrm{NH}_{3}=\frac{2}{5} \times 100=40$ mole $\%$
(viii) Formality (F) -

It may be defined as the number of gram formula masses of the ionic solutes dissolved per litre of the solution. Mathematically
Formality $(F)=\frac{\text { Mass of the ionic solute in gram per litre }}{\text { Formula mass of the solution }}$
Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecule but as network of ions.
(ix) Mass fraction -

If $W_{A}$ is the mass of component $A$ and $W_{B}$ the mass of component $B$ in the solution, then the mass fraction of component $A$ and $B$ is Wlitten as
Mass fraction of $A=\frac{W_{A}}{W_{A}+W_{B}}$
Mass fraction of $B=\frac{W_{B}}{W_{A}+W_{B}}$
(x) Parts per million (ppm) -

When a solute is present in trace amounts, its concentration is expressed in parts per million. It may be defined as the number of parts by mass oj solute per million parts by mass oj the solution.

$$
\text { Parts per million }(\mathrm{ppm})=\frac{\text { Mass of solute }}{\text { Mass of solution }} \times 10^{6}
$$

## 4. Vapour Pressure

The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called vapour pressure of the liquid.

### 4.1 Vapour Pressure of Solutions and Raoult's Law

When a small amount of a non-volatile solute is added to the liquid (solvent). it is found that the vapour pressure of the solution is less than that of the pure solvent. This is due to the fact that the solute particles occupy a certain surface area and as the evaporation is to take place from the surface only. the particles of the solvent will have a less tendency to change into vapour i.e. the vapour pressure of the solution will be less than that of the pure solvent and it is termed as lowering of vapour pressure.
The vapour pressure of the solutions of non-volatile solutes can be obtained by applying Raoult's law.
According to this law. the vapour pressure of a solution containing non-volatUe solute is proportional to mole fraction of the solvent.
For a two component solution A (volatile) and B (non-volatile) the vapour pressure of solution is given by Vapour pressure of solution $=$ Vapour pressure of solvent in solution $\propto$ Mole fraction of solvent.
$P=P_{A} \propto X_{A}$
or $P_{A}=K X_{A}$
Where K is proportionality constant.
For pure liquid $X_{A}=1$. then $K$ becomes equal to the vapour pressure of the pure solvent which is denoted by $\mathrm{P}_{\mathrm{A}}$.

$$
\text { Thus } P_{A}=P_{A}^{0} X_{A}
$$

or $P_{\text {solution }}=P_{\text {pure solvent }} \times$ mole fraction of solvent
In a solution of two miscible non-volatile liquids. $A$ and $B$ the partial vapour pressure $P_{A}$ of the liquid $A$ is proportional to its mole fraction $X_{A}$ and the partial vapour pressure $P_{B}$ of liquid $B$ is proportional to its mole fraction $X_{B}$.
Thus $\quad \mathrm{P}_{\mathrm{A}} \propto \mathrm{X}_{\mathrm{A}}$
$P_{A}=P_{A}{ }_{A} X_{A}$
Also $\quad P_{B} \propto X_{B}$
$P_{B}=P_{B}^{0} X_{B}$
Where $\mathrm{P}_{\mathrm{A}}^{\circ}$ and $\mathrm{A}_{\mathrm{B}}^{0}$ are the vapour pressures of pure components A and B respectively.
This relation is called Raoult's law. It states that "For a solution of two or more miscible liquids, the partial vapour pressure of each component is directly proportional to its mole fraction".
Total vapour pressure of solution $\mathrm{P}=\mathrm{P}_{\mathrm{A}}^{0} \mathrm{X}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}} \mathrm{X}_{B}$
The solutions which obey Raoult's law are called Ideal solutions. For such solution, vapour pressure of the solution always lies between the vapour pressure of the pure components. Raoult's law is applicable only in case of dilute solutions.

### 4.2 Relative Lowering of Vapour Pressure

For a solution of non-volatile solute with volatile solvent.
$P=P_{A} \propto X_{A} \quad P=$ vapour pressure of solution
$P_{A}=P_{A}^{0} X_{A} \quad P_{A}=$ vapour pressure of solvent
If mole fraction of solute is $X_{B}$, then $X_{A}=$ mole fraction of solvent and $P_{A}^{\circ}=$ vapour pressure of pure solvent.

$$
\begin{aligned}
& X_{A}+X_{B}=1 \text { or } X_{A}=1-X_{B}^{\circ} \quad \text { or } \\
& P_{A}=P_{A}^{o}\left(1-X_{B}\right)=P_{A}^{0}-P_{A}^{o}-P_{A}^{o} X_{B} \\
\text { or } & P_{A}^{\circ}-P_{A}=P_{A}^{\circ} X_{B} \quad \text { or } \quad X_{B}=\frac{P_{A}^{o}-P_{A}}{P_{A}^{0}}
\end{aligned}
$$

$\left(P_{A}^{o}-P_{A}\right)$ is the lowering of vapour pressure whereas $\left(\frac{P_{A}^{o}-P_{A}}{P_{A}^{0}}\right)$ is called relative lowering of
vapour pressure. So Raoult's law can also be defined as "For a solution containing non-volatile solute, at a particular temperature. the relative lowering of vapour pressure is equal to mole fraction of the solute".

### 4.3 Ideal Solutions

An ideal solution may be defined as the solution which obeys Raoult's law over the entire range of concentration and temperature and during the formation of which no change in enthalpy or volume takes place. So for ideal solutions
(i) It should obey Raoult's law.
i.e. $P_{A}=P_{A}^{0} X_{A}$ and $P_{B}=P_{B}^{0} X_{B}$
(ii) $\Delta \mathrm{H}_{\text {mixture }}=0$
(iii) $\Delta V_{\text {mixture }}=0$

There is no solution which behaves strictly as the ideal solution. However. the solution in which solvent solvent and solute-solute interactions are almost of the same type as solvent-solute interactions. behaves as ideal solutions. Example.
(a) n-heptane and n-hexane
(b) Chlorobenzene and bromobenzene
(c) Benzene and toluene
(d) Ethyl bromide and ethyl iodide

Only very dilute solutions behave as ideal solutions.
4.4 Non-ideal Solutions

For a non-ideal solutions, the conditions are
(i) Raoult's law is not obeyed

$$
\text { i.e. } P_{A} \neq P_{A}^{0} X_{A} \text { and } P_{B} \neq P_{B}^{o} X_{B}
$$

(ii) $\Delta \mathrm{H}_{\text {mixture }} \neq 0$
(iii) $\Delta \mathrm{V}_{\text {mixture }} \neq 0$

The non-ideal solutions are further classified into two catagories
(a) Solutions with positive deviation and
(b) Solutions with negative deviation.
4.5 Solution with positive deviation : - It has the following characteristics
(i) Solution in which solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions.
(ii) At intermediate composition vapour pressure of the solution is maximum.
(iii) At intermediate composition boiling point is minimum.

So for the non-ideal solutions exhibiting positive deviations
(i) $P_{A}>P_{A}^{\circ} X_{A}$ and $P_{B}>P_{B}^{\circ} X_{B}$
(ii) $\Delta \mathrm{H}_{\text {mixture }}=+\mathrm{ve}$
(iii) $\Delta V_{\text {mixture }}=+$ ve
4.6 Azeotrope or azeotropic mixture - A solution which distills without change in composition is called azeotropic mixture or azeotrope.
Example of positive deviation - A mixture of nhexane and ethanoL
4.7 Solution with negative deviation - It has the following characteristics
(i) Solutions in which solvent-solvent and solutesolute interactions are weaker than solute-solvent interactions.
(ii) At intermediate composition vapour pressure of the solution is minimum.
(iii) At intermediate composition boiling point is maximum.

So for non-ideal solutions exhibiting negative deviations
(i) $\mathrm{P}_{\mathrm{A}}<\mathrm{P}_{\mathrm{A}}{ }^{\circ} \mathrm{X}_{\mathrm{A}}$ and $\mathrm{P}_{\mathrm{B}}<\mathrm{P}_{\mathrm{B}}^{\circ} \mathrm{X}_{\mathrm{B}}$ (ii) $\Delta \mathrm{H}_{\text {mixture }}=-\mathrm{ve}$
(iii) $\Delta V_{\text {mixture }}=-\mathrm{ve}$
5. Colligative Properties

The properties of dilute solutions containing nonvolatile solute, which depends upon relative number of solute and solvent particles but do not depend upon their nature are called colligative properties. Some of the colligative properties are
(i) Relative lowering of vapour pressure:
(ii) Elevation of boiling point;
(iii) Depression of freezing point; and'
(iv) Osmotic pressure.

### 5.1 Relative Lowering of Vapour Pressure

As shown earlier the mathematical expression for relative lowering of vapour pressure is as follows
$\frac{\Delta \mathrm{P}}{\mathrm{P}_{\mathrm{A}}^{0}}=\mathrm{X}_{\mathrm{B}}=$ mole fraction of solute
$\Delta \mathrm{P}=\mathrm{P}_{\mathrm{A}}^{0}-\mathrm{P}_{\mathrm{A}}=$ lowering of vapour pressure
$P_{A}=$ vapour pressure of pure solvent
Molecular mass of non-volatile substance can be determined from relative lowering of vapour pressure
$\frac{\mathrm{P}_{\mathrm{A}}^{0}-\mathrm{P}}{\mathrm{P}_{\mathrm{A}}^{0}}=\frac{\mathrm{W}_{\mathrm{B}} / \mathrm{M}_{\mathrm{B}}}{\mathrm{W}_{\mathrm{A}} / \mathrm{M}_{\mathrm{A}}+\mathrm{W}_{\mathrm{B}} / \mathrm{M}_{\mathrm{B}}}$
For dilute solution $W_{B} / M_{B}<W_{A} / M_{A}$ and hence $W_{B} / M_{B}$ may be neglected in the denominator. So

$$
\begin{aligned}
& \quad \frac{\mathrm{P}_{\mathrm{a}}^{\mathrm{o}}-\mathrm{P}_{\mathrm{A}}}{\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}}=\frac{\mathrm{W}_{\mathrm{B}} / \mathrm{M}_{\mathrm{B}}}{\mathrm{~W}_{\mathrm{A}} / \mathrm{M}_{\mathrm{A}}}=\frac{\mathrm{W}_{\mathrm{B}}}{\mathrm{~W}_{\mathrm{A}}} \times \frac{\mathrm{M}_{\mathrm{A}}}{\mathrm{M}_{\mathrm{B}}} \\
& \text { or } \mathrm{M}_{\mathrm{B}}=\frac{\mathrm{W}_{\mathrm{B}} / \mathrm{M}_{\mathrm{A}}}{\mathrm{~W}_{\mathrm{A}}}\left(\frac{\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}}{\mathrm{P}_{\mathrm{A}}^{0}-\mathrm{P}_{\mathrm{A}}}\right)
\end{aligned}
$$

### 5.2 Elevation of Boiling Point

The boiling points elevates when a non-volatile solute is added to a volatile solvent. Which occurs due to lowering of vapour pressure.
The boiling point of a liquid may be defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure.
So when a non-volatile solute is added to a volatile solvent results lowering of vapour pressure and consequent elevation of boiling point

$$
\begin{array}{ll}
\Delta T_{b} \propto \Delta P \propto X_{B} ; & \Delta T_{b}=\text { elevation in B.P. } \\
\text { or } \Delta T_{b}=K X_{B} & \Delta P=\text { lowering of V.P. } \\
& X_{B}=\text { mole fraction of solute } \\
& K=\text { elevation constant } \\
\text { or } \Delta T_{b}=K \frac{W_{B}}{M_{B}} \times \frac{M_{A}}{W_{A}}=K \frac{n_{B}}{W_{A}} \times M_{A}
\end{array}
$$

If $W_{A}$ is the weight of solvent in kg . then $\frac{\mathrm{n}_{\mathrm{B}}}{W_{A}}$ is equal to molality $(\mathrm{m})$ of the solution.

$$
\Delta T_{b}=K M_{A} m \text { or } \Delta T_{b}=K_{b} m
$$

Where $\mathrm{K}_{\mathrm{b}}$ is molal elevation constant or molal ebullioscopic constant.
When molality of the solution is equal to one. then

$$
\Delta \mathrm{T}_{\mathrm{b}}=\mathrm{K}_{\mathrm{b}}
$$

Hence molal elevation constant of the solvent may be defined as the elevation in its boiling point when one mole of non-volatile solute is dissolved per $\mathrm{kg}(1000 \mathrm{gm})$ of solvent. The unit of $\mathrm{K}_{\mathrm{b}}$ are $\mathrm{K} \mathrm{kg} \mathrm{mol}^{-1}$.
Because molality of solution $m=\frac{W_{B}}{M_{B}} \cdot \frac{1000}{W_{A}}$
So $\Delta T_{b}=K_{b} \frac{W_{B}}{M_{B}} \cdot \frac{1000}{W_{A}} \quad M_{B}=\frac{1000 \times K_{b} \times W_{B}}{\Delta T_{b} \times W_{A}}$
When the volume is taken as 1000 ml ., then elevation in boiling point is known as molar elevation constant.

### 5.3 Depression in Freezing Point

The freezing point of a pure liquid is fixed. If a non-volatile solute is dissolved in a liquid the freezing point of the solution is lowered. The freezing point is that temperature at which the solvent has the same vapour pressure in two phases. liquid solution and solid solvent. Since the solvent vapour pressure in solution is depressed. its vapour pressure will become equal to that of the solid solvent at a lower temperature So $\Delta T_{f} \propto \Delta P \propto X_{B}$
or $\Delta T_{f}=K X_{B}=K \frac{n_{B}}{n_{A}+n_{B}}=K \frac{W_{B} / M_{B}}{W_{A} / M_{A}+W_{B} / M_{B}}$
For dilute solution $\frac{W_{B}}{M_{B}}<\frac{W_{A}}{M_{A}}$ and hence $\frac{W_{B}}{M_{B}}$ can be neglected in the denominator So.

$$
\Delta T_{f}=K \frac{W_{B} / M_{B}}{W_{A} / M_{A}}=K \frac{n_{B} \times M_{A}}{W_{A}}
$$

If $W_{A}$ is the mass of solvent in kg . then $\frac{n_{B}}{W_{A}}$ is equal to molality $(m)$ of the solution.
$\Delta T_{f}=K M_{A} m$ or $\Delta T_{f}=K_{f} m\left(K \times M_{A}=K_{f}\right)$
Where $K_{f}$ is molal depression constant. When molarity $(m)$ of the solution is one. then $\Delta T_{f}=K_{f}$
Hence molal depression constant or molal cryoscopic constant may be defined as "the depression in freezing point when one mole of non-volatile solute is dissolved per kilogram ( 1000 gm ) of solvent" and molar depression constant is defined as "the depression in freezing point when one mole of non-volatile solute is dissolved per litre ( 1000 ml ) of solvent."
The molecular mass of the non-volatile solute may be calculated by the use of following mathematical equation

$$
M B=\frac{K_{f} \times W_{B} \times 1000}{W_{A} \times \Delta T_{f}}
$$

| Solvent | B.P. | $\mathbf{K}_{\mathbf{b}}$ | F.P. | $\mathbf{K}_{\mathbf{f}}$ |
| :--- | :--- | :--- | :--- | :--- |
| Acetic acid | $118.1^{\circ} \mathrm{C}$ | 2.93 | $17^{\circ} \mathrm{C}$ | 3.9 |
| Benzene | $80.2^{\circ} \mathrm{C}$ | 2.53 | $5.4^{\circ} \mathrm{C}$ | 5.13 |
| Water | $100^{\circ} \mathrm{C}$ | 0.53 | $0^{\circ} \mathrm{C}$ | 1.86 |

5.4 Antifreeze solutions -

Water is used in radiators of vehicles as cooling liquid. If the vehicle is to be used at high altitudes where temperature is sub-zero. water would freeze in radiators. To avoid this problem. a solution of ethylene glycol in water is used in radiators which will lower the freezing point lower than zero.
The molar mass of ethylene glycol required per kilogram of solvent is calculated by the following formula

$$
\begin{aligned}
& \mathrm{M}=\frac{-\Delta \mathrm{T}_{\mathrm{f}}}{\mathrm{~K}_{\mathrm{r}}} \mathrm{~K}_{\mathrm{r}} \text { (water) }=1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1} \\
& \Delta \mathrm{~T}_{\mathrm{f}}=\text { depression of freezing point }
\end{aligned}
$$

6. Osmotic Pressure

When a solution is separated from the pure solvent with the help of a semipermeable membrane. there occurs the flow of solvent molecules from the pure solvent to the solution side. The flow of solvent molecules from a region of higher concentration of solvent to the region of lower concentration of solvent is termed as the phenomenon of osmosis. This also happens when two solution of different concentrations are separated by a semipermeable membrane.
As a result of osmosis a pressure is developed which is termed as osmotic pressure. It is defined in various methods.
(1) The excess hydrostatic pressure which builds up as a result of osmosis is called osmotic pressure.
(2) The excess pressure that must be applied to the solution side to prevent the passage of solvent into it through a semipermeable membrane.
(3) Osmotic pressure of a solution is equal to the negative pressure which must be applied to the solvent in order to just stop the osmosis.
(4) The osmotic pressure of a solution may be defined as the extra pressure which should be applied to the solution to increase the 'chemical potential of solvent in solution equal to the chemical poteatial of the pure solvent at the same temperature.

## 7. Isotonic solution -

The two solutions having equal osmotic pressure are termed as isotonic solution.
Hypertonic solution -
A solution having higher osmotic pressure than some' other solution is said to be called hypertonic solution.

## Hypotonic solution -

A solution having a lower osmotic pressure relative to some other solution is called hypotonic solution.
Semipermeable Membrane
A membrane which allows the passage of solvent molecules but not that of solute. when a solution is separated from the solvent by it is known as semipermeable membrane.
Some example of it are as follows
(a) Copper ferrocyanide $\mathrm{Cu}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$;
(b) Calcium phosphate membrane; and
(c) Phenol saturated with water.
8. Theory of Dilute Solutions

The osmotic pressure of a dilute solution was the same as the solute would have exerted if it were a gas at the same temperature as of the solution and occupied a volume equal to that of the solution. This generalization is known as Van't Hoff theory of dilute solutions.
The osmotic pressure is a colligative property. So the osmotic pressure is related to the number of moles of the solute by the following relation
$\pi \mathrm{V}=\mathrm{nR} T$
$\pi=\frac{\mathrm{n}}{\mathrm{V}} \mathrm{RT} \quad\left(\therefore \frac{\mathrm{n}}{\mathrm{V}}=\mathrm{C}\right)$
$\pi=\mathrm{CRT}$
Here $C=$ concentration of solution in moles per litre;
$\mathrm{R}=$ solution constant;
$\mathrm{T}=$ temperature in Kelvin degree;
$\mathrm{n}=$ number of moles of solute; and
$\mathrm{V}=$ volume of solution.
Equation A is called Van't Hoff's solution equation.
8.1 Van't Hoff-Boyle's law - if the temperature remaining constant the osmotic pressure of the solution is directly proportional to the molar concentration of the solute. ie.
$\pi \propto C \quad$ (T constant)
or $\pi \propto \frac{\mathrm{n}}{\mathrm{V}} \quad$ (T constant)
For a solution containing same amount at different volume. we will have $\pi \propto \frac{1}{\mathrm{~V}}$ (T constant)
i.e. osmotic pressure is inversely proportional to the volume.
8.2 Van't Hoff-Charle's law - At constant volume. the osmotic pressure of a solution is directly proportional to its absolute temperature. i.e.
$\pi \propto \mathrm{T}$ (C constant)
Berkeley and Hartley's method is used to determine the osmotic pressure.
8.3 Determination of molecular mass from. osmotic pressure - The molecular mass of a substance i.e. solute can be calculated by applying the following formula

$$
\mathrm{M}=\frac{\mathrm{WRT}}{\pi \mathrm{~V}}
$$

Accurate molecular mass will only be obtained under following conditions
(i) The solute must be non-volatile;
(ii) The solution must be dilute; and
(iii) The solute should not undergo dissociation or association in the solution.

Solution constant $R$ - The solution constant $R$ has the same significance and value as the gas canstant. i.e.
$\mathrm{R}=0.0821$ litre-atm $\mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$=8.314 \times 10^{-7} \mathrm{erg} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$
$=8.314 \mathrm{Nm} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$

Abnormal molecular masses - When the substances undergo dissociation or association in solution then the value of observed colligative property and value of calculate calligative property are quite different. As the dissociation and association cause changes in the number of particles as compared to usual condition.

### 8.4 Van't Hoff Factor

In 1886, Van't Hoff introduced a factor i called Van't Hoff joctor to express the extent of association or dissociation of solute in solution.

Van't Hoff factor $\mathrm{i}=\frac{\text { Normal molecular mass }}{\text { Observed molecular mass }}$
In case of association, observed molecular mass being more than the normal the factor $i$ has a value less than 1. But in case of dissociation, the Van't Hoff factor is more than 1 because the observed molecular mass has a lesser magnitude. In case there is no association or dissociation the value i becomes equal to 1. Therefore
$i=\frac{\text { Observed value of colligative property }}{\text { Calculated value of colligative property }}$
Introduction of the Van't Hoff factor modifies the equations for the colligative properties as follows
Elevation of B.P. $\Delta \mathrm{T}_{\mathrm{b}}=\mathrm{i} \mathrm{K}_{\mathrm{b}} \mathrm{m}$
Depression of F.P. $\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{iK} \mathrm{K}_{\mathrm{f}} \mathrm{m}$
Osmotic pressure $\mathrm{p}=\frac{\mathrm{inRT}}{\mathrm{V}}$
From the value of'[ it is possible to calculate degree of dissociation or degree of association of substance in solution by the following formula
$i=\frac{(1-\alpha)+m \alpha}{1}=1+(m-1) \alpha$
So $\alpha=\frac{i-1}{(m-1)}$
Where $\alpha$ is the degree of disSociation and $m$ is the number of particles per molecule.
Similarly degree of association is calculated from ' $i$ ' by the following mathematical formula
$\alpha=\frac{i-1}{1 /(m-1)}$
The ratio ofVan't Hoff factor ,i to the number of ions furnished by. one molecule of the electrolyte! ' $n$ ' is known as the osmotic coefficient. It is denoted by g. Mathematically

Osmotic coefficient ' $g$ ' $=\frac{\text { Van't Hoff factor ' } \mathrm{i} \text { ' }}{\text { ' } n \text { ' }}$
(.) (.) (๑)

