

Chapter 4

Solution & Colligative properties

"A solution is a mixture in which substances are intermixed so intimately that they can not be observed as separate components". The dispersed phase or the substance which is to be dissolved is called **solute**, while the dispersion medium in which the solute is dispersed to get a homogenous mixture is called the **solvent**.

Solubility

"Solubility of a substance may be defined as the amount of solute dissolved in 100gms of a solvent to form a saturated solution at a given temperature". A **saturated solution** is a solution which contains at a given temperature as much solute as it can hold in presence of dissolving solvent. Any solution may contain less solute than would be necessary to saturate it. Such a solution is known as **unsaturated solution**. When the solution contains more solute than would be necessary to saturate it then it is termed as **supersaturated solution**.

Kinds of solutions

All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Depending on the state of solute or solvent, mainly there may be following nine types of binary solutions.

Solvent	Solute	Example
Gas	Gas	Mixture of gases, air.
Gas	Liquid	Water vapours in air, mist.
Gas	Solid	Sublimation of a solid into a gas, smoke.
Liquid	Gas	CO ₂ gas dissolved in water (aerated drinks).
Liquid	Liquid	Mixture of miscible liquids, e.g., alcohol in water.
Liquid	Solid	Salt in water, sugar in water.
Solid	Gas	Adsorption of gases over metals; hydrogen over palladium.
Solid	Liquid	Mercury in zinc, mercury in gold, CuSO ₄ ·5H ₂ O.
Solid	Solid	Homogeneous mixture of two or more metals (alloys), e.g., copper in gold, zinc in copper.

Among these solutions the most significant type of solutions are those which are in liquid phase and may be categorised as, (1) Solid in liquid solutions, (2) Liquid in liquid solutions and (3) Gas in liquid solutions.

Methods of expressing concentration of solution

Concentration of solution is the amount of solute dissolved in a known amount of the solvent or solution. The concentration of solution can be expressed in various ways as discussed below,

(i) **Percentage** : It refers to the amount of the solute per 100 parts of the solution. It can also be called as parts per hundred (*pph*). It can be expressed by any of following four methods,

(i) **Weight to weight percent**

$$\% \text{ w/w} = \frac{\text{Wt. of solute}}{\text{Wt. of solution}} \times 100$$

Example : 10% Na₂CO₃ solution w/w means 10g of Na₂CO₃ is dissolved in 100g of the solution. (It means 10g Na₂CO₃ is dissolved in 90g of H₂O)

(ii) **Weight to volume percent**

$$\% \text{ w/v} = \frac{\text{Wt. of solute}}{\text{Volume of solution}} \times 100$$

Example : 10% Na₂CO₃ (w/v) means 10g Na₂CO₃ is dissolved in 100cc of solution.

(iii) **Volume to volume percent**

$$\% \text{ v/v} = \frac{\text{Vol. of solute}}{\text{Vol. of solution}} \times 100$$

Example : 10% ethanol (v/v) means 10cc of ethanol dissolved in 100cc of solution.

(iv) **Volume to weight percent**

$$\% \text{ v/w} = \frac{\text{Vol. of solute}}{\text{Wt. of solution}} \times 100$$

Example : 10% ethanol (v/w) means 10cc of ethanol dissolved in 100g of solution.

(2) **Parts per million (ppm) and parts per billion (ppb)** : When a solute is present in trace quantities, it is convenient to express the concentration in parts per million and parts per billion. It is the number of parts of solute per million (10⁶) or per billion (10⁹) parts of the solution. It is independent of the temperature.

$$\text{ppm} = \frac{\text{mass of solute component}}{\text{Total mass of solution}} \times 10^6$$

$$ppb = \frac{\text{mass of solute component}}{\text{Total mass of solution}} \times 10^9$$

(3) **Strength** : The strength of solution is defined as the amount of solute in grams present in one litre (or dm^3) of the solution. It is expressed in g/litre or (g/dm^3) .

$$\text{Strength} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$$

(4) **Normality (N)** : It is defined as the number of gram equivalents (equivalent weight in grams) of a solute present per litre of the solution. Unit of normality is gram equivalents/litre. Normality changes with temperature since it involves volume. When a solution is diluted x times, its normality also decreases by x times. Solutions in term of normality generally expressed as,

N = Normal solution; $5N$ = Penta normal,

$10N$ = Deca normal; $N/2$ = semi normal

$N/10$ = Deci normal; $N/5$ = Penti normal

$N/100$ or $0.01 N$ = centinormal,

$N/1000$ or 0.001 = millinormal

Mathematically normality can be calculated by following formulas,

$$(i) \text{ Normality (N)} = \frac{\text{Number of g.eq. of solute}}{\text{Volume of solution (l)}}$$

$$(ii) N = \frac{\text{Weight of solute in g.}}{\text{g.eq. weight of solute} \times \text{Volume of solution (l)}}$$

$$(iii) N = \frac{\text{Wt. of solute per litre of solution}}{\text{g eq. wt. of solute}}$$

$$(iv) N = \frac{\text{Wt. of solute}}{\text{g.eq. wt. of solute}} \times \frac{1000}{\text{Vol. of solution in ml}}$$

$$(v) N = \frac{\text{Percent of solute} \times 10}{\text{g eq. wt. of solute}},$$

$$(vi) N = \frac{\text{Strength in } g\ l^{-1} \text{ of solution}}{\text{g eq. wt. of solute}}$$

$$(vii) N = \frac{\text{Wt\%} \times \text{density} \times 10}{\text{Eq. wt.}}$$

(viii) If volume V_1 and normality N_1 is so changed that new normality and volume N_2 and V_2 then,

$$N_1 V_1 = N_2 V_2 \text{ (Normality equation)}$$

(ix) When two solutions of the same solute are mixed then normality of mixture (N) is

$$N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(x) Vol. of water to be added i.e., $(V_2 - V_1)$ to get a solution of normality N_2 from V_1 ml of normality N_1

$$V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2} \right) V_1$$

(xi) If W g of an acid is completely neutralised by V ml of base of normality N

$$\frac{\text{Wt. of acid}}{\text{g eq. wt. of acid}} = \frac{VN}{1000}$$

$$\text{Similarly, } \frac{\text{Wt. of base}}{\text{g eq. wt. of base}} = \frac{\text{Vol. of acid} \times N \text{ of acid}}{1000}$$

(xii) When V_a ml of acid of normality N_a is mixed with V_b ml of base of normality N_b

(a) If $V_a N_a = V_b N_b$ (Solution neutral)

(b) If $V_a N_a > V_b N_b$ (Solution is acidic)

(c) If $V_b N_b > V_a N_a$ (Solution is basic)

$$(xiii) \text{ Normality of the acidic mixture} = \frac{V_a N_a + V_b N_b}{(V_a + V_b)}$$

$$(xiv) \text{ Normality of the basic mixture} = \frac{V_b N_b + V_a N_a}{(V_a + V_b)}$$

$$(xv) N = \frac{\text{No. of meq} \times \text{of solute}}{\text{Vol. of solution in ml}}$$

(* 1 equivalent = 1000 milliequivalent or meq.)

(5) **Molarity (M)** : Molarity of a solution is the number of moles of the solute per litre of solution (or number of millimoles per ml. of solution). Unit of molarity is **mol/litre** or **mol/dm** For example, a molar (1M) solution of sugar means a solution containing 1 mole of sugar (i.e., 342 g or 6.02×10^{23} molecules of it) per litre of the solution. Solutions in term of molarity generally expressed as,

1M = Molar solution, 2M = Molarity is two,

$\frac{M}{2}$ or 0.5 M = Semimolar solution,

$\frac{M}{10}$ or 0.1 M = Decimolar solution,

$\frac{M}{100}$ or 0.01 M = Centimolar solution

$\frac{M}{1000}$ or 0.001 M = Millimolar solution

• Molarity is most common way of representing the concentration of solution.

• Molarity is depend on temperature as, $M \propto \frac{1}{T}$

• When a solution is diluted (x times), its molarity also decreases (by x times)

Mathematically molarity can be calculated by following formulas,

$$(i) M = \frac{\text{No. of moles of solute (n)}}{\text{Vol. of solution in litres}},$$

$$(ii) M = \frac{\text{Wt. of solute (in gm) per litre of solution}}{\text{Mol. wt. of solute}}$$

$$(iii) M = \frac{\text{Wt. of solute (in gm)}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{Vol. of solution in ml.}}$$

$$(iv) M = \frac{\text{No. of millimoles of solute}}{\text{Vol. of solution in ml}}$$

$$(v) M = \frac{\text{Percent of solute} \times 10}{\text{Mol. wt. of solute}}$$

$$(vi) M = \frac{\text{Strength in } gL^{-1} \text{ of solution}}{\text{Mol.wt. of solute}}$$

$$(vii) M = \frac{10 \times \text{Sp. gr. of the solution} \times \text{Wt. \% of the solute}}{\text{Mol.wt. of the solute}}$$

(viii) If molarity and volume of solution are changed from M_1, V_1 to M_2, V_2 . Then,

$$M_1 V_1 = M_2 V_2 \text{ (Molarity equation)}$$

(ix) In balanced chemical equation, if n_1 moles of reactant one react with n_2 moles of reactant two. Then,

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

(x) If two solutions of the same solute are mixed then molarity (M) of resulting solution.

$$M = \frac{M_1 V_1 + M_2 V_2}{(V_1 + V_2)}$$

(xi) Volume of water added to get a solution of molarity M_2 from V_1 ml of molarity M_1 is

$$V_2 - V_1 = \left(\frac{M_1 - M_2}{M_2} \right) V_1$$

Relation between molarity and normality

$$\text{Normality of solution} = \text{molarity} \times \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

$$\text{Normality} \times \text{equivalent mass} = \text{molarity} \times \text{molecular mass}$$

$$\text{For an acid, } \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \text{Basicity}$$

$$\text{So, Normality of acid} = \text{molarity} \times \text{basicity.}$$

$$\text{For a base, } \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \text{Acidity}$$

$$\text{So, Normality of base} = \text{Molarity} \times \text{Acidity.}$$

(6) **Molality (m)** : It is the number of moles or gram molecules of the solute per 1000 g of the solvent. Unit of molality is mol/kg . For example, a 0.2 molal (0.2m) solution of glucose means a solution obtained by dissolving 0.2 mole of glucose in 1000gm of water. *Molality (m) does not depend on temperature* since it involves measurement of weight of liquids. *Molal solutions are less concentrated than molar solution.*

Mathematically molality can be calculated by following formulas,

$$(i) m = \frac{\text{Number of moles of the solute}}{\text{Weight of the solvent in grams}} \times 1000$$

$$(ii) m = \frac{\text{Strength per 1000 grams of solvent}}{\text{Molecular mass of solute}}$$

$$(iii) m = \frac{\text{No. of gm moles of solute}}{\text{Wt. of solvent in kg}}$$

$$(iv) m = \frac{\text{Wt. of solute}}{\text{Mol.wt. of solute}} \times \frac{1000}{\text{Wt. of solvent in g}}$$

$$(v) m = \frac{\text{No. of millimoles of solute}}{\text{Wt. of solvent in g}}$$

$$(vi) m = \frac{10 \times \text{solubility}}{\text{Mol.wt. of solute}}$$

$$(vii) m = \frac{1000 \times \text{wt. \% of solute}(x)}{(100 - x) \times \text{mol. wt. of solute}}$$

$$(viii) m = \frac{1000 \times \text{Molarity}}{(1000 \times \text{sp. gravity}) - (\text{Molarity} \times \text{Mol.wt. of solute})}$$

Relation between molarity (M) and molality (m)

$$\text{Molality } (m) = \frac{\text{Molarity}}{\text{Density} - \frac{\text{Molarity} \times \text{molecular mass}}{1000}}$$

$$\text{Molarity } (M) = \frac{\text{Molality} \times \text{density}}{1 + \frac{\text{Molality} \times \text{molecular mass}}{1000}}$$

(7) **Formality (F)** : Formality of a solution may be defined as the number of gram formula masses of the ionic solute dissolved per litre of the solution. It is represented by F . Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecules but exist as network of ions. A solution containing one gram formula mass of solute per litre of the solution has formality equal to one and is called formal solution. It may be mentioned here that the *formality of a solution changes with change in temperature.*

$$\text{Formality } (F) = \frac{\text{Number of gram formula masses of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of ionic solute (g)}}{(\text{gm. formula mass of solute}) \times (\text{Volume of solution (l)})}$$

$$\text{Thus, } F = \frac{W_B(g)}{GFM \times V(l)} \quad \text{or} \quad \frac{W_B(g) \times 1000}{GFM \times V(ml)}$$

(8) **Mole fraction (X)** : Mole fraction may be defined as the ratio of number of moles of one component to the total number of moles of all the components (solvent and solute) present in the solution. It is denoted by the letter X . It may be noted that *the mole fraction is independent of the temperature. Mole fraction is dimensionless.* Let us suppose that a solution contains the components A and B and suppose that W_A g of A and W_B g of B are present in it.

$$\text{Number of moles of } A \text{ is given by, } n_A = \frac{W_A}{M_A} \text{ and}$$

$$\text{the number of moles of } B \text{ is given by, } n_B = \frac{W_B}{M_B}$$

where M_A and M_B are molecular masses of A and B respectively.

$$\text{Total number of moles of } A \text{ and } B = n_A + n_B$$

$$\text{Mole fraction of } A, X_A = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of } B, X_B = \frac{n_B}{n_A + n_B}$$

The sum of mole fractions of all the components in the solution is always one.

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1.$$

Thus, if we know the mole fraction of one component of a binary solution, the mole fraction of the other can be calculated.

Relation between molality of solution (m) and mole fraction of the solute (X).

$$X_A = \frac{m}{55.5 + m}$$

(9) **Mass fraction** : Mass fraction of a component in a solution is the mass of that component divided by the total mass of the solution. For a solution containing $w_A \text{ gm}$ of A and $w_B \text{ gm}$ of B

$$\text{Mass fraction of } A = \frac{w_A}{w_A + w_B}; \text{ Mass fraction of } B = \frac{w_B}{w_A + w_B}$$

It may be noted that molality, mole fraction, mass fraction etc. are preferred to molarity, normality, etc. because the former involve the weights of the solute and solvent where as later involve volumes of solutions. Temperature has no effect on weights but it has significant effect on volumes.

(10) **Demal unit (D)** : The concentrations are also expressed in "Demal unit". One demal unit represents one mole of solute present in one litre of solution at 0°C .

Colligative properties

Certain properties of dilute solutions containing non-volatile solute do not depend upon the nature of the solute dissolved but depend only upon the concentration *i.e.*, the number of particles of the solute present in the solution. Such properties are called colligative properties. The four well known examples of the colligative properties are,

- (1) Lowering of vapour pressure of the solvent.
- (2) Osmotic pressure of the solution.
- (3) Elevation in boiling point of the solvent.
- (4) Depression in freezing point of the solvent.

Since colligative properties depend upon the number of solute particles present in the solution, the simple case will be that when the solute is a *non-electrolyte*. In case the solute is an electrolyte, it may split to a number of ions each of which acts as a particle and thus will affect the value of the colligative property.

Each colligative property is exactly related to other, Relative lowering of vapour pressure, elevation in boiling point and depression in freezing point are directly proportional to osmotic pressure.

Lowering of 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*. The vapour pressure of a liquid depends on,

(1) **Nature of liquid** : Liquids, which have weak intermolecular forces, are volatile and have greater vapour pressure. For example, dimethyl ether has greater vapour pressure than ethyl alcohol.

(2) **Temperature** : Vapour pressure increases with increase in temperature. This is due to the reason that with increase in temperature more molecules of the liquid can go into vapour phase.

(3) **Purity of liquid** : Pure liquid always has a vapour pressure greater than its solution.

Raoult's law : When a non-volatile substance is dissolved in a liquid, the vapour pressure of the liquid (solvent) is lowered. According to *Raoult's law* (1887), *at any given temperature the partial vapour pressure (p) of any component of a solution is equal to its mole fraction (X) multiplied by the vapour pressure of this component in the pure state (p_A^0)*. That is, $p_A = p_A^0 \times X_A$

The vapour pressure of the solution (P_{total}) is the sum of the partial pressures of the components, *i.e.*, for the solution of two volatile liquids with vapour pressures p_A and p_B .

$$P_{\text{total}} = p_A + p_B = (p_A^0 \times X_A) + (p_B^0 \times X_B)$$

Alternatively, Raoult's law may be stated as "*the relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution*".

Relative lowering of vapour pressure is defined as the ratio of lowering of vapour pressure to the vapour pressure of the pure solvent. It is determined by Ostwald-Walker method.

Thus according to Raoult's law,

$$\frac{p^0 - p}{p^0} = \frac{n}{n + N} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

where, p = Vapour pressure of the solution

p^0 = Vapour pressure of the pure solvent

n = Number of moles of the solute

N = Number of moles of the solvent

w and m = weight and mol. wt. of solute

W and M = weight and mol. wt. of the solvent.

Limitations of Raoult's law

- Raoult's law is applicable only to *very dilute solutions*.
- Raoult's law is applicable to solutions containing non-volatile solute only.
- Raoult's law is not applicable to solutes which dissociate or associate in the particular solution.

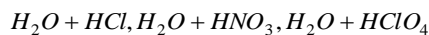
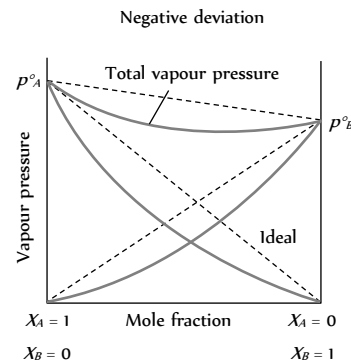
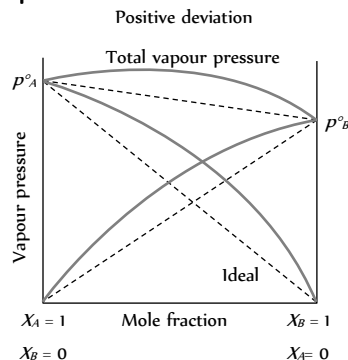
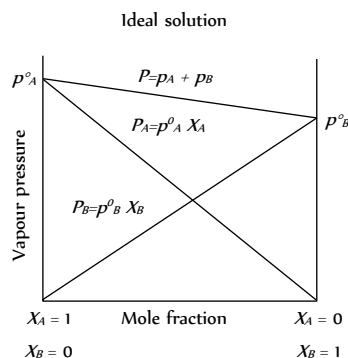
Ideal and Non-Ideal solution

Table: 4.1 Ideal and non-ideal solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
1. Obey Raoult's law at every range of concentration.	1. Do not obey Raoult's law.	1. Do not obey Raoult's law.
2. $\Delta H_{\text{mix}} = 0$; neither heat is evolved nor absorbed during dissolution.	2. $\Delta H_{\text{mix}} > 0$. Endothermic dissolution; heat is absorbed.	2. $\Delta H_{\text{mix}} < 0$. Exothermic dissolution; heat is evolved.
3. $\Delta V_{\text{mix}} = 0$; total volume of solution is equal to sum of volumes of the components.	3. $\Delta V_{\text{mix}} > 0$. Volume is increased after dissolution.	3. $\Delta V_{\text{mix}} < 0$. Volume is decreased during dissolution.

4. $P = p_A + p_B = p_A^0 X_A + p_B^0 X_B$ i.e.,
 $p_A = p_A^0 X_A$; $p_B = p_B^0 X_B$
5. $A-A$, $A-B$, $B-B$ interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character.
6. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.
- Examples:
 Dilute solutions;
 benzene + toluene;
n-hexane + *n*-heptane;
 chlorobenzene + bromobenzene;
 ethyl bromide + ethyl iodide;
n-butyl chloride + *n*-butyl bromide
4. $p_A > p_A^0 X_A$; $p_B > p_B^0 X_B$
 $\therefore p_A + p_B > p_A^0 X_A + p_B^0 X_B$
5. $A-B$ attractive force should be weaker than $A-A$ and $B-B$ attractive forces. 'A' and 'B' have different shape, size and character.
6. 'A' and 'B' escape easily showing higher vapour pressure than the expected value.
- Examples:
 Acetone + ethanol
 acetone + CS_2 ;
 water + methanol;
 water + ethanol;
 CCl_4 + toluene;
 $CCl_4 + CHCl_3$;
 acetone + benzene;
 $CCl_4 + CH_3OH$;
 cyclohexane + ethanol
4. $p_A < p_A^0 X_A$; $p_B < p_B^0 X_B$
 $\therefore p_A + p_B < p_A^0 X_A + p_B^0 X_B$
5. $A-B$ attractive force should be greater than $A-A$ and $B-B$ attractive forces. 'A' and 'B' have different shape, size and character.
6. Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.
- Examples:
 Acetone + aniline;
 acetone + chloroform;
 $CH_3OH + CH_3COOH$;
 $H_2O + HNO_3$
 chloroform + diethyl ether;
 water + HCl ;
 acetic acid + pyridine;
 chloroform + benzene

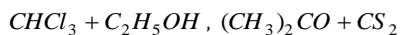
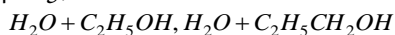
Graphical representation of ideal and non-ideal solutions



Azeotropic mixture

Azeotropes are defined as the mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as in vapour phase. Azeotropes are also called constant boiling mixtures because whole of the azeotropes changes into vapour state at constant temperature and their components can not be separated by fractional distillation. Azeotropes are of two types as described below,

(i) **Minimum boiling azeotrope** : For the solutions with positive deviation there is an intermediate composition for which the vapour pressure of the solution is maximum and hence, boiling point is minimum. At this composition the solution distills at constant temperature without change in composition. This type of solutions are called minimum boiling azeotrope. e.g.,



(2) **Maximum boiling azeotrope** : For the solutions with negative deviations there is an intermediate composition for which the vapour pressure of the solution is minimum and hence, boiling point is maximum. At this composition the solution distill's at constant temperature without the change in composition. This type of solutions are called maximum boiling azeotrope. e.g.,

Osmosis and Osmotic pressure of the solution

(i) **Osmosis** : The flow of solvent from pure solvent or from solution of lower concentration into solution of higher concentration through a semi-permeable membrane is called *Osmosis*. Osmosis may be divided in following types,

(i) **Exo-Osmosis** : The outward osmotic flow of water from a cell containing an aqueous solution through a semi-permeable membrane is called as Exo-osmosis. For example, egg (after removing hard shell) placed in conc. $NaCl$ solutions, will shrink due to exo-osmosis.

(ii) **Endo-osmosis** : The inward flow of water into the cell containing an aqueous solution through a semi-permeable membrane is called as endo-osmosis. e.g., an egg placed in water swells up due to endo-osmosis.

(iii) **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 semi-permeable 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.

Differences between osmosis and diffusion

Osmosis	Diffusion
In osmosis movement of molecules	In diffusion there is no role of semi-

takes place through a semi-permeable membrane.	permeable membrane.
It involves movement of only solvent molecules from one side to the other.	It involves passage of solvent as well as solute molecules from one region to the other.
Osmosis is limited to solutions only.	Diffusion can take place in liquids, gases and solutions.
Osmosis can be stopped or reversed by applying additional pressure on the solution side.	Diffusion can neither be stopped nor reversed

(2) **Osmotic pressure (π)**

The osmotic pressure of a solution at a particular temperature may be defined as the excess hydrostatic pressure that builds up when the solution is separated from the solvent by a semi-permeable membrane. It is denoted by π .

or

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 semi-permeable membrane.

or

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.

(i) **Measurements of osmotic pressure** : Following methods are used for the measurement of osmotic pressure,

(a) Pfeffer's method, (b) Morse and Frazer's method, (c) Berkeley and Hartley's method, (d) Townsend's negative pressure method, (e) De Vries plasmolytic method.

(ii) **Determination of molecular mass of non-volatile solute from osmotic pressure (π)** : The osmotic pressure is a colligative property. For a given solvent the osmotic pressure depends only upon the molar concentration of solute but does not depend upon its nature. The following relation relates osmotic pressure to the number of moles of the solute,

According to Boyle Van't Hoff law (at conc. temp.)

$$\pi \propto C \quad \text{.....(i)}$$

According to Gaylussac Van't Hoff law (at conc. temp.)

$$\pi \propto T \quad \text{.....(ii)}$$

From equation (i) and (ii)

$$\pi \propto CT, \pi = CRT \quad (\text{Van't Hoff equation})$$

$$\pi = \frac{n}{V} RT \quad \left(\because C = \frac{n}{V} \right); \pi = \frac{w}{m} \frac{RT}{V} \quad \left(\because n = \frac{w}{m} \right)$$

Here, C = concentration of solution in moles per litre

R = gas constant ; T = temperature

n = number of moles of solute ; V = volume of solution

m = molecular weight of solute ; w = weight of solute

(iii) Conditions for getting accurate value of molecular mass are,

(a) The solute must be non-volatile.

(b) The solution must be dilute.

(c) The solute should not undergo dissociation or association in the solution.

(iv) **Relation of osmotic pressure with different colligative properties** : Osmotic pressure is related to relative lowering of vapour pressure, elevation of boiling point and depression of freezing point according to the following relations,

$$(a) \pi = \left(\frac{P_A^o - P_A}{P_A^o} \right) \times \frac{dRT}{M} \quad (b) \pi = \Delta T_b \times \frac{dRT}{1000 \times K_b}$$

$$(c) \pi = \Delta T_f \times \frac{dRT}{1000 \times K_f}$$

In the above relations, π = Osmotic pressure; d = Density of solution at temperature T ; R = Universal gas constant; M = Mol. Mass of solute; K_b = Molal elevation constant of solvent; K_f = Molal depression constant of solvent

(v) **Isotonic, Hypertonic and Hypotonic solutions**

(a) **Isotonic or iso-osmotic solutions** : Two solutions of different substances having same osmotic pressure at same temperature are known as isotonic solutions.

For isotonic solutions, $\pi_1 = \pi_2$ Primary Condition(i)

$$\left. \begin{array}{l} \text{Also, } C_1 = C_2 \\ \text{or } \frac{n_1}{V_1} = \frac{n_2}{V_2} \\ \text{or } \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2} \end{array} \right\} \text{Secondary Conditions} \quad \text{.....(ii)}$$

Eq. (ii) holds good only for those solutes which neither possess the tendency to get associate nor dissociate in solution, e.g.,

Urea and glucose are isotonic then, $\pi_1 = \pi_2$ and $C_1 = C_2$

Urea and NaCl (dissociate) are isotonic then, $\pi_1 = \pi_2$ but $C_1 \neq C_2$

Urea and Benzoic acid (associate) are isotonic then, $\pi_1 = \pi_2$ but $C_1 \neq C_2$

(b) **Hypertonic and hypotonic solution** : The solution which has more osmotic pressure than the other solution is called as hypertonic solution and the solution which has lesser osmotic pressure than the other is called as hypotonic solution.

The flow of solvent is always from lower osmotic pressure to higher osmotic pressure i.e. from hypotonic to hypertonic solution.

Elevation in b.pt. of the solvent (Ebullioscopy)

Boiling point of a liquid may be defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure, i.e., 760 mm. Since the addition of a non-volatile solute lowers the vapour pressure of the solvent, solution always has lower vapour pressure than the solvent and hence it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure with the result *the solution boils at a higher temperature than the pure solvent*. Thus sea water boils at a higher temperature than distilled water. If T is the boiling point of the solvent and T is the boiling point of the solution, the difference in the boiling point (ΔT or ΔT) is called the elevation of boiling point.

$$T - T_b = \Delta T_b \text{ or } \Delta T$$

Elevation in boiling point is determined by Landsberger's method and Cottrell's method. Study of elevation in boiling point of a liquid in which a non-volatile solute is dissolved is called as ebullioscopy.

Important relations concerning elevation in boiling point

(1) *The elevation of boiling point is directly proportional to the lowering of vapour pressure, i.e., $\Delta T_b \propto p^0 - p$*

$$(2) \Delta T_b = K_b \times m$$

where K_b = molal elevation constant or ebullioscopic constant of the solvent; m = Molality of the solution, i.e., number of moles of solute per 1000 g of the solvent; ΔT_b = Elevation in boiling point

$$(3) \Delta T_b = \frac{1000 \times K_b \times w}{m \times W} \text{ or } m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

where, K_b is *molal elevation constant* and defined as the elevation in b.pt. produced when 1 mole of the solute is dissolved in 1 kg of the solvent.

w and W are the weights of solute and solvent and m is the molecular weight of the solute.

$$(4) K_b = \frac{0.002(T_0)^2}{l_v}$$

where T_0 = Normal boiling point of the pure solvent; l_v = Latent heat of evaporation in cal/g of pure solvent; K_b for water is $0.52 \text{ deg-kg mol}^{-1}$.

Depression in f.pt. of the solvent (Cryoscopy)

Freezing point is the temperature at which the liquid and the solid states of a substance are in equilibrium with each other or it may be defined as the temperature at which the liquid and the solid states of a substance have the same vapour pressure. It is observed that the freezing point of a solution is always less than the freezing point of the pure solvent. Thus the freezing point of sea water is low than that of pure water. The depression in freezing point (ΔT or ΔT_f) of a solvent is the difference in the freezing point of the pure solvent (T_s) and the solution (T_{sol}).

$$T_s - T_{sol} = \Delta T_f \text{ or } \Delta T$$

NaCl or CaCl_2 (anhydrous) are used to clear snow on roads. They depress the freezing point of water and thus reduce the temperature of the formation of ice.

Depression in freezing point is determined by Beckmann's method and Rast's camphor method. Study of depression in freezing point of a liquid in which a non-volatile solute is dissolved in it is called as cryoscopy.

Important relations concerning depression in freezing point.

(1) Depression in freezing point is directly proportional to the lowering of vapour pressure. $\Delta T_f \propto p^0 - p$

$$(2) \Delta T_f = K_f \times m$$

where K_f = molal depression constant or cryoscopic constant; m = Molality of the solution (i.e., no. of moles of solute per 1000g of the solvent); ΔT_f = Depression in freezing point

$$(3) \Delta T_f = \frac{1000 \times K_f \times w}{m \times W} \text{ or } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

where K_f is *molal depression constant* and defined as the depression in freezing point produced when 1 mole of the solute is dissolved in 1kg of the solvent. w and W are the weights of solute and solvent and m is the molecular weight of the solute.

$$(4) K_f = \frac{R(T_0)^2}{l_f 1000} = \frac{0.002(T_0)^2}{l_f}$$

where T_0 = Normal freezing point of the solvent; l_f = Latent heat of fusion/g of solvent; K_f for water is $1.86 \text{ deg-kg mol}^{-1}$

Colligative properties of electrolytes

The colligative properties of solutions, viz. lowering of vapour pressure, osmotic pressure, elevation in b.p. and depression in freezing point, depend on the total number of solute particles present in solution. Since the electrolytes ionise and give more than one particle per formula unit in solution, the colligative effect of an electrolyte solution is always greater than that of a non-electrolyte of the same molar concentration. All colligative properties are used for calculating molecular masses of non-

volatile solutes. However osmotic pressure is the best colligative property for determining molecular mass of a non-volatile substance.

Colligative properties are depending on following factors

- (1) Colligative properties \propto Number of particles
 - \propto Number of molecules
(in case of non-electrolytes)
 - \propto Number of ions
(In case of electrolytes)
 - \propto Number of moles of solute
 - \propto Mole fraction of solute

(2) For different solutes of same molar concentration, the magnitude of the colligative properties is more for that solution which gives more number of particles on ionisation.

(3) For different solutions of same molar concentration of different non-electrolyte solutes, the magnitude of the colligative properties will be same for all.

(4) For different molar concentrations of the same solute, the magnitude of colligative properties is more for the more concentrated solution.

(5) For solutions of different solutes but of same percent strength, the magnitude of colligative property is more for the solute with least molecular weight.

(6) For solutions of different solutes of the same percent strength, the magnitude of colligative property is more for that solute which gives more number of particles, which can be known by the knowledge of molecular weight and its ionisation behaviour.

Abnormal molecular masses

Molecular masses can be calculated by measuring any of the colligative properties. The relation between colligative properties and molecular mass of the solute is based on following assumptions.

- (1) The solution is dilute, so that Raoult's law is obeyed.
- (2) The solute neither undergoes dissociation nor association in solution.

In case of solutions where above assumptions are not valid we find discrepancies between observed and calculated values of colligative properties. These anomalies are primarily due to

- (i) Association of solute molecules.
- (ii) Dissociation of solute molecules.
- (i) **Association of solute molecules** : Certain solutes in solution are found to associate. This eventually leads to a decrease in the number of molecular particles in the solutions. Thus, it results in a decrease in the values of colligative properties.

$$\text{Colligative property} \propto \frac{1}{\text{molecular mass of solute}}$$

therefore, higher values are obtained for molecular masses than normal values for unassociated molecules.

(ii) **Dissociation of solute molecules** : A number of electrolytes dissociate in solution to give two or more particles (ions). Therefore, the number of solute particles, in solutions of such substances, is more than the expected value. Accordingly, such solutions exhibit higher values of colligative properties. Since colligative properties are inversely proportional to molecular masses, therefore, molecular masses of such substances as calculated from colligative properties will be less than their normal values.

Van't Hoff's factor (i) : In 1886, Van't Hoff introduced a factor ' i ' called Van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. It is ratio of the normal and observed molecular masses of the solute, i.e.,

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

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's factor is more than 1 because the observed molecular mass has a lesser value than the normal molecular mass. In case there is no dissociation the value of ' i ' becomes equal to one.

Since colligative properties are inversely proportional to molecular masses, the Van't Hoff's factor may also be written as,

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property assuming no association or dissociation}}$$

$$i = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before association or dissociation}}$$

Introduction of the Van't Hoff factor modifies the equations for the colligative properties as follows,

$$\text{Relative lowering of vapour pressure} = \frac{P_A^o - P_A}{P_A^o} = iX_B$$

$$\text{Elevation of boiling point, } \Delta T_b = ik_b m$$

$$\text{Depression in freezing point, } \Delta T_f = ik_f m$$

$$\text{Osmotic pressure, } \pi = \frac{i n R T}{V}; \quad \pi = i C R T$$

From the value of ' i ', it is possible to calculate degree of dissociation or degree of association of substance.

Degree of dissociation (α) : It is defined as the fraction of total molecules which dissociate into simpler molecules or ions.

$$\alpha = \frac{i - 1}{m - 1}; \quad m = \text{number of particles in solution}$$

Degree of association (α) : It is defined as the fraction of the total number of molecules which associate or combine together resulting in the formation of a bigger molecules.

$$\alpha = \frac{i - 1}{1/m - 1}; \quad m = \text{number of particles in solution.}$$