

Solution

Homogeneous mixture of two or more non reacting components whose composition can be varied within certain limits is known as solution.

Expressing Concentration of Solutions:

Composition of a solution can be described by expressing its concentration. The latter can be expressed either qualitatively or quantitatively. For example, qualitatively we can say that the solution is dilute (i.e., relatively very small quantity of solute) or it is concentrated (i.e., relatively very large quantity of solute). But in real life these kinds of description can add to lot of confusion and thus the need for a quantitative description of the solution. There are several ways by which we can describe the concentration of the solution quantitatively.

(i) Mass percentage (w/w): The mass percentage of a component of a solution is defined as:

Mass % of a component

$$= \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

(ii) Volume percentage (V/V): The volume percentage is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100$$

(iii) Mass by volume percentage (w/V): Another unit which is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

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 =

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

v) Mole fraction: Commonly used symbol for mole fraction is x and subscript used on the right hand side of x denotes the component. It is defined as:

Mole fraction of a component =

$$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

For example, in a binary mixture, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

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

For a solution containing i number of components, we have:

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

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

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

vi) Molarity: Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution,

$$\text{Molarity (M)} = \frac{\text{wt. of solute} \times 1000}{\text{M. wt of solute} \times \text{volume in mL}}$$

(vi) **Normality (N)** : Number of gram equivalents of the solute dissolved per litre of the solution.

$$\text{Normality (N)} = \frac{\text{wt. of solute} \times 1000}{\text{E. wt of solute} \times \text{volume in mL}}$$

(viii) **Molality:** Molality (m) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\begin{aligned} \text{Molality (m)} \\ = \frac{\text{wt. of solute} \times 1000}{\text{M. wt of solute} \times \text{wt. of solvent in grams}} \end{aligned}$$

SOME IMPORTANT RELATIONS :

$$(i) \quad M = \frac{md}{1 + m \frac{M_2}{1000}} \quad \text{or} \quad d = M \left(\frac{1}{m} + \frac{M_2}{100} \right)$$

$$(ii) \quad m = \frac{1000x_2}{x_1M_1}$$

$$(iii) \quad M = \frac{1000 dx_2}{x_1M_1 + x_2M_2}$$

$$(iv) \quad \text{Mole fraction (} x_2 \text{)} = \frac{m}{m + \frac{1000}{M_1}}$$

M = molarity

m = molality

d = density of solution

x_1 = mole fraction of solvent

x_2 = mole fraction of solute

M_1 = molecular mass of solvent

M_2 = molecular mass of solute

Normality = n × Molarity

$$\text{where } n = \frac{\text{Molecular Mass}}{\text{Equivalent mass}}$$

Solubility: Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends upon the nature of solute and solvent as well as temperature and pressure.

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. 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 out of solution. This process is known as crystallisation. A stage is

reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.



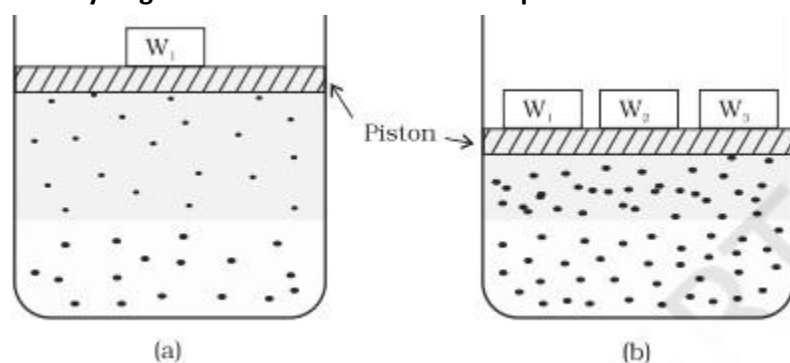
At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution**. The concentration of solute in such a solution is its solubility.

Effect of temperature on solubility: The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by the saturated solution. This, being dynamic equilibrium, must follow Le Chateliers Principle. In general, if in a nearly saturated solution, the dissolution process is endothermic ($\Delta_{\text{sol}}H > 0$), the solubility should increase with rise in temperature. If it is exothermic ($\Delta_{\text{sol}}H < 0$), the solubility should decrease. These trends are also observed experimentally.

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

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 which sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. Solubility of gases in liquids is greatly affected by pressure and temperature. **The solubility of gases increase with increase of pressure.**



For solution of gases in a solvent, consider a system as shown above in Fig. (a). The lower part is solution and the upper part is 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 [Fig. (b)]. 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 solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.

Henry's law: Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent.

The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

The most commonly used form of Henry's law states that **"the partial pressure of the gas in 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 K_H is the Henry's law constant. Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas. It is obvious the above equation that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

Applications of Henry's Law: Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of CO_2 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 blood. When the divers come towards 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 life. 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: Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt in the last Section that dissolution process involves dynamic equilibrium and thus must follow **Le Chatelier's Principle**. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

Vapour Pressure of Liquid Solutions :

Liquid solutions are formed when solvent is a liquid. The solute can be a gas, a liquid or a solid. We shall discuss the properties of only binary solutions, that is, the solutions containing two components, namely, the solutions of (i) liquids in liquids and (ii) solids in liquids.

Vapour Pressure of Liquid-Liquid Solutions:

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be p_{total} and p_1 and p_2 be the partial vapour pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the **Raoult's law** which states that

For a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

Thus, for component 1

$$p_1 \propto x_1$$

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

where p_1^0 is the vapour pressure of pure component 1 at the same temperature. Similarly, for component 2

$$p_2 \propto x_2$$

$$\text{and } p_2 = p_2^0 x_2$$

where p_2^0 is the vapour pressure of pure component 2 at the same temperature.

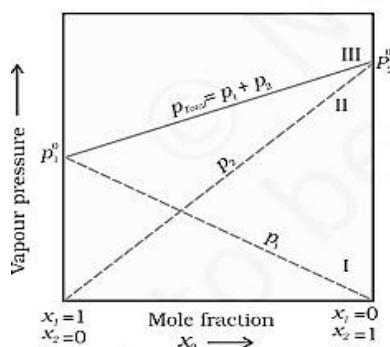
According to **Dalton's law** of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

$$\begin{aligned} p_{\text{total}} &= p_1 + p_2 \\ &= p_1^0 x_1 + p_2^0 x_2 \\ &= (1 - x_2) p_1^0 + p_2^0 x_2 \\ \therefore p_{\text{total}} &= p_1^0 + (p_2^0 - p_1^0) x_2 \end{aligned}$$

Following conclusions can be drawn from the above equation.

- (i) Total vapour pressure over the solution can be related to the mole fraction of any one component.
- (ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.
- (iii) Depending on the vapour pressures of the pure components 1 and 2, total vapour 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 below. These lines (I and II) pass through the points for which x_1 and x_2 are equal to unity. Similarly



the plot (line III) of p_{total} versus x_2 is also linear.

The minimum value of p_{total} is p_1^0 and the maximum value is p_2^0 , assuming that component 1 is less volatile than component 2, i.e., $p_1^0 < p_2^0$.

The composition of 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 vapour 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 vapour 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

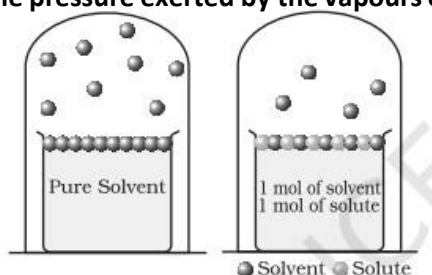
$$p = K_H x.$$

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. Only the proportionality constant K_H differs from p_i^0 . Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_i^0 .

Vapour Pressure of Solutions of Solids in Liquids:

Another important class of solutions consists of solids dissolved in liquid, for example, sodium chloride, glucose, urea and cane sugar in water and iodine and sulphur dissolved in carbon disulphide. Some physical properties of these solutions are quite different from those of pure solvents. For example, vapour pressure. We have learnt that **liquids at a given temperature vapourise and under equilibrium conditions the pressure exerted by the vapours of the liquid over the liquid phase is called vapour pressure.**

In a pure liquid the entire surface is occupied by the molecules of the liquid. If a non-volatile solute is added to a solvent to give a solution, the vapour pressure of the solution is solely from



the solvent alone. This vapour pressure of the solution at a given temperature is found to be lower than the vapour 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 vapour pressure is also reduced.

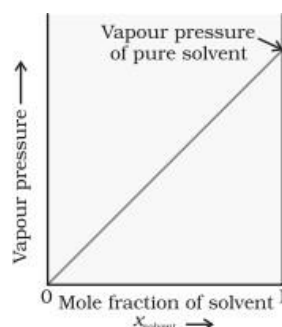
The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature.

Raoult's law in its general form can be stated as, **for any solution the partial vapour 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 vapour phase and contribute to vapour pressure.

Let p_1 be the vapour pressure of the solvent, x_1 be its mole fraction, p_1^0 be its vapour pressure in the pure state. Then according to Raoult's law

$$p_1 \propto x_1$$

and $p_1 = x_1 p_1^0$



The proportionality constant is equal to the vapour pressure of pure solvent, p_1^0 .

Ideal and Nonideal Solutions:

Ideal Solutions: The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$\Delta_{\text{mix}}H = 0, \Delta_{\text{mix}}V = 0$$

It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If

the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

Fractional Distillation: The constituents of an ideal solution can be completely separated by fractional distillation. Distillate gives more volatile component and residue gives less volatile component.

KONOWALOFF'S RULE : The mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.

RELATION BETWEEN THE TOTAL PRESSURE AND MOLE FRACTIONS OF VOLATILE COMPONENTS IN LIQUID PHASE :

$$P = p_A^0 \cdot x_A + p_B^0 \cdot x_B$$

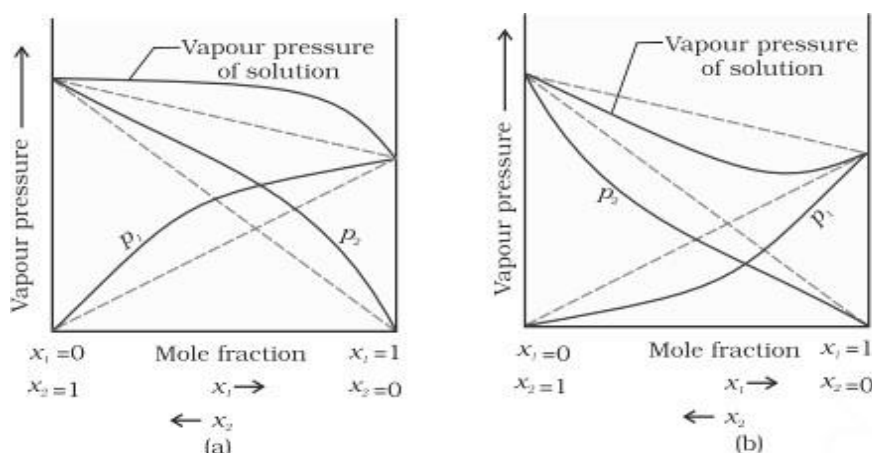
RELATION BETWEEN THE TOTAL PRESSURE AND MOLE FRACTIONS OF VOLATILE COMPONENTS IN VAPOUR PHASE :

$$\frac{1}{P} = \frac{Y_A}{p_A^0} + \frac{Y_B}{p_B^0}$$

Non-ideal Solutions:

When a solution does not obey Raoult's law over the entire range of concentration, then it is called non-ideal solution. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits **positive deviation** and if it is lower, it exhibits **negative deviation** from Raoult's law. The plots of vapour pressure as a function of mole fractions for such solutions are shown in the following figure.

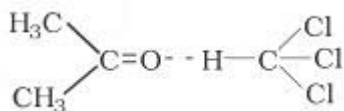
The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state.



The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.

This will increase the vapour pressure and result in positive deviation. Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.

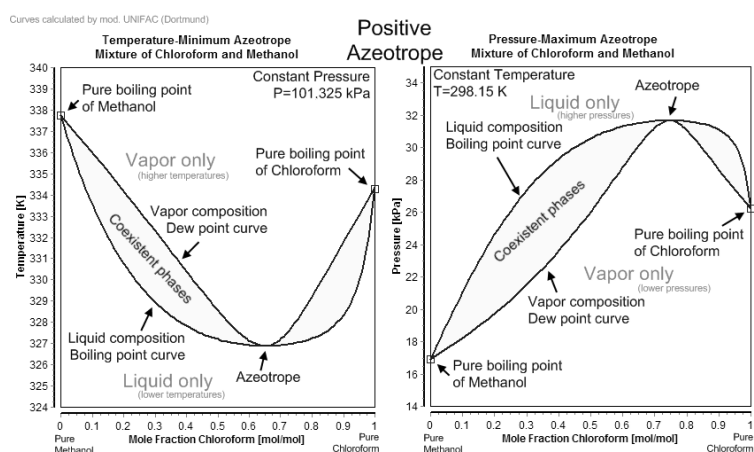
In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.



This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law [Fig. (b)].

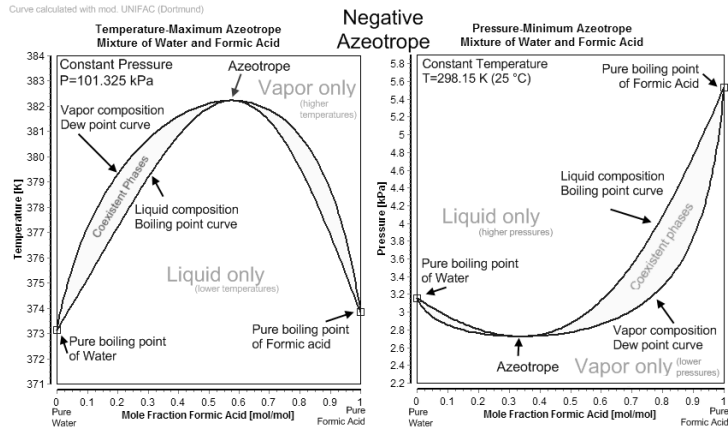
Azeotropes: An azeotrope is a mixture of two or more liquids which displays the same level of concentration in the liquid and vapour phase. Simple distillation cannot alter their proportions. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called **minimum boiling azeotrope (positive Azeotrope)** and **maximum boiling azeotrope (Negative Azeotrope)**.

The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.



Forexample, 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 vapour have the same composition, and no further separation occurs.

The solutions that show 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.

Colligative Properties and Determination of Molar Mass:

There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (1) relative lowering of vapour pressure of the solvent (2) depression of freezing point of the solvent (3) elevation of boiling point of the solvent and (4) osmotic pressure of the solution. All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called **colligative properties** (colligative: from Latin: co means together, ligare means to bind).

1. Relative Lowering of Vapour Pressure: We have learnt that the vapour pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The following equation establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent, i.e.,

$$p_1 = x_1 p_1^0$$

The reduction in the vapour pressure of solvent (Δp_1) is given as:

$$\begin{aligned}\Delta p_1 &= p_1^0 - p_1 = p_1^0 - p_1^0 x_1 \\ &= p_1^0 (1 - x_1)\end{aligned}$$

Knowing that $x_2 = 1 - x_1$, the above equation reduces to

$$\Delta p_1 = x_2 p_1^0$$

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Vapour pressure depends on the sum of the mole fraction of different solutes.

The above equation can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2$$

The expression on the left hand side of the equation as mentioned earlier is called relative lowering of vapour pressure and is equal to the mole fraction of the solute. The above equation can be written as:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \quad \left(\text{since } x_2 = \frac{n_2}{n_1 + n_2} \right)$$

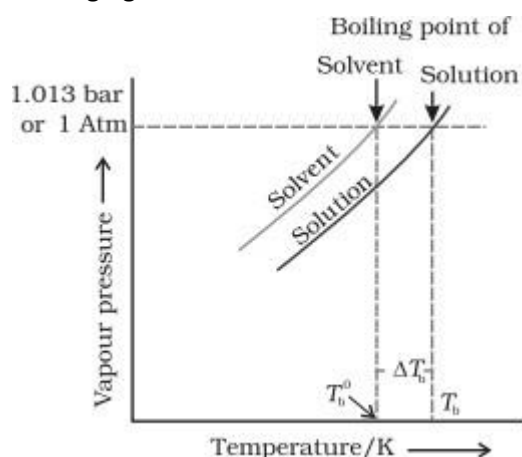
Here n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_2 \ll n_1$, hence neglecting n_2 in the denominator we have

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

or $\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$

Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute respectively. From the above equation knowing all other quantities, the molar mass of solute (M_2) can be calculated.

Elevation of Boiling Point: We have learnt that the vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. We have also learnt in the last section that vapour pressure of the solvent decreases in the presence of non-volatile solute. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar (1 atmosphere) by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in the following figure.



Let T_b^0 be the boiling point of pure solvent and T_b be the boiling point of solution. The increase in the boiling point $\Delta T_b = T_b - T_b^0$ is known as elevation of boiling point.

For dilute solutions the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m$$

$$\text{or } \Delta T_b = K_b m$$

Here m (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, K_b is called **Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant)**. The unit of K_b is K kg mol^{-1} .

If w_2 gram of solute of molar mass M_2 is dissolved in w_1 gram of solvent, then molality, m of the solution is given by the expression:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1}$$

Substituting the value of molality in the above equation, we get

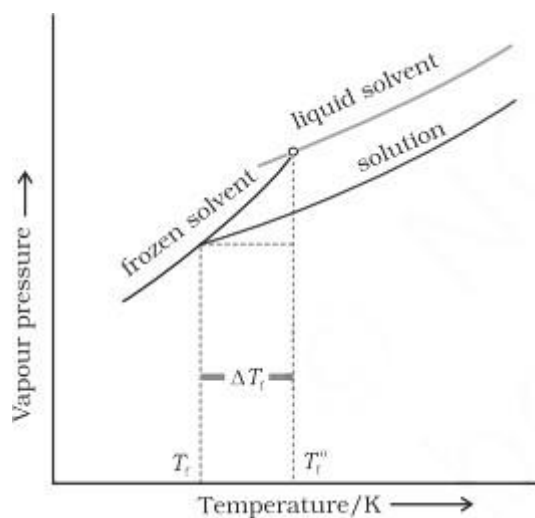
$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1}$$

Thus, in order to determine M_2 , molar mass of the solute, known mass of solute in a known mass of

the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

Depression of Freezing Point: The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent. We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, **the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase.** A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.



Let T_f^0 be the freezing point of pure solvent and T_f be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point

$$\Delta T_f = T_f^0 - T_f$$

is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point (ΔT_f) for dilute solution (ideal solution) is directly proportional to molality, m of the solution. Thus,

$$\Delta T_f \propto m$$

$$\text{or } \Delta T_f = K_f m$$

The proportionality constant, K_f , which depends on the nature of the solvent is known as **Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant**. The unit of K_f is K kg mol^{-1} .

If w_2 gram of the solute having molar mass as M_2 , present in w_1 gram of solvent, produces the depression in freezing point ΔT_f of the solvent then molality of the solute is given by the equation

$$m = \frac{w_2 / M_2}{w_1 / 1000}$$

Substituting this value of molality in the above equation we get:

$$\Delta T_f = \frac{K_f \times w_2 / M_2}{w_1 / 1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

Thus for determining the molar mass of the solute we should know the quantities w_1 , w_2 , ΔT_f , along with the molal freezing point depression constant.

The values of K_f and K_b , which depend upon the nature of the solvent, can be ascertained from the following relations

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{\text{fus}} H}$$

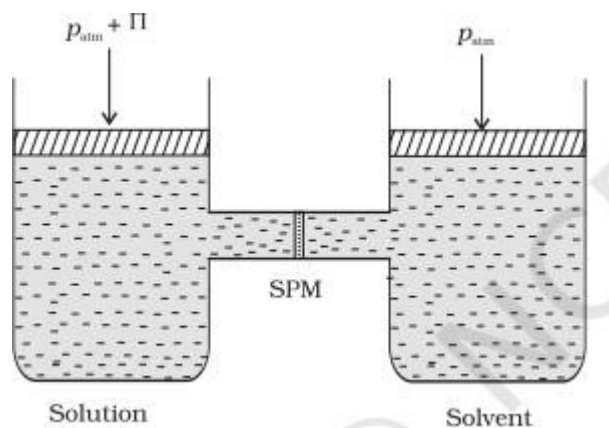
$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{\text{vap}} H}$$

Here the symbols R and M_1 stand for the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further, ΔH_{fus} and ΔH_{vap} represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

Osmosis and Osmotic Pressure:

If a semipermeable membrane is placed between the solvent and solution, the solvent molecules will flow through the membrane from pure solvent to the solution. This process of flow of the solvent is called **osmosis**.

The flow will continue till the equilibrium is attained. The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. This excess pressure that just stops the flow of solvent is called **osmotic pressure** of the solution.



Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity.

For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T . Thus:

$$\Pi = CRT$$

Here Π is the osmotic pressure and R is the gas constant.

$$\Pi = (n_2 / V) R T$$

Here V is volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2 / M_2$ and we can write,

$$\Pi V = \frac{w_2 R T}{M_2}$$

or
$$M_2 = \frac{w_2 R T}{\Pi V}$$

Thus, knowing the quantities w_2 , T , Π and V we can calculate the molar mass of the solute.

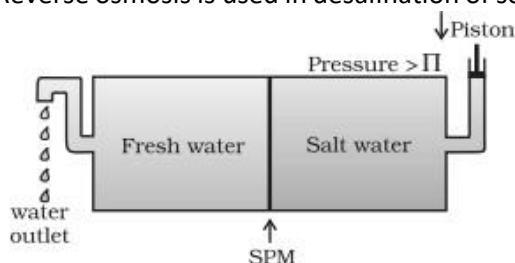
Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other macromolecules. **The osmotic pressure method has the advantage** over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

Two solutions having same osmotic pressure at a given temperature are called **isotonic solutions**. When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/ volume) sodium chloride solution, called **normal saline solution** and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

Several phenomena can be explained on the basis of osmosis. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into its cells through osmosis. When placed in water containing less than 0.9% (mass/ volume) salt, blood cells swell due to flow of water in them by osmosis. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called **edema**. Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis. The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

Reverse Osmosis and Water Purification:

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis and is of great practical utility. Reverse osmosis is used in desalination of sea water.



The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.

PLASMOLYSIS : The flow of the fluid from the plant cell when placed in a hypertonic solution is called plasmolysis. The plant cell undergoes shrinkage.

EXO-OSMOSIS : Outward osmotic flow of fluid from a cell through semipermeable membrane e.g. grape in conc. NaCl solution.

ENDO-OSMOSIS : Inward osmotic flow of fluid from a cell through semipermeable membranes e.g. grape in water.

SILICA GARDEN : When coloured salts e.g. Copper Sulphate, Cobalt Nitrate, Manganese Chloride, Nickel Chloride and Ferrous sulphate etc. are placed in Sodium silicate solution of density 1.1, a colloidal and semipermeable shell of Silicates is formed round the crystal. Inside this, there is strong solution of salt and outside weak solution of sodium silicate. Water permeates into the shell, pressure rises and the shell bursts out, the salt solution escapes but immediately reacts with sodium silicate to form again semipermeable shell of the metallic silicate. The process is repeated again and again and projection of coloured silicates continues to grow.

Abnormal Molar Masses:

In some cases, experimental (normal) values of colligative properties and molar mass of solute is found to be different from the theoretical (abnormal) values. This is due to either association or dissociation of solute particles in solution.

In 1880 van't Hoff introduced a factor i , known as the van't Hoff factor, to account for the extent of dissociation or association. This factor i is defined as:

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated. In case of association, value of i is less than unity while for dissociation it is greater than unity. For example, the value of i for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows: Relative lowering of vapour pressure of solvent

$$\frac{p_1^0 - p_1}{p_1^0} = i \cdot \frac{n_2}{n_1}$$

$$\text{Elevation of Boiling point, } \Delta T_b = i K_b m$$

$$\text{Depression of Freezing point, } \Delta T_f = i K_f m$$

$$\text{Osmotic pressure of solution, } \Pi = i n_2 R T / V$$

MCQ:

1. A 0.0020 m aqueous solution of an ionic compound $\text{Co}(\text{NH}_3)_5(\text{NO}_2)\text{Cl}$ freezes at -0.00732°C .

Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be ($K_f = -1.86^\circ\text{C}/m$)

- (a) 3
- (b) 4
- (c) 1
- (d) 2

2. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase?

- (a) Addition of NaCl
- (b) Addition of Na_2SO_4
- (c) Addition of 1.00 molal KI
- (d) Addition of water

3. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be (K_f for water = $1.86 \text{ K kg mol}^{-1}$).

- (a) -0.372°C
- (b) -0.520°C
- (c) $+0.372^\circ\text{C}$
- (d) -0.570°C

4. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of sodium ions, Na^+ and carbonate ions, CO_3^{2-} are respectively (Molar mass of $\text{Na}_2\text{CO}_3 = 106 \text{ g mol}^{-1}$)

- (a) 0.955 M and 1.910 M
- (b) 1.910 M and 0.955 M
- (c) 1.90 M and 1.910 M
- (d) 0.477 M and 0.477 M

5. The freezing point depression constant for water is $-1.86^\circ\text{C m}^{-1}$. If 5.00 g Na_2SO_4 is dissolved in 45.0 g H_2O , the freezing point is changed by -3.82°C . Calculate the van't Hoff factor for Na_2SO_4

- (a) 2.05
- (b) 2.62
- (c) 3.11
- (d) 0.381

6. The van't Hoff factor i for a compound which undergoes dissociation in one solvent and association in other solvent is respectively :

- (a) less than one and greater than one.
- (b) less than one and less than one.
- (c) greater than one and less than one.
- (d) greater than one and greater than one.

7. Mole fraction of the solute in a 1.00 molal aqueous solution is

- (a) 0.1770
- (b) 0.0177
- (c) 0.0344
- (d) 1.7700

8. A 0.1 molal aqueous solution of a weak acid is 30% ionized. If K_f for water is 1.86°C/m , the freezing point of the solution will be :

- (a) -0.18°C
- (b) -0.54°C
- (c) -0.36°C
- (d) -0.24°C

9. 200 mL of an aqueous solution of a protein contains its 1.26 g. The osmotic pressure of this solution at 300 K is found to be $2.57 \times 10^{-3} \text{ bar}$. The molar mass of protein will be ($R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$)

- (a) 51022 g mol^{-1}
- (b) $122044 \text{ g mol}^{-1}$
- (c) 31011 g mol^{-1}
- (d) 61038 g mol^{-1}

10. P_A and P_B are the vapour pressure of pure liquid components, A and B, respectively of an ideal binary solution. If X_A represents the mole fraction of component A, the total pressure of the solution will be.

- (a) $P_A + X_A (P_B - P_A)$
- (b) $P_A + X_A (P_A - P_B)$
- (c) $P_B + X_A (P_B - P_A)$
- (d) $P_B + X_A (P_A - P_B)$

11. Freezing point of an aqueous solution is $(-0.186)^{\circ}\text{C}$. Elevation of boiling point of the same solution is $K_b = 0.512^{\circ}\text{C}$, $K_f = 1.86^{\circ}\text{C}$, find the increase in boiling point.

- (a) 0.186°C
- (b) 0.0512°C
- (c) 0.092°C
- (d) 0.2372°C .

12. In mixture A and B components show -ve deviation as

- (a) $\Delta V_{\text{mix}} > 0$
- (b) $\Delta H_{\text{mix}} < 0$
- (c) A – B interaction is weaker than A – A and B – B interaction
- (d) A – B interaction is stronger than A – A and B – B interaction.

13. A pressure cooker reduces cooking time for food because

- (a) boiling point of water involved in cooking is increased
- (b) the higher pressure inside the cooker crushes the food material
- (c) cooking involves chemical changes helped by a rise in temperature
- (d) heat is more evenly distributed in the cooking space

14. In a 0.2 molal aqueous solution of a weak acid HX the degree of ionization is 0.3. Taking k_f for water as 1.85, the freezing point of the solution will be nearest to

- (a) -0.360°C
- (b) -0.260°C
- (c) $+0.480^{\circ}\text{C}$
- (d) -0.480°C

15. Which one of the following aqueous solutions will exhibit highest boiling point ?

- (a) 0.015 M urea
- (b) 0.01 M KNO_3
- (c) 0.01 M Na_2SO_4
- (d) 0.015 M glucose

16. 6.02×10^{20} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is

- (a) 0.02 M
 - (b) 0.01 M
 - (c) 0.001 M
 - (d) 0.1 M
- (Avogadro constant, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

17. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the value of 0.1 M aqueous KOH solution required is

- (a) 40 mL
- (b) 20 mL
- (c) 10 mL
- (d) 60 mL

18. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour)

- (a) Boiling points
- (b) Vapour pressure at the same temperature
- (c) Heat of vapourization
- (d) Gaseous densities at the same temperature and pressure

19. Which of the following liquid pairs shows a positive deviation from Raoult's law ?

- (a) Water - nitric acid
- (b) Benzene - methanol
- (c) Water - hydrochloric acid
- (d) Acetone – chloroform

20. Which one of the following statements is FALSE?

- (a) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH > Sucrose$
- (b) The osmotic pressure (p) of a solution is given by the equation $p = MRT$, where M is the molarity of the solution
- (c) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction
- (d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

Answer Key:

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans	d	d	a	b	b	c	b	d	d	d	b	b	a	d	c	b	a	d	b	d