Unit

2

Solution

2.1 Introduction

When two or more than two substances mix and form a uniform or homogeneous mixture, such a mixture is called solution. The proportion of a component or components which is less in a solution is/are called solute and the proportion of component which is more in the solution is called a solvent. There can be one solvent and one or more than one solute components in a solution. The solution having one solute and one solvent component is called binary solution. In a homogeneous mixture the diameter of the molecular particles is 10^{-9} meter. In a homogeneous mixture the different components cannot be separated by physical methods, like filteration, sedimentation, boiling or centrifugation.

2.2 Types of Solutions

The solutions can be found in three states; Solid, Liquid and Gas. The solute and solvent can also be in three states. The physical state of the resulting solution can be decided on the basis of physical state of solute and solvent. The types of solution and their examples are given in table 2.1

Table 2.1 Types of solutions and their examples

Sr. No.	Type of solution	Physical state		Examples
		Solute	Solvent	
1.	Solid solution	Solid	Solid	Alloy formed from copper and zinc (Brass),
		Liquid	Solid	Zinc amalgam-Zinc dissolved in mercury (Zn/Hg)
		Gas	Solid	adsorption of H_2 gas on Pd.
2.	Liquid solution	Solid	Liquid	Homogeneous mixture of sugar and water.
		Liquid	Liquid	Homogeneous mixture of water and ethanol.
		Gas	Liquid	Homogeneous mixture of CO_2 gas in water.
3.	Gaseous solution	Solid	Gas	Homogeneous mixture of camphor in N_2 gas.
		Liquid	Gas	Air containing moisture
		Gas	Gas	Mixture of H_2 and O_2 gas.

When solute and solvent molecules experience attractive interaction between them, a solution is formed. For example solution is formed by strong attractive interaction between water and ethanol molecules but there is almost negligible interaction between water and benzene, their solution is not formed (it remains insoluble). Thus, solution can be formed if the solute or solvent has following characteristics.

(i) If the number of –OH group in organic compound is more in a solute, it is more soluble in water. More the number of –OH group more is the solubility e.g., Glycerol is more soluble in water than ethanol.

(ii) Most of the polar solutes dissolve in polar solvents. e.g., HCl in water.

(iii) Most of the non-polar solutes dissolve in non-polar solvents. e.g., Napthalene in benzene.

(iv) Most of the ionic solutes are soluble in water because they are ionic even in solid state. e.g., NaCl in water.

If water is the solvent in the solution, the solution is known as an aqueous solution, If water is not the solvent, the solution is known as non-aqueous solution. In a non-aqueous solution, generally benzene, ether, carbon tetrachloride etc. are used as non-aqueous solvents.

2.3 Units of Concentration

The quantitative proportion of solute and solvent are different in different solutions. The amount of solute in a unit volume of solution or unit weight of solvent is called concentration of solution. There are different ways to express concentration of solutions. Normality formality, molarity, molality mole-fraction, weight-fraction (% W / W) are units of concentration which you have studied in unit 1.9 of Semester-I. You will study some other units of concentration in this unit.

(1) Formality : Ionic compounds are in ionic form even in the solid state and not in molecular form. Hence formula mass is taken instead of molecular mass and so the concentration is known as formality. The sum of the atomic masses of the atom, in the proportion formula of the compound is called its formula mass. e.g. compounds like potash alum, the molecular formula of alum is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; hence its molecular mass will be 948 gram mole^{-1} the proportion formula of alum is $KAl(SO_4)_2 \cdot 12H_2O$ and so the value of its formula proportion mass is 474 gram formula mass. Hence, at normal temperature if one gram formula mass of the substance (solute) is dissolved in one litre solution it is called one formal solution and this type of concentration is called formality. It is indicated by the symbol F.

$$\text{Formality (F)} = \frac{1000 \times \text{mass of solute (gram)}}{\text{Formula mass of solute} \times \text{volume of solution (ml)}}$$

When 474 gram potash alum is dissolved in water and the solution is made to one litre, its concentration is called one formal. Formality unit is more used in pharmacy and medicinal science disciplines.

Example 1 : Calculate the formality of solution in which 948 gram potash alum is dissolved in 5 litre solution.

Solution : The formula mass of potash alum is 474 gram (formula mass)$^{-1}$.

$$\text{Formality of potash alum (F)} = \frac{1000 \times \text{mass of solute (gram)}}{\text{Formula mass of solute} \times \text{volume of solution (ml)}}$$

$$= \frac{1000 \times 948}{474 \times 5000} = 0.4 \text{ F}$$

The formality of this potash alum solution will be 0.4 F

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(2) Volume percentage (% V / V) : The volume of solute (ml) dissolved in 100 ml solution, is expressed as volume percentage (% V / V). Such a solution is called, percent proportion with reference to the volume of solute.

Mathematically it is written as below :

$$\% \text{ V/V} = \frac{100 \times \text{volume of solute}}{\text{volume of solute} + \text{volume of solvent}} = \frac{100 \times \text{volume of solute (ml)}}{\text{volume of solution (ml)}}$$

For example 10% V/V solution of ethanol in water means 10 ml ethanol dissolved in water and made the volume of solution equal to 100 ml. Generally solution in which solute and solvent both are in liquid form gives liquid solution. The concentration of such solutoin is indicated by this unit.

Example 2 : Calculate the % V / V of a solution in which 200 ml ethanol is dissolved in 2 litre aqueous ethanol solution.

Solution : 2 litre aqueous ethanol solution means 2000 ml aqueous solution.

Now, $\% \text{ V / V} = \dfrac{100 \times \text{volume of ethanol (ml)}}{\text{volume of solution (ml)}} = \dfrac{100 \times 200}{2000} = 10 \%$

The concentration of aqueous ethanol solution is 10% V/V.

Example 3 : How many ml of kerosene is required to prepare 5 litre of 15% V/V kerosene in petrol solution ?

Solution : 5 litre solution = 5000 ml solution

Now, $\% \text{ V/V} = \dfrac{100 \times \text{volume of kerosene (ml)}}{\text{volume of solution (ml)}}$

$$\therefore \ 15 = \frac{100 \times \text{volume of kerosene}}{5000}$$

Volume of kerosene $= \dfrac{15 \times 5000}{100} = 750$ ml

$\therefore$ 750 ml kerosene will be required to prepare 15% V/V 5 litre solution.

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(3) Mass by volume percentage (% W/V) : The mass of solute dissolved in 100 ml solution is called mass by volume percentage (% W/V). Such a solution is called percent weight proportion with reference to the mass of solute. Mathematically, it is written as below :

$$\% \text{ W/V} = \frac{100 \times \text{mass of solute (gram)}}{\text{volume of solution (ml)}}$$

For example 5% W/V aqueous solution of sugar means 5 gram sugar is dissolved in 100 ml. solution. Generally the concentration of solutions is expressed by this unit in pharmacy and medicinal fields.

Example 4 : How many gram of sugar will be required to prepare 5% W/V 2 litre aqueous solution ?

Solution : 2 litre solution = 2000 ml solution

Now, $\% \, W/V = \dfrac{100 \times \text{weight of sugar (gram)}}{\text{volume of solution (ml)}}$

$\therefore \, 5 = \dfrac{100 \times \text{weight of sugar}}{2000}$

$\therefore$ The weight of sugar $= \dfrac{5 \times 2000}{100} = 100$ gram.

100 gram of sugar will be required to prepare 5% W/V 2 litre solution.

Example 5 : Calculate the % W/V, containing 200 gram urea dissolved in 5 litre solution.

Solution : 5 litre solution = 5000 ml solution.

$\% \, W/V = \dfrac{100 \times \text{weight of urea (gram)}}{\text{volume of solution (ml)}} = \dfrac{100 \times 200}{5000} = 4 \, \%$

The concentration of urea solution will be 4 % W/V.

(4) Parts per million : (ppm) : Some times the amount of the solute in solution is very much less, and so the concentration is expressed as parts per million. (ppm) viz. Pollutant in pollution of air, the amount of O_2 gas dissolved in sea-water pollutants in pollution of water etc. are expressed by this unit. Parts per million can be expressed by three different ways as parts per million by mass to mass, parts per million by mass to volume and parts per million by volume to volume.

Parts per million by mass to volume : The amount of solute in milligram dissolved, in one litre solution is called parts per million by mass to volume.

$$\text{parts per million by mass to volume} = \dfrac{\text{amount of solute (mg)}}{\text{amount of solution (litre)}} \qquad (2.1)$$

So the unit of parts per million by mass to volume can be written as mg litre^{-1}

Now to express the amount of solute in gram and volume of solution in ml in equation (2.1),

$$\text{Parts per million by weight to volume} = \dfrac{\text{amount of solute (gram)}}{\text{amount of solution (ml)}} \times 10^6$$

$$= \dfrac{\text{amount of solute (micro gram)}}{\text{volume of solution (ml)}} \qquad (2.2)$$

So the unit of parts per million by mass to volume can also be written as micro gram ml^{-1}

Example 6 : Calculate the parts per million by mass to volume for 2 litre solution in which 2×10^{-6} kg sulphur is dissolved.

Solution : 2 litre solution = 2×10^3 ml

mass of sulphur (solute) = 2×10^{-6} kg = 2×10^{-3} gram

$\therefore$ parts per million by mass of volume = $\dfrac{\text{amount of solute (gram)}}{\text{volume of solution}} \times 10^6$

$$= \dfrac{2 \times 10^{-3}}{2 \times 10^3} \times 10^6 = 1$$

Parts per million by mass to volume for soultion will be 1 micro gram ml^{-1}

With the change in temperature the values of molality, mole fraction, percentage by mass, parts per million by mass to mass are not changed because these units do not include the term volume which depends on temperature; while with the change in temperature the molarity, normality, percentage by volume to volume, percentage by mass to volume, formality, parts per million by volume to volume, parts per million by mass to volume values are changed; because these units include the term volume which depends on temperature.

2.4 Solubility of Gases (Solubility of Gaseous Solute in Liquid Solvent)

At a given temperature and pressure the maximum amount of gaseous solute that can be dissolved in a specified amount of solvent is called solubility of gaseous solute. Factors which effect the solubility of gaseous solute in liquid solution formed by homogeneous mixture of gaseous solute and liquid solvent are given as under.

(i) **Nature of gaseous solute and the solvent :** The solubility of gases like H_2, O_2 and N_2 are less in water but their solubility is more in ethyl alcohol; also the solubility of gaseous solute like H_2S and NH_3 is more in water, while their solubility is less in ethyl alcohol. So the solubility depends on the nature of gaseous solute and then also the nature of solvent.

(ii) **Effect of temperature :** The solubility decreases with increase in temperature for gaseous solute in liquid solvent. Generally with increase in temperature the solute dissolved in solution bubbles out and hence, with the increase in temperature the solubility of a gaseous solute decreases. Such an effect can also be explained by Le-Chatelier principle for an equilibrium as follows.

gaseous solute + liquid solvent $\rightleftharpoons$ solution + energy.

The dissolution of gaseous solute in liquid solvent is an exothermic process. On increasing the temperature for such a reaction, according to Le-Chatelier principle the equilibrium shifts towards left hand side i.e., reverse direction. So the solubility of solute decreases.

(iii) **Effect of pressure :** The solubility of gaseous solute in liquid solvent increases by increasing pressure of gaseous solute present on the surface of solution. The concentration of gas dissolved in solution increases as shown in 2.1 (a) the upper part is gaseous solute while the lower part is solution obtained by dissolving gaseous solute in liquid solvent. Equilibrium is established between gaseous solute
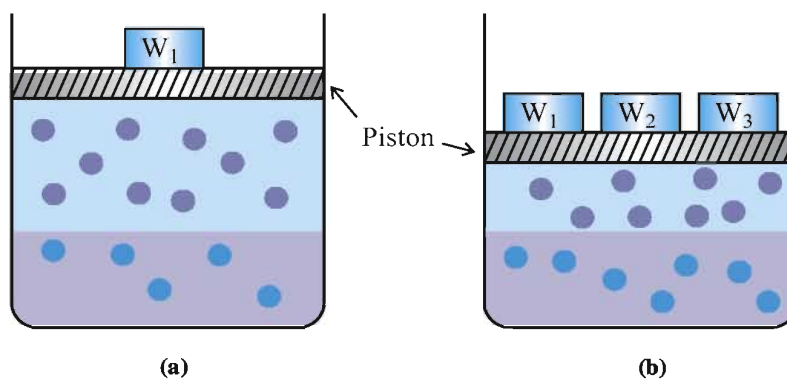
Fig. 2.1

The effect of pressure on solubility of gas. The concentration of dissloved gas is directly propertional to the pressure of gas upon the solution

and solution at temperature T_1 and pressure P_1, and hence the rates of molecules entering into solution and the dissolved gaseous molecules leaving the solution are equal. Now as shown in figure 2.1 (b) at temperature T_1, the pressure increases from P_1 to P_2, the volume accomodated by gaseous solute on the surface of solution decreases and hence the number of molecules of solute in unit volume increases. So the number of gaseous molecules striking the surface of solution increases and thus increases the solubility and at the end equilibrium is established. Hence, the solubility of gaseous solute increases due to the increase in the pressure of gaseous molecules in the solution.

Henry's law : The quantitative relation betwen solubility of gaseous solute in liquid solvent and pressure was given by Henry in 1803. It can be expressed as "The solubility of a gaseous solute in a liquid solvent at definite temperature is directly proportional to the pressure of the gas." On the basis of this, Henry's law can be expressed as **"The solubility of a gaseous solute in a liquid solvent at constant temperature is directly proportional to the pressure of gaseous solute."**
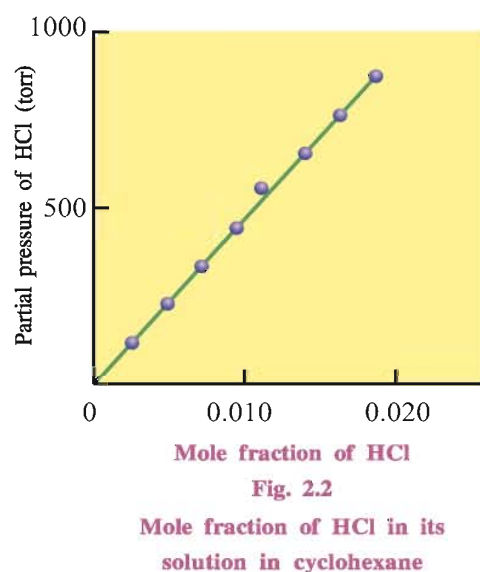

Fig. 2.2

Mole fraction of HCl in its solution in cyclohexane

Contemporarily Dalton independently concluded that the solubility of a gaseous solute in liquid solution is a function of the partial pressure of the gas. "If the mole fraction is considered for the solubility of gaseous solute then the partial pressure of a gaseous solute over the solution is directly proportional to the mole-fraction of the gaseous molecules". In the solution X is mole fraction of gaseous solute dissolved in unit volume of solvent and its partial pressure is p, then according to Henry's law it is expressed as

$$p \propto X$$

$$p = K_H \cdot X \qquad \text{where, } K_H \text{ is Henry's constant.}$$

If in the solution mole-fraction of gas is X and its partial pressure is p and graph is plotted betwen them, the graph is a stright line as indicated in fig 2.2. The value of the slope is equal to value of K_H. The unit of K_H is bar. The values of Henry's constant are different for different gaseous solutes, at constant temperature. This indicates that K_H is a function of the nature of the gas. The values of K_H also change with change in temperature for all the gaseous solutes which are given in table 2.2

Table 2.2 Values of Henary's Constant for Some Selected Gases in Water

Gas	Temperature (K)	K_H(kbar)	Gas	Temperature (K)	K_H(kbar)
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	1.83×10^{-5}
N_2	303	88.4	Methane	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611
O_2	303	46.82			

The following results can be obtained from the K_H values shown in table 2.2

(1) The solubility of gaseous solute is lower with the higher values of K_H.

(2) The K_H values increase as temperature increase which means the decrease in solubility of gaseous solute.

Limitations of Henry's law :

(i) This law is applicable to the gaseous solutes which show only ideal behaviour at high temperature and low pressure.

(ii) This law is applicable to solute which does not undergo association or dissociation when the solute is dissolved in solvent.

(iii) This law is applicable to gaseous solute which does not form any product by the chemical reaction, when gaseous solute is dissolved in liquid solvent.

Uses of Henry's law : Henry's law is used in industrial field and to explain some biochemical reactions :

(i) To increase the solubility of CO_2 gas in cold-drinks, soda-water, beer, champagne, the gases are filled in bottle at high presures and then sealed.

(ii) Due to higher partial pressure of oxygen gas entering into the lungs, it reacts with haemo-globin and forms oxyhaemoglobin. The partical pressure of oxygen gas is low in tissue. Hence, the oxygen is released from the oxohaemoglobin itself and is useful in the utilisation of the function of cell.

(iii) The sea-divers use the cylinders filled with mixture of 2 % dioxygen gas and 98% helium gas during the diving in sea. Nowadays a cylinder filled with 11.7 % He, 56.2 % N_2 and 32.1 % O_2 gas mixture are used.

Example 7 : Calculate the solubility of CO_2 in water in term of mole fraction if partial pressure of CO_2 is 2×10^{-8} bar at 298 K temperature, the K_H value for CO_2 is 6.02×10^{-4} bar.

Solution : According to Henry's law $p_{CO_2} = K_H \cdot X_{CO_2}$

$$\therefore X_{CO_2} = \frac{p_{CO_2}}{K_H} = \frac{2 \times 10^{-8} \text{ bar}}{6.02 \times 10^{-4} \text{ bar}}$$

$$= 3.322 \times 10^{-5}$$

The solubility of CO_2 gas in water in terms of mole fraction will be 3.322×10^{-5}

Example 8 : Calculate the partial pressure of He gas over the solution, having 2.4×10^{-3} mole fraction of gas in its saturated solution at 273 K temperature. The value of Henry's constant is 6.71×10^{-6} bar.

Solution : According to Henry's law, $p_{He} = K_H \cdot X_{He}$

$$= 6.71 \times 10^{-6} \times 2.4 \times 10^{-3}$$

$$= 1.61 \times 10^{-8} \text{ bar}$$

The partial pressure of the gas will be 1.61×10^{-8} bar.

Example 9 : How many millimoles of CO_2 gas will dissolve when CO_2 gas is passed in 900 ml water at 298 K temperature. The value of K_H is 6.02×10^{-4} bar and partial pressure of CO_2 gas is 2×10^{-8} bar.

Solution : Mole fraction of CO_2 $= \dfrac{P_{CO_2}}{K_H} = \dfrac{2 \times 10^{-8}}{6.02 \times 10^{-4}}$

$$= 3.322 \times 10^{-5}$$

Now the density of water is 1gm ml^{-1}. Hence, the mass of 900 ml water can be taken as 900 gram.

$$\therefore \text{ Mole of } H_2O = \frac{w}{M} = \frac{900}{18} = 50 \text{ mole}$$

Suppose the moles of CO_2 is n then the total moles $= (n + 50) \cong 50$ can be taken.

$$\therefore \text{ Mole fraction of } CO_2 = \frac{\text{mole of } CO_2}{\text{total mole}}$$

$$3.322 \times 10^{-5} = \frac{n}{50}$$

$$\therefore \text{ n } = 3.322 \times 10^{-5} \times 50$$

$$= 1.661 \times 10^{-3} \text{ mole}$$

$$= 1.661 \times 10^{-3} \times 10^{+3} \text{ millimole}$$

$$= 1.661 \text{ millimole}$$

$\therefore CO_2$ dissolved in 900 ml water will be 1.661 millimole.

2.5 Solubility of Solid Solute in Solid Solvent

When solid solute is dissoved in solid solvent it gives solid solution. The molecules are arranged in two ways :

(1) Substituted solid solution : As shown in fig 2.3, the size of solid solute and solid solvent are almost the same, then the solute atoms are arranged in solvent atoms and the solute atoms are substituted in arrangement of atoms forming solid solution. Such type of solution is known as substituted solid solution, e.g. brass, bronze, steel, monel metal etc.
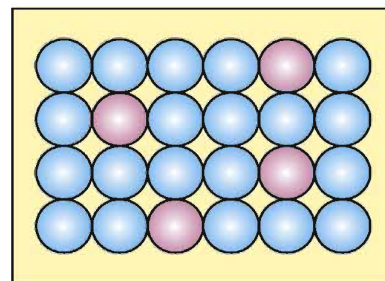

atoms of solvent   atoms of solute

Fig. 2.3

(2) Interstitial solid solution : As shown in figure 2.4 when the sizes of solid solute and solid solvent have vast difference then the small atoms are arranged in the interstitial holes formed between big atoms. Such type of solutions are called interstitial solid solution. e.g. Tungsten carbide (WC).

Solubility of solid solute in liquid solvent : At constant temperature and presure when the maximum amount of solid solute is dissolved in given liquid solvent then the concentration of solute is called its solubility. Now, no more solute can be dissolved in solution, so such a solution is called saturated solution. In a saturated solution the equilibrium is established between solid solute and solution.

atoms of solvent   O   atoms of solute

Fig. 2.4

Solid solute + Liquid solvent $\rightleftharpoons$ Liquid solution

It is not necessary that all the solid solutes will dissolve in all the liquid solvents. For example ionic solids like NaCl or KCl are solube in polar solvent like water but not soluble in non-polar solvent like benzene or carbon tetrachloride, because generally ionic solid solutes, dissolve in polar liquid solvents. Similarly non-ionic compounds like napthalene will dissolve in non-polar solvents like benzene, but does not dissolve in polar solvent like water. Thus the solubility of solute depends on the nature of solute and solvent. Moreover the solubility depends upon another two important factors like temperature and pressure.

Effect of temperature : When solid solute is dissolved in liquid solvent and solution is obtained then the equilibrium is established as given below :

Solute (Solid) + Solvent (Liquid) $\rightleftharpoons$ Solution (Liquid)

If such reaction in equilibirium is endothermic then according to Le-Chatelier's principle, on increasing the temperature, the forward reaction will occur and hence the solubility will increase, and if such reaction is exothermic, then on increasing the temperature according to Le-Chatelier's principle, the reverse reaction will occur and hence the solubility will decrease.

Effect of pressure : Solid solute substances when dissolved in liquid solvents give liquid solutions. Here, the substances are related with reactions may be in solid or liquid state which possess the non-compressible property, so the effect of pressure is very less or negligible.
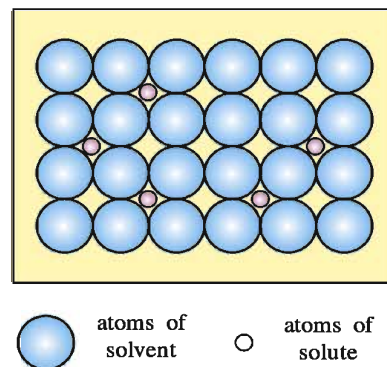
2.6 Solution-Colligative Properties

When solute substances are dissolved in pure solvent, the solutions are obtained. Some properties of solvent change viz. the vapour pressure of a solution prepared from a solvent is less than that of pure solvent, while the boiling point increases and freezing point decreases. The osmotic presure also changes. The change in these properties depend on number of molecules of solute but not on nature of solute. Such properties are called colligative properties of solution. For example by taking 1m aqueous solution of glucose, NaCl and $BaCl_2$ and if the colligative properties are studied, it is observed that all the solutons have equal molal concentration, yet the number of particles present are not equal. In glucose solution the concentration of number of particles of solute are 1 m, in NaCl solution the concentration of number of particles are 2 m and in $BaCl_2$ solution the concentration of number of particles is 3 m, Hence, their colligative properties are in proportion of 1:2:3 respectively. So these colligative properties do not depend upon the concentration of solution but depend on the concentration of the number of particles of solute present in the solution.

2.7 Vapour pressure of solution

A solid solute on dissolving in liquid solvent forms a solution. We have studied, such solutions. Now, let us study the vapour pressure of binary solutions which are obtained by dissolving solid solute in liquid solvent and liquid solute dissolved in liquid solvent. Solid solutes do not have remarkable vapour pressure but liquid solute and liquid solvent have vapour presures. At certain temperature the rate for the process of vapour to liquid phase and liquid to vapour phase becomes equal and hence equilibrium is established. Due to this at certain temperature pressure of vapour on surface on the solution become constant which is called vapour pressure of solution at that temperature. The factors which affect the vapour pressure are given below.

(i) The nature of liquid : The weaker the intermolecular forces between the molecules of liquid, the greater is the vapour pressure. This is because more and more molecules of liquid are converted into vapour phase and hence the vapour pressure is more.

(ii) Temperature : Higher the temperature of liquid, more is the vapour pressure, because the kinetic energy of the molecules increases due to increase in temperature and hence more and more molecules leaving the surface of liquid and obtain the vapour phase and its vapour pressure increses.

2.8 Raoult's Law (For Non-volatile Solute)

When solid solute dissolve in liquid solvent and liquid solution is formed its vapour pressure can be understood by simple experiment given below. As shown in figure 2.5, take two equal containers A and B and fill pure solvent and solution of non-volatile solute in same solvent in the containers respectively. Initially in both containers, keep the level of both the liquids (solvent and solution) same, it will be found that the level of solvent is more reduced than the level of solution, because in container A having solvent, its surface has totally solvent molecules and hence more vapour is formed. While in container B having solution, the surface has both solute and solvent molecules. So in

(a) Vapour pressure of
pure solvent

(b) Vapour pressure
of solution

Fig. 2.5 Vapour pressure of solution

containers B the fraction of surface covered by solvent molecules gets reduced as a result the number of molecules escaping from the surface is reduced and hence vapour pressure is reduced in container B. Thus, the vapour pressure of a solution prepared from a solvent is always less than that of pure solvent. The lowering of vapour pressure of solution was studied by Raoult and a law was proposed in 1887, which is called Raoult's law. According to Raoult's law "If dilute and ideal solution is prepared by dissolving non-volatile solute in a volatile solvent, the relative lowering of vapour pressure of the solution is equal to the mole fraction of the dissolved solute."

Proof of Raoult's law : For binary solution, Raoult's law is generally experessed as. "For any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction." The binary solution in which non-volatile solute is dissolved in the solution, the vapour is only due to solvent. If the vapour pressure of solvent is denoted by p_1 and its mole-fraction by X_1 then mathematical form is
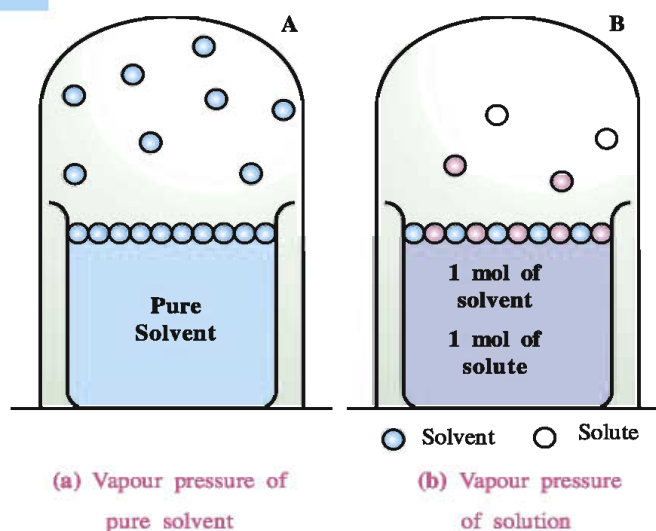
$$p_1 \propto X_1$$

$$p_1 = X_1 \cdot p_1^0 \qquad (2.3)$$

(where p_1^0 is proportionality constant and its value is equal to the vapour pressure of pure solvent)

As shown in fig 2.6 the graph of vapour pressure against mole-fraction of solvent is straight line, which states the Raoult's law-when the value of mole fraction X_1 is one, then $p_1 = p_1^0$ which is clear from the graph. Now from equation (2.3).

$$\frac{p_1}{p_1^0} = X_1 \qquad (2.4)$$

But $X_1 = \dfrac{n_1}{n_1 + n_2}$ where, n_1 and n_2 are the moles of solvent and solute respectively. Putting value of X_1 in equation (2.4) the equation is $\dfrac{p_1}{p_1^0} = \dfrac{n_1}{n_1 + n_2}$. Now subtracting each side from 1.

$$1 - \frac{p_1}{p_1^0} = 1 - \frac{n_1}{n_1 + n_2}$$

$$\therefore \frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \qquad (2.5)$$

but $\dfrac{n_2}{n_1 + n_2} = X_2$ i.e., mole fraction of solute. Putting this value in equation (2.5)

$$\frac{p_1^0 - p_1}{p_1^0} = X_2 \qquad (2.6)$$

Thus, the solution obtained by dissolving non-volatile solute in pure volatile solvent the relative lowering of vapour pressure of the solution is equal to the mole-fraction of the dissolved solute (X_2).

For very dilute solution $n_2 \ll n_1$, hence putting $n_1 + n_2 \approx n_1$ in equation (2.5)

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \qquad (2.7)$$

but $n_2 = \dfrac{w_2}{M_2}$ and $n_1 = \dfrac{w_1}{M_1}$; putting this values in equation 2.7

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \qquad (2.8)$$

where, w_1 = mass of solvent, M_1 = molecular mass of solvent

w_2 = mass of solute, M_2 = molecular mass of solute

For very dilute solutions, the molecular mass of solute can be calculated from equation (2.8).
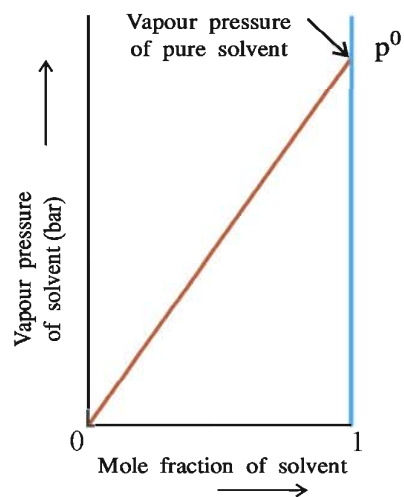

Fig. 2.6 Rault's law.
The relation between mole fraction of solvent and vapour pressure of solution

Limitations of Raoult's law :

(1) This law is applicable to very dilute solutions.

(2) This law is applicable to ideal solution.

(3) This law is applicable to solutions, whose heat of dilution does not change.

(4) It is applicable to solutions whose total volume is equal to the sum of the volumes of solute and solvent, if they are in liquid state.

(5) This law is applicable to the non-electrolyte aqueous solutions which do not undergo any dissociation or association when solute is dissolved in solvent.

2.9 Raoult's Law (For Volatile Solute and Volatile Solvent)

When both volatile liquids are the solute and the solvent then the vapour pressure of the solution is due to vapour pressure of both solute and solvent. According to Raoult's law for such a solution the vapour pressure of both the solute and solvent will be proportional to their mole-fractions.

Suppose in a binary solution X_A is the mole-fraction of solute A and its partial pressure is p_A and X_B is the mole fraction of the solvent B and its partial pressure is p_B then according to Raoult's law $p_A \propto X_A$ and $p_B \propto X_B$.

According to experimental observations Raoult's law can be proved that if the vapour presure of solute is p_A^0 and vapour pressure of pure solvent is p_B^0 then,

$$p_A = p_A^0 \, X_A \qquad (2.9) \qquad \text{and} \quad p_B = p_B^0 \, X_B \qquad (2.10)$$

Now according to Dalton's law of partial pressure the total pressure in the closed vessel will be,

Total pressure $P = p_A + p_B$

Now putting values of p_A and p_B from equation (2.9) and (2.10)

$$
\begin{aligned}
\text{Total pressure} \quad p &= p_A^0 \, X_A + p_B^0 \, X_B \\
&= p_A^0 \, (1 - X_B) + p_B^0 \, X_B \qquad (\because X_A = 1 - X_B) \\
&= p_A^0 - p_A^0 \, X_B + p_B^0 \, X_B \\
&= p_A^0 + (p_B^0 - p_A^0) X_B \qquad\qquad (2.11)
\end{aligned}
$$

In the same way,

$$
\begin{aligned}
\text{total pressure} \quad p &= p_A + p_B \\
p &= p_A^0 \, X_A + p_B^0 \, X_B \\
&= p_A^0 \, X_A + p_B^0 \, (1 - X_A) \qquad (\because X_B = 1 - X_A) \\
&= p_A^0 \, X_A + p_B^0 - p_B^0 \, X_A \\
&= p_B^0 + (p_A^0 - p_B^0) X_A \qquad\qquad (2.12)
\end{aligned}
$$

Following conclusions can be drawn from the equations (2.11) and (2.12).

(1) Total vapour pressure of the solution can be related to mole fraction X_A or X_B of any component.

(2) The total vapour pressure of the solution varies linearly with the mole fraction of the component A or B.

(3) Dependning on the vapour pressure of the pure components A and B, the total vapour pressure of the solution change with the change of the mole fraction of component A or B.

If graph is plotted between p_A or p_B with mole fraction X_A or X_B then as shown in fig 2.7, according to equation (2.11) if $p_B^0 > p_A^0$ i.e., components is more volatile compared to component A then minimum total vapour pressure obtained of the solutoin is p_A^0 and the maximum total vapour pressure is p_B^0. When $X_A = 1$ then the total vapour pressure over the solution is p_A^0 and when $X_B = 1$ then total vapour pressure over the solution is p_B^0 which is clear from equation (2.11) and (2.12).
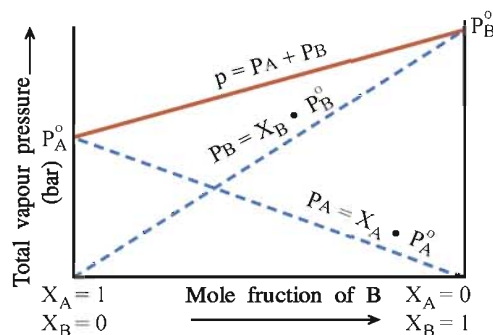

Fig. 2.7 Total vapour pressure → mole fraction

If at equilibrium stage, Y_A and Y_B are the mole-fractions of component A and componant B in vapour phase respectively then at equilibrium the partial pressure p_A and p_B of each component can be obtained by equations given below :

$$p_A = Y_A \cdot P_{total}$$

$$p_B = Y_B \cdot P_{total}$$

Raoult's law (for gaseous solute and liquid solvent) : When gaseous solute is dissolved in liquid solvent and solution is prepared, then according to Raoult's law its vapour pressure can be given as follows :

$$p_A = p_A^0 \cdot X_A \tag{2.13}$$

But if gaseous solute is dissolved in liquid solvent, then its solubility can be given by Henry's law as given below:

$$\text{Solubility } p = K_H \cdot X_A \tag{2.14}$$

By comparing Raoult's law-equation (2.13) and Henry's law-equation (2.14) if both the constant (like p_A^0 and K_H) are different but the volatile component or partial presure of gas is directly proportional to its mole fraction. It can therefore be said that solubility of a gas and vapour pressure of solution follows Henry's law and Raoult's law respectively.

Ideal solution : The solution which obeys the Raoult's law over the entire range of concentrations is known as ideal solution. The ideal solution has two other important proporties like.

(i) On mixing solute and solvent if solution is obtained, then for this reaction, change in enthapy (ΔH) is zero.

(ii) If solute and solvent are in liquid state then on preparing solution, the change in volume (ΔV) is zero. For understanding ideal behaviour of solution, the components A and B of solution, when they are in pure form, there are A–A and B–B type intermolecular interaction forces. Besides that in binary solution also A–B type attractive intermolecular interactions will also be present. If the intermolecular, attractive forces between A–A and B–B are nearly equal to the intermolecular attractive force between A–B, the solution becomes ideal. (This leads to the formation of an

ideal solution). For example mixture of Bromoethane and chloroethane, Benzene and toluene, Hexane and heptane, Chlorobenzene and bromobenzene.

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. This solution is also called real solution. The vapour pressure of such solution is either higher or lower than that predicted by Raoult's law. The intermolecular attractive forces between A–A and B–B are not equal to the intermolecular attractive forces between A–B for such solution. The value of ΔH and ΔV will not be zero. For example mixture of phenol and aniline, mixture of chloroform and acetone, mixture of HCl and water, mixture of HNO_3 and water give non-ideal solutions.

Example 10 : Calculate the vapour pressure for 4% W / W aqueous solution of urea at 298 K temperature. The vapour pressure of water is 0.025 bar.

Solution : According to Raoult's law,

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

Now 4 % W/W urea solution means 4 gram urea in 96 gram water and $p_1^0 = 0.025$ bar

$$\therefore n_1 = \frac{w_1}{M_1} = \frac{96}{18} = 5.33 \ \text{mole of water}$$

$$n_2 = \frac{w_2}{M_2} = \frac{4}{60} = 0.0667 \ \text{mole of urea}$$

Now putting these values of p_1^0, n_1 and n_2 in Raoult's law equation,

$$\frac{0.025 - p_1}{0.025} = \frac{0.0667}{5.33}$$

$$\therefore 0.025 - p_1 = \frac{0.0667 \times 0.025}{5.33} = 0.000313$$

$$\therefore p_1 = 0.025 - 0.000313 = 0.02469 \ \text{bar}$$

The vapour pressure of 4 % W/W aqueous solution of urea will be 0.02469 bar.

Example 11 : The vapour pressure of chlorobenzene and bromobenzene are 0.350 bar and 0.500 bar respectively. Find the vapour pressure of solution obtained by mixing 11.25 gram chlorobenzene with 31.4 gram bromobenzene.

Solution : The molecular masses of chlorobenzene and bromobenzene are 112.5 and 157 gm mol^{-1} respectively.

$$\therefore \ \text{mole of chlorobenzene} = \frac{w}{M} = \frac{11.25}{112.5} = 0.1 \ \text{mole}$$

$$\text{mole of bromobenzene} = \frac{w}{M} = \frac{31.4}{157} = 0.2 \ \text{mole}$$

$$\therefore \text{Total moles} = (0.1 + 0.2) = 0.3$$

$\therefore$ The mole fraction of chlorobenzene $= X_1 = \dfrac{0.1}{0.3} = \dfrac{1}{3}$

mole fraction of bromobenzene $= X_2 = \dfrac{0.2}{0.3} = \dfrac{2}{3}$

Here, $p_1^0 = 0.350$ bar and $p_2^0 = 0.500$ bar

Now according to Raoult's law,

total vapour pressure $= p_1^0 + (p_2^0 - p_1^0)\, X_2$

$$= 0.350 + (0.500 - 0.350) \times \dfrac{2}{3}$$

$$= 0.350 + \dfrac{0.150 \times 2}{3}$$

$$= 0.350 + 0.100 = 0.450 \text{ bar}$$

$\therefore$ The vapour pressure of solution will be 0.450 bar.

2.10 Elevation in Boiling Point

The temperature at which the vapour pressure of any liquid (solvent or solution) becomes 1 bar (1 atmorphere), is known as boiling point of that liquid. (solvent or solution). At any temperature the vapour pressure of solution is less than that of pure solvent from which it is prepared, and vapour pressure increases on increasing temperature. At 373 K (373.15 K) temperature the vapour pressure of pure water becomes 1 bar and hence it starts boiling . Now if solution is prepared by adding non-volatile solute (like sugar), the vapour pressure of solution decreases. So as to make its vapour pressure equal to 1 bar it has to be heated. On heating solution starts boiling. Thus the boiling point of solution is higher than that of pure solvent. The increrase in boiling point is called **elevation in boiling point (ΔT_b)**.

Molal elevation constant : Increase in boiling point of a solution prepared by dissolving one gram molar mass of non-volatile solute in one kilogram of solvent is called molal elevation constant (K_b). For example 342 gram sugar or 60 gram urea or 180 gram glucose is dissolved in one kilogram water means by dissolving one molecular mass of a substance the increase in boiling points (ΔT_b) of these solutions are same. Thus, increase in boiling point depends upon the number of molecules of solute and not on the nature of solute, so it is colligative property of solution.

Molal elevation and molal elevation constant : Figure 2.8 shows the relation between vapour pressure and temperature for pure solvent and its solutions.

Suppose the boiling point of pure solvent is T_b^0 and the boiling point of solution is T_b, then increrase in boiling point $\Delta T_b = T_b - T_b^0$ is elevation in boiling point. Experimental observation
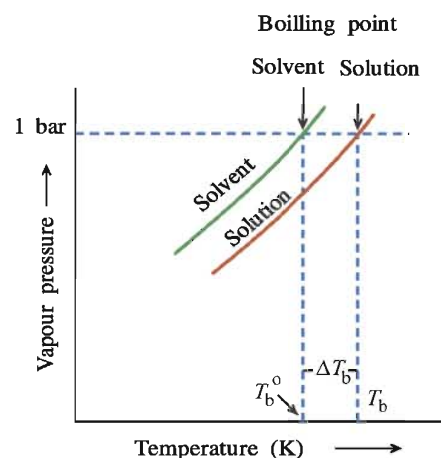

Fig. 2.8 The relation between vapour pressure and temperature

indicates that molal elevation (ΔT_b) is directly proportional to the molal concentration of solute dissolved in dilute and ideal solution. So it is written in mathematical form as

$$\Delta T_b \, \alpha \, m$$

$$\Delta T_b = K_b \times m \qquad\qquad (2.15)$$

$$\text{but molality } m = \frac{1000 \times w_2}{M_2 \times w_1}$$

Putting this value in equation 2.15

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

$$\therefore K_b = \frac{\Delta T_b \times w_1 \times M_2}{1000 \times w_2} \qquad\qquad (2.16)$$

where K_b = Molal elevation constant w_1 = mass of solvent

w_2 = mass of solute M_2 = molecular mass of solute

ΔT_b = elevation in boiling point.

Elevation in boiling point for one molal solution is called solvent's molal elevation constant (K_b). Its unit is Kelvin kilogram mole^{-1} (K kg mole^{-1}).

Example 12 : Calculate the boiling point of solution which is prepared by dissolving 6 gram of urea in 2 kg of water. Molal elevation constant for solution is 3.2 K kg mole^{-1}.

Solution : $\Delta T_b = \dfrac{K_b \times 1000 \times w_2}{M_2 \times w_1}$

K_b = 3.2 K kg mole^{-1} w_2 = 6 Gram

w_1 = 2 Kilogram = 2000 gram M_2 = 60 gram mole^{-1}

$$= \frac{3.2 \times 1000 \times 6}{60 \times 2000} = 0.16 \text{ Kelvin}$$

$\therefore$ The boiling point of urea solution = boiling poing of solvent + T_b

$$= 373 \text{ K} + 0.16 \text{ K} = 373.16 \text{ K}$$

$\therefore$ The boiling point of urea solution will be 373.16 K.

Example 13 : How many gram of glucose should be added to 5 kg of water, so that the boiling point increases from 373 K to 373.5 K. The molal elevation constant of solvent is 2.2 K kg mole^{-1}.

Solution : Elevation in boiling point

$$\Delta T_b = 373.5 \text{ K} - 373 \text{ K} = 0.5 \text{ K}$$

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

$$\Delta T_b = 0.5 \text{ K} \qquad\qquad K_b = 2.2 \text{ K kg mole.}^{-1}$$

$$w_2 = ? \qquad\qquad M_2 = 180 \text{ gram mole}^{-1}$$

$$w_1 = 5 \text{ kg} = 5000 \text{ gram}$$

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

$$= \frac{0.5 \times 180 \times 5000}{2.2 \times 1000} = 204.5 \text{ gram}$$

$\therefore$ 204.5 gram glucose should be dissolved in 5 kg water.

2·11 Depression in freezing point

Freezing point of substance (solvent or solution) is a temperature at which the solid and liquid phase of the substance (solvent or solution) are in equilibrium and at that temperature (Freezing point) the vapour pressure of the solid and liquid phase of the substance (solvent or solution) are same.

The freezing point of solution is lower than that of pure solvent from which the solution is prepared. Thus, decrease in freezing point of solution from solvent is called depression in freezing point (ΔT_f). Freezing point of solution is less than that of solvent from which it is prepared, because according to Raoult's law vapour pressure of solution is less compared to that of solvent to which the non-volatile solute is added to form that solution. So at lower temperature the vapour pressure of liquid. Solution and pure solid solvent becomes equal, that temperature is the freezing point of solution. Thus, the freezing point of solution is less than freezing point of pure solvent.

Molal depression constant : "Decrease in freezing point of a solution prepared by dissolving one gram molar mass of non-volatile solute into one kilogram of solvent is called molal depression constant (K_f)." For example 60 gram urea or 180 gram glucose or 342 gram sugar i.e. one gram molar mass of solute on dissolving in 1 kg of solvent, the lowering in freezing points are equal, because depression in freezing point depends on number of molecules of solute dissolved in the solution and not on the nature of solute, so it is a coilligative property.

Depression in freezing point and molal depression constant : The values of vapour pressure at different temperatures for pure solvent and solution prepared from that solvent are shown in figure 2.9.

Suppose the freezing point of pure solvent is T_f^0 and freezing point of solution is T_f then depression in freezing point $\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point. Experimental results shows that it is directly proportional to the molal concentration of solute. So it is written in mathematical form as

Fig. 2.9 The relation between vapour pressure and temperature (mole depression constant)

$$\Delta T_f \propto m$$

$$\therefore \Delta T_f = K_f \times m \qquad\qquad (2.17)$$

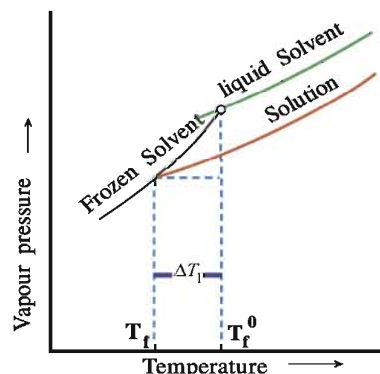But molality $m = \dfrac{1000 \times w_2}{M_2 \times w_1}$. Putting values in equation (2.17)

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

$$\therefore K_f = \frac{\Delta T_f \times w_1 \times M_2}{1000 \times w_2} \qquad (2.18)$$

where, K_f = molal depresion constant $\qquad$ w_1 = mass of solvent

$\qquad$ w_2 = mass of solute $\qquad$ M_2 = molar mass of solute

$\qquad$ ΔT_f = depression in freezing point.

Depression in freezing point for one molal solution is called molal depression constant (K_f) and its unit is Kelvin kilogram mole^{-1} (K kg mol^{-1}).

Example 14 : Find the freezing point of solution obtained by dissolving 1.8 gram glucose in 500 gram water. The value of K_f for solvent is 1.8 K kg mol^{-1}.

Solution : $\Delta T_f = \dfrac{K_f \times 1000 \times w_2}{M_2 \times w_1}$

K_f = 1.8 K kg mol^{-1} $\qquad$ w_2 = 1.8 gram

M_2 = 180 gram mol^{-1} $\qquad$ w_1 = 500 gram

$$= \frac{1.8 \times 1000 \times 1.8}{180 \times 500} = 0.036$$

Now freezing point of pure solvent is 273 K.

$\therefore$ Freezing point of solution = freezing point of solvent $- \Delta T_f$

$$= 273 - 0.036 \text{ K} = 272.964 \text{ K}$$

$\therefore$ The freezing point of solution will be = 272.964 K.

Example 15 : How many grams of urea must be dissolved in 2000 grams of water so that depression in freezing point is 0.2 K. The K_f for solvent is 2.0 Kkgmol^{-1}.

Solution : $\Delta T_f = \dfrac{K_f \times 1000 \times w_2}{M_2 \times w_1}$

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

K_f = 2 K kg mol^{-1} $\qquad$ w_2 = ?

M_2 = 60 gram mol^{-1} $\qquad$ w_1 = 2000 gram

ΔT_f = 0.2 K

$$\therefore \quad w_2 = \frac{0.2 \times 60 \times 2000}{1000 \times 2} = 12 \text{ gram}$$

$\therefore$ 12 gram urea will have to be dissolved in 2000 gram water.

2.12 Osmosis, Osmotic pressure and its Uses

When a semipermeable membrane is kept between two solutions having different concentrations or between a solvent and a solution, a spontaneous flow of solvent starts from a solution, having lower concentration to higher concentration, or from a solvent to a solution respectively. This phenomenon is called **Osmosis.** The meaning of Greek word osmosis is to push. Semipermeable membrane can allow only solvent molecules but will not allow solute molecules. As shown in figure 2.10, $CuSO_4$ solution is filled on one side and on other otherside pure water or dilute $CuSO_4$ solution.

After some time it is observed that spontanoeusly the water molecules flow towards the $CuSO_4$ solution and hence the difference is observed in level of liquids on both the sides of semipermeable membrane. Such spontaneous flow will just stop when equilibrium is established between them.

Fig. 2.10 Osmosis

Some examples of osmosis are found in nature and in daily life. For example the dry grapes get swollen when kept in water, wilted flower revives when placed in water; blood cell collapse when placed in salty water. In all these phenomena the boundry of all the substances bounded by semipermeable membrane and hence osmosis is observed. Some examples of natural semipermieable membranes are animal cell wall, plant cell wall, urinary bladder of animal. While artificial semipermeable membrane are parchment paper, cellophane, butter paper, copper ferrocyanide $Cu_2[Fe(CN)_6]$. In such artificial semiper-meable membranes, the copper ferrocyanide is one of the best artificially prepared semipermiable membrane.

Osmotic pressure : As shown in fig 2.11 on one side of semipermeable membrane (SPM) a solution and on other side pure water are filled. As the time passes, the spontaneous flow of solvent starts towards solution, hence the difference in levels of the pure solvent (water) and solution is observed. Hence by applying minimum pressure on the solution that just stops the flow of solvent towards the solution across the semipermeable membrane is called osmotic pressure of solution.

Fig. 2.11 Osmosis pressure

Example of osmotic pressure :

(1) Plants absorb water from soil through their roots is due to osmosis.

(2) Water assimilated by the plants moved into the different parts of plant is due to osmosis.

(3) Due to osmosis the water reaches into the different parts of the animal body.

(4) Opening of flower and closing of flower is also controlled by osmosis.

(5) Bursting of red blood cell when placed in water is also due to osmosis.

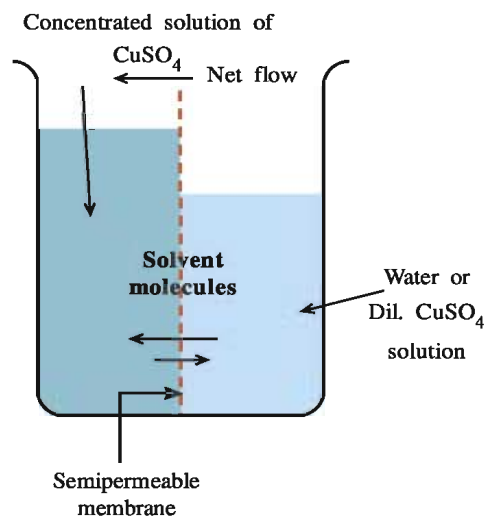(6) Rapid growth of the plants and germination of seeds is due to osmosis.

2.13 Laws of osmotic pressure
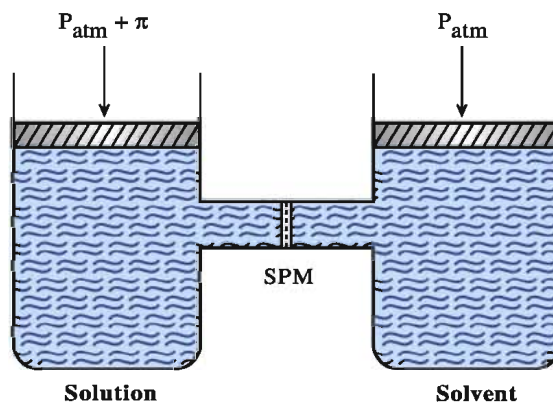
van't-Hoff and Pfeiffer suggested that the solute in the dilute solution behaves like a gas. The osmotic pressure of dilute solution is equal to pressure of gas if the solute is in gaseous form at that temperature and occupy the volume equal to that of solution. So van't Hoft derived laws similar to gas laws like Boyle, Gay-Lussac and Avogadro's law for dilute solution.

(i) **Boyle's-van't Hoff Law** : "At constant temperature the osmotic pressure (π) is directly proportional to the molar concentration of the solution." It can be written mathematically as follow :

Putting this value

$$\pi \propto C \text{ but } C = \frac{n}{V}$$

$$\pi \propto \frac{n}{V} \tag{2.19}$$

where, n = number of moles of solute   V = volume of solution (litre)

$$\frac{n}{V} = \text{ molar concentration}$$

Putting in equation (2.19) n = 1 mole,

$$\pi \propto \frac{1}{V} \tag{2.20}$$

$$\pi = K \frac{1}{V}$$

$$\therefore \pi V = K \tag{2.21}$$

Eequation (2.21) is similar to Boyle's law : PV = K

(ii) **Gay-Lussac-van't Hoff law** : If the concentration of solution is constant then osmotic pressure of solution is directly proportional to absoulte temperature. It can be written mathematically as

$$\pi \propto T \tag{2.22}$$

$$\pi = KT \quad \text{where, K = proportionality conctant.}$$

$$\frac{\pi}{T} = K \tag{2.23}$$

Equation (2.23) is of the form $\frac{P}{T} = K$ regarding Gay-Lussac's law for gases.

(iii) **Avogadro's-van't-Hoff law** : The number of molecules in the same volume of different solutions having the same osmotic pressure at the same temperature. It can be written mathematically as

$$\pi \propto n \tag{2.24}$$

Now, according to equation (2.20).

$$\pi \alpha \frac{1}{V} \quad \text{(Boyle-van't-Hoff Law)}.$$

According to equation (2.22)

$\pi \alpha T$ (Gay-Lussac-van't-Hoff Law)

$\pi \alpha n$ (Avogadro-van't-Hoff Law)

$$\pi \alpha \frac{nT}{V}$$

$$\pi = \frac{nRT}{V} \quad \text{where, R is proportionality constant and its value is equal to that of gas constant.}$$

$$\therefore \pi V = nRT \tag{2.25}$$

where π = Osmotic pressure in bar   V = volume of solution in litres

n = number of moles of solute   R = gas constant

T = absoulte temperature in Kelvin.

Equation 2.25 is similar to simple gas equation PV = nRT

Now, putting value of $n = \dfrac{w}{M}$ in equation (2.25)

$$\pi V = \frac{wRT}{M}$$

$$\pi = \frac{wRT}{MV} \tag{2.26}$$

where w = mass of solute,   M = molar mass of solute

2.14 Iso-Osmotic (Isotonic)Solutions

The solutions having same osmotic pressure at given temperature are called Iso−osmotic (Isotonic) solutions. If such solutions are separated by semipermeable membrance no osmosis occurs, between them. The vapour pressures of iso-osmotic solutions are equal so such solution are known as iso-osmotic or isotonic solutions. Concentration of isotonic solutions are equal. For example the osmotic pressure associated with fluid inside blood cell is equivalent to that of 0.91 % W/V NaCl solution, same way 0.1 M H_2SO_4 solution is isotonic with 0.3M glucose solution. If the osmotic pressures of two different solutions are different it means that concentrations are different then, solution whose osmotic pressure is less it is known as hypotonic with comparison to higher osmotic pressure solution. A solution whose osmotic pressure is higher, in comparison to solution having less osmotic pressure is called hypertonic solution. This means that for the solution having less osmotic pressure the prefix hypo and for the solution having more osmotic pressure the prefix hyper is used. For example less than 0.91% W/V pure NaCl solution is hypotonic compared to fluid inside human blood but pure NaCl solution having concentration more than 0.91 % W/V is hypertonic with respect to fluid inside human body.

Example 16 : Calculate the osmotic pressure at 300 K temperature of a solution having 18 gram glucose dissolved in 5 litre solution.

Solution : Osmostic pressure $\pi = \dfrac{wRT}{MV}$

M = 180 gram   w = 18 gram   V = 5 Litre

T = 300 K   R = 8.314 × 10^{-2} bar lit K^{-1} mol^{-1}

$$\therefore \pi = \frac{18 \times 8.314 \times 10^{-2} \times 300}{180 \times 5}$$

$$\therefore \pi = \frac{18 \times 8.314 \times 10^{-2} \times 300}{900} = 0.4988 \text{ bar}$$

$\therefore$ The osmotic pressure of the glucose solution will be 0.4988 bar.

Example 17 : 6 gram of urea is dissolved in 2 litre solution at 300 K temperature. How many grams of NaCl should be dissolved in 5 litre solution so that it becomes iso-osmotic with urea solution ?

Solution : As the temperature and gas constant R have same values, for both solutions; so for such iso-osmotic solutions, it can be written directly.

$$\frac{\text{mole of urea}}{\text{volume of urea solution}} = \frac{\text{mole of NaCl}}{\text{volume of NaCl solution}}$$

$$\therefore \frac{0.1}{2} = \frac{\text{moles of NaCl}}{5} \qquad \left(\because \text{ moles of urea } \frac{w}{M} = \frac{6}{60} = 0.1 \text{ mole} \right)$$

$$\therefore \text{ moles of NaCl} = \frac{0.1 \times 5}{2} = 0.25 \text{ mole}$$

Now in NaCl, $(Na^+ + Cl^-)$ the number of particles is two and for isotonic solution the number of particles required is 0.25 mole number of particles, so the mole of NaCl will be half

$$\text{number of mole of NaCl } = \frac{0.25}{2}$$

$$= 0.125 \text{ mole}$$

Amount of NaCl in gram $= $ no. of mole $\times$ molar mass

$$= 0.125 \times 58.5$$

$$= 7.31 \text{ gram}$$

$\therefore$ 7.31 gram NaCl should be dissolved so that it becomes isotonic with urea solution.

2.15 Methods of Determining the Molecular Mass

To determine the molecular mass of any substance, the different methods used are as given below :

(1) Using Raoult's law.

(2) Molal elevation measurement method.

(3) Molal depression measurement method.

(4) Osmotic pressure measurement method.

Let us study these methods in detail.

(1) Using Raoult's law : For the solution obtained by dissolving non-volatile solute in pure volatilc solvent equation (2.8) was derived earlier. Using this equation the molecular mass can be determined.

According to equation (2.8)

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \qquad \text{OR}$$

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

At given temperature the solution is prepared by dissolving w_2 gram non-volatile solute into w_1 gram solvent having vapour pressure. p_1^0 and molecular mass M_1. Now the vapour pressure of the solution (p_1) is determined and putting the values obtained at the end of the experiment in equation (2.8) the molar mass (M_2) of solute can be found.

Example 18 : Calculate the molar mass of unknown substance, when 20 gram non-volatile substances dissolved in 360 gram water at 298 K temperature. The vapour pressure of water is reduced to 0.0238 bar from 0.0242 bar.

Solution : According to Raoult's law

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

$p_1^0 = 0.0242$ bar $p_1 = 0.0238$ bar

$w_2 = 20$ gram $M_2 = ?$

$w_1 = 360$ gram $M_1 = 18$ gram mole^{-1}

$$\therefore \frac{0.0242 - 0.0238}{0.0242} = \frac{20 \times 18}{M_2 \times 360}$$

$$\therefore \frac{0.0004}{0.0242} = \frac{1}{M_2}$$

$$\therefore M_2 = \frac{0.0242}{0.0004} = 60.5 \text{ gram mole}^{-1}$$

Molar mass of unknown substance will be 60.5 gram mole^{-1}.

(2) Molal elevation measurement method : When solution is prepared by dissolving non-volatile solute in pure volatile solvent, for such a solution according to equation (2.16) molar mass of non-volatile solute can be determined. According to equation (2.16).

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

$$\therefore M_2 = \frac{K_b \times 1000 \times w_2}{\Delta T_b \times w_1} \qquad\qquad (2.27)$$

At given temperature the solution is prepared by dissolving w_2 gram solute in w_1 gram solvent having molal elevation constant K_b and by experimental observation for that solution elevation in boiling point (ΔT_b) is obtained. Putting these values in equation (2.27) molar mass of solute is obtained by the calculation.

Example 19 : 0.75 gram unknown substance is dissolved in 200 gram water and solution is prepared. If the elevation in boiling point is 0.15 K and molal elevation constant is 7.5 K kg mole^{-1} then find the molar mass of unknown substance.

Solution : The molar mass of unknown substance

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

$K_b = 7.5$ K kg mol^{-1} $w_2 = 0.75$ gram

$\Delta T_b = 0.15$ K $w_1 = 200$ gram

$$\therefore M_2 = \frac{7.5 \times 1000 \times 0.75}{0.15 \times 200}$$

$$= 187.5 \text{ gram mole}^{-1}$$

∴ The molar mass of unknown substance will be 187.5 gram mole^{-1}.

(3) Molal depression measurement method : When non-volatile solute is dissolved in pure volatile solvent and solution is prepared then, for such solution equation (2.18) as derived earlier, can be used so that the molar mass of non-volatile solute (M_2) can be determined. According to equation (2.18.)

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

$$\therefore M_2 = \frac{K_f \times 1000 \times w_2}{\Delta T_f \times w_1} \qquad\qquad (2.28)$$

At given temperature the solution is prepared by dissolving w_2 gram solute in w_1 gram solvent having molal depression constant K_f and by experimental observation in depression of temperature for that solution (ΔT_f) is obtained. Putting these values in equation 2.28 molar mass of solute can be obtained by the calculation.

Example 20 : 2 gram unknown substance is dissolved in 500 gram water and solution is prepared. The depression in freezing point is 0.06 K. If the molal depression constant for solvent is 5 K kg mole^{-1}, then find the molar mass of unknown substance.

Solution : Molar mass of unknown substance $M_2 = \dfrac{K_f \times 1000 \times w_2}{\Delta T_f \times w_1}$

$K_f = 5$ Kkgmole^{-1} $w_1 = 500$ gram

$\Delta T_f = 0.06$ $w_2 = 2$ gram

$$M_2 = \frac{5 \times 1000 \times 2}{0.06 \times 500}$$

$$= 333.3 \text{ gram mole}^{-1}$$

The molar mass of unknown substance will be 333.3 gram mole^{-1}

(4) Osmotic pressure measurement method : In fixed amount of solvent if fixed amount of solute is dissolved and solution is prepared at fixed temperature and the osmotic pressure is noted and then by using formula given below, the molar mass of substance can be calculated.

Molar mass of unknown solute substance $M = \dfrac{\text{mass of unknown solute} \times RT}{\text{osmotic pressure} \times \text{volume of solution}}$

This method is more useful for the determination of molar masses of protein polymer and macromolecules; because during experimental observation the values obtained for elevation in boiling point, depression in freezing point is very less (nearly 10^{-5} K); So it is difficult to measure them accurately; nearly the pressure as small as 10^{-3} bar can be measured in mm unit. Besides this the biomolecules like protein are not stable at high temperature, so their molar masses can not be obtained by molal elevation method or molal depression method, but at room temperature can be obtained by osmotic pressure measurement method, besides this the solubility of polymer substances is very less so they can be prepared as dilute solutions and for dilute solutions the observation which are obtained can be easily noted in the osmotic pressure measurement method.

While in other methods the observation values obtained are very small, so it is difficult to measure them. In osmotic pressure measurement method the concentration of solution is measured in molarity instead of molality. So the osmotic pressure measurement method is more useful than other methods.

Example 21 : At 300 K temperature 1.5 gram unknown substance is dissolved in solvent and made the volume 1.5 litre of the solution. Its osmotic pressure is found to be 0.2 bar. Calculate the molar mass of unknown substance.

Solution : Molar mass of unknown substance

$M = \dfrac{\text{mass of unknown substance} \times RT}{\text{osmotic pressure} \times \text{volume of solution}}$

$= \dfrac{1.5 \times 8.314 \times 10^{-2} \times 300}{0.2 \times 1.5} = 124.71$ gram mole^{-1}

Molar mass of unknown substance will be 124.71 gram mole^{-1}

2.16 Abnormal molecular mass and van't Hoft factor

The various relations for the colligative properties are applicable to the non-electrolyte solution and also the solutes which do not undergo any dissociation or association in the solution; because due to dissociation or association of solute the number of particles, which indicate concentration gets decreased or increased. When polar solute is dissolved in polar solvent; the solute is polar so it is ionised in solution and number of particles in solution increases e.g. $NaCl$, K_2SO_4, $FeCl_3$ and $Fe_2(SO_4)_3$ when dissolved in water get ionised, and the number of particles obtained are 2, 3, 4 and 5 respectively. It is called dissociation. Due to increase in number of particles; using colligative properties; the value of molar mass obtained is less than the actual molar mass. The molar mass obtained by experimental method is called abnormal molar mass. Besides this some solute molecules when dissolved in solvent, more than two molecules combine and form associated molecules, and this process is called association. e.g. Acetic acid or benzoic acid when dissolved in solvent like benzene, then two molecules of solute associate and hence the number of molecules in solution decreases. For such type of solution the real molar mass of solute can not be obtained, by using method based on colligative properties. The experimental molar mass value is more than real molar mass value and such experimental molar mass obtained is also called

abnormal molar mass. The colligative properties of solution is applicable to only dilute solution because concentrated solution means the concentration of solution is higher, so the solute molecules are so close to each other that they exert appreciable molecular forces of attraction. As a result real molar mass can not be obtained on the basis of colligative properties; So abnormal molar mass is obtained.To obtain real molar mass scientist van't-Hoff in 1880 introduced one factor which is known as van't Hoff's factor (i).

$$\text{van't Hoff factor (i)} = \frac{\text{Normal molar mass of solute}}{\text{Abnormal molar mass of solute}}$$

$$= \frac{\text{Theoretical moral mass of solute}}{\text{Experimental molar mass of solute}}$$

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

By introducing van't Hoff factor (i) the formula to obtain molar mass can be written as follows:

Raoult's law : $\dfrac{p_1^0 - p_1}{p_1^0} = i \dfrac{n_2}{n_1 + n_2} \simeq i \dfrac{n_2}{n_1}$

Elevation in boiling point : $\Delta T_b = i \, K_b \cdot m$

Depression in Freezing point : $\Delta T_f = i \, K_f \cdot m$

Osmotic pressure of solution : $\pi = i \dfrac{nRT}{V}$

The value of van't Hoff factor (i) is less than one; when there is an association of the solute and it is more than one when there is dissociaton. The value of (i) is equal to 1 when there is no association or dissociation of solute. The values of van't Hoft factor (i) for some solutions are given in table 2.3

Table 2.3 Values of van't Haff factor (i) at various concentrations for NaCl, KCl, MgSO$_4$ and K$_2$SO$_4$

Salt	values of i			van't Hoff Factor i for complete
	0.1 m	0.01 m	0.001 m	dissociation of solute
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
MgSO$_4$	1.21	1.53	1.82	2.00
K$_2$SO$_4$	2.32	2.70	2.84	3.00

Degree of dissociation : The proportion of the mass of the given solute in the solution which gets dissociated is called degree of dissociation (α)

$$\text{Degree of dissociation } (\alpha) = \frac{i-1}{n-1}$$

where i = van't Hoff factor

Degree of association (X) : The proportion of the mass of the given solute in the solution which gets associated, is called degree of asociation (X).

Degree of association $(X) = (1-i)\dfrac{n}{n-1}$

where i = van't Hoff factor, n = no. of molecules combined due to association.

Example 22 : The depression in freezing point is 0.24 K obtained by dissolving 1 gram KCl in 200 gram water, calculate van't-Hoff factor. The molal depression costant is 1.86 K kg mole^{-1}.

Solution : Molar mass of solute (KCl)

$$= \dfrac{1000 \times K_f \times \text{mass of KCl}}{\Delta T_f \times \text{mass of solvent}}$$

$$= \dfrac{1000 \times 1.86 \times 1}{0.24 \times 200} = 38.75 \text{ gram mole}^{-1} \text{ (experimental value)}$$

Now the molar mass $= 39 + 35.5 = 74.5$ gram mole^{-1}

van't Hoff factor (i) $= \dfrac{\text{Theoretical molar mass of KCl}}{\text{Experimental molar mass of KCl}}$

$$= \dfrac{74.5}{38.75} = 1.92$$

The value of van't Hoff factor (i) for KCl will be 1.92

Example 23 : Find the degree of association when 1.0 gram benzoic acid, dissolved in 25 gram benzene is having depression in freezing point 0.81 K. The molal depression constant for solvent is 4.9 K kg mole^{-1}.

Solution : molar mass of benzoic acid,

$$= \dfrac{1000 \times K_f \times \text{mass of benzoic acid}}{\Delta T_f \times \text{mass of solvent}}$$

$$= \dfrac{1000 \times 4.9 \times 1}{0.81 \times 25}$$

$$= 242 \text{ gram mole}^{-1}$$

$\qquad\qquad\qquad = $ abnormal (experimental) molar mass of benzoic acid.

van't Hoff facator (i) $= \dfrac{\text{Theoretical molar mass of benzoic acid}}{\text{Experimental molar mass of benzoic acid}}$

$$= \dfrac{122}{242} \cong 0.5$$

van't Hoff factor (i) for benzoic acid is 0.5

Now, degree of association

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

$$= (1 - 0.5) \left(\frac{2}{2-1} \right)$$

$$= 0.5 \times 2 = 1$$

Example 24 : Calculate degree of dissociation (α) for $K_3[Fe(CN)_6]$ when depression in freezing pont is 0.062 K for 0.01 m $K_3[Fe(CN)_6]$ aquesous solution. The molal depression constant (K_f) for solvent is 1.86 K kg mole^{-1}.

Solution : The depression in freezing point (theoretical) of solution.

$$\Delta T_f = K_f \cdot m \quad = 1.86 \times 0.01 = 0.0186 \text{ K}$$

van't Hoff factor (i) $= \dfrac{\text{Experimental depression in freezing point}}{\text{Theoretical depression in freezing point}}$

$$= \frac{0.062}{0.0186} = 3.33$$

When $K_3[Fe(CN)_6]$ is dissolved in water the total number of ions $= 3 + 1 = 4$ due to its ionisation .

$$K_3[Fe(CN)_6](aq) \rightleftharpoons 3K^+(aq) + [Fe(CN)_6]^{3-}(aq)$$

The degree of dissociation (α) $= \dfrac{i-1}{n-1}$

$$= \frac{3.33-1}{4-1} = 0.778$$

The degree of dissociation for $K_3[Fe(CN)_6]$ will be 0.778

Example 25 : The depression in freezing point is 0.69 K when 2 gram phenol is dissolved in 100 gram benzene. If it is associated as dimeric then find its degree of associatoin. The molal depression constant for solvent is 5.12 K kg mole^{-1}.

Solution : The theoretical molar mass = 94 gram mole^{-1}.

The experimental molar mass of phenol $= \dfrac{1000 \times K_f \times \text{mass of solute}}{\Delta T_f \times \text{mass of solvent}}$

$$= \frac{1000 \times 5.12 \times 2}{0.69 \times 100}$$

$$= 148.4 \text{ gram mole}^{-1} = \text{abnormal molar mass of phenol}$$

van't Hoff factor (i) $= \dfrac{\text{Theoretical molar mass of phenol}}{\text{Experiemental molar mass of phenol}}$

$$= \frac{94}{148.4}$$

$$= 0.633$$

The degree of association for phenol $(X) = (1-i) \dfrac{n}{n-1}$

$$= (1-0.633) \dfrac{2}{2-1}$$

The degree of association for phenol will be 0.734

SUMMARY

- When two or more than two substances are mixed and they form a uniform or homogeneous mixture, it is called solution.

- The proportion of component which is more in the solution is called a solvent and the proportion of a component or components which is less in a solution is/are called solute.

- There can be one solvent and one or more solute components.

- The solution having one solute and one solvent component, is called binary solution.

- There are three types of solution solid solution, liquid solution, gaseous solution.

- The physical state of a solvent in a given solution becomes the physical state of that solution.

- Polar solute dissolves in polar solvent and non polar solute dissolves in non polar solvent and forms homogeneous mixture (solution).

- If the number of −OH group is more in a solute, then it is more solube in water.

- Most of polar solutes dissolve in polar solvents.

- If water is the solvent, the solution is called an aqueous solution, but if water is not the solvent, the solution is called as non-aqueous solution.

- **Formality :** One gram formula mass of the substance (solute) dissolved in one litre solution is called one formal solution.

$$\text{Formality (F)} = \frac{1000 \times \text{mass of solute (gram)}}{\text{formula mass of solute} \times \text{volume of solution (ml)}}$$

- **Volume percentage (% V/V) :** The volume of solute (ml) dissolved in 100 ml solution is expressed as volume percentage (% V/V).

$$\% \text{ V/V} = \frac{100 \times \text{volume of solute}}{\text{volume of solution}}$$

- **Mass by volume percentage : (% W/V) :** The mass of solute dissolved in 100 ml solution is called mass by volume percentage (% W/V).

$$\% \text{ W/V} = \frac{100 \times \text{mass of solute}}{\text{volume of solution}}$$

- **Parts per million (ppm) :** Sometimes the amount of the solute in solution is very much less and so the concentration is expressed as parts per million (ppm).

  parts per million can be expressed in three different ways : (1) Parts per million by mass to mass, (2) Parts per million by mass to volume and (3) Parts per million by volume to volume.

- **Parts per million by mass to volume :** The amount of solute in milligram dissolved in one litre solution is called parts per million by mass to volume.

- Parts per million by mass to volume $= \dfrac{\text{amount of solute (mg)}}{\text{amount of solution(litre)}}$

  Unit of parts per million by mass to volume can be written mg litre^{-1}

- At given temperature and pressure the maximum amount of solute dissolved in a solvent is called its solubility

- There is effect of temperature on solubility of solid, liquid or gas.

- **Henry law :** "The solubility of gaseous solute in a liquid solvent at definite temperature is directly proportional to the pressure of the gas."

- Partial pressure of gaseous solute $p = K_H \cdot X$ where K_H is Henry's constant which depends on temperature

- Limitation and uses of Henry's law are as given in unit.

- When solid solute dissolves in solid solvent, substitutional solid solution, (brass, bronze, steel, monel metal etc.) as well as interstitial solid solution (WC) is formed.

- The solution prepared by dissolving solid solute in liquid solvent, the factor that affect the solulity are temperature and pressure these are known as colligative properties of solution.

- If a solution is prepared by dissolving solid in a solvent, vapour pressure decreases, boiling point increases and freezing point decreases.

- **Raoult's law :** Relative lowering of vapour pressure of the solution is equal to the mole fraction of the dissolved solute.

$$X_2 = \frac{p_1^0 \quad p_1}{p_1^0}$$

- Raoult's law has some limitations but the solution which obey Raoult's law, over the entire range of concentration is known as ideal solution and the solutions which do not obey Raoult's law are called non-ideal or real solutions.

- When volalite solute is dissolved in volalite solvent the vapour pressure of solution is the total of vapour pressure of solute and solvent both.

- When solute dissolved in solvent the increase in boiling point of solution is called elevation in boiling point.

- **Molal elevation constant :** Increase in boiling point of a solution prepared by dissolving one gram molar mass solute in one kilogram of solvent is called molal elevation constant (K_b).

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

- The depression in freezing point when one gram molar mass solute is dissolved in one kilogram of non-volatite solvent is called molal depression constant (K_f).

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

- **Osmosis :** When two solutions having different concentrations are separated by semi-permeable membrance the spontaneous flow of solvent starts from a solution with lower concentration to higher concentration it is called osmosis.

- **Osmotic pressure :** Such a sponteneous flow as above which can be stopped by applying pressure is called osmotic presure (π).

- **Boyle's-van't Hoff law :** At constant temperature the osmotic pressure is directly proportional to the molar concentration of the solution.

- **Gay-Lussac-van't Hoff law :** If the concentration of the solution is constant then osmotic pressure of solution is directly proportional to absolute temperature. $\pi \propto T$

- **Avogadro-van't Hoff law :** In the same volumes of different solutions having similar osmotic pressure at the same temperature have same number of molecules; of the solute.

- By combining these three laws the equation $\pi = \dfrac{nRT}{V}$ or $\pi = \dfrac{wRT}{MV}$ can be derived

- The solutions having same osmotic pressure at given temperature are called iso-osmotic (Isotonic) solutions.

- The solution having lower osmotic pressure in comparision with higher concentration is called hypotonic solution. The solution having higher osmotic pressure in comparison with lower concentration is called hypertonic solution.

- **Methods to determine molar mass :**

(i) Using Raoult's law : $\dfrac{p_1^0 - p_1}{p_1^0} = \dfrac{w_2 \times M_1}{M_2 \times w_1}$

(ii) Molal elevation constant method :

$$\text{molar mass of solute} = \frac{1000 \times \text{mass of solute} \times K_b}{\text{elevation in boiling point} \times \text{mass of solvent}}$$

(iii) Molal depression constant method :

$$\text{molar mass of solute} = \frac{1000 \times \text{mass of solute} \times K_f}{\text{depressing in freezing point} \times \text{mass of solvent}}$$

(iv) Osmotic pressure measurement method :

molar mass of unknown substance =

$$\frac{\text{mass of solute} \times RT}{\text{osmotic pressure of solution} \times \text{volume of solution}}$$

- The colligative properties are applicable to solutions which do not undergo dissociation or association.

- van't Haff factor (i) is introduced for the deviation from normal behaviour.

- van't Hoff factor (i) = $\dfrac{\text{theoretical molar mass of solute}}{\text{experimental molar mass of soulte}}$

- Raoult's law : $\dfrac{p_1^0 - p_1}{p_1^0} = i\,\dfrac{n_2}{n_1 + n_2} \simeq i\,\dfrac{n_2}{n_1}$

- Elevation in boiling point : $\Delta T_b = i\,K_b \cdot m$

- Depression in freezing point : $\Delta T_f = i\,K_f \cdot m$

- The osmotic pressure : $\pi = i\,\dfrac{nRT}{V}$

- Degree of association (X) = $(1-i)\,\dfrac{n}{n-1}$

- Degree of dissociation (α) = $\dfrac{i-1}{n-1}$

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which unit of concentration value is changed with change in temperature ?

(A) Normality   (B) Molarity   (C) % V/V   (D) all of these

(2) Which type of solution is petrol ?

(A) solid-liquid   (B) liquid-liquid   (C) gas-liquid   (D) all of these

(3) What is the concentration of solution in ppm when 2×10^{-6} gram CO_2 is dissolved in 10 ml solution ?

(A) 2   (B) 0.2   (C) 200   (D) 2×10^{-6}

(4) Which of the following gas has highest solubility in ethyl alcohol ?

(A) H_2S (B) NH_3 (C) N_2 (D) CO_2

(5) Which of the following substance has the highest solubility in water?

(A) ethanol   (B) ethylene glycol   (C) glycerine   (D) propanol

(6) On increasing temperature, the solubity of gaseous solute in liquid solvent

(A) Increases   (B) Decreases   (C) Remains constant (D) Uncertain

(7) On increasing temperature the value of Henry's constant

(A) Decreases   (B) Increases   (C) Remains constant (D) Uncertain

(8) Which solution has the highest effect of temperature on its vapour pressure ?

(A) Sugar solution   (B) NaCl solution   (C) $BaCl_2$ Solution   (D) Aqueous H_2S

(9) Which of the following aqueous solution has the highest boiling point having concentration 0.02 m ?

(A) Urea   (B) NaCl   (C) Na_2SO_4 (D) $K_4[Fe(CN)_6]$

(10) 0.05 M glucose solution is iso-osmotic with which of the following solutions ?

(A) 0.10 M NaCl   (B) 0.05 NaCl   (C) 0.025 M NaCl   (D) 1M NaCl

(11) What is the value of van't Hoff factor for dilute $FeCl_3$ (aqueous) solution ?

(A) 1   (B) < 1   (C) >1   (D) zero

(12) What is the value of van't Hoff factor when acetic acid is dissolved in benzene?

(A) Zero   (B) 1   (C) >1   (D) < 1

(13) What is the molality for 10% W/W NaOH(aq) solution ?

(A) 2.778   (B) 2.5   (C) 10   (D) 5

(14) For which solution the value of van't Hoff factor is one ?

(A) NaCl   (B) KNO_3 (C) glucose   (D) CH_3COOH

(15) For which solution the value of van't Hoff factor is not 1 ?

(A) Glucose   (B) Sugar   (C) Fructose   (D) Acetic acid

(16) The real vapour pressure for non-ideal solution is .... than by Raoult's law

(A) more   (B) less   (C) equal   (D) (A) and (B) both

(17) Which of the following solutions is hypotonic ?

(A) 0.1 M NaCl   (B) 0.1 M sugar   (C) 0.1M Na_2SO_4 (D) 0.1 M $FeCl_3$

(18) The total pressure for volatile components A and B is 0.02 bar at equilibrium. If the mole fractions of component A is 0.2, then what will be partial pressure of componant B ?

(A) 0.02 bar   (B) 0.04 bar   (C) 0.016 bar   (D) 0.2 bar

(19) Which of the following solutions is hypertonic ?

(A) 0.1 M $FeCl_3$ (B) 0.1 M NaOH   (C) 0.1 M Urea   (D) 0.1 M Na_2SO_4

2. **Write the answers of the following questions in short :**

(1) Define solution.

(2) What is solvent and solute in solution ?

(3) Write types of solutions.

(4) Which type of solutions are air containing moisture, zinc amalgam and dry air ?

(5) Define : Formality, Solubility, ppm

(6) Write effect of temperature on solubilty of solute.

(7) Give example of interstitial solid solution.

(8) Define saturated solution.

(9) What is molal elevation ?

(10) What is molal depression ?

(11) Write Boyle-van't Hoff law.

(12) What is osmosis ?

(13) What is osmostic pressure ?

(14) What is abnormal molecular mass ?

(15) Write formula for degree of association (X).

(16) What is binary solution ?

(17) When the value of van't Hoff factor will be more than one ?

(18) What is iso-osmotic solution ?

(19) To determine the molar mass of polymer; which method is more useful ?

(20) What is freezing point ?

3. **Answer the following questions :**

(1) Write about types of solid solution with examples.

(2) Write about gaseous solution with examples.

(3) Explain % V/V in short.

(4) Explain unit ppm with example.

(5) Write the factors affecting the solubility of solute in aqueous H_2S solution ?

(6) Write uses of Henry's law.

(7) Explain substitutional solid solution in short.

(8) Explain interstitial solid solution in short.

(9) Write any two uses of osmotic pressure.

(10) Explain molal elevation measurement method.

(11) Explain association and dissociation.

(12) What are colligative propeties of solution ?

(13) Why van't Hoff factor (i) was introduced ?

4. **Explain following questions in detail :**

(1) Write Henry's law, derive the formula and write its limitation.

(2) Explain molal elevation constant. Derive its formula.

(3) Write Raoult's law and derive its equation.

(4) Explain the factors affecting the solubility of solute in solution obtained by dissolving gaseous. solute in liquid solvent.

(5) Derive the formula of Raoult's law for a solution having volatile solute and solvent.

(6) Derive the formula for molal depression constant.

(7) Explain the different methods to determine the molar mass.

(8) Write law of osmotic pressure and derive formula.

(9) Explain iso-osmotic solution and write uses of osmotic pressure.

(10) Explain abnormal molar mass and explain van't Hoft factor.

(11) Explain and write the formula for colligative properties introducing van't Hoft factor (i).

(12) **Solve the examples :**

(1) Calculate the formality of solution when 4.78 gram potash alum is dissolved in 2 litre solution.

(2) How many ml ethanol is required to prepare 2 litre aqueous solution of ethanol solution having concentration 5% V/V.

(3) Calculate the percentage by mass to volume for 0.2 M NaOH solution.

(4) Calculate the ppm for solution in which 2×10^{-7} kg calcium bicarbonate is dissolved in 2 litre solution.

(5) Calculate the solubity in mole- fraction at 300 K temperature; the partial pressure of Cl_2 gas in water is 2.5×10^{-8} bar. For Cl_2 gas the value of K_H is 7.1×10^{-4} bar.

(6) How many millimoles of H_2S gas will dissolve in water when passed through 1 litre water, the K_H value is 5.6×10^{-4} bar and the partial pressure is 3×10^{-8} bar.

(7) Calculate the vapour pressure of aqueous 0.1m glucose solution at 300 K temperature, the vapour pressure of water is 0.03 bar at 300 K temperature.

(8) The vapour pressures of benzene and toluene are 0.9 and 0.85 bar respectively. Calculate the vapour pressure of solution obtained by mixing 7.8 gram benzene with 180 gram toluene.

(9) Find the boiling point of 2.5% W/W sugar solution; the molal elevation constant for solvent is 4 K kg mole^{-1}.

(10) How many grams of urea should be dissolved in 500 gram water so that the depression in freezing point is 0.2 K ? K_f for solvent is 3.2 K kg mole^{-1}.

(11) How many grams of glucose should be dissolved in 2 litre aqueous solution at 298 K temperature so that the osmotic pressure of solution is 0.5 bar.

(12) Calculate the osmotic pressure of 2% W/V aqueous solution of urea at 300 K temperature. This solution is iso-osmotic with what % W/V of NaOH aqueous solution.

(13) At 298 K temperature 10 gram non-volatile unknown substance is added to 540 gram water so that the change in vapour pressure will be from 0.0335 bar to 0.033 bar; find the molar mass of unknown substance.

(14) Elevation in boiling point is 0.2 K when 1.5 gram unknown substance is dissolved in 500 gram water. Find the molar mass of unknown substance. Molal elevation constant for solvent is 3 K kg mole^{-1}.

(15) 2 gram of unknown substance is dissolved in 1kg water, the depression in freezing point is 0.4 K. If the molal elevation constant is 4.5 K kg mole^{-1}, find the molar mass of solute.

(16) When 5 gram unknown substance is dissolved in 10 litre solution the osmotic pressure of solution is 0.2 bar at 300 K temperature. Find the molar mass of unknown substance.

(17) The depression in freezing point observed is 0.3 K, when 2 grams FeCl$_3$ is dissolved in 250 ml water. Find the van't Hoff factor. The molal elevation constant for solvent is 1.5 K kg mole^{-1}.

(18) Find the degree of dissociation when 0.02M aqueous Al$_2$(SO$_4$)$_3$ solution having elevation in boiling point of 0.04 K. The molal elevation constant for solvent is 1.9 K kg mole^{-1}.

(19) The depression in freezing point is 0.56 K when 1.5 gram phenol is dissolved in 100 gram toluene. If its association is dimeric then find the degree of association. Molal depression constant for solvent is 4 K kg mole^{-1}.