2
Solution

2.1 Solution

A Solution is a homogeneous mixture of two or more pure substances whose composition may be altered within certain limits. The substances which make up the solution are generally called its components.

Depending upon the total components present in the solution, it is called the binary solution (two components), ternary soution (three components), quaternary solution (four compoents), etc.

The two compoents of the binary soutions are called a solvent and a solute. solvent is a component which is present in excess while the component which is present in lesser quantity is termed as solute.

For example in case of solution of glucose and water, gulcose is the solute and water is the solvent.

2.1.1 Types of Solutions

1. **Gaseous Solutions –** When a gas is mixed with another gas then gaseous solution is obtained. All gaseous mixtures are homogeneous solutions.
2. **Liquid Solutions –** When a gas or liquid or solid is dissolved in another liquid then liquid solution is obtained. The solutions in which water is the solvent are called aqueous solutions while those in which water is not the solvent are called non aqueous solutions.
3. **Solid Solutions –** When a gas or liquid or solid is dispersed irreguarly in another solid then it is known as solid solutions.

Depending upon the physical states of the solute and the solvent, the solutions can be cassified into the following nine types :–

Types of Solutions	Solute	Solvent	Example
Gaseous Solutions	Gas	Gas	mixture of gases, air
	Liquid	Gas	water vapour in air, vaporization of liquids
	Solid	Gas	sublimation of Solids into a gas e.g. camphor, I_2, NH_4Cl
Liquid Solutions	Gas	Liquid	aerated drinks, Ammonical water
	Liquid	Liquid	mixture of miscible liquids e.g. alcohol in water
	Solid	Liquid	salt in water, sugar in water, sulphur in alcohol
Solid Solutions	Gas	Solid	absorption of gases over metals e.g. H_2 over Pd
	Liquid	Solid	mercury in Zn, Mercury in Cu
	Solid	Solid	alloys e.g. Cu – Au, Zn – Cu (brass)

2.2 Units of Concentration

The concentration of a solution may be defined as the amount of solute present in the given quantity of the solution. It can be expressed in any of the following ways :

1. **Mass Percentage (w/W)–** It is defined as the number of parts by mass of solute (in g) per hundred parts by mass of solution.

If W_B be the mass of solute (B) and W_A be the mass of solvent (A) then

$$\text{Mass Percentage of B} = \frac{W_B}{W_B + W_A} \times 100$$

Example. A solution is prepared by adding 11g of oxalic acid to 500ml. of water. Calculate the mass percentage of solution. (assume density of solution = 1.1 gml^{-1})

Solution :

Mass of oxalic acid i.e. $W_B = 11\text{g}$

Mass of Solution $= 500 \text{ ml} \times 1.1 \text{ g ml}^{-1}$

$= 550\text{g}$

Mass Percentage of oxalic acid

$$= \frac{11}{550} \times 100 = 2\% \left(\frac{w}{W}\right)$$

2. **Volume Percentage (v/V)–** It is defined as the number of parts by volume of solute per hundred parts by volume of solution.

If V_B be the volume of solute (B) and V_A be the volume of solvent (A), then

$$\text{Volume percentage of B} = \frac{V_B}{V_B + V_A} \times 100$$

Example. A 25% aqheous solution of ethyl alcohol (by volume) means 100ml of solution contain 25ml. of ethyl alohol and 75ml. of water.

3. **Mass-volume Percentage (w/V)–** It is defined as the number of parts by mass of solute, per hundred parts by volume of soution.

If w_B be the mass of solute (B) and V_A be the volume of solvent (A), then

$$\text{Mass volume percentage of B} = \frac{W_B}{V_B + V_A} \times 100$$

Example. Calculate the mass of NaCl required to make 500ml. aqueous solution of $2\% \frac{w}{V}$ NaCl

Solution :

$$\text{Mass - volume Percentage} = \frac{W_B}{\text{Volume of Solution in ml}} \times 100$$

$$= \frac{W_B}{500} \times 100, \quad W_B = 10\text{g}$$

4. **Parts Per Million (ppm) –** When a solute is present in very minute amounts then its concentration is expressed in parts per million.

It may be defined as the mumber of parts by mass of solute per million parts by mass of the solution.

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

Example. Calculate the concentration of chlorine in ppm when a litre of public supply water contains about 3×10^{-3}g of chlorine.

Solution :

$$\text{ppm} = \frac{\text{mass of } Cl_2}{\text{mass of solution}} \times 10^6$$

$$= \frac{3 \times 10^{-3}}{10^3} \times 10^6 = 3\text{ppm}$$

Atmospheric pollution in cities due to harmful gases is generally expressed in ppm though in this case the values refer to volume rather than masses. e.g. the concentration of SO_2 in Delhi has been found to be as high as 10ppm. This means that 10 cm^3 of SO_2 are present in 10^3L (or 10^6 cm^3) of air.

5. **Molarity (M)–** Molarity of a solution is defined as the number of gram moles of the solute dissolved per litre of the solution.

$$\text{Molarity} = \frac{\text{Gram moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{mass of solute in Gram}}{\text{molar mass of solute}} \times \frac{1}{\text{Volume of solution in liter}}$$

$$= \frac{\text{mass of solute in Gram}}{\text{molar mass of solute}} \times \frac{1000}{\text{Volume of solution in ml or Cm}^3}$$

Molarity is expressd in units of mol L^{-1} or ML^{-1}

Example. Calculate the molarity of a solution containing 5g of NaOH dissolved in 500 ml of solution.

Solution :

$$\text{Molarity} = \frac{\text{mass of NaOH}}{\text{molar mase of NaOH}} \times \frac{1000}{\text{Volume of solution in ml.}}$$

$$= \frac{5}{40} \times \frac{1000}{500} = 0.25ML^{-1}$$

If V_1 ml of a solution of molarity M_1 is mixed with another, Solution of some substance with volume V_2 and Molarity M_2, then molarity of the resulting mixture solution (M) can be obtained from.

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

6. **Normality (N) -** Normality of a solution is defined as the number of g-equivalents of the solute dissolved per litre soultion.

$$\text{Normality} = \frac{\text{Gram equivalents of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{mass of solute in grams}}{\text{Gram eq. mass of solute}} \times \frac{1}{\text{Volume of solution in liters}}$$

$$= \frac{\text{mass of solute in grams}}{\text{Gram eq. mass of solute}} \times \frac{1000}{\text{Volume of solution in ml. or cm}^3}$$

The units of normality are gm equivalent per litre or NL^{-1}

$\frac{N}{2}, \frac{N}{5}, \frac{N}{10}, \frac{N}{100}$, N, 5N and 10N solutions are known as semi normal, pentinormal, decinormal, centinormal, normal, penta normal and deca normal solutions respectively.

Example. Calculate the normality of a solution containing 6.3 g oxalic acid dissolved in 250ml. of solution.

Solution.

$$\text{Normality} = \frac{\text{mass of oxalic acid}}{\text{Gam eq. mass of oxalic acid}} \times \frac{1000}{\text{Volume of solution in ml.}}$$

$$= \frac{63}{63} \times \frac{1000}{250} = 0.4NL^{-1}$$

7. **Molality (m)-** It is the number of moles of solute dissolved per 1000g (or 1Kg) of the solvent.

$$\text{Molality} = \frac{\text{Gram moles of solute}}{\text{weight of solvent in Kg}}$$

$$= \frac{\text{mass of solute in grams}}{\text{molar mass of solute}} \times \frac{1}{\text{Weight of solvent in Kg}}$$

$$= \frac{\text{mass of solute in grams}}{\text{molar mass of solute}} \times \frac{1000}{\text{Weight of solvent in gram}}$$

The units of molality is moles/Kg. solvent (MKg–1 solvent).

Example. Calculate the molality of 93% $\frac{W}{V}$ H_2SO_4 solution (assume density of solution = 1.8g ml^{-1}).

Solution. 93%$\frac{W}{V}$ H_2SO_4 solution means that 93 g of H_2SO_4 are present in 100 ml of solution in water.

Mass of solution = volume × density

= 100 × 1.8 = 180 g

Mass of solvent water = 180 – 93 = 87g

$$\text{molality} = \frac{\text{mass of } H_2SO_4}{\text{molar mass of } H_2SO_4} \times \frac{1000}{\text{weight of solvent water in gram}}$$

$$= \frac{93}{98} \times \frac{1000}{87} = 10.9 \text{ moles/Kg. solvent}$$

8. **Mole Fraction (x) -** it is the ratio of number of moles of one component to the total number of moles (solute and solvent) present in the solution. It is denoted by x. Let us suppose that a solution contains n_A moles of solute and n_B moles of the solvent. Then,

$$\text{Mole fraction of solute } (x_A) = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of solute } (x_B) = \frac{n_B}{n_A + n_B}$$

The sum of mole fractions of all the components in solution is always equal to one as shown below :

$$x_A + x_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

Thus, if the mole fraction of one component of a binary solution is known, that of the other can be calculated. For example, the mole fraction x_A is related to x_B as :

$$x_A = 1 - x_B \quad \text{or} \quad x_B = 1 - x_A$$

It may be noted that the mole fraction is independent of temperature.

Example. A solution is prepared by adding 60g of methyl alcohol to 120g of water. Calculate the mole fraction of methanol and water.

Solution. Mass of methanol = 60g

$$\text{Moles of methanol} = \frac{60}{32} = 1.875$$

(Molar mass = 32)

Mass of water = 120g

$$\text{Moles of water} = \frac{120}{18} = 6.667$$

(Molar mass = 18)

Total number of moles = 1.875 + 6.667
= 8.542

$$\text{Mole fraction of methanol} = \frac{1.875}{8.542} = 0.220$$

$$\text{Mole fraction of water} = \frac{6.667}{8.542} = 0.780$$

9. **Some Important Relationship -**

1. Molarity × molar mass of solute = Normality × Eq. mass of solute

For Acids, Normality = Basicity × molarity

For Bases, Normality = Acidity × molarity

Basicity is the number of H^+ ions given by each molecule of acid in solution.

Acidity is the number of OH^- ions given by each molecule of base in solution.

2. Relationship between molarity and molality - Molarity (M) and molality (m) are related to each other by the following relation where, d is th density of solution.

$$m = \frac{1000 \times M}{(1000 \times d) - (M \times \text{molar mass of solute})}$$

2.3 Solubility

2.3.1 Solution of Solids in Liquids

In binary solution of solid in liquid, solid is referred to as solute and liquid is solvent.

Cause of solubility of solids in liquids

Dissolution of any substance in a liquid is governed by the basic principle that solute-solvent interactions are either similar or of greater magnitude than solute-solute and solvent-solvent interactions. Let us consider th dissolution of **ionic solids** in **water.** The attractive forcs in ionic solids are *interionic attractions.* When an ionic solid is dissolved in water, the cations and anions get attractd by the opposite ends of water dipoles. If

ion-dipole attractive forces are stronger enough to overcome the interionic attraction, the ions are pulled out of crystal lattice and they pass into solution. In the solution, the ions behave as independent entities, but they remain surrounded by the envelop of water dipoles. This process is referred to as **hydration of ions**. Molecular solids, on the other hand, do not ionise but they dissolve in water because of their ability to form *hydrogen-bonds* with water molecules.

The energy required to dismentle crystal lattice is represented by $\Delta H_{Lattice}$ and energy released during hydration is represented by $\Delta H_{Hydration}$.

In general, $\Delta H_{Solution} = \Delta H_{Lattice} + \Delta H_{Hydration}$

Solubility of Solids

Solubility of a substance is defined as the amount of solid that can be dissolved in 100 g of the solvent at a particular temperature. In fact, solubility refers to concentration of solute in a **saturated solution** at particular temperature. Solubility of a solid solute in liquid depends upon the following factors.

(i) Nature of solute - Dissolution of solid solute in liquids can be summed up in a phrase **"like dissolves like".** This means that, polar solutes dissolve in polar solvents and non polar solutes dissolve in non-polar solvents.

For example, ionic substances such as NaCI, KCl, KNO_3, etc., have larger solubilities in polar solvents like water but they have poor solubilities in non-polar solvents like CCl_4, CS_2, etc. On the other hand, non-polar solids such as I_2, S_8, etc., are more soluble in non polar solvents like CCl_4, CS_2 but they are almost insoluble in polar solvents like water.

(ii) Temperature - Saturated solution represents equilibrium between undissolved solute and dissolved solute.

$$\text{Undissolved Solute + Solvent} \rightleftharpoons \text{solution}; \quad \Delta H_{Sol} = \pm \text{x}.$$

If the value of $\Delta H_{Sol} < 0$; *i.e.*, the solution process is **exothermic**, then by Le-chatelier's principle, the solubility of such a solute will **decrease** with the *rise in temperature.* On the other hand, if $\Delta H_{Sol} > 0$; *i.e.,* solution process is **endothermic**, then, solubility of such a solute will *increase* with rise in temperature.

2 Solution of Gases in Liquids

Most of the gases are soluble in water and also in some other liquids to different extent. Solutions of gases in water are very common in our daily routine. The familiar examples are, carbonated beverages, i.e., solution of CO_2 in water, formaline (an aqueous solation of formaldehyde), variety of household cleaners which contains aqueous solutions of ammonia. All natural waters also contain dissolved O_2, N_2 and traces of other gases.

Solubility of Gases

Solubility of gases are generally expressed in terms of absorption coefficient. It is defined as the volume of gas (reduced at STP) that can be dissolved by a unit-volume of a liquid solvent at the temperature of the experiment at I bar pressure.The absorption coefficients of some gases in water, ethanol, and benzene solvents at 298K are given below

	H_2	N_2	O_2	CO_2
Water	0.017	0.015	0.028	0.88
Ethanol	0.080	0.130	0.143	3.0
Benzene	0.060	0.140	0.165	–

Factors affecting the solubility of gases

The following factors affect the solubilities of gases in liquids :

(i) The nature of gas and the nature of solvent - In general, the gases which are easily liquefiable are relatively more soluble in common solvents. For example, carbon dioxide is more soluble in water than dihydrogen or dioxygen. The gases which are capable of undergoing ionisation in water are more soluble in water than in other solvents. For example, HCl gas is more soluble in water than in benzene.

(ii) Effect of Temperature - The solubilities of majorities of gases in water diminishes with the rise in temperature because their dissolution processes are exothermic. For example, the amount of O_2 dissolved in water at 298 K is about one half of that at 273 K. The solubilities of some gases in organic solvents do follow the reverse trends *i.e.*, their solubilities are found to increase with rise in temperature.

(iii) Effect of Pressure- Henry's Law - The effect of pressure on the solubility of gases in water at constant temperature is governed by Henry's Law. The law states that at constant temprature, the ***mass* of the gas (m) dissolved per unit volume of a solvent is directly proportional to the pressure of gas in equilibrium with the aqueous solution (P_m).**

Mathematically, $m \propto P_m$ or $m = k.P_m$

Where k is constant of proportionality.

It may be noted that solubility of a gas has a linear relationship with pressure of gas above the aqueous solution.

Limitations of Henry's law : It has been observed that Henry's law is valid if

(i) pressure is not high

(ii) the temperature is not too low

(iii) the gas is not highly soluble, and

(iv) the gas neither reacts chemically with the solvent nor dissociates or associates in the solvent.

2.4 Vapour Pressure of Solutions

When a liquid placed in a beaker is covered with a bell jar, part of the liquid evaporates and fills the available space with the vapours. As the evaporation proceeds, the number of gaseous molecules in the vapour phase increases gradually. These molecules move about at random in a limited space and during their random movement, some of these strike the surface of liquid and get condensed. The process of condensation acts in opposite direction to the process of evaporation. Thus, both evaporation and condensation processes go on simultaneously. Ultimately, a stage is reached when the rate of evaporation become equal to rate of condensation and an quilibrium gets established between liquid and vapour phases. The pressure exerted by the vapours at the equilibrium is called vapour pressure. Thus, the pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperatur is called **vapour pressure.**

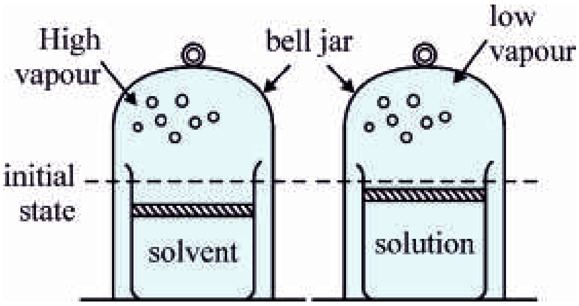


Fig. 2.1

The vapour pressure of a liquid depends upon followings:

(i) **Nature of the liquid-** Each liquid has a characteristic vapour pressure because each liquid has different magnitude of intermolecular forces. The liquids, which have weaker intermolcular forces, tend to escape readily into vapour phase and, therefore, have greater vapour pressure. For example, dimethylether and alcohol have higher vapour pressure than water at a given temperature because of weaker intermolecular forces in them as compared to water.

(ii) **Temperature -** The vapour pressure of a liquid increases with increase in temperature. This is due to the fact that with increase in temperature, more molecules will have larger kinetic energies. Therefore, larger number of molecules will have larger kinetic energies. Therefore, larger number of molecules will escape from the surface of the liquid to the vapour phase resulting in higher vapour pressure.

2.5 Vapour Pressure of Solution

Let us add a small amount of a non-volatile solute to the solvent (e.g. sugar in water) to form the solution. When evaporation of this solution takes place, the vapour phase again consists of vapours of the solvent (*i.e.*, of water) because the solute is non-volatile. However, the vapour pressure of the solution is found to be less than that of the pure solvent. This can be explained as follows :

We know that evaporation is a surface phenomenon. The vapour pressure depends on the escape of solvent molecules from the surface of the liquid. In the case of solution, the non-volatile sugar molecules as shown by small black spheres in Fig. 2.1, also occupy a certain surface area. As a result, lesser number of solvent molecules will escape into vapours. In other words, vapour pressure of the solution will be less than that of the pure solvent or there will be a lowering in vapour pressure.

Raoult's Law

(1) Raoult's law for Binary Solutions of Volatile Liquids -

In the binary solution of volatile liquid, the vapour phase consists of vapours of both the components. The Raoult's law for such binary solution may be stated as.

At a given temperature, for a solution of volatile liquids, the partial pressure of each component is directly proportional to its mole fraction.

suppose a binary solution consists of two volatile liquids A and B. If P_A and P_B are the partial vapour pressure of the two liquids and x_A and x_B are their mole fraction in solution, then

$$P_A \propto X_A$$

$$P_A \propto P_A^o X_A \qquad \ldots(i)$$

$$P_B \propto X_B$$

$$P_B \propto P_B^o X_B \qquad \ldots(ii)$$

where $P_A{}^o$ and $P_B{}^o$ are the vapour pressures of pure components A and B, respectively. This relationship is called **Raoult's law.** It states that for a solution of two or more miscible volatile liquids, the partial vapour pressure of each component of the solution at a particular temperature is directly proportional to its mole fraction.

Accoring to Raoult's law, a plot of P_A against X_A should give a straight line passing through $P_A{}^o$ when X_A=1 (shown by broken line I in Fig. 2.2). Similarly, a plot of P_B against X_B is a straight line passing through P_B when $X_B = 1$ (broken line II in Fig. 2.2). The total vapour pressure, P exerted by the solution is the sum of P_A and P_B as required by Dalton's law of partial pressures.

$$P = P_A + P_B$$

$$\text{or } P = P_A^o X_A + P_B^o X_B \qquad (\because X_A + X_B = 1) \qquad \ldots(iii)$$

$$= P_A^o (1 - X_B) + P_B^o X_B$$

$$= P_A^o - P_A^o X_B + P_B^o X_B$$

$$= (P_B^o - P_A^o)\, X_B + P_A^o \qquad \ldots(iv)$$

Similarly, by putting $X_B = 1 - X_A$, we can arrive at the following relation–

$$P = (P_A^o - P_B^o) X_A + P_B^o$$

Since P_B^o and P_A^o are constants at particular temperature, therefore, the equations (iii) and (iv) reveal that the total pressure, P is a linear function of X_B (or X_A). This means that plot of P v/s X_B or P v/s X_A should be a straight line. The variation of P with mole fraction is given by the solid line III in the graph.

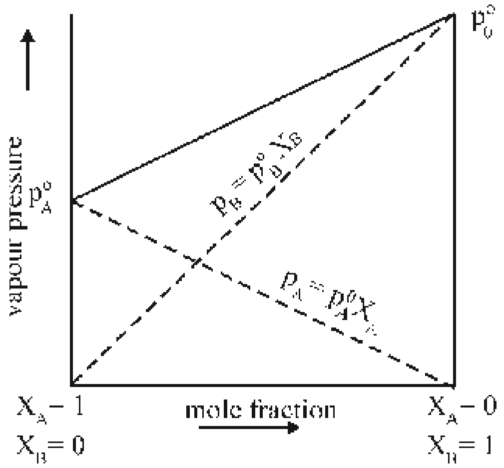


Fig. 2.2 : Graph between mole fraction of solute and solvent in solution v/s total pressure

The solutions which obey Raoult's law are called **ideal solutions.** For such solutions, the vapour pressure of the solution always lies between the vapour pressures of the pure components.

2.6 Ideal Solutions

An ideal solutions may by defined as the solution which obeys Raoult's law exactly at all concentrations and at all temperatures. Such solutions are formed by mixing the two components which are identical in molecular size, in structure and have almost identical intermolecular forces. In these soltuions, the intermolecular interactions between the components (A–B attractions) are of same magnitude as the intermolecular interactions in pure components (A–A and B–B attractions). According to Raoult's law, the partial vapour pressure of two components of the solution may be given as :

$$p_A = p_A^o\ x_A$$

and $$p_B = p_A^o\ x_B$$

Total pressure p is given by

$$p = p_A + p_B$$
$$= P_A^o\ x_A + P_B^o\ x_B$$

The ideal solutions also have the following characteristics :

(i) Heat change on mixing is zero - Since there is no change in magnitude of the attractive forces in the two components present, the heat change on mixing *i.e.* ΔH_{mixing} in such solutions must be zero.

(ii) Volume change on mixing is zero – In ideal solutions, the volume of the solution is the sum of the volumes of the components before mixing *i.e.* there is no change in volume on mixing or ΔV_{mixing} is zero.

For example, when we mix 100 cm^3 of benzene with 100 cm^3 of toluene, the volume of the solution is found to be exactly 200 cm^3. Therefore, there is no change in volume on mixing i.e. $\Delta V_{mixing} = 0$. It has been noticed that the solutions generally tend to become ideal when they are dilute.

The characteristics of an ideal solution may be summed up as follows :

(i) It must obey Raoult's law.

(ii) ΔH_{mixing} should be zero.

(iii) ΔV_{mixing} should be zero.

Example.

(a) n-hexane + n-heptane (Alkane)

(b) methanol + ethanol (Alcohol)

(c) 1-chloro butane + 1-bromobutane (Alkyl halide)

(d) benzene + toluene (Aromatic hydrocarbon)

(e) $CCl_4 + SiCl_4$ (Chlorides of group 14 elements)

(f) Chlorobenzene + bromobenzene (Aryl halide)

2.7 Non Ideal Solution

The solution which do not obey Raoult's law are called non ideal solutions.

For binary non ideal solution.

(i) $p_A \neq p_A^o\ x_A$ and $p_B \neq p_B^o\ x_B$

(ii) $\Delta V_{mixing} \neq 0$

(iii) $\Delta H_{mixing} \neq 0$

Non ideal solutions are of two types :-

2.7.1 Non ideal solution with positive deviations–

Consider a binary solution of two components A and B. If the A–B interactions in the solutions are weaker than the A–A and B–B interactions in the two liquids forming the solution, then the escaping tendency of A and B types of molecules from the solution becomes more than from pure liquids. As a result, each compoents of solution has a partial vapour pressure greater than expected on the basis of Raoult's law.

For positive deviations

(i) $p_A > P_A^o\, x_A$ and $p_B > p_B^o\ x_B$

(ii) ΔV_{mixing} = positive (endothermic)

(iii) ΔH_{mixing} = positive (increase in volume on mixing)

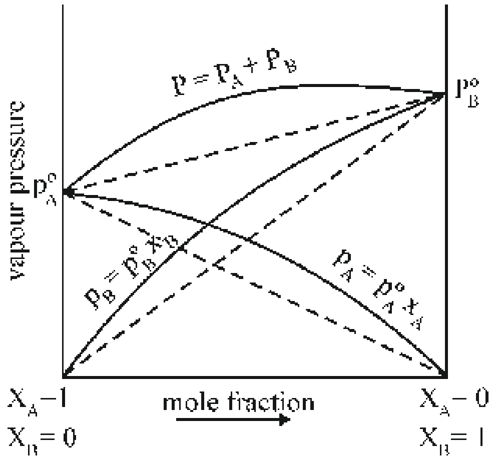


Fig. 2.3

Few examples of solutions showing positive deviation are:

(i) methanol + water
(ii) methanol + carbontetrachloride
(iii) ethanol + water
(iv) acetone + ethanol
(v) acetone + carbondisulphide

2.7.2 Non ideal solution with negative deviations–

Consider a binary solution of two components A and B. If the A–B interactions in the solutions are stronger than the A–A and B–B interactions in the two liquids forming the solution, then the escaping tendency of A and B types of molecules from the solution becomes less than from pure liquids. As a result, each compoents of solution has a partial vapour pressure lesser than expected on the basis of Raoult's law.

For negative deviations

(i) $p_A < P^o_A\ x_A$ and $p_B < P^o_B\ x_B$
(ii) ΔV_{mixing} = negative (exothermic)
(iii) ΔH_{mixing} = negative (decrease in volume on mixing)

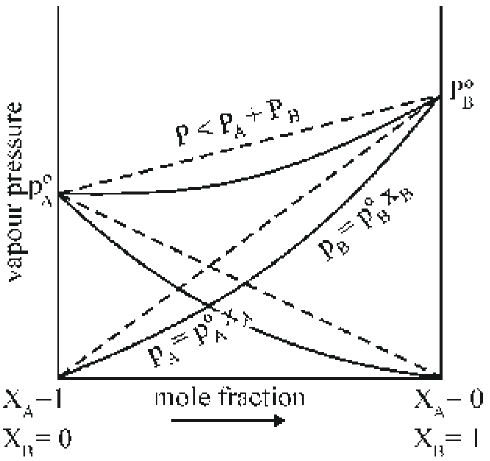


Fig. 2.4

Few examples of solutions showing negative deviation are:

(i) chloroform + acetone
(ii) water + hydrochloric acid
(iii) acetone + aniline
(iv) methanol + acetic acid
(v) chloroform + benzene

2.8 Azeotropic Mixtures

When a binary solution of two volatile liquids is boiled, its vapours, in general, do not have the same composition of the componenents as that in solution. The mole fraction of the more volatile component is generally higher in vapours. This forms the basis of fractional distillation. But many binary solutions at definite compositions behave like pure liquids because their vapours have the same composition of the two components as in solution. Such solutions are called *azeotropic mixtures* or *azeotropes*. Thus, azeotropes are defined as the mixture of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as in vapour phase. Azeotropes are also called constant boiling mixtures because whole of the azeotrope changes in vapour state at constant temperature and their components cannot be separatd by fractional distillation. Azeotropes are of two types as described below :

(i) Minimum boiling azeotropes – These azeotropes are formed by those liquid pairs which show positive deviation from ideal behaviour. Such azeotropes have boiling points lower than either of the components.

(ii) Maximum boiling azeotropes - These azeotropes are formed by those liquid pairs which show negative deviations from the idal behaviour. Such azeotropes have boiling points higher than either of the components.

2.9 Colligative Properties

The properties of the solutions which depend only on the number of solute particles but not on the nature of the solute are called colligative properties.

The important colligative properties are :

(i) Relative lowering in vapour pressure

(ii) Elevation in boiling point

(iii) Depression in Freezing point

(iv) Osmotic pressure

2.9.1 Relative lowering in Vapour Pressure

It has already been shown that for an ideal solution, the relative lowering of vapour pressure is equal to mole fraction of the solute *i.e.*

$$\frac{p_A^o - p_A}{p_A^o} = x_B$$

$$x_B = \frac{n_B}{n_A + n_B} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

Where n_B = number of moles of solute n_A = number of moles of solvent. W_B and W_A are masses of solute and solvent. M_B and M_A are molecular mass of solute and solvent.

Substituting the value of x_B, we get

$$\frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} = \frac{p_A^o - P_A}{p_A^o}$$

For the ideal solutions which are dilute, the molar concentration of solute being very small $\left[\frac{W_B}{M_B} << \frac{W_A}{M_A}\right]$ and can be neglectd as compared to that of the solvent. Thus

$$\frac{W_A}{M_A} + \frac{W_B}{M_B} \simeq \frac{W_A}{M_A}$$

The eq. becomes

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

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

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

Thus the molar mass of the solute can be determined if the other quantities in above equation are known.

Example. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. At the same temperature the vapour pressure of a solution containing 0.5g of non volatile solid in 39g of benzene at 0.845 bar. what is the molecular weight of solid ? (molar mass of benzene = 78 g mol^{-1})

Solution. Given $p_{C_6H_6}^o = 0.850\,\text{bar}$

Vapour pressure of solution is P_A= 0.845 bar

$W_B = 0.5g,\ M_{C_6H_6} = 78g,$

$W_{C_6H_6} = 39\,g,\ \ M_B = ?$

$$M_B = \frac{W_B \times M_A}{W_A}\left(\frac{p_{C_6H_6}^o}{p_{C_6H_6}^o - p_A}\right)$$

$$= \frac{0.5\times 78}{39}\times\frac{0.850}{0.850-0.845}=170\text{g}$$

2.9.2 Elevation of Boiling Point –

The boiling point of a liquid is the temprature at which its vapour pressure becomes equal to the atmospheri pressure.

We have learnt that the vapour pressure of the solution containing non-volatile solute is less than that of the solvent. Therefore, the solution has to be heated to a higher temprature so that its vapour pressure becomes equal to the atmospheric pressure. Thus the boiling point of the solution is always higher than that of the pure solvent. The diffrence in boiling points of the solution (T_b) and pure solvent (T_b^o) is called the elevation in boiling point (ΔT_b) i.e.

$$\Delta T_b = T_b - T_b^o$$

graphically,

$$\Delta T_b \propto \Delta P$$

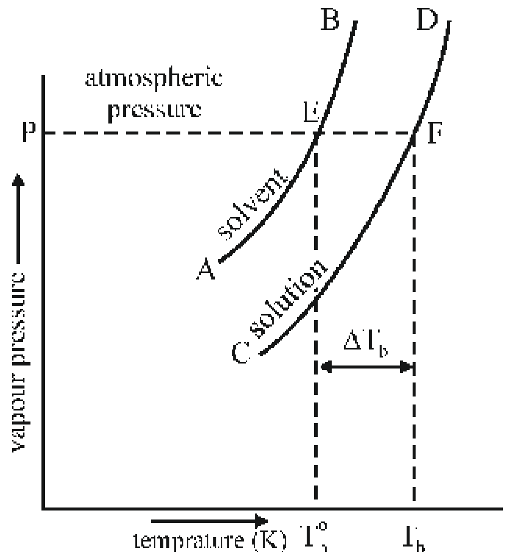


Fig. 2.5

According to Raoult's law $\Delta P \propto x_B$ (x_B = mole fraction of solute), so, we have

$$\Delta T_b \propto x_B$$

$$\Delta T_b \propto K x_B$$

$$x_B = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}+\frac{W_B}{M_B}}$$

$$\Delta T_b = k\frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}+\frac{W_B}{M_B}}$$

For dilute solutions, $\frac{W_B}{M_B} <<< \frac{W_A}{M_A}$

$$\Delta T_b = K\frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}}$$

$$\Delta T_b = K.M_A\frac{W_B}{M_B\times W_A}$$

$$\Delta T_b = K_b.m$$

where m is molality of solution and K_b is molal elevation constant.

Calculation of molecular mass of an unknown non–volatile compound from elevation of boiling point

Molality of solution $m = \frac{W_B\times 1000}{M_B\times W_A}$

We know that, $\Delta T_b = K_b.m = K_b.\frac{W_B\times 1000}{M_B\times W_A}$

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

Where, W_B = mass of solute

M_B = Molar mass of solute

W_A = Mass of solvent

K_b is related to molar enthalpy of vaporisation of solvent according to the relation

$$K_b = \frac{M_A R T_b^2}{\Delta H_{vap.} \times 1000}$$

Where,

M_A = Molecular mass of solvent

R = Universal gas constant

T_b = Boiling point of solvent

$\Delta H_{vap.}$ = Enthalpy of vaporisation of solvent

Example. The boiling point of benzene (353.23k) becomes 354.11 K if 1.80 g of a non-volatile solute is dissolved in 90g of it. Find the molar mass of the unknown solute.

(K_b for benzene = 2.53 K Kg mol^{-1})

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

given $K_b = 2.53$ K Kg mol^{-1},

$w_b = 1.8g$

$w_A = 90g$

$\Delta T_b = T_b - T_b^o = 354.11 - 353.23 = 0.88K$

$$M_B = \frac{2.53}{0.88} \times \frac{1.8}{90} \times 1000 = 58 \text{ g mol}^{-1}$$

2.9.3 Depression in Freezing Point

The freezing point is the temperature at which the solid and the liquid states of the substance have the same vapour pressure. It has been observed that when a non volatile solution is added to a solvent, the freezing point of the solution is always lower than that of the pure solvent. This may be illustrated graphically as shown in Fig. 2.6

In the figure the curve BC gives the vapour pressure of pure solvent, we know that the addition of a non-volatile solute lowers the vapour pressure and the curve DE gives the vapour pressure curve for the solution at different temperatures. The curve AB corresponds to the vapour pressure of the solid at different temperatures.

The temperature corresponding to the point B where the solid and liquid solvent meet (i.e., solid and liquid states have the same vapour pressure) represents the freezing point temprerature of pure solvent (T_f^o). The temperature corresponding to the point D where the solid solvent and liquid solution meet (i.e., solid and liquid states have the same vapour pressure) represents the freezing point temperature of the solution (T_f).

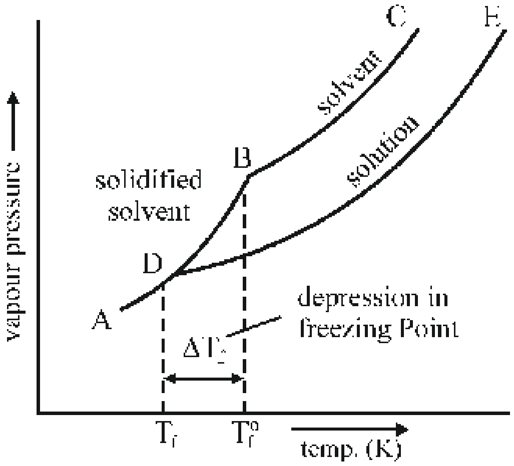


Fig. 2.6

It is clear from graph that $\Delta T_f \propto \Delta P$

According to Raoult's law $\Delta T_f \propto x_B$

$\therefore \Delta T_f = K x_B$

$$x_B = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\Delta T_f = K \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

For dilute solutions, $\frac{W_B}{M_B} <<< \frac{W_A}{M_A}$

$$\Delta T_f = K \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}}$$

$$\Delta T_f = K.M_A \frac{W_B}{M_B \times W_A}$$

$\Delta T_f = K_f.m$

where, m is molality of solution and K_f is molal elevation constant.

Calculation of molecular mass of an unknown non volatile compound from depression of freezing point can be done as–

$$\text{Molality of solution } m = \frac{W_B \times 1000}{M_B \times W_A}$$

$$\text{We know, } \Delta T_f = K_f \frac{W_B \times 1000}{M_B \times W_A}$$

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

Where W_B = Mass of solute

M_B = Molar mass of solute

W_A = Mass of solvent

$$K_f = \frac{M_A R T_f^2}{\Delta H_{vap.} \times 1000}$$

Where,

M_A = Molecular mass of solvent

T_f = Freezing point of solvent

R = Universal gas constant

$\Delta H_{vap.}$ = Enthalpy of freezing of solvent

Example. A solution containing 25.6 g of sulphur dissolved in 1000 g of naphthalene whose melting point is 80.1°C gave the freezing point lowering of 0.68°C. Calculate the formula of sulphur. (K_f for naphthalene = 6.8 K Kg mol^{-1})

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

given $K_f = 6.8$ k kg mol^{-1},

$\Delta T_f = 0.68°C \simeq 0.68$ K

$W_B = 25.6$ g

$W_A = 1000$ g

$$M_B = \frac{6.8}{0.68} \times \frac{25.6}{1000} \times 1000 = 256$$

Let molecular formula of sulphur is S_x

∴ Molar mass = x × 32, Therefore,

x = 8 so the formula of sulphur is S_8

2.10 Diffusion

In diffusion, the molecules move from a region of highr concentration into the region of lower concentration. It is common in gases as well as in liquids. It cannot be stopped or reversed.

2.10.1 Osmosis

The phenomenon of osmosis was studied for the first time by Jean-Antoine Nollet in 1748. Let us consider an aqueous solution of sugar placed in an intverted thistle funnel having a semi-permeable membrane such as animal bladder or parchment paper, attached to its bottom. The thistle funnel is lowered into a beaker containing water. The membrane is such that it allows only the molecules of the solvent and not of the solute to pass through it. Thus, there will be movement of water molecules from pure solvent into the solution. As a result, water passes into the thistle funnel and level of solution in the thistle funnel rises gradually (fig. 2.7). This process is called osmosis. Thus, the phenomenon of the flow of solvent through a semi phermeable membrane from pure solvent to the solution is called **osmosis**.

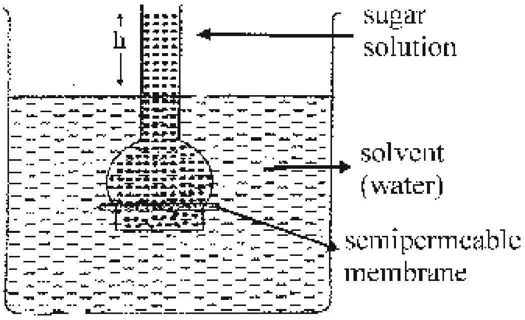


Fig. 2.7

2.11 Osmotic pressure

Alternatively, to understand the concept of osmotic pressure, consider an apparatus shown in

Fig. 2.8. It consists of a vessel divided into two compartments by a semi-permeable membrane. These two compartments are fitted with water-tight frictionless pistons. Let us take solution in one compartment and pure solvent in the other compartment. Due to osmosis, there will be flow of solvent into the solution compartment through the semi-permeable membrane. As a result, the piston on the solution side will tend to move outwards. To stop this movement of piston outwards, we have to apply pressure on the solution side. This pressure, just sufficient to stop osmosis will be equal to the osmotic pressure. Thus, osmotic pressure may be defined as the excess pressure which may be applied to a solution to prevent the passage of solvent into it through a semi-permeable membrane.

Thus, osmotic pressure is the pressure applied to prevent osmosis. It is generally denoted by π.

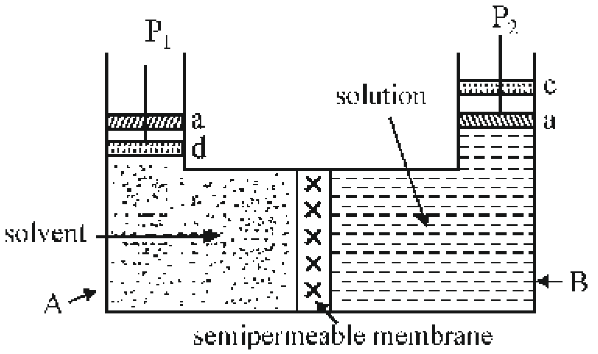


Fig. 2.8

2.11.1 Osmotic pressure-a colligative property–

Van't Hoff made a thorough study of the osmotic pressure of the dilute or ideal solutions. He concluded that a dilute or ideal solution behaves like an ideal gas and the different gas laws are applicable to the dilute solution as well.

(i) **Van't Hoff Boyle rule-** For a solution at a given temperature, osmotic pressure is directly proportional to its concentration.

$$\pi \propto C \qquad \because \text{ Concentration} = \frac{1}{\text{dilution (V)}}$$

$$\therefore \qquad \pi \propto \frac{1}{V}$$

(ii) **Van't Hoff pressure temperature rule–** For a solution of definite concentration or dilution, osmotic pressure is directly proportional to absolute temperature.

$$\pi \propto T$$

From the above two rules.

$$\pi \propto \frac{T}{V}$$

$$\pi = \frac{ST}{V}$$

$\pi V = ST$ for 1 mole

$\pi V = nST$ for n mole

S = Solution constant whose value is equal to gas constant (R). Therefore,

$$\pi V = nRT$$

2.11.2 Determination of molar mass from osmotic pressure-According to Van't Hoff equation

$$\pi V = nRT$$

$$\pi = \frac{n}{V} RT$$

The number of moles of solute (n) may be given as $n = \frac{W_B}{M_B}$

Substituting the value of n in the above expression

Where

W_B = mass of solute

M_B = molecular weight of solute

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

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

Example– Calculate the osmotic pressure of $\frac{M}{10}$ solution of urea at 27° C

(R = 0.0821 L atm K^{-1} $mole^{-1}$)

Solution– $\pi V = nRT$

$$\pi = \frac{n}{V}RT$$

$$\pi = CRT$$

given $C = \frac{1}{10}$ mole, $R = 0.0821$ L atm $K^{-1}mol^{-1}$

$$T = 27 + 273 = 300\ K$$

$$\pi = \frac{1}{10} \times 0.0821 \times 300$$

$$= 2.46 \text{ atm}$$

2.11.3 Isotonic solutions–

The two solutions having equal osmotic pressure are called isotonic solutions.

2.11.4 Hypertonic solutions–

If a solution has more osmotic pressure than some other solution, it is called hypertonic solution.

2.11.5 Hypotonic solutions–

If a solution has less osmotic pressure than some other solution, it is called hypotonic solution.

Example– A 12% solution of compound A is isotonic with 4% solution of urea. Calculate the molar mass of compound A.

Solution– Osmotic pressure

$$\pi = \frac{W_B RT}{MV}$$

Osmotic pressure of 4% solution of urea (NH_2CONH_2)

$$\pi_1 = \frac{4 \times R \times T}{60 \times 100} \times 1000$$

Osmotic pressure of 12% solution of compound A

$$\pi_2 = \frac{12 \times R \times T}{M \times 100} \times 1000$$

Isotonic solutions have the same osmotic pressure, so

$$\therefore\ \pi_1 = \pi_2$$

$$\frac{4 \times R \times T}{60 \times 100} \times 1000 = \frac{12 \times R \times T}{M \times 100} \times 1000$$

$\frac{4}{60} = \frac{12}{M}$ and M = 180 g, Hence,

Molar mass of compound A is 180 g

2.12 ABNORMAL MOLAR MASSES–

The various relations between colligative property and molecular mass are applicable only to the solutions of non electrolytes and are based on the following assumptions :

(i) The solution is dilute, so that Raoult's law is obeyed.

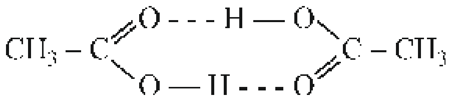
(ii) The solute neither undergoes dissociation nor association in solution.

When we measure the colligative properties of electrolytic solutions we find discrepencies between the observed and calculated values of colligative properties.

These anomalies are primarily due to dissociation of the solute particle and association of solute molecules.

A number of electrolytes dissociate in solution to give two or more particles (ions). For example 1mole each of NaCl, $CaCl_2$, $K_4[Fe(CN)_6]$ dissociates into 2, 3 and 5 ions when dissolved in water. Since colligative properties are inversely proportional to molecular masses therefore molecular masses of such substances equals to $\frac{1}{2}, \frac{1}{3}, \frac{1}{5}$ of its normal molecular masses.

Similary certain solutes like formic acid, acetic acid, benzoic acid assoicates in benzene due to formation of intra molecular hydrogen bond.



Since colligative properties are inversely proportional to molecular masses thus the above acids is found to have molecular mass double of its normal molecular mass.

2.12.1 Van't Hoff's Factor–

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

Since colligative properties are inversly proportional to molecular masses, the van't Hoff's factor may be written as-

$$i = \frac{\text{observed colligative property}}{\text{theoretical colligative property}}$$

$$i = \frac{\text{ionization/no. of particles after association}}{\text{ionization/no. of particles before association}}$$

$$i = \frac{\Delta P_{\text{observed}}}{\Delta P_{\text{theoritical}}} = \frac{\Delta T_{b\,\text{observed}}}{\Delta T_{b\,\text{theoritical}}} = \frac{\Delta T_{f\,\text{observed}}}{\Delta T_{f\,\text{theoritical}}} = \frac{\pi_{\text{observed}}}{\pi_{\text{theoritical}}}$$

In case there is no dissociation or association the value of i become equal to one (unity).

In case of dissociation, the Van't Hoff factor is more than 1.

In case of association, the Van't Hoff factor is less than 1.

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

(i) Relative lowering of vapour pressure

$$\frac{P_A^o - P_A}{P_A^o} = ix_B$$

(ii) Elevation of boiling point

$\Delta T_b = iK_bm$

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

(iii) Depression of freezing point

$\Delta T_f = iK_fm$

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

(iv) Osmotic pressure

$\pi = icRT$

$$\pi = \frac{i \times W_B \times R \times T}{M_B \times V}$$

2.12.2 Van't Hoff factor and extent of dissociation

Suppose a molecule of an electrolyte A gives n ions after dissociation. Then if we start with 1 mole of the solute and α is the degree of dissociation then at equilibrium.

$$\underset{1}{A} \rightleftharpoons \underset{0}{nB}$$

Number of moles of solute left undissociated = 1 - α

Number of moles of ions formed = nα

observed number of moles of solute = 1-α+nα
= 1+α(n-1)

$$i = \frac{\text{No. of moles after ionization}}{\text{No. of moles before ionization}}$$

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

$$\text{or } \alpha = \frac{i-1}{n-1}$$

Example– 0.1M solution of $K_4[Fe(CN)_6]$ at 27°C is 46% dissociated. Calculate the osmotic pressure of the solution. (R = 0.082 atm ×L×$K^{-1}$$mole^{-1}$)

Solution– $\pi = icRT$

degree of dissociation α is given by

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

α = 46% or $\alpha = \frac{46}{100}$, for ionic compound $K_4[Fe(CN)_6]$ n = 5

$$i = 1 + \frac{46}{100}(5-1) = 2.84$$

C = 0.1, R = 0.082 T = 27 + 273 = 300

$\pi = 2.84 \times 0.1 \times 0.082 \times 300$

$= 6.98$ atm

2.12.3 Van't Hoff factor and extent of association–

Suppose n simple molecules of the solute associate to form the assoicated molecule An

$nA \rightleftharpoons [An]$

If we start with 1 mole of A and α is the degree of association, the concentration of the species after association is

$[A] = 1 - \alpha \qquad [An] = \frac{\alpha}{n}$

∴ observed number of moles of solute

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

$$i = \frac{\text{observed number of moles of solute}}{\text{Normal number of moles of solute}}$$

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

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

$in = n - n\alpha + \alpha$

$in - n = \alpha - n\alpha$

$n(i-1) = \alpha(1-n)$

$$\alpha = \frac{n(i-1)}{1-n}$$

Example– The freezing point of a solution containing 0.3 of benzoic acid in 20 g of benzene is lowered by 0.317 K. Calculate the degree of association of benzoic acid in benzene.

(K_f for benzene = 5.1 K Kg mol^{-1})

Solution– $M_{\text{Bप्रेक्षित}} = \frac{K_f}{\Delta T_f} \times \frac{W_B}{W_A} \times 100$

$K_f = 5.1$ K Kg $mole^{-1}$

$\Delta T_f = 0.317$ K

$W_B = 0.3$ g

$W_A = 20$ g

$$M_{\text{Bप्रेक्षित}} = \frac{5.1 \times 0.3 \times 1000}{0.317 \times 20}$$

$M_{\text{Bप्रेक्षित}} = 241$

Normal molar mass of benzoic acid = 122g

$$i = \frac{\text{normal molar mass}}{\text{observed molar mass}}$$

$$= \frac{122}{241} = 0.506$$

Benzoic acid forms dimer in benzene therefore n = 2

$$\alpha = \frac{n(i-1)}{1-n}$$

$$\alpha = \frac{2(0.506-1)}{1-2}$$

$$= \frac{2 \times (-)0.494}{(-)1}$$

$= 0.988 = 98.8$ %

EXERCISE QUESTIONS

Multiple Choice Questions

1. Liquid NaOH dissolved in 500g water. The molality of solution will be :

(a) 8 g/Litre (b) 0.2N

(c) 0.2m (d) 0.2 M

2. Which liquid pair solution show positive deviations.

(a) Water + HCl

(b) Water + HNO_3

(c) benzene + methanol

(d) acetone + chloroform

3. The molarity of pure water is

(a) 55.5M (b) 100M

(c) 18M (d) 1M

4. Arrange following 0.1M solutions in their increasing order of boiling point.

(i) NaCl (iii) Urea

(ii) $MgCl_2$ (iv) $AlCl_3$

(a) (i) < (ii) < (iii) < (iv)

(b) (ii) < (i) < (iii) < (iv)

(c) (iii) < (i) < (ii) < (iv)

(d) (iv) < (iii) < (ii) < (i)

5. The property of an ideal solution is-

(a) It obey Raoult's law

(b) $\Delta H_{mixture} = O$

(c) $\Delta V_{mixture} = O$

(d) All of above

6. The vapour pressure of a substance by increasing temperature is :

(a) always increases

(b) decreases

(c) does not depend on temperature

(d) partially depends on temperature

7. Osmotic pressure of 5% solution of sugar at 25 °C is

(a) 3.48 atm (b) 5.07 atm

(c) 4.03 atm (d) 2.09 atm

8. Solubility of H_2 gas in water by increasing temprature is

(a) increases

(b) decreases

(c) remains unchanged

(d) non of the above

Very Short Answer Questions

1. Determine molality of 10% $\left(\frac{w}{W}\right)$ H_2SO_4 aqueous solution.
2. Define molarity and what is the effect of temperature.
3. Define mole fraction of a substance in solution.
4. Can ethylene glycol be used in radiators of car?
5. What is reverse osmosis? Describe its application.

Short Answer Type Questions

1. Explain the effect of temperature of solubility of solid in liquid. Write an equation of Van't Hoff factor for abnormal molecular weight. How it is affected by association and dissociation.
2. Normal molar mass and observed molar mass of ionic compound AB is 58.2g and 30g. Calculate Van't Hoff factor and degree of dissociation.
3. What is the difference between diffusion and osmosis, give examples of each.
4. 1.26g protein is present is 0.2L aqueous solution. The osmotic pressure of the solution at 300K is 2.57×10^{-3} bar. Determine its molar mass (R = 0.0821 L bar mol^{-1} K^{-1})
5. For a non volatile solute's solution, prove that

$$\Delta T_b = K_b.m$$

6. Explain the determination of molar mass of a solute from Relative lowering in vapour pressure.
7. Explain the solubility of gases in liquids. Discuss the factors affecting the solubility of gases in liquids.
8. Calculate the temprature at which the solution (of 54 glucose in 250g water) freezes.

($K_f = 1.86$ K. Kg mol^{-1})

9. Draw a graph for an ideal solution formed from solute and solvent.

Answers (Multiple Choice Questions)

1. (c) 2, (d) 3. (a) 4. (c)

5. (d) 6. (a) 7. (a) 8. (a)