# SOLUTIONS

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# **1. INTRODUCTION**

A solution may contain varying amounts of the components. Hence, a solution may be defined as follows:

**Solution** is a homogenous mixture of two or more chemically non-reacting substances on molecular level, whose composition can be varied within certain limits.

In a homogeneous mixture, all the particles are of molecular size, i.e., up to  $10^{-9}$  m in diameter and the different constituents of the mixture cannot be separated by any of the physical methods like filtration, settling or centrifuging. Every solution is made up of a **solvent** and one or more **solutes**. **A solvent** is that component of the solution which is present in larger amount by mass than the other component, termed as **solute**. A solution containing only one solute dissolved in a solvent is called **binary solution**.

Solutions in water are called **aqueous solutions**, and the solutions in which water is not the solvent are called non-aqueous solutions. The solvents in the non-aqueous solutions are usually benzene, ether, carbon tetrachloride, etc.

#### Importance of solutions.

The use of a particular solution in everyday life depends upon its composition. For example,

- (i) Brass is a homogeneous mixture of copper and zinc, German silver is that of copper, zinc and nickel while bronze is that of copper and tin. They have different properties and hence are put to different uses.
- (ii) 1 part per million parts (1 ppm) of fluoride ions in water prevents tooth decay, 1.5 ppm causes the teeth to become mottled (coloured) and still higher concentration can be used as poison, e.g., for rats, in the form of sodium fluoride.
- (iii) Solutions of intravenous injections should have the same ionic concentration as that of the blood plasma.

When we mix two liquids, they may or may not form a homogenous mixture depending upon the nature of the liquids. Hence, liquid - liquid mixtures are generally classified into the following three types:

- (a) **Completely miscible liquids.** When both the liquids are polar (e.g., ethyl alcohol and water) or both are non-polar (e.g., benzene and hexane), they mix completely in all proportions to form a homogeneous mixture. They are said to be completely miscible liquids.
- (b) Completely immiscible liquids. When one liquid is polar and the other is non-polar, e.g., benzene and water or cyclohexane and water etc., they do not mix at all and form separate layers. They are said to be completely immiscible liquids.
- (c) Partially miscible liquids. When two liquids are not exactly similar in nature and also not completely dissimilar in nature e.g., ether and water, they dissolve in each other to a limited extent only. They are said to be partially miscible. Similarly, we have phenol and water or nitrobenzene and hexane.

Whereas on the basis of solubility solutions may be divided into three types:

- (1) Unsaturated solution: A solution in which more solute can be dissolved without raising temperature is called unsaturated solution.
- (2) Saturated solution: A solution in which no solute can be dissolved further at a given temperature is called saturated solution.
- (3) **Super-saturated solution:** When the temperature of the saturated solution is increased, its solubility will also be increased and more solute can be dissolved into it. Hence, this hot concentrated solution is called super-saturated solution.

# The maximum amount of a solute that can be dissolved in a given amount of solvent (generally 100 gram) at a given temperature is termed as its "solubility" at that temperature.

The solubility of a solute in a solvent depends upon the following factors:

- (a) Nature of the solute
- (b) Nature of the solvent
- (c) Temperature of the solution
- (d) Pressure (in case of gases)

# 2. METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION

The term **"concentration"** of a solution is defined as the relative amount of solute present in a given amount of solution.

 $concentration = \frac{Quantity \ of \ solute}{volume \ of \ solution}$ 

Solutions with relatively low concentration of solutes are called **dilute solutions** while those of with relatively high concentration of solutes are called **concentrated solutions**. The concentration of a solution can be expresses in a number of ways. The important methods are:

# 2.1 Percentage:

The percentage of a solution is usually expressed either as 'percentage by mass' or 'percentage by volume' or 'percentage mass by volume'.

# 2.1.1 Mass Percentage or Percent by Mass (Percent by weight):

It is defined as the amount of solute in grams present in 100 grams of the solution.

Mass percentage = 
$$\frac{Mass \ of \ Solute}{Mass \ of \ Solution} \times 100$$

 $= \frac{Mass \ of \ solute}{Mass \ of \ solute + Mass \ of \ solvent} \times 100$ 

 $= \frac{\text{Mass of solute}}{\text{Volume of Solution} \times \text{Density of solution}} \times 100$ 

It has the same meaning for solid and liquid solutes.

# 2.1.2 Volume percentage or Percent by Volume:

Percentage by volume has different meanings for solid and liquid solutes. In case of solid solutes, percentage by volume means mass of the solute in grams dissolved in 100 mL of the solution, i.e. it is weight/volume (w/V) percent.

Percent by volume (for solids) =  $\frac{Mass \ of \ solute}{Volume \ of \ solution} \times 100$ 

It is also known as **percent mass by volume** or **percent strength**. Whereas in case of liquid solutes, it has a meaning that volume of the solute in mL dissolved in 100 mL of the solution, hence it is volume/volume (v/V) percent.

Percent by volume (for liquids) = 
$$\frac{Volume \ of \ solute}{Volume \ of \ solution} \times 100$$

# Note:

- (i) It is so because the volume of solids is taken as negligible.
- (ii) This method is not always correct, because sometimes volume of solute mixed with a certain volume of solvent does not give the total volume equal to sum of volumes of solute and solvent.

# 2.2 Strength (Concentration in grams per litre):

It is defined as the amount of the solute in grams present in one litre (or  $dm^3$ ) of the solution.

 $Concentration (strength) of solution = \frac{Mass of solute in grams}{Volume of the solution in litres}$ 

 $= \frac{\text{Mass of solute in grams}}{\text{Volume of the solution in mL}} \times 1000$ 

**Strength or concentration** of the solution  $= w/V gL^{-1}$ 

# 2.3 Parts per million (ppm):

When the solute is present in trace quantities, it is convenient to express the concentration in parts per million (ppm). It is defined as the quantity of the solute in grams present in 10<sup>6</sup> grams of the solution (i.e. 1 mg in solute present in 1 kg of solution).

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

Atmospheric pollutants are expressed in ppm by volume. It refers to the volume of the pollutant in  $10^6$  units of volume. 10 ppm of SO<sub>2</sub> in air means 10 mL of SO<sub>2</sub> is present in  $10^6$  mL of air.

# 2.4 Parts per billion (ppb):

For even more dilute solutions parts per billion (ppb =  $10^9$ ) is used rather than parts per million (ppm =  $10^6$ ).

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

#### 2.5 Molarity (Molar concentration M):

It is defined as the number of moles of the solute present in 1 litre or 1  $dm^3$  of the solution, i.e.,

Molarity (M) = 
$$\frac{\text{Number of moles of solute}}{\text{Volume of the solution (in litres)}}$$

Let  $w_A$  g of the solute of molecular mass  $M_A$  is dissolved in V litre of solution.

Molarity of the solution (M) =  $\frac{w_A}{M_A \times V}$ 

or Molarity  $\times$  M<sub>A</sub> = w<sub>A</sub>/V

but  $w_A/V$  = strength of solution; hence, M can be calculated from the strength as below:

$$M = \frac{\text{strength in } gL^{-1}}{M}$$

If V is taken in mL (cm<sup>3</sup>), then Molarity of the solution =  $\frac{w_A}{M_A \times V} \times 1000$ 

The unit of molarity is mol litre<sup>-1</sup> or mol dm<sup>-3</sup>

The number of moles can be calculated as:

Number of moles =  $M \times V(in litre) = \frac{Weight}{Molecular weight}$ 

Number of milli moles =  $M \times V(in mL) = \frac{Weight}{Molecular weight} \times 1000$ 

#### 2.5.1 Molarity of dilution:

If  $V_1$  mL of solution with molarity  $M_1$  is diluted to volume  $V_2$  mL and the molarity of the diluted solution is  $M_2$ , then

Before dilution  $M_1V_1 = M_2V_2$ 

This is called **molarity equation**.

However, if the two different solutions are taken, first the balanced equation is written, i.e.

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

Where,  $n_1$  = number of moles of solute in solution 1

 $n_2$  = number of moles of solute in solution 2

#### 2.5.2 Molarity of mixing:

Let there be three samples of solution (containing same solvent and solute) with their molarity  $M_1$ ,  $M_2$ ,  $M_3$  and volumes  $V_1$ ,  $V_2$ ,  $V_3$  respectively. These solutions are mixed; molarity of mixed solution may be given as:

$$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$$

Where,  $M_R$  = resultant molarity

Molarity is dependent on volume; therefore, it depends on temperature.

#### 2.6 Normality (N):

It is defines as the number of gram equivalents of solute present per litre of solution; i.e.

Normality  $(N) = \frac{No.of gram equivalents of solute}{Volume of solution (in litres)}$ 

Let  $w_A$  gram of the solute of equivalent mass  $E_A$  be present in V litre of the solution, then, Normality  $(N) = \frac{w_A}{E_A \times V}$ 

But  $w_A/V$  = strength of solution; hence, N can be calculated from the strength as below:

$$N = \frac{\text{strength in } g \ L^1}{Equivalent \text{ mass of the solute in } g \ eq^{-1}}$$

The unit of normality is g eq litre<sup>-1</sup> or g eq dm<sup>-3</sup>

The number of equivalents can be calculated as:

Number of equivalents = 
$$N \times V(in litre) = \frac{Weight}{Equivalent weight}$$

Number of milli equivalents =  $N \times V(in mL) = \frac{Weight}{Equivalent weight} \times 1000$ 

#### 2.6.1 Normality of dilution:

Same, as shown in case of molarity, when a solution  $(N_1)$  is diluted from  $V_1$  mL volume to  $V_2$  mL and the normality of the diluted solution is  $N_2$ , then

Before dilution After dilution  $N_1V_1 = N_2V_2$ 

This is called **normality equation**.

Weight

# 2.6.2 Normality of mixing:

Similarly, if normalities are used,  $N_1V_1 + N_2V_2 + N_3V_3 = N_R (V_1 + V_2 + V_3)$ Where,  $N_R$  = resultant normality

# Relationship between normality and molarity:

As, Molarity × Molecular mass = Strength of solution (g/L) Similarly, Normality × Equivalent mass = Strength of the solution (g/L) Hence, Molarity × Molecular mass = Normality × Equivalent mass or Normality/Molarity = Molecular mass/Equivalent mass = n

Here, n=valance factor

So Normality = n × Molarity

**Note:** To dilute  $V_1cc$  of a solution having molarity  $M_1$  to molarity  $M_2$  and the final volume is  $V_2$ , volume of water to be added, i.e.,

$$V_2 - V_1 = \left(\frac{M_1 - M_2}{M_2}\right) V_1$$
, Similarly,  $V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2}\right) V_1$ 

# 2.7 Molality (m)

It is defined as the number of the moles of the solute present in 1 kg of the solvent, it is denoted by m.

$$Molality = \frac{Number of moles of solute}{Mass of solvent in kg}$$

Let  $w_A$  grams of the solute of molecular mass  $M_A$  be present in  $w_B$  grams of the solvent, then

Molality (m) = 
$$\frac{W_A}{M_A \times W_B} \times 1000$$

Unit of molality is mol kg<sup>-1</sup>

**Molality** is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

#### 2.8 Formality (F)

It is the concentration unit for ionic compounds which dissolve in a polar solvent to give pair of ions. It represents number of gram-formula-weight of the substance dissolved per liter of the solution. It is almost same as the molarity .It describes the solute that is mixed in a liquid rather than the solute present in solution after the dissolution process.

$$Formality = \frac{Moles \ of \ substance \ added \ to \ solution}{Volume \ of \ solution \ in \ L}$$

# 2.9 Mole Fraction

It is defined as the ratio of number of moles of one component to the total number of moles of the solution (i.e., all the components).

Let n moles of solute (A) and N moles of solvent (B) be present in a solution.

Mole fraction of solute  $(x_A) = \frac{n}{N+n} = x_A$ 

Mole fraction of solvent  $(x_B) = \frac{N}{N+n} = x_B$ 

Evidently,  $x_A + x_B = 1$ 

Hence, the sum of mole fractions of all the constituents of a solution is always equal to unity.

Mole fraction is independent of temperature of the solution.

# 2.10 Mole Percentage

It represents the number of moles of a solute in a solution as a percentage of the total number of moles in the solution (i.e., all the components). Multiplying mole fraction by 100 gives the mole percentage, also referred as amount percent.

$$Mole \% = \frac{Moles of solute}{Moles of solute + Moles of solvent} \times 100$$

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#### 2.11 Mass Fraction:

It is the ratio of the mass of one component to the total mass of the solution. Let w gram is the weight of solute and W gram is the weight of solvent. Hence,

Mass fraction of solute (X<sub>solute</sub>) =  $\frac{w}{w+W}$ 

Mass fraction of solvent (X<sub>solvent</sub>) =  $\frac{W}{W + W}$ 

Evidently,  $X_{solute} + X_{solvent} = 1$ 

Also, Mass percentage = mass fraction × 100

# Some Important Relationship:

#### (i) Relationship between molarity (M) and molality (m):

Molarity M means M moles of the solute are present in 1000 mL of the solution. If density of the solution is d g mL<sup>-1</sup>, mass of solution = 1000 d grams. Mass of solute =  $MM_2$  g ( $M_2$  is molar mass of the solute). Hence, mass of solvent = 1000 d -  $MM_2$  gram.

$$\therefore \text{ Molality (m)} = \frac{M}{1000d-MM_2} \times 1000$$
$$= \frac{1000 \text{ M}}{1000d-MM_2}$$
Thus, m=  $\frac{M}{d-MM_2/1000}$ or m $\left(d - \frac{MM_2}{1000}\right) = M$ or md -  $\frac{m MM_2}{1000} = M$ or M $\left(1 + \frac{mM_2}{1000}\right) = md$ or M $\left(1 + \frac{mM_2}{1000}\right) = md$ or M=  $\frac{md}{1+mM_2/1000}$ 

# (ii) Relationship between molality (m) and mole fraction (x<sub>2</sub>):

Molality (m) means m moles of the solute in 1000 g of the solvent =  $1000/m_1$  moles (M<sub>1</sub> = molar mass of the solvent). Hence,

Mole fraction 
$$(x_2) = \frac{m}{m + 1000 / M_1} = \frac{m M_1}{1000 + m M_1}$$

 $x_2 = \frac{mM_1}{1000 + m M_1}$ Thus,  $\frac{1}{x_2} = \frac{1000 + mM_1}{mM_1} = \frac{1000}{mM_1} + 1$  $\frac{1000}{mM_1} = 1 - \frac{1}{m} = \frac{1 - x_2}{m} = \frac{x_1}{m}$ or

or 
$$\frac{1000}{mM_1} = 1 - \frac{1}{x_2} = \frac{1}{x_2} = \frac{1}{x_2} = \frac{1000x_2}{x_1M_1}$$

# (iii) Relationship between molarity (M) and mole fraction (x<sub>2</sub>):

Referring to calculations in (ii) above,

Mole fraction  $(x_2) = \frac{M(Moles of solute)}{(1000 d - MM_2)/M_1} +$ М (Moles of solvent) (Moles of solute) or  $x_2 = \frac{MM_1}{(1000d - MM_2) + MM_1}$  $=\frac{MM_{1}}{M(M_{1}-M_{2})+1000\,d}$ Thus,  $x_2 = \frac{MM_1}{M(M_1 - M_2) + 1000 d}$ 

On rearranging we get,

$$M = \frac{1000 \, d \, x_2}{x_1 M_1 + x_2 M_2}$$

It should be noted here if molarity (M) is in moles/litre and density d is in kg/litre and molality m is in moles kg of the solvent, 1000 will be replaced by 1 in the above formulae.

#### Note:

- 1. Demal (D) is another unit for expressing the concentration solution. It is equal to molar concentration at 0°C, i.e., 1 D represents one mole of the solute present in one litre of the solution at 0°C.
- 2. When normality of solution is 1 N, it is called a normal solution. When normality of a solution is 0.1 N it is called a deci-normal solution. Similarly we defined semi-normal solution as 0.5 N solutions.
- 3. It may be noted that molality, mole fraction, etc. are preferred to molarity, normality etc. because the former involve the weight of solute and solvent whereas latter involve volumes of solution. Temperature has no effect on weights but it has significant effect on volumes.
- **Example:** Calculate the molality and mole fraction of 2.5 g of ethanoic acid (CH<sub>3</sub>COOH) in 75 g of benzene.

**Solution:** Mass of solute  $(CH_3COOH) = 2.5 g$ Mass of solvent  $(C_6H_6) = 75 g = 0.075 kg$ Molar mass of  $CH_3COOH = 60 \text{ g mol}^{-1}$ Molar mass of  $C_6H_6 = 78 \text{ g mol}^{-1}$ 

#### **Calculation of molality**

Moles of the solute (CH<sub>3</sub>COOH) =  $\frac{2.5}{60}$  = 0.0417 *Molality* =  $\frac{Moles \ of \ the \ solute}{Mass \ of \ the \ solvent \ in \ kg}$ 

 $=\frac{0.0417 \,mol}{0.075 \,kg}=0.556 \,mol \,kg^{-1}$ 

# **Calculation of mole fraction**

Mole of solute  $(n_{CH,COOH}) = 0.0417$ 

Mole of solvent 
$$(n_{C_6H_6}) = \frac{75}{78} = 0.961$$

Moles fraction of CH<sub>3</sub>COOH in the solution

$$= \frac{n_{CH_{B}COOH}}{n_{CH_{B}COOH+n_{C_{6}H_{6}}}} = \frac{0.0417}{0.0417+0.961}$$
$$= 0.0416$$

**Example:** Calculate the molarity and normality of a solution containing 5 g of NaOH in 450 mL solution.

**Solution:** Mass of NaOH dissolved = 5 g Volume of the solution =  $450 \text{ cm}^3 = 0.45 \text{ L}$ Calculation of molarity:

5 g of NaOH =  $\frac{5}{40}$  mole of NaOH

(" Molar mass of NaOH = 40 g mol<sup>-1</sup>)

$$= 0.125 \text{ mole}$$

$$Molarity = \frac{No \text{ of moles of solute}}{Volume \text{ of the solution in litres}}$$

$$=\frac{0.125\,mol}{0.45\,L}=\ 0.278\,mol\ L^{1}$$

Hence, molarity of the solution = 0.278 M

# **Calculation of normality:**

Since NaOH is monoacidic.

 $\therefore$  Eq. mass of NaOH = Mol. Mass of NaOH = 40

5 g of NaOH = 
$$\frac{5}{40}$$
 g equivalent

= 0.125 g equivalent

Normality =  $\frac{No. of g eq. of the solute}{Volume of solution in litres}$ =  $\frac{0.125 g eq}{0.45 L}$  = 0.278 g equivalent L<sup>-1</sup> Hence, normality of the solution = 0.278 N

# **3. TYPES OF SOLUTIONS**

When two or more chemically non-reacting substances are mixed, they form mixtures. A mixture may be heterogeneous or homogenous (true solution).

Every solution consists of a solvent and one or more solutes. Generally, the component present in greater amount than any or all the other components is called the solvent and the other components are the solutes.

All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Mainly there may be the following seven types of binary solutions.

S. No.	Solute	Solvent	Example
1.	Gas	Gas	Air
2.	Gas	Liquid	Aerated water ( $CO_2 + H_2O$ )
3.	Gas	Solid	Hydrogen in palladium
4.	Liquid	Liquid	Alcohol in water, benzene in toluene
5.	Liquid	Solid	Mercury in zinc amalgam
6.	Solid	Liquid	Sugar in water, common salt in water
7.	Solid	Solid	Various alloys

It should be noted that the formation of solution is not a chemical process. It is purely a physical change and it is separable into its components by altering the state of one of them (freezing or boiling of one of them).Based upon the physical state of the solvent and solute, solutions are classified into the following types:

# (i) Gaseous Solutions.

These solutions contain gas as a solvent. Three types of gaseous solutions are:

- (a) Solid in gas: Iodine vapours in air, camphor in  $N_2$  gas.
- (b) Liquid in gas: Humidity in air, chloroform mixed with  $N_2$  gas.
- (c) Gas in gas: Air  $(O_2+N_2)$ .

#### (ii) Liquid Solutions.

Liquid solutions are the solutions in which solvent used is liquid. There are three types of Liquid solutions:

- (a) Solid in liquid: sugar solution in water.
- (b) Liquid in liquid: Methanol or ethanol in water.
- (c) Gas in liquid: Aerated drinks, O<sub>2</sub> in water.

#### (iii) Solid Solutions.

In this type of solutions the solid is used as solvent. These are of further three types:

- (a) Solid in solid: Alloys (brass, German silver, bronze etc.)
- (b) Liquid in solid: Hydrated salts, Amalgam of Hg with Na and Zn.
- (c) Gas in solid: Dissolved gases in minerals.

#### 3.1 Solutions of Gases in Liquids

Almost all gases are soluble in water though to different extents. The existence of aquatic life in lakes, rivers, sea etc. is due to dissolution of oxygen gas of the air in water. Some gases are also soluble in solvents like ethyl alcohol, benzene, etc.

"The solubility of any gas in a particular liquid is the volume of the gas in ml (converted to S.T.P.) that can dissolve in unit volume (1 ml) of the liquid to form the saturated solution at the temperature of the experiment and under a pressure of one atmosphere."

This method of expressing the concentration is called **absorption coefficient** of the gas and is usually represented by  $\alpha$ .

Solubility of a gas in a liquid at a particular temperature is also expressed in terms of molarity (moles of the gas dissolved per litre of the solvent to form the saturated solution, i.e., in terms of mol  $L^{-1}$ ) or in terms of mole fraction ( $x_A$ ) of the gas.

The solubility of a gas in liquids depends upon the following factors:

(i) Nature of the gas: Generally, the gases, which can be easily liquefied, are more soluble in common solvents. For example, CO<sub>2</sub>, HCl, NH<sub>3</sub> are more soluble than hydrogen or oxygen in water.

The gases which are capable of forming ions are much more soluble in water than in other solvents. Gases like HCl and  $NH_3$  are highly soluble in water but not in organic solvents.

- (ii) Nature of the solvent: O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> are much more soluble in ethyl alcohol than in water at the same temperature and pressure while H<sub>2</sub>S and NH<sub>3</sub> are more soluble in water than in ethyl alcohol. The greater solubility of gas in a solvent is again due to the chemical similarity between the gas and the solvent.
- (iii)**Temperature:** The solubility of most gases in liquids decreases with increase of temperature. Hence, the dissolution of a gas in a liquid is exothermic process, i.e., accompanied by evolution of heat. Thus,

Gas + Solvent ≓ Solution + Heat

Applying Le Chatelier's principle, it is evident that increase of temperature would shift the equilibrium in the backward direction, i.e., the solubility would decrease.

Though  $O_2$  gas is more soluble than  $N_2$  gas at any temperature, the solubility of both the gases decreases with increase of temperature as represented in Fig.



Figure: Variation of Solubility of  $O_2$  and  $N_2$  gases with temperature at constant pressure of 1 atm

However, some gases are more soluble at higher temperature than at lower. For example: the solubility of some sparingly soluble gases, such as hydrogen and inert gases increases slightly with increase of temperature especially in the non-aqueous solvents such as hydrocarbons, alcohols and acetone.

(iv) Pressure: The quantitative relation between the solubility and pressure is given by Henry's law.

# 3.1.1 Henry's Law of Vapour Pressure

According to this law, the mass of a gas dissolved by a given volume of a liquid, at constant temperature, is proportional to the pressure of the gas. Hence, According to Henry's law,

 $m \propto p$  (at constant temperature)

here, m = the mass of gas dissolved per unit volume of a solvent

p =the pressure of the gas in equilibrium

or m = Kp .....(i)

where K is proportional constant.

Where,  $x_A$  = the mole fraction of the gas in the solution

 $p_A$  = the partial pressure of the gas

and K' = proportionality constant.

From eq.(ii),  $p_A = 1/K' \times x_A$ 

Or  $p_A = K_H x_A$  .....(iii)

Where  $K_H = 1/K'$ , is called Henry's constant.

Thus Henry's Law may be defined as:

The partial pressure of a gas in vapour phase (p) is directly proportional to the mole fraction (x) of the gas in the solution.

# Characteristics of Henry's constant, $K_{\rm H}$

- (i) Henry's constant,  $K_{H_1}$  is a function of the nature of the gas.
- (ii) Greater the value of  $K_H$ , lower is the solubility of the gas at the same partial pressure [according to eqn. (iii)] at a particular temperature.
- (iii) The value of  $K_H$  increases with increases of temperature implying that the solubility decreases with increase of temperature at the same pressure.

It is for the reason that aquatic species feel more comfortable in cold water (in which  $O_2$  gas dissolved is more) than in warm water (in which  $O_2$  dissolved is less).

# 3.1.1.1 Applications of Henry's law

# (i) In the production of carbonated beverages.

To increase the solubility of  $CO_2$  in soft drinks, soda water as well as beer, champagne, etc. the bottles are sealed under high pressure. When the bottles are opened to air, the partial pressure of  $CO_2$  above the solution decreases. As a result, solubility decreases and hence  $CO_2$  bubbles out.

# (ii)In the deep sea diving.

Deep-sea divers (or Scuba divers) depend upon compressed air for their oxygen supply. According to Henry's law, solubilities of gases increase with pressure. Thus, both  $N_2$  and  $O_2$  will dissolve considerably in the blood and other body fluids. Oxygen is used up for metabolism, but due to high partial pressure and greater solubility,  $N_2$  will remain dissolved and will form bubbles when the diver comes to the atmospheric pressure. These bubbles affect nerve impulses and give rise to a disease called **bends** or **decompression sickness**. To avoid bends and also the toxic effects of high concentration of nitrogen in the blood, the cylinders used by the divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

#### (iii) In the function of lungs.

When air enters the lungs, partial pressure of oxygen is high. This oxygen combines with haemoglobin to form oxyhaemoglobin. Partial pressure of  $O_2$  in tissues is low. Hence.  $O_2$  is released from oxyhaemoglobin, which is utilized from functions of the cells.

#### (iv) For climbers or people living at high altitudes.

At high altitudes, the partial pressure of oxygen is less than at the ground level. As a result, there is a low concentration of oxygen in the blood and tissues of the people living at high altitudes or climbers. Consequently, they feel weak and are unable to think properly, a disease called anoxia.

# 3.1.1.2 Limitations of Henry's law

Henry's law is applicable only if the following conditions are satisfied:

- (i) The pressure should be low and the temperature should be high, i.e., the gas should behave like an ideal gas.
- (ii) The gas should not undergo compound formation with the solvent or association or dissociation in the solvent.

For example, the law is not applicable in case of dissolution of ammonia in water because it undergoes compound formation followed by dissociation:

$$NH_3$$
 (g) +  $H_2O \rightarrow NH_4OH$  (aq)

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Similarly, the law is not applicable to the dissolution of HCl gas in water because it undergoes dissociation after dissolution:

$$HCl(g) + aq \rightarrow HCl (aq)$$
$$HCl (aq) \rightarrow H^{+} (aq) + Cl^{-} (aq)$$

**Example:** At what partial pressure, oxygen will have a solubility of 0.05 g L<sup>-1</sup> in water at 293 K? Henry's constant ( $K_H$ ) for  $O_2$  in water at 293 K is 34.86 kbar. Assume the density of the solution to be same as that of the solvent.

# Solution: Calculation of mole fraction $(x_{0_2})$

Mass of 1 L of solution = 1000 g ( $: d = 1 \text{ g mL}^{-1}$ )

 $\therefore$  Mass of solvent (water) = 1000 g - 0.05 g

$$\therefore n_{H_20} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.5 \text{ moles}$$
$$n_{O_2} = \frac{0.05 \text{ g}}{32 \text{ g mol}^{-1}} = 1.56 \times 10^{-3} \text{ moles}$$

$$\therefore \quad x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} \quad ; \quad \frac{n_{O_2}}{n_{H_2O}}$$
$$= \frac{1.56 \times 10^{-5}}{55.5} = 2.81 \times 10^{-5}$$

# Calculation of partial pressure.

Applying Henry's Law  $p_{O_2} = K_H \times x_{O_2}$ = (34.86 × 10<sup>3</sup> bar) × (2.81 × 10<sup>-5</sup>) = 0.98 bar.

- **Example:** Air contains O<sub>2</sub> and N<sub>2</sub> in the ratio of 1:4. Calculate the ratio of solubilities in terms of mole fractions of O<sub>2</sub> and N<sub>2</sub> dissolved in water at atmospheric pressure and room temperature at which Henry's constant for O<sub>2</sub> and N<sub>2</sub> are  $3.30 \times 10^7$  torr and  $6.60 \times 10^7$  torr respectively.
- Solution: At 1 bar pressure,

Partial pressure of  $O_2(p_{O_2}) = \frac{1}{5} \times 1 \text{ bar} = 0.2 \text{ bar}$ Partial pressure of  $N_2(p_{N_2}) = \frac{4}{5} \times 1 \text{ bar} = 0.8 \text{ bar}$ Applying Henry's law,  $p_{O_2} = K_H(O_2) \times x_{O_2} \text{ or } x_{O_2} = \frac{p_{O_2}}{K_H(O_2)}$  $p_{N_2} = K_H(N_2) \times x_{N_2} \text{ or } x_{N_2} = \frac{p_{N_2}}{K_H(N_2)}$ 

$$\therefore \quad \frac{x_{o_2}}{x_{N_2}} = \frac{p_{o_2}}{K_H(o_2)} \times \frac{K_H(N_2)}{P_{N_2}} = \frac{p_{o_2}}{p_{N_2}} \times \frac{K_H(N_2)}{K_H(o_2)}$$
$$= \frac{0.2 \text{ bar}}{0.8 \text{ bar}} \times \frac{6.60 \times 10^7 \text{ torr}}{3.30 \times 10^7 \text{ torr}}$$
$$= \frac{1}{2}$$
$$i.e., x_{o_2} : x_{N_2} = 1:2$$

# **3.2 Solutions of Liquids in Liquids**

These are the solutions in which the solvent and solute, both are liquids. Here, we shall confine our study only to the binary solutions.

A liquid may or may not be soluble in another liquid. Depending upon the relative solubility of a liquid in another, the following three cases are possible.

# Liquid-Liquid Systems

Liquids those are completely miscible.	Liquids those are partially miscible.	Liquids those are practically immiscible.
Examples:	Examples:	Examples:
Benzene and toluene; Ethyl	Ether and water; Phenol	Benzene and water; carbon
alcohol and water; carbon	and water; Nicotine and	tetrachloride and water;
tetrachloride and benzene.	water.	Benzene and alcohol

Miscible liquids form two types of solutions, which can be ideal or non-ideal solutions.

When two liquids are immiscible they exist as the two separate layers of liquids in solution. These are known as **conjugate solutions**. At increasing temperature both these layers become miscible.

# 3.2.1 Solubility principles for liquid-liquid solution

The extent to which a liquid will dissolve in another liquid is influenced by:

(a)Nature of solvent and solute: The basic concept of solubility based on the fact 'like dissolves like'. Polar solvents like water, NH<sub>3</sub>, liquid HF etc. dissolves polar and ionic liquid solutes, whereas non-polar solvents like C<sub>6</sub>H<sub>6</sub>, CCl<sub>4</sub>, CS<sub>2</sub>, etc. dissolves non-polar liquid solutes.

The solubility of some solutes in a solvent is also due to H-bonding, e.g., ethanol in water.

(b)**Temperature:** Many liquids are partially miscible and thus form two liquid layers at a particular temperature (conjugate solutions). The miscibility increases with temperature.

At a certain temperature the two layers become completely miscible. This temperature is called **critical temperature**.

#### 3.2.2 Vapour Pressure of Liquid Solutions

The main property of liquids to be studied here is their **vapour pressure**.

If a pure liquid or a solution is taken in an evacuated vessel placed in a thermostat at a particular temperature and the vessel is connected to a manometer, the amount of the vapour in the space above the liquid/solution keeps on increasing and ultimately becomes constant (as indicated by the pressure in the monometer). This is because equilibrium is attained, i.e., rate of evaporation becomes equal to the rate of condensation. The pressure thus exerted by the vapour pressure. Hence,

The pressure exerted by the vapours of a solvent while in equilibrium with pure solvent, at a given temperature is called **Vapour pressure** at a particular temperature. Vapour pressure of a liquid depends on:

(1) Temperature of liquids: Increase in temperature increases the kinetic energy of solvent molecules thus resulting an increase in vapour pressure. Variation in vapour pressure with temperature is given by Clapeyron-Clausius equation:

2.303 
$$\log_{10} \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[ \frac{T_2 - T_1}{T_2 T_2} \right]$$

 $P_1$  and  $P_2$  are vapour pressures at temperature  $T_1$  and  $T_2, \, \Delta H_V$  is heat of vaporization and R is gas constant.

- (2) External pressure: When external pressure is applied on a liquid, its vapour pressure decreases. Because due to external pressure more vapours are condensed into liquid state.
- (3) Nature of the liquids: Solvents with higher boiling points have higher forces of attraction among their molecules and thus have low vapour pressures.
- (4) Surface area of liquids: The number of solvent molecules that escape the liquid surface is proportional to the surface area of liquid. Due to the presence of some solute molecules on the surface, the molecules of solvent are replaced by them. Therefore, the available surface area for evaporation and so as vapour pressure decrease.

#### 3.2.3 Raoult's Law of Vapour Pressure for Volatile Solutes

For a solution of liquids as both the constituents of solution are volatile, each constituent will form vapours above the solution. At equilibrium, each constituent exert a vapour pressure, i.e., its partial vapour pressure, which is studied by F.M.Raoult in 1886.

According to this law, "The partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution."

Let a mixture (solution) be prepared by mixing  $n_A$  moles of liquid A and  $n_B$  moles of liquid B. Let  $p_A$  and  $p_B$  be the partial pressures of two constituents A and B in solution and  $p_A^0$  and  $p_B^0$  are the vapour pressures in pure state respectively.

Thus, according to Raoult's law,

$$\begin{aligned} p_A &= \frac{n_A}{n_A + n_B} \times p_A^\circ = mole \ fraction \ of \ A \times p_A^\circ = x_A p_A^0 \\ and \ p_B &= \frac{n_B}{n_A + n_B} \times p_B^0 = mole \ fraction \ of \ B \times \ p_B^0 = x_B p_B^0 \end{aligned}$$

If the total pressure be P, then P can be calculated applying **Dalton's law of partial** pressures.

$$P = p_A + p_B$$
  
=  $\frac{n_A}{n_A + n_B} \times p_A^\circ + \frac{n_B}{n_A + n_B} \times p_B^\circ$   
$$P = x_A p_A^0 + x_B p_B^0$$
  
or  $P = (1 - x_B) p_A^0 + x_B p_B^0$ 

This law, in fact, is the major deciding factor, whether a solution will be ideal or non-ideal. Ideal solutions obey Raoult's law at every range of concentration. Non-ideal solutions do not obey Raoult's law. They show either positive or negative deviation from Raoult's law.

#### The composition of the vapor phase in equilibrium:

The composition of the vapour phase in equilibrium with the solution can be calculated from the vapour pressures of the constituents (in the vapour phase). Let the mole fractions of vapours A and B is  $y_A$  and  $y_B$  respectively. Let  $p_A$  and  $p_B$  be the partial pressures of vapours A and B respectively and total pressure  $P_{total}$ .

$$p_{A} = y_{A} P_{total} \qquad ..(i)$$

$$p_{B} = y_{B} P_{total} \qquad ..(ii)$$

$$p_{A} = x_{A} p_{A}^{0} \qquad ..(iii)$$

$$p_{B} = x_{B} p_{B}^{\circ} \qquad ..(iv)$$

Equating (i) from (iii)

$$\mathbf{y}_{\mathsf{A}} \, \mathsf{P}_{\mathsf{total}} = \mathbf{x}_{\mathsf{A}} \, p_{\mathsf{A}}^{\circ}$$

or 
$$y_A = \frac{\mathbf{x}_A p_A^0}{P_{total}} = \frac{p_A}{P_{total}}$$

Similarly, equating (iii) from (iv)

$$y_B = \frac{\mathbf{X}_B \boldsymbol{p}_B^0}{\boldsymbol{P}_{total}} = \frac{\boldsymbol{p}_B}{\boldsymbol{P}_{total}}$$

Thus, in case of ideal solution the vapour phase is richer with more volatile component i.e., the one having relatively greater vapour pressure.

Note: The Raoult's law is not valid when solute shows association or dissociation in solution.

**Example:** Ethylene dibromide (C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>) and 1, 2 dibromo-propane form a series of ideal solutions over the whole range of composition. At **85**°C, the vapour pressures of these two liquids are 173 and 127 torr respectively. What would be the mole fraction of ethylene dibromide in a solution at **85**°C equilibrated with 1 : 1 molar mixture in the vapour?

**Solution:** suppose the mole fraction of ethylene dibromide in the liquid phase = x. Then mole fraction of 1, 2-dibromo propane will be = 1 - x. Vapour pressure of ethylene dibromide =  $x \times p^\circ = x \times 173 \ torr$ = 173 x torr

Vapour pressure of 1, 2-dibromo propane

 $= (1 - x) \times 127$  torr

As they have 1 : 1 molar ratio in the vapour phase,

 $173 x = (1 - x) \times 127$ 

Or 
$$x = \frac{127}{300} = 0.423.$$

# 3.2.4 Ideal and Non-ideal Solutions

As the solute and solvent molecules are brought together, energy is released because of the attractive forces between them. When solute and solvent molecules are strongly attracted by each other, more energy is released in the final step. Three cases may arise under these circumstances. The overall dissolution process results either in evolution of heat or absorption of heat, or energy released in the final step is the same as the absorbed in the first two, i.e., net change is zero. On the basis of heat of reaction evolved or absorbed the solutions are classified as **ideal or non-ideal solutions**.

#### 3.2.4.1 Ideal solutions

A solution composed of two components A and B will be an ideal one if the forces between A - A, B - B and A - B should be the same. An ideal solution possesses the following characteristics:

(i) Both the components (i.e. the volatile liquids) should form a homogenous solution.

(ii) Volume change of mixing should be zero.

 $\Delta V_{mix} = 0$ ;  $V_{solvent} + V_{solute} = V_{solution}$ 

(iii) Heat change on mixing should be zero.

 $\Delta H_{mix} = 0$  (Heat is neither absorbed nor evolved).

(iv) For these solutions,  $p_A = x_A p_A^0$  and  $p_B = x_B p_B^0$ 

If **P** is the total pressure of the system at the same temperature, then by **Dalton's law** of partial pressures,

 $P = p_A + p_B$ or  $P = x_A p_A^0 + x_B p_B^0 \qquad \dots(i)$ 

Since  $p_A^0$  and  $p_B^0$  are constant at a particular temperature, it is evident from the equation (i) that the total vapour pressure is a linear function of mole fractions  $x_A$  or  $x_B$ . Thus a straight line should be obtained, when P is plotted against  $x_A$  or  $x_B$ . The broken lines (I) and (II) give the plot of partial pressure versus composition and the solid line (III) that of the total pressure versus mole fraction.



Figure: Relationship between vapor pressure and mole fraction of an ideal solution at constant temperature

(v) There should be no chemical reaction between solvent and solute. Solvent + solute  $\rightarrow$  solution

 $H_2O + NH_3 \rightarrow NH_4OH$  (Non-ideal)

(vi) Solute molecules should not be dissociated in the ideal solution.

$$NaCl \xrightarrow{Aqueous mean main Mathematical} Na^+ + Cl^- (Non - ideal)$$

(vii) Solute molecules should not associate in ideal solution.



(viii) Ideal solutions must obey Raoult's law at all concentrations. Hence, the total vapour pressure of the solution is the sum of the partial pressures of its components.

# Examples:

- (a) Benzene and toluene.
- (b) Carbon tetrachloride and silicon tetrachloride,
- (c) n-Hexane and n-heptane,
- (d) Ethyliodide and ethylbromide
- (e) Chlorobenzene and bromobenzene

# Note:

Practically no solution is ideal. However, very dilute solutions are nearly ideal. Substances having similar structures and polarities form nearly ideal solutions.

# 3.2.4.2 Non-Ideal solutions

In the non-ideal solution, the forces between two components A and B i.e., A - B, are different as exist in pure component A i.e., A - A and B i.e., B - B.

It has the following characteristics:

- (i)  $\Delta V_{\text{mixing}} \neq 0$
- (ii)  $\Delta H_{\text{mixing}} \neq 0$ .
- (iii) For these solutions,  $p_A \neq x_A p_A^0$ ,  $p_B \neq x_B p_B^0$  and  $P \neq x_A p_A^0 + x_B p_B^0$

(iv) Non-ideal solutions do not obey Raoult's law.

# Types of Non-Ideal solutions:

# (i) Non-Ideal solutions showing positive deviation:

When a component B is added to another component A, sometimes the partial vapour pressures of each component is found to be more than expected on the basis of Raoult's law. The total vapour pressure for these solutions is greater than that corresponding to an ideal solution of the same composition. Such behavior of solutions is described as **positive deviation** from Raoult's law.

If attraction between A and B molecules is less than the attractive forces between A-A and B-B, the escaping tendency in solution is higher than in either of the pure component.



#### Figure: A vapor pressure graph showing positive deviation from ideal behaviour

The boiling points of such solutions are relatively lower as compared to those of the pure components (because higher the vapor pressure, lowering is the boiling point).

To sum up, for a non-ideal solution showing positive deviation,

$$p_A > x_A p_A^0, p_B > x_B p_B^0$$
$$P_{total} > x_A p_A^0 + x_B p_B^0$$

(i) 
$$\Delta H_{mixing} = +ve \text{ or } \Delta H_{mixing} > 0$$

(ii)  $\Delta V_{mixing} = +ve \text{ or } \Delta V_{mixing} > 0$ 

As the new bonds formed are weaker, hence energy is absorbed and there is increase in volume.

A few examples of non-ideal solutions showing positive deviation showing below:

- (a) Acetone and ethyl alcohol
- (b) Methyl alcohol and water
- (c) CCl<sub>4</sub> and CHCl<sub>3</sub>
- (d) Acetone and benzene
- (e) Acetone and carbon disulphide
- (f) Ethyl alcohol and water
- (g) CCl<sub>4</sub> and benzene
- (h) CCl<sub>4</sub> and toluene
- (ii) Non-Ideal solutions showing negative deviation: For any composition of the solution, the partial vapour pressure of each component is lesser than that corresponding to the components of an ideal solution of the same composition and the total vapour pressure of the solution will also be less than expected from Raoult's law.

In such mixtures, the attraction between molecules of A and B is greater than the force between A-A molecules or B-B hence the escaping tendencies of both the components are lowered from the pure liquids.



#### Figure: A vapor pressure graph showing negative deviation from ideal behaviour

Such solutions have relatively higher boiling points as compared to those of the pure components (because lower the vapor pressure, higher is the boiling point).

To sum up, for a non-ideal solution showing negative deviation,

$$(i) p_A < x_A p_A^0, p_B < x_B p_B^0$$

$$(ii)P_{total} < x_A p_A^0 + x_B p_B^0$$

(iii)  $\Delta H_{mixing} = -ve \text{ or } \Delta H_{mixing} < 0$ 

(iv) 
$$\Delta V_{\text{mixing}} = -ve \text{ or } \Delta V_{\text{mixing}} < 0$$

Heat is evolved due to formation of stronger bonds and hence there is a decrease in volume.

A few examples of non-ideal solutions showing negative deviation showing below:

- (a)  $CHCl_3$  and benzene
- (b) HCl and water
- (c) Acetic acid and pyridine
- (d) Acetone and aniline
- (e) HNO<sub>3</sub> and water
- (f)  $CHCl_3$  and diethyl ether

# **Comparison Between Ideal and Non-ideal Solutions**

	Non-ideal solutions			
Ideal solutions	Positive deviation from Raoult's law	Negative deviation from Raoult's law		
1)Obey Raoult's law at every range of concentration. 2) $\Delta H_{mix} = 0$ ; neither heat is evolved nor absorbed during	<ol> <li>Do not obey Raoult's law.</li> <li>ΔH<sub>mix</sub>&gt;0. Endothermic dissolution; heat is absorbed.</li> </ol>	<ol> <li>Do not obey Raoult's law.</li> <li>ΔH<sub>mix</sub>&lt;0. Exothermic dissolution; heat is</li> </ol>		
dissolution. 3) $\Delta V_{mix} = 0$ ; total volume of solution is equal to sum of volumes of the components.	3) $\Delta V_{mix} > 0$ . Volume is increased after dissolution.	evolved. 3) $\Delta V_{mix}$ <0. Volume is decreased during dissolution.		
4) $P = p_A + p_B = p_A^0 x_A + p_B^0 x_B$	4) $p_A > p_A^0 x_A; p_B > p_B^0 x_B$ $\therefore p_A + p_B > p_A^0 x_A + p_B^0 x_B$	4) $p_A < p_A^0 x_A; p_B < p_B^0 x_B$ $\therefore p_A + p_B < p_A^0 x_A + p_B^0 x_B$		
5) A—A, A—B, B—B interactions should be same, i.e., 'A' and 'B' are identical in	5) A—B attractive force should be weaker than A—A and B—B attractive forces. 'A' and 'B'	5) A—B attractive force should be greater than A— A and B—B attractive		

have different shape, size and character.	forces. 'A' and 'B' have different shape, size and character
6) 'A' and B' escape easily showing higher vapour pressure than the expected value.	6) Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.
Examples:	Examples:
acetone + ethanol	acetone + aniline;
acetone + $CS_2$ ;	acetone + chloroform;
water + methanol;	$CH_3OH + CH_3COOH;$
water + ethanol;	$H_2O + HNO_3;$
$CCl_4$ + toluene;	Chloroform + diethyl ether
$CCI_4 + CHCI_3;$	water + HCI;
	have different shape, size and character. 6) 'A' and B' escape easily showing higher vapour pressure than the expected value. <b>Examples:</b> acetone + ethanol acetone + $CS_2$ ; water + methanol; water + ethanol; CCl <sub>4</sub> + toluene; CCl <sub>4</sub> + CHCl <sub>3</sub> ;

**Example:** The vapour pressure of two pure liquids A and B that forms an ideal solution are 300 and 800 torr respectively at temperature T. A mixture of the vapours of A and B for which the mole fraction A is 0.25 is slowly compressed at temperature T. Calculate:

- (a) The composition of the first drop of condensation.
- (b) The total pressure of this drop formed.
- (c) The composition of the solution whose normal boiling point is T.
- (d) The pressure when only the last bubble of vapours remains.
- (e) Composition of the last bubble.

**Solution:** (a)  $p_A^0 = 300 \text{ torr } p_B^0 = 800 \text{ torr}$ 

$$y_A = \frac{p_A}{P} = \frac{p_A^0 x_A}{P}$$
$$y_B = \frac{p_B^0 x_B}{P}$$

Where  $y_A$  and  $y_B$  are mole fraction of A and B in the vapour phase

$$\frac{y_A}{y_B} = \frac{p_A^0 x_A}{p_B^0 x_B}$$
$$\frac{0.25}{0.75} = \frac{300 x_A}{800 x_B}$$

i.e., 
$$\frac{x_A}{x_B} = \frac{8}{9}$$

 $x_A = 8/17 = 0.47,$ 

 $x_B = 9/17 = 0.53$  i.e., composition of the first drop.

# (B) Pressure of the drop:

 $P = p_A^0 x_A + p_B^0 x_B$ = 300 × 0.47 + 800 × 0.53 = 141 + 424 =565 torr (c) At boiling point T: p = 760 760 = 300  $x_A$  + 800 (1- $x_A$ )  $x_A$  = 0.08,  $\therefore x_B$  = 0.92 (d) For last drop:  $x_A$  = 0.25,  $x_B$  = 0.75 P = 300 × 0.25 + 800 × 0.75 = 675 torr. (e)  $y_A$  =  $p_A/P$   $y_A$  = 300×0.25/675 = 0.111  $y_B$  = 0.889 Here,  $y_A$  and  $y_B$  are composition of vapour of last drop.

# 3.2.4.3 Azeotropic Mixtures or Constant Boiling Mixtures

In case of solutions showing positive deviations from Raoult's law, at one of the intermediate compositions, the total vapour pressure is the highest and the boiling point is the lowest.



Figure: Non-ideal solutions showing positive deviations from Raoult's law

In case of solutions showing negative deviations from Raoult's law, for one intermediate composition, the vapour pressure is least and boiling point is highest.



#### Figure: Non-ideal solutions showing negative deviations from Raoult's law

For liquid pairs of such intermediate compositions, the composition of the liquid and vapour phases is the same. So, if liquid mixture of such a composition vaporizes without change in composition, the liquid obtained by the condensation of the vapour also has same composition i.e. the mixture distils over as if it were a pure liquid. The composition of such a mixture is, of course, fixed.

This type of liquid mixture, having a definite composition, and boiling like a pure liquid, is called a **constant boiling mixture** or an **azeotropic mixture**.

In case of positive deviations we get **minimum boiling azeotropes** whereas in case of negative deviations we get **maximum boiling azeotropes**.

In case of minimum boiling azeotropes, the boiling point of the azeotrope is less than the boiling point of either of the pure components. For example, a mixture of ethanol (b. pt. 351.3 K) and water (b.pt 373 K) containing 95.4% of ethanol forms an azeotrope with boiling point 351.15 K. similarly, in case of maximum boiling azeotropes, the boiling point of the azeotrope is higher than that of either of the pure components, for example, a mixture of nitric acid (b.pt. 359 K) and water (b.pt. 373 K) containing 68% nitric acid forms an azeotrope with boiling point 393.5 K.

Azeotopic mixtures cannot be separated into their constituents by fractional distillation. For example, if we try to concentrate a dilute solution of alcohol, we can do so only till it becomes 95.4% because after that it becomes a constant boiling mixture (azeotrope). Other methods have to be used to get 100% ethanol.

# 3.3 Solutions of solids in liquids

In solutions of solids in liquids, the liquid is invariably referred to as a solvent and the solid dissolved in it as the solute. An unsaturated solution is one in which more solute can be dissolved at the same temperature **.A solution which remains in contact with undissolved solute is termed as saturated.** It can also be defined as **one which is in equilibrium with the excess of solid at a particular temperature.** The amount of solute dissolved in 100 g of a solvent to form a saturated solution at a given temperature is termed the solubility of the solute in the given solvent at that temperature.

When a solid is added to the solvent, the particles from the solid diffuse into it. However, some of the particles of the solute return to the solid state due to collisions. Thus, two opposite processes operate simultaneously.

# (a) Dissolution:

Particles of solute leaving the solid and dissolving in the solvent.

# (b) Recrystallisation:

Solute particles returning to the solid form.

When these two processes move with same speed, a dynamic equilibrium stage is reached.

Solute (solid)  $\Rightarrow$  Solute (dissolved)

Thus, a dynamic equilibrium exists in a saturated solution. When a saturated solution prepared at a higher temperature is cooled, it gives a solution, which contains usually more of solute than required for the saturated solution at that temperature. Such a solution is referred to as a supersaturated solution.

The following factors influence the solubility of a solute in a liquid:

- (i) Nature of solute,
- (ii) Nature of solvent,
- (iii) Temperature.

# 1. Nature of solute:

The solutes (solids) can be classified as ionic and non-ionic solids. It is the force of attraction between the ionic solids, i.e., lattice energy which opposes the tendency of a solute to dissolve. The ionic solutes having high solvation energy have more solubility. The ions are solvated by the solvent molecules and in this process energy (known as hydration energy) is released. When the hydration energy is high, the ionic solid is more soluble. Many non-ionic substances dissolve in polar solvents due to hydrogen bonding. Generally, if the solute and solvent have similar characteristics, i.e. both polar or both non-polar, the solubility is high.

#### 2. Nature of solvent:

Ionic solids dissolve to a larger extent in a solvent having a high dielectric constant as compared to solvents of low dielectric constants. Dielectric constant of water is 80 while that of methyl alcohol is 33.5.

An ionic solid, therefore, dissolves more readily in water than in methyl alcohol.

For non-ionic solids, the guiding principle is 'like dissolves like, i.e., if the solvent is polar, it will dissolve the polar solutes and if it is non-polar, it will dissolve the non-polar solutes in it.

# 3. Temperature:

The solubility of a solute in a given solvent varies appreciably with temperature. A few curves drawn between solubility in water and temperature are given in Fig.



Solubility curves.

When the solubility is plotted against temperatures, the curves obtained are called solubility curves.

On the basis of the effect of temperature on solubility in water, the various ionic substances are divided into three categories.

(a) Those whose solubility increases continuously with increase of temperature. Most of the substances like NaNO<sub>3</sub>, KNO<sub>3</sub>, NaCl, KCl, etc. fall into this category. The reason for this behaviour is that in case of all such substance, the process of dissolution is endothermic., i.e.,

Applying Le Chatlier's principle, as the temperature is increased, equilibrium will shift in a direction in which the heat is absorbed, i.e., in the forward direction; consequently, more of the solute passes into the solution.

- (b) Those whose solubility decreases continuously with increase of temperature. There are a few substances like cerium sulphate, lithium carbonate, sodium carbonate monohydrate (Na<sub>2</sub>CO<sub>3</sub>.H<sub>2</sub>O), etc. whose solubility decrease with increase of temperature. Obviously, it is due to the fact that the process of dissolution of these substances is exothermic, i.e., it is accompanied by evolution of heat.
- (c) Those substances whose solubility does not increase or decrease continuously. There are some substances which on heating change at a particular temperature from one polymorphic from to another (like  $\alpha$  to  $\beta$  –form as in the case of ammonium nitrate) or from one hydrated form to another (like CaCl<sub>2</sub>.6H<sub>2</sub>O  $\rightarrow$  CaCl<sub>2</sub>.4H<sub>2</sub>O  $\rightarrow$  CaCl<sub>2</sub>.2H<sub>2</sub>O) or from hydrated to anhydrous form (e.g., Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O  $\rightarrow$  Na<sub>2</sub>SO<sub>4</sub>). Such substances do not show a continuous increase or decrease of solubility. From example, in case of

sodium sulphate, the solubility first increases upto 32.4°C and then begins to decrease. The temperature at which one from of the substance changes into another is called transition temperature. Thus, in case of sodium sulphate,

Above 
$$32.4^{\circ}C$$
  
 $Na_2SO_4.10H_2O \qquad f \qquad Na_2SO_4$   
 $Below 32.4^{\circ}C$ 

Generally, solubility depends on heat of solution. If a substance dissolves with absorption of heat, the solubility increases with rise of temperature. On the other hand, if a substance dissolves with evolution of heat, the solubility decreases with rise of temperature.

#### 3.3.1 Raoult's Law of Vapour Pressure for Non-volatile Solutes

Quantitatively, the effect of adding a solid (non-volatile) on the lowering of vapour pressure can be derived from the general definition of Raoult's law, according to which

now, if the solute is non-volatile and non-electrolyte (e.g., glucose, urea, etc.), it will not contribute to the total vapour pressure of the solution. Thus, the vapour pressure of the solution will be the vapour pressure due to solvent in the solution only, i.e.,

combining results (i) and (ii), we have for a solution containing non-volatile solute, Vapour pressure of the solution

or 
$$p_s = x_1 p^0$$
 ...(iii)  
or  $p_s/p^0 = x_1$  ...(iv)

the above expression  $(p_s = x_1 p^0)$  implies that

$$p_s \propto x_1$$

i.e., vapour pressure of solution  $\propto$  mole fraction of the solvent in the solution.

If the solution contains  $n_2$  moles of the solute dissolved in  $n_1$  moles of the solvent, we have Mole fraction of the solvent in solution

$$x_1 = \frac{n_1}{n_1 + n_2}$$

Substituting this value in equation (iv), we get

$$\frac{p_s}{p^0} = \frac{n_1}{n_1 + n_2}$$

Substrating each side from 1,

$$\begin{aligned} 1 - \frac{p_s}{p^0} &= 1 - \frac{n_1}{n_1 + n_2} \\ or \ \frac{p^0 - p_s}{p^0} &= \ \frac{n_2}{n_1 + n_2} \quad \dots \dots (v) \end{aligned}$$

In this expression,  $p^0 - p_s$  expresses the lowering of vapour pressure,  $\frac{p^0 - p_s}{p^0}$  is called

relative lowering of vapour pressure and  $\frac{n_2}{n_1 + n_2}$  represents the mole fraction of the solute.

Hence,

The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

# 3.3.2 Colligative properties of dilute solutions

The dilute solutions show more or less ideal behaviour as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as **colligative properties**. The colligative properties are:

(i) Relative Lowering in the vapour pressure,

(ii) Elevation in the boiling point,

(iii) Depression in the freezing point, and

(iv) Osmotic pressure

All such properties of the solutions are thus linked with each other and hence are called colligative properties (co – together, ligare – to link)

The importance of these properties lies in the fact that they provide methods for the determination of molecular masses of dissolved solutes. The results are excellent if the following three conditions are satisfied.

(i) The solution should be very dilute.

(ii) The solute should be non-volatile.

(iii) The solute does not dissociate or associate in solution.

# 3.3.2.1 Relative Lowering in the Vapour Pressure

# (Raoult's Law for Non-volatile solutes):

When a non-volatile solute is added to a pure solvent, its vapour pressure is lowered due to the following reasons:

- (i) Percentage surface area occupied by the solvent decreases. Thus the rate of evaporation and vapour pressure decreases.
- (ii) According to Graham's law of evaporation,

Rate of evaporation  $\propto 1/\sqrt{\text{density}}$ 

When a non-volatile solute is dissolved in a liquid, its density increases. Thus both rate of evaporation and vapour pressure are lowered.

If  $p^0$  is the vapour pressure of pure solvent and  $p_s$  is the vapour pressure of the solution, the

difference (p<sup>0</sup> – p<sub>s</sub>) is termed lowering in vapour pressure and the ratio  $\frac{p^{\nu} - p_s}{p^0}$  is termed

relative lowering in vapour pressure.

Raoult, in 1886, established a relationship between relative lowering in vapour pressure and composition of the solution. The relationship is known as **Raoult's law**. It states that *the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution.* 

If n moles of solute be dissolved in N moles of the solvent, the mole fraction of the solute will be  $\frac{n}{n+N}$ .

According to Raoult's law,  $\frac{p^0 - p_s}{p^0} = \frac{n}{n+N}$ 

This is the mathematical expression for Raoult's law.

Modified form of Raoult's law: The above relationship can be written as,

$$\frac{p^{0}}{p^{0} - p_{s}} = \frac{n + N}{n} = 1 + \frac{N}{n}$$

$$or \frac{p^{0}}{p^{0} - p_{s}} - 1 = \frac{N}{n} or \frac{p_{s}}{p^{0} - p_{s}} = \frac{N}{n}$$

$$\frac{p^{0} - p_{s}}{p_{s}} = \frac{n}{N} = \frac{w_{A}M_{B}}{w_{B}M_{A}}$$

 $w_A$  = mass of solute (molecular mass  $M_A$ )

 $w_{B}$  = mass of the solvent (molecular mass  $M_{B}$ )

This relationship is useful in the determination of the molecular mass of dissolved solute by measuring relative lowering of vapour pressure in dilute as well as concentrated solutions.

**Example:** What mass of non-volatile solute (urea) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 5%. What will be the molality of solution?

Using Raoult's law in the following form, Solution:

$$\frac{p^0 - p_s}{p_s} = \frac{n}{N} = \frac{w_A M_B}{w_B M_A}$$

If  $p_0 = 100 \text{ mm}$ , then  $p_s = 75 \text{ mm}$ 

$$\frac{100-75}{75} = \frac{w_A \times 18}{100 \times 60}$$
  
w<sub>A</sub> = 111.1 g  
Molality (m) =  $\frac{w_A \times 1000}{w_B \times M_A} = \frac{111.1 \times 1000}{60 \times 100} = 18.52g$ 

#### Measurement of relative lowering of vapour pressure.

Pure dry air is first passed through bulbs containing solution and then through bulbs containing pure solvent and finally through tubes containing anhydrous CaCl<sub>2</sub> (if solvent used is water).



Passing dry air first through the solution and then through the solvent.

Loss in weight of solution bulbs  $(w_1) \propto vapour pressure of the solution <math>(p_s)$ 

Loss in weight of solvent bulbs  $(w_2) \propto V.P.$  of solvent – V.P. of solution.

Thus,  $p_s \propto w_1$  and  $p^0 - p_s \propto w_2$ .

This gives 
$$\frac{p^0 - p_s}{p^0} = \frac{w_2}{w_1 + w_2}$$
  
=  $\frac{Loss \ in \ weight \ of \ solvent \ bulb}{Total \ loss \ in \ weight \ of \ solution \ bulbs \ and \ solvent \ bulbs}$ 

The above method is called **Ostwald-Walker dynamic method** or transpiration method.

#### 3.3.2.2 Elevation of Boiling point (Ebullioscopy):

The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Hence, the temperature of the solution when its vapour pressure will be equal to atmospheric pressure will be higher than the temperature of the pure solvent. In other words, the boiling point of the solvent is elevated by the addition of non-volatile solute. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed elevation of boiling point.

Elevation of boiling point,

 $(\Delta T_b)$  = Boiling point of the solution  $(T_b)$  – Boiling point of pure solvent  $(T_b^0)$ 

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and a solution having a certain concentration of solute.



Figure: Elevation in boiling point

It is evident from the graph that greater the lowering in vapour pressure ( $\Delta P$ ), higher the elevation in boiling point ( $\Delta T_b$ ), i.e.,

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

From Raoult's law for dilute solution

$$\frac{p^0 - p_s}{p^0} = \frac{w_A \times M_B}{M_A \times w_B}$$

(p<sub>s</sub> = vapour pressure of solution)

$$\text{Or} \qquad p^0 - p_s = \frac{w_A \times M_B \times p^0}{M_A \times w_B}$$

For the pure solvent,  $P_0$  (its vapour pressure at the boiling point) and  $M_B$  (its molecular mass) are constant. Therefore,

$$p^{0} - p_{s} = \frac{w_{A}}{M_{A}w_{B}}$$
  
or  $\Delta p \propto \frac{w_{A}}{M_{A}w_{B}}$   
or  $\Delta T_{b} = K \cdot \frac{w_{A}}{M_{A}w_{B}}$  ...(i)

(because  $\Delta T_b \propto \Delta P$ )

where K is a constant, called as elevation constant.

When,  $w_A/M_A = 1$  (one mole of solute) and  $w_B = 1$  g, then

$$\Delta T_{b} = K$$

Thus, boiling point constant is equal to the elevation in boiling point which would be theoretically produced when 1 mole of a non-volatile solute is dissolved in 1000 g of the solvent.

If  $\frac{w_{A}}{M_{A}} = 1$  (one mole of solute) and w\_{B} = 1000 g.

 $\Delta T_{b} = K/1000 = K_{b}$ 

 $K_b$  is called **molal elevation constant**. It is defined as the elevation in boiling point produced when 1 mole of the solute is dissolved in 1000 g of the solvent.

Thus,  $K = 1000 K_b$ 

Putting this value in Eq. (i),

$$\Delta T_b = \frac{1000K_b W_A}{M_A W_B} \qquad \dots (ii)$$

or  $\Delta T_b = Molality \times K_b$ 

$$(\sin ce \frac{W_A}{M_A W_B} \times 1000 = molality).$$

The elevation in boiling point of a solution of non-electrolyte is proportional to its molality and equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points. There are known as Raoult's laws of elevation of boiling point.

If  $K_b$ ,  $w_A$ ,  $\Delta T_b$  and  $w_B$  are known, molecular mass of a non-volatile solute can be determined.

#### **Molal Elevation Constant:**

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_{b} = \frac{R(T_{b}^{0})^{2}}{1000l_{v}} = \frac{M_{A}R(T_{b}^{0})^{2}}{1000\Delta_{vap}H} \qquad \left(Q \ l_{v} = \frac{\Delta_{vap}H}{M_{A}}\right)$$

Where R is molar gas constant,  $T_b^0$  is the boiling point of the solvent on Kelvin scale,  $I_v$  the latent heat of vaporization of solvent in calories per gram,  $\Delta_{vap}H$  is the latent heat of vaporization per mole of the solvent and M<sub>A</sub> is the molecular mass of the solvent.

 $\begin{array}{l} \mathsf{R} = \mathsf{gas}\;\mathsf{constant} \\ = 8.314\;\mathsf{J}\;\mathsf{K}^{\text{-1}}\;\mathsf{mol}^{\text{-1}} \\ (\mathsf{if}\;\mathsf{I}_{\mathsf{v}}\;\mathsf{or}\;\Delta_{\mathsf{vap}}\mathsf{H}\;\mathsf{are}\;\mathsf{in}\;\mathsf{joules}) \\ = 2\;\mathsf{cal}\;\mathsf{deg}^{\text{-1}}\;\mathsf{mol}^{\text{-1}} \\ (\mathsf{if}\;\mathsf{I}_{\mathsf{v}}\;\mathsf{or}\;\Delta_{\mathsf{vap}}\mathsf{H}\;\mathsf{are}\;\mathsf{in}\;\mathsf{calories.}) \end{array}$ 

- **Example:** Calculate the molal elevation constant of water, it being given that its latent heat of vaporization is 2.257 kJ/g.
- Solution:

$$\mathbf{K}_{\mathrm{b}} = \frac{\mathbf{R}\mathbf{T}_{0}^{2}}{1000\mathbf{I}_{\mathrm{V}}}$$

$$= \frac{8.314 \text{ J K}^{-1} \text{mol}^{-1} \times (373 \text{ K})^2}{1000 \text{ g kg}^{-1} \times 2257 \text{ J g}^{-1}}$$
  
= 0.512 K kg mol^{-1}

- **Example:** Calculate the molal elevation constant of water, it being given that 0.1 molal aqueous solution of a substance boiled at 100.052°C.
- **Solution:** Here, we are given that

M = 0.1

Boiling point of solution = 100.052°C

 $\therefore \Delta T_{b} = 100.052 - 100 = 0.052$ °C

Applying the relationship,

$$\Delta I_{b} = K_{b}.m$$

We get 
$$K_b = \frac{\Delta T_b}{m} = \frac{0.052°C}{0.1 m}$$
  
= 0.52°C/m

**Example :** The boiling point of benzene is 353.23 K. when 1.80 g of a non-volatile solute dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. calculate molar mass of the solute.  $K_b$  for benzene is 2.53 kg mol<sup>-1</sup>

Solution: here, we are given

 $w_2 = 1.80g, w_1 = 90 g$   $\Delta T_b = 354.11 - 353.23 K = 0.88 K$  $K_b = 2.53 K kg mol^{-1}$ 

Substituting these values in the formula,

$$M_2 = \frac{1000K_bw_2}{w_1\Delta T_b}, \text{ we get}$$
$$= 58 \text{ g mol}^{-1}$$

# 3.3.2.3 Depression of Freezing point (Cryoscopy)

Since the addition of a non-volatile solute always lowers the vapour pressure of solvent, therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of the pure solvent and its solution is called depression of freezing point.

Depression of freezing point

 $(\Delta T_f)$  = Freezing point of the solvent  $(T_f^0)$  – Freezing point of the solution  $(T_f)$ 

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and a solution.



#### Figure: Depression in freezing point

It is evident from the graph that greater the lowering in vapour pressure ( $\Delta P$ ), higher the depression of freezing point ( $\Delta T_f$ ), i.e.,

or  $\Delta T \propto \Delta P$ From Raoult's law for dilute solutions,

$$\frac{p^{\circ} - p_s}{p^{\circ}} = \frac{w_A \times M_B}{M_A \times w_B}$$
$$p^{\circ} - p_s = \frac{w_A \times M_B \times p_0}{M_A \times w_B}$$

For the pure solvent,  $p_0$  and  $M_B$  are constant. Therefore,

$$or\Delta P = \frac{w_A}{M_A w_B}$$
  
or  $\Delta T_f = \frac{K . w_A}{M_A w_B}$  ....(i)

(because  $\Delta T_f \propto \Delta P$ )

where K is a constant, called depression constant.

When  $w_A/M_A = 1$  (or mole of solute) and  $w_B = 1$  g

$$\therefore \Delta T_f = K$$

Thus, depression constant is equal to the depression of the freezing point, which would be theoretically produced when one mole of a non-volatile solute is dissolved in 1 g of the solvent.

If  $\frac{W_A}{M_A} = 1$  and  $w_B = 1000$  g

$$\Delta T_{\rm f} = \mathrm{K}/1000 = \mathrm{K}_{\rm f}$$

K<sub>f</sub> is called molal depression constant.

It is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

Thus,  $K = 1000K_f$ 

Putting this value in Eq. (i),

$$\Delta T_{\rm f} = \frac{1000 \, K_f w_A}{M_A w_B} \qquad \dots (ii)$$

or  $\Delta T_f$  = molality × K<sub>f</sub>

If  $K_f$ ,  $w_A$ ,  $\Delta T_f$  and  $w_B$  are known, molecular mass of a non-volatile solute can be determined.  $\Delta T_f$  is measured by Beckmann's method in the laboratory.

 $K_{\rm f}$  is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_{f} = \frac{R(T_{f}^{0})^{2}}{1000l_{f}} = \frac{M_{A}R(T_{f}^{0})^{2}}{1000\Delta_{fus}H} \qquad \left(Q \ l_{f} = \frac{\Delta_{fus}H}{M_{A}}\right)$$
  
or  $K_{f} = \frac{0.0002(T_{f}^{0})^{2}}{l_{f}}$ 

where  $T_f^0$  is the freezing point of solvent in absolute scale,  $I_f$  is the latent heat of fusion in calories per gram of the solvent,  $\Delta_{fus}H$  is the latent heat of fusion in calories per mole of the solvent and  $M_A$  is the molecular mass of the solvent.

R = gas constant= 8.314 JK<sup>-1</sup> mol<sup>-1</sup> if 1<sub>f</sub> or  $\Delta_{fus}H$  are in joules = 2 cal deg<sup>-1</sup> mol<sup>-1</sup> if 1<sub>f</sub> or  $\Delta_{fus}H$  are in calories.

- **Example:** Latent heat of fusion of ice is 1436.3 cal mol-1 . Calculate the molal depression constant of water.
- Solution:

$$K_{f} = \frac{M_{1}RT_{0}^{2}}{1000 \Delta_{fus}H}$$
  
=  $\frac{18 \text{ g mol}^{-1} \times 2 \text{ cal } \text{K}^{-1} \text{ mol}^{-1} \times (273 \text{ K})^{2}}{1000 \text{ g kg}^{-1} \times 1436.3 \text{ cal mol}^{-1}}$   
= 1.87 K kg mol<sup>-1</sup>

**Example:** The molal elevation constant for water is  $0.56 \text{ K kg mol}^{-1}$ . Calculate the boiling point of a solution made by dissolving 6.0 g of urea (NH<sub>2</sub>CONH<sub>2</sub>) in 200 g of water.

Solution:

$$\Delta T_{b} = \frac{M_{A} W_{B}}{M_{A} W_{B}}$$
Given, K<sub>b</sub> = 0.56 K kg mol<sup>-1</sup>, w<sub>A</sub> = 6.0 g, w<sub>B</sub> = 200 g, M<sub>A</sub> = 60  
 $\Delta T_{b} = 1000 \times 0.56 \times 6.0/200 \times 60 = 0.28^{\circ}C$ 

Thus, The boiling point of solution  $(T_b^0)$  = b.pt. of water  $(T_b) + \Delta T_b = (100^{\circ}C + 0.28^{\circ}C) = 100.28^{\circ}C$ 

**Example:** A solution of 2.5 g of a non-volatile solid in 100 g benzene boiled at 0.42°C higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is 2.67 K kg mol<sup>-1</sup>.

**Solution:** Given,  $K_b = 2.67$ ,  $w_A = 2.5$  g,  $w_B = 100$  g,  $\Delta T_b = 0.42$ 

$$M_{A} = \frac{1000 \times K_{b} w_{A}}{\Delta T_{b} w_{B}}$$
$$M_{A} = \frac{1000 \times 2.67 \times 2.5}{0.42 \times 100} = 158.9$$

The molecular mass of substance is 158.9.

# **3.3.2.4 Osmotic pressure**

# (a) Osmosis:

It is observed that if two solutions of unequal concentrations are separated by a semi permeable membrane, the solvent molecules from a solution of lower concentration move towards a solution of higher concentration. This phenomenon was first observed by Abbe Nollet (1748) and termed as Osmosis (Greek, osmos = to push). Osmosis is defined as the spontaneous flow of solvent molecules through semi permeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

# **Difference between Osmosis and Diffusion**

The two processes, diffusion and osmosis, can be distinguished in terms of the following aspects:

(i) In diffusion, solute as well as solvent molecules flows in opposite directions while in osmosis the flow of solvent molecules occurs in one direction only.



Figure: Demonstration of osmotic pressure

(ii) For osmosis, a semi permeable membrane is required while for diffusion it is not required.

# (b) Osmotic pressure:

A porous pot is taken and a semi permeable membrane of copper Ferrocyanide is deposited in its walls. It is fitted with a long glass with the help of a rubber stopper. It is filled with concentrated aqueous sugar solution and placed in distilled water. Osmosis occurs and the level of the solution in glass tube rises over a period of time. After a few days, the level becomes stationery. At this equilibrium state the hydrostatic pressure of the liquid column exactly balances the tendency, which enables the water molecules to pass through semi permeable membrane. The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution. Osmotic pressure is also defined as the hydrostatic pressure built up on the solution, which just stops the osmosis.

Osmosis pressure = hydrostatic pressure

 $\pi = hdg$ 

where h = increase in level in the tube of unit cross section, d = density of solution and g = acceleration due to gravity.

Actually, this will not be an exact measure of osmotic pressure of the solution originally taken because sufficient dilution has taken place with time.

# (c) Reverse Osmosis

When a solution is separated from pure water by a semipermeable membrane, water moves towards solution on account of osmosis. This process continues till osmotic pressure becomes equal to hydrostatic pressure or osmosis can be stopped by applying external pressure equal to osmotic pressure on solution. If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis. This type of osmosis is termed reverse osmosis. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

# (d) Determination of osmotic pressure: Berkeley and Hartley's method

Various methods are employed for the measurement of osmotic pressure but the bestknown method was suggested by Berkeley and Hartley. The apparatus used is shown in Figure. A porous tube having copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. The porous tube is fitted with a reservoir of pure solvent at one end and a capillary tube at the other end. In a metallic jacket is an arrangement for applying external pressure, which is measured with the help of pressure gauge.



Berkeley and Hartley's apparatus

# **Procedure:**

The porous tube is filled with pure solvent and the metallic jacket with solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.

# Advantages:

- (i) It is a quick and accurate method.
- (ii) The concentration of the solution does not change because flow of solvent is not permitted into solution; so the results obtained by this method are reliable.

(iii) As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated. So, this method can be used to measure high osmotic pressure also.

# (e) Van't Hoff Theory of Dilute Solutions

Van't Hoff presumed that the osmotic pressure is due to the bombardment of solute molecules against the semi permeable membrane.

He showed that for dilute solutions of non-electrolytes the following laws hold good provided osmotic pressure of solutions is used in place of ordinary gas pressure.

# 1. Boyle-van't Hoff law:

The osmotic pressure (P or  $\pi$ ) of a solution is directly proportional to its concentration (C) when the temperature is kept constant. The concentration of the solution containing one gram mole in V litre is equal to 1/V (C = 1/V)

Thus  $P \propto C$  (when temperature is constant)

or P  $\propto$  1/V or PV = constant or  $\pi$  V = constant

# 2. Pressure-Temperature law (Charles-van't Hoff law / Gay-Lussac law):

Concentration remaining same; the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), i.e.,

 $T \propto P$ 

or P/T = constant or  $\pi$  /T = constant

# 3. Avogadro-van't Hoff Law:

Equal volume of dilute solutions of different solutes, having the same temperature and osmotic pressure contain equal number of molecules i.e., isotonic solutions at a given temperature have same molar concentration.

P ∝ n

Or P/n = constant

n = number of moles of solute

# Expression for the osmotic pressure.

Combining the three laws, i.e., when concentration and temperature both are changing and 1 mole of solute is taken, the osmotic pressure will be given by:

 $P \propto CT$ 

or P = kCT

or P = kT/V (since C = 1/V)

or PV = ST or  $\pi$  V = nST

S is called molar solution constant. Its value is found to be same as that of the 'Gas constant  $\mathsf{R}'.$ 

Here V is the volume of solution containing one gram mole of the solute (i.e.,n=1). The value of S comes out to 0.082 lit atm  $K^{-1}$  mol<sup>-1</sup> which is in agreement with the value of R, the molar gas constant. In case the solution contains n gram moles in V litres, the general equation would become

PV = nSTor  $\pi V = nST$ 

This equation is called van't Hoff equation for dilute solutions.

This led van't Hoff to suggest that a solute in dissolved state (i.e., in solution) behaves as a gas and the osmotic pressure of the solution is equal to the pressure which the solute would

exert if it were a gas at the same temperature and occupying the same volume as that of the solution. This statement is known as **van't Hoff law**.

# (f) Isotonic Solutions

Equimolar solutions of different solutes exert equal osmotic pressure under identical conditions of temperature. Such solutions, which have the same osmotic pressure, are termed **isotonic or iso-osmotic**. When two isotonic solutions are separated by a semipermeable membrane, no flow of solvent molecules is observed on either side.

For solution I, 
$$PV = n_1ST$$

For solution II,  $PV = n_2ST$ 

Thus,  $n_1$  must be equal to  $n_2$  when P, V and T are same.

Therefore, **Isotonic solutions** have the same osmotic pressure .If two solutions have different osmotic pressure the one having lower pressure is called **hypotonic solution** and the other with higher pressure is called **hypertonic solution**.

**Example:** Arginine vasopressin is a pituitary hormone. It helps to regulate the amount of water in the body by reducing the flow of urine from kidneys. An aqueous containing 21.6 mg of vasopressin in 100 mL of solution had an osmotic of 3.70 mm Hg at 25°C. What is molecular weight of hormone?

**Solution:** We know  $\pi V = nRT$  (or  $\pi V = nST$ )

$$\pi V = \frac{w_B RT}{M_B}$$
  
or  $M_B = \frac{w_B RT}{\pi V}$ .....

where  $w_B = mass$  of solute (21.6× 10<sup>-3</sup> g)

 $M_B$  = molar mass of solute

$$R = 0.0821 L atm K^{-1} mol^{-1}$$

V = 100/1000 = 0.1 L :  $\pi = 3.70/760 \text{ atm.}$ 

From (i),  $M_B = 21.6 \times 10^{-3} \times 0.0821 \times 298/(3.70/760) \times 0.1 = 1085 \text{ g/mol}$ 

#### Some of the processes regulated by osmosis in plants and animals are as under:

.(i)

- (i) Plants absorb water from the soil through their roots due to osmosis because concentration of cell sap inside root hair cells is higher than that of the water present in the soil.
- (ii) Water assimilated by the plants moves into the body of the plants and reaches even to the top of a tall tree due to osmosis.
- (iii) In animals, water moves into different parts of the body under the effect of the process of osmosis.
- (iv) Stretching of leaves, flowers etc. is also controlled by osmosis.
- (v) Osmosis helps in rapid growth of the plants and germination of seeds.
- (vii) Different movements of plants such as opening and closing of flowers etc. are ontrolled by osmosis.
- (viii) Bursting of red blood cells when placed in water is also due to osmosis.
- (ix) It is interesting to note that the salt concentration in blood plasma due to different species present in it is equivalent to 0.9% aqueous solution of NaCl (mass/volume). Hence, we may conclude the following.

(a) A 0.9% solution of pure NaCl is isotonic with human red blood cells (RBC). Therefore, in this solution, RBC neither swells nor undergoes plasmolysis.

**(b)** A pure NaCl solution with concentration less than 0.9% is called hypotonic solution. On placing RBC in this solution, they will swell and even burst.

(c) A pure NaCl solution with concentration more than 0.9% is called hypertonic solution. On placing RBC's in this solution, they shrink due to plasmolysis.

Thus, it is essential that the solutions that flow into the blood stream have the same osmotic pressure as that of the blood. A proper osmotic pressure balance inside and outside the cell of the organisms is maintained by  $Na^+$  and  $K^+$  ions.

In general, if two solutions have same osmotic pressure and hence same molar concentration, they are called isotonic. If one solution is of lower osmotic pressure, it is called hypotonic with respect to the more concentrated solution. The more concentrated solution is said to be hypertonic with respect to the dilute solution.

# **3.4 Abnormal Colligative Properties**

The colligative properties of solutions depend on the number of solute particles present in solution. Various relations derived for colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case the total number of particles of the solute changes in solution, the colligative property shall also change accordingly. The number of particles in solution may change in two ways:

# (i) By dissociation:

When the substance is an electrolyte, i.e., the substance undergoes ionization and number of particles increases in solution, the ions act as particles. The number of particles, thus, increases on ionization and the value of colligative property increases accordingly.

# (ii) By association:

When the substance undergoes association, i.e., two or more molecules of the solute associate to form single giant particle, the number of particles decreases and consequently the value of colligative property decreases.

Thus,

Normal value of colligative property  $\infty$  No. of particles of solute taken

Abnormal value of colligative property  $\propto$  No. of particles of solute after ionization or association

Thus, the ratio, abnormal colligative property/ normal colligative may have the value either more than 1 or less than 1. The ratio is termed van't Hoff factor which is represented by `i'. Thus,

$$i = \frac{p_{obs}}{p_{normal}} = \frac{(\Delta P)_{obs}}{(\Delta P)_{normal}} = \frac{(\Delta T_b)_{obs}}{(\Delta T_b)_{normal}} = \frac{(\Delta T_f)_{obs}}{(\Delta T_f)_{normal}}$$

= Actual no. of particles in solution/No. of particles taken

# 3.4.1 van't Hoff factor (i) in case of dissociation

Suppose one molecule of an electrolyte gives `n' ions on dissociation and ` $\alpha$ ' is its degree of ionization. Obviously,

$$\begin{array}{rrrr} A &\rightleftharpoons nB \\ 1mol & 0 & initially \\ (1-\alpha)mole & n\alpha & after dissociation \end{array}$$

At equilibrium, Number of ions produced =  $n\alpha$ 

and Number of unionized molecules =  $1 - \alpha$ 

Total number of particles in solution =  $1 - \alpha + n\alpha$ 

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

Thus,

van't Hoff factor 'i' =  $1 + (n-1)\alpha/1 > 1$ , if n is 2 or more and  $\alpha = \frac{i-1}{n-1}$ 

But 
$$i = \frac{Normal (calculated)molecular mass}{Observed molecular mass} = \frac{M_c}{M_0}$$
  
 $\therefore \quad \alpha = \frac{M_c - M_0}{M_0 (n-1)}$ 

From this equation, the apparent degree of dissociation ( $\alpha$ ) can be easily calculated.

# 3.4.2 van't Hoff factor (i) in case of association

Suppose 'n' molecules of the solute A associate to form one giant molecule  $A_n$  and '  $\alpha'$  is the degree of association; the

$$nA \rightleftharpoons (A)_n$$

$$1mol \qquad 0 \qquad initially$$

$$(1-\alpha) \qquad \frac{\alpha}{n} \qquad at \ equilibrium$$

At equilibrium, number of moles of A=  $(1 - \alpha)$ 

and number of moles of  $A_n = \alpha/n$ 

Total number of particles in solution =  $1 - \alpha + \alpha/n$ 

$$= 1 + (1/n - 1) \alpha$$
  
Thus, Van't Hoff factor,  $i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$ 

Whence 
$$\alpha = (1-i)\frac{n}{n-1}$$
  
Also  $i = \frac{M_c}{M_o}$   
 $\therefore \quad 1 - \alpha + \frac{\alpha}{n} = \frac{M_c}{M_o} \text{ or } 1 - \frac{M_c}{M_o} = \alpha - \frac{\alpha}{n}$   
 $or \frac{M_o - M_c}{M_o} = \alpha \left(1 - \frac{1}{n}\right) = \alpha \left(\frac{n-1}{n}\right)$   
 $\alpha = \frac{M_o - M_c}{M_o} \cdot \frac{n}{(n-1)}$ 

From this equation, the apparent degree of association ( $\alpha$ ) can be calculated.

# van't Hoff factor for different solutes undergoing ionization and dissociation

Solute ty	vpe Example	Ionisation or association	No. of particles in the solution from1 mole solute	van't Hoff factor `i'	Abnormal molecular mass
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1.	Non electrolyte	Urea, sucrose, glucose	-	1	1	M <sub>normal</sub>
2.	Binary electrolyte AB type	NaCl, KCl, CH <sub>3</sub> COOH, etc.	$\begin{array}{c} AB \to A^{+} + B^{-} \\ 1 - \alpha  \alpha  \alpha \end{array}$	2	1+α	$M_{normal}/1+lpha$
3.	Ternary electrolyte AB <sub>2</sub>	$CaCl_2, BaCl_2 H_2SO_4,$	$\begin{array}{ccc} AB_2 \rightarrow & A^{2+}+2B^{-}\\ 1-\alpha & \alpha & 2\alpha \end{array}$	3	$1+2\alpha$ $1+2\alpha$	$M_{normal}/1+2lpha$ $M_{normal}/1+2lpha$
	type or A <sub>2</sub> B type	K <sub>2</sub> [PtCl <sub>6</sub> ]	$\begin{array}{ccc} A_2B \rightarrow & 2A^+ + 2B^- \\ 1 - \alpha & 2\alpha & \alpha \end{array}$	3	1+3α 1+3α	$M_{normal}/1+3lpha$ $M_{normal}/1+3lpha$
4.	Quaternary electrolyte AB <sub>3</sub>	AICI <sub>3</sub> , K <sub>3</sub> [Fe(CN <sub>3</sub> )] FeCla KaPO	$\begin{array}{c} AB_{3} \rightarrow A^{3+} + 3B^{-} \\ 1 - \alpha  \alpha  3\alpha \end{array}$	4	[1-(1-1/n) α]	M <sub>normal</sub> /[1-(1- 1/n) α]
		1 (13, 13) (4	$\begin{array}{c} A_3B \to 3A^+ + B^{3-} \\ 1 - \alpha  \alpha  2\alpha \end{array}$	4	[1+(n-1) α]	M <sub>normal</sub> /[1+(n- 1) α]
5.	Association of solute	Benzoic acid forming dimer in benzene	$\begin{array}{ccc} nA \rightarrow & A_n \\ 1-\alpha & \alpha/n \end{array}$	1/n	$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$	-

#### Determination of Molecular mass from Osmotic pressure Measurements.

According to van't Hoff equation for dilute solution,

 $\pi V = nRT \qquad \dots (i)$ 

Where  $\pi$  is the osmotic pressure at temperature T for a solution containing n moles of the solute dissolved in V litres of the solution, R is a constant (sometimes called 'solution constant').

If  $w_2$  grams of the solute are dissolved in V litres of the solution and  $\mathsf{M}_2$  is the molecules mass

of the solute, then  $n = \frac{w_2}{M_2}$ 

Substituting this value in equation (i), we get

Thus, measuring the osmotic pressure  $\pi$  of a solution containing w<sub>2</sub> grams of the solute in V litres of the solution, at temperature T, the molecular mass, M<sub>2</sub>, of the solute can be calculated using equation.

For the determination of molecular masses of proteins, polymers and other macromolecules, it is considered to be one of the most suitable methods. For such substances, the other

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methods based upon colligative properties (elevation in boiling point, depression in freezing point, etc.) cannot be used because of the following reasons:

- (i) The changes observed in these properties are very small. (e.g., 0.00001 K for substances having molar masses of the order of 10<sup>6</sup>g mol<sup>-1</sup>). On the other hand, osmotic pressures of the order of 10<sup>-3</sup> atm can be easily measured in terms of mm.
- (ii) Elevation in boiling point method for biomolecules such as proteins is not suitable because these molecules are not stable at higher temperatures whereas the advantage of the osmotic pressure is that it can be measured at room temperature.
- (iii) The osmotic pressure method has the advantage that it used molarities instead of molalities.
- **Example:** 2.0 g of benzoic acid dissolved in 25.0 g of benzene shows a depression in point equal to 1.62 K. Molal depression constant ( $K_f$ ) of benzene is 4.9 K kg mol<sup>-1</sup>. What is the percentage association of the acid ?
- Solution: Given,

Mass of solute  $(w_2) = 2.0 \text{ g}$  (for benzoic acid)

Mass of solvent  $(w_1) = 25.0 \text{ g}$  (for benzene)

Observed  $\Delta T_f = 1.62 \text{ K}$ 

 $K_{f} = 4.9 \text{ K kg mol}^{-1}$ 

. Observed molecular mass of benzoic acid

$$(m_2) = \frac{1000 \times K_f \times w_2}{\Delta T_f \times w_1} \\ = \frac{1000 \times 4.9 \times 2.0}{1.62 \times 25.0} = 242$$

Calculated molecular mass of benzoic acid

 $(C_6H_5COOH) = 72 + 5 + 12 + 32 + 1 = 122$ 

vant's Hoff factor,  $i = \frac{Calculate \ mol. \ mass}{Observea \ mol. \ mass}$ 

$$=\frac{122}{242}=0.504$$

If  $\alpha'$  is the degree of association of benzoic acid, then we have

$$\begin{array}{rcl} 2C_6H_5COOH \eqref{eq:H_5COOH_2} \\ Initial moles & 1 & 0 \\ after association & 1-\alpha & \frac{\alpha}{2} \end{array}$$

. Total number of moles after association

$$= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$
  
$$\therefore \qquad i = \frac{1 - \frac{\alpha}{2}}{1} = 0.504$$
  
or, 
$$1 - \frac{\alpha}{2} = 0.504$$

- $\therefore \quad \alpha = (1 0.504) \times 2 = 0.992$
- or, % of association = 99.2%
- **Example:** calculate the boiling point of a one-molar aqueous solution (density 1.04 g L<sup>-1</sup>) of potassium chloride ( $K_b$  for water = 0.52 K kg mol<sup>-1</sup>. Atomic masses: K = 39, Cl = 35.5)

# Solution: Given,

Concentration of solution = 1 MDensity of solution =  $1.04 \text{ g L}^{-1}$ Let us first calculate the molality of the solution Amount of solute (KCl) =  $1 \mod = 74.5 \text{ g}$ Volume of the solution = 1 L = 1000 mLMass of the solution =  $1000 \times 1.04 = 1040$  g ∴ mass of solvent = 1040 - 74.5 = 965.5 g 965.5 g of the solvent contain solute = 1 mol  $\therefore$  1000 g of the solvent contain solute  $=\frac{1}{965.6} \times 1000 \text{ mol} = 1.0357 \text{ mol},$ i.e., molality of the solution = 1.0357 m KCI dissociates as:  $KCI \rightarrow K^+ + CI^-$ Number of particles after dissociation = 2 .: van't Hoff-factor, i = 2 Now,  $\Delta T_b = i \times K_b \times m$ = 2 × 0.52 × 1.0357 = 1.078°C : Boiling point of the solution = 100 + 1.078

= 101.078° C