

# Theory of Solutions

## BASICS

## Section - 1

A *solution* is defined as homogenous mixture of two or more substances (*called as components*), the relative proportion or composition of which may vary between certain limits.

The component in small quantity is called as *solute* and the component in excess is called as *solvent*. A solution consisting of two components is known as *binary solution* and of three components is known as *ternary solution*.

The solutions may be *gaseous, liquids and solids*. The most common type of solution is liquid solution (*gas in liquid, liquid in liquid, solid in liquid*). In all, we can divide solutions into nine different classes as follows :

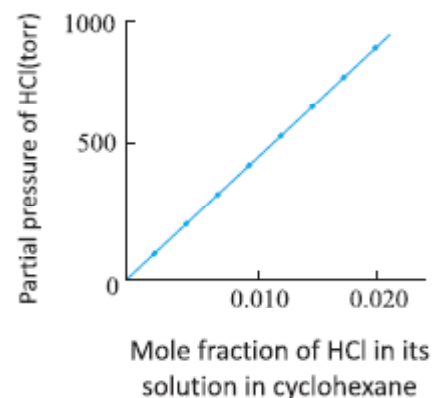
| Types of Solutions | Solute in Solvent | Examples  |
|--------------------|-------------------|---|
| Gaseous Solutions  | Gas in Gas        | air, mixture of all gases   |
|                    | Liquid in Gas     | water in air, bromine in chlorine, acetic acid in nitrogen                    |
|                    | Solid in Gas      | Naphthalene in methane, iodine in air, camphor in air                         |
| Liquid Solutions   | Gas in Liquid     | CO <sub>2</sub> in water, HCl in benzene                                      |
|                    | Liquid in Liquid  | Alcohols in water, bromine in CS <sub>2</sub> or in CCl <sub>4</sub>          |
|                    | Solid in Liquid   | Sugar in water, iodine in CCl <sub>4</sub> , lead in mercury, NaCl in water   |
| Solid Solutions    | Gas in Solid      | Hydrogen in palladium   |
|                    | Liquid in Solid   | Mercury in Thallium   |
|                    | Solid in Solid    | Co in Ni, gold in silver, PbCl <sub>2</sub> in PbBr <sub>2</sub> , all alloys |

**Note :** In general, the physical state of a solution is the physical state of solvent.

There are various ways in which one can express the concentration of a solution. We have already learnt about these in [Stoichiometry - 1](#). These are Strength (g/L), Molarity (mol/L), Normality (gm-eq/L), mole fraction, mass fraction and molality (mol/kg).

## 1. Solubility of Gases

The solubility of a gas in a liquid is determined by several factors. In addition to the nature of the gas and the liquid, solubility of the gas depends on the temperature and pressure of the system. The solubility of a gas in a liquid is governed by *Henry's Law* which states that the *solubility of a gas in a liquid is directly proportional to the pressure of the gas*. Dalton, a contemporary of the Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of the mole fraction of the gas in the solution as a measure of its solubility, then :



*Mole fraction of the gas in a solution is proportional to the partial pressure of the gas above the solution.*

$$P = K_H \chi \quad \text{where } K_H \text{ is Henry's law constant and } \chi \text{ is the mole fraction of the gas in the solution.}$$

It is obvious that the higher the value of  $K_H$  at a given pressure, the lower is the solubility of the gas in the liquid. The  $K_H$  value for both  $N_2$  and  $O_2$  increases with increase of temperature indicating that solubility of gases decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than warm waters. Dissolution of gas in liquid is accompanied by release of heat i.e. the dissolution of gas is exothermic reaction.

### Illustrating the concept :

The Henry's law constant for the solubility of  $N_2$  gas in water at 298 K is  $1.0 \times 10^5 \text{ atm}$ . The mole fraction of  $N_2$  in air is 0.8. The number of moles of  $N_2$  from air dissolved in 10 moles of water at 298 K and 5 atm pressure is :

- (A)  $4.0 \times 10^{-4}$       (B)  $4.0 \times 10^{-5}$       (C)  $5.0 \times 10^{-4}$       (D)  $4.0 \times 10^{-6}$

### SOLUTION : (A)

As per Henry's law :

$$p_{N_2} = K_H (\chi_{N_2})_{\text{in solution}}$$

$$\Rightarrow (\chi_{N_2})_{\text{in solution}} = 4 \times 10^{-5} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}} \approx \frac{n_{N_2}}{n_{H_2O}}$$

$$\text{Now, } p_{N_2} = p_{\text{Total}} \times (\chi_{N_2})_{\text{in air}} = 5 \times 0.8 = 4 \text{ atm}$$

$$\Rightarrow (\chi_{N_2})_{\text{in solution}} = 4 \times 10^{-5} \times n_{H_2O} = 4 \times 10^{-4}$$

$$\Rightarrow 4 = 10^5 \times (\chi_{N_2})_{\text{in solution}}$$

## 2 Vapour Pressure of a Solution

Consider a pure liquid in a container covered with a lid. The molecules of liquids at the surface escape (vapourisation) and fill the space available to them. After sometime, equilibrium is established between the vapour and the liquid phases. The pressure exerted by the vapours in such a state (vapour  $\rightleftharpoons$  liquid) of equilibrium is known as *vapour pressure* of a liquid.

Now if some solute (B) is added to such a solvent (A) to make a solution, two possibilities arises:

- (i) If the solute is volatile (solid or liquid)                      (ii) If the solute is non-volatile (solid or liquid).

- (i) **When solute is volatile** : The surface molecules of both solute and solvent escape (vapourise) and fill the vacant space. The vapour phase now consists of vapours of solute (B) and vapours of solvent (A). At vapour liquid equilibrium, the pressure exerted by the vapours of solute and solvent is known as *vapour pressure* of the solution.

### Raoult's Law

The partial vapour pressure of a component in such type of solution is given by **Raoult's Law**. It states that the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

Let  $\chi_A$  and  $\chi_B$  be the mole fractions of solvent (A) and solute (B) molecules in the solution and  $P_A$  and  $P_B$  be the partial vapour pressures of A and B respectively. Then according to Raoult's Law :

$$P_A \propto \chi_A \quad \text{and} \quad P_B \propto \chi_B$$

From the results of various experiments, it has been observed that :

$$P_A = P_A^0 \chi_A \quad \text{and} \quad P_B = P_B^0 \chi_B \quad \text{where } P_A^0 \text{ and } P_B^0 \text{ are vapour pressures of pure A and B.}$$

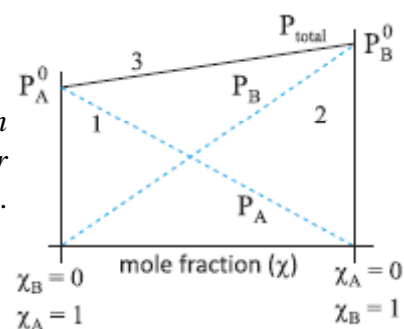
Now the total vapour pressure ( $P_{\text{Total}}$ ) of the solution is given by Dalton's Law of partial pressures as follows :

$$P_{\text{Total}} = P_A + P_B \quad \Rightarrow \quad P_{\text{Total}} = P_A^0 \chi_A + P_B^0 \chi_B$$

For a solution of different compositions made from A and B, the plot of  $P_A$ ,  $P_B$  against  $\chi_A$  and  $\chi_B$  is shown as follows :

In the graph :

Two dotted lines 1 and 2 show variations in partial pressure with increasing mole fraction and the solid line 3 gives the total vapour pressure  $P_{\text{Total}}$  exerted by the solution as a whole at any composition.



**Note :**  $\chi_{A(\text{Liquid phase})} = \frac{P_A}{P_A^0}$ ,  $\chi_{A(\text{Vapour phase})}^V = \frac{P_A}{P_A + P_B}$

**Note:** The solutions which obey Raoult's Law at all compositions of solute in solvent are called as *Ideal Solutions*. The plot of partial pressure (P) vs mole fraction ( $\chi$ ) of such solution is typical and in general like the graph shown here.

**Illustration - 1**

At a certain temperature, the vapour pressure of pure ether is 646 mm and that of pure acetone is 283 mm. Calculate the mole fraction of each component in the vapour state if the mole fraction of ether in the solution is 0.50.

**SOLUTION :**

In the given solution, both ether and acetone are volatile, so from Raoult's Law, we can have vapour pressure of solution ( $P_{\text{Total}}$ ).

Let A : ether and B : acetone.

$$P_{\text{Total}} = P_A + P_B = P_A^0 \chi_A + P_B^0 \chi_B$$

$$\Rightarrow P_{\text{Total}} = 646 \times 0.5 + 283 \times 0.5$$

$$= 464.5 \text{ mm}$$

Now mole fraction in vapour state is given as follows :

$$\chi_{A(\text{vapour})}^V = \frac{P_A}{P_{\text{Total}}} = \frac{P_A^0 \chi_A}{P_{\text{Total}}}$$

$$= \frac{646 \times 0.5}{464.5} = 0.695$$

$$\chi_{B(\text{vapour})}^V = \frac{P_B}{P_{\text{Total}}} = \frac{P_B^0 \chi_B}{P_{\text{Total}}}$$

$$= \frac{283 \times 0.5}{464.5} = 0.305$$

- (ii) **When solute is non-volatile :** In such a solution, the surface molecules of only solvent will escape and contribute to the vapour phase i.e. there is no contribution from solute in the vapour phase. The vapour pressure of such a solution is equal to the partial vapour pressure of solvent molecules ( $= P_A$ ).

$$P_{\text{Total}} = P_A^0 \chi_A + P_B = P_A^0 \chi_A \quad (\because P_B = 0).$$

$$\text{For binary solution : } \chi_A + \chi_B = 1 \Rightarrow \chi_A = 1 - \chi_B$$

$$\Rightarrow \frac{P_A^0 - P_A}{P_A^0} = \chi_B$$

The expression  $\frac{P_A^0 - P_A}{P_A^0}$  is called as *Relative Lowering of Vapour Pressure for a solution usually expressed as  $\frac{\Delta p}{p^0}$* .

Another form of Raoult's Law can now be stated as :

*Relative Lowering of vapour pressure for a solution containing non-volatile solute is equal to the mole fraction of the solute.*

### Illustrating the concept :

4.375 g of a substance when dissolved in 36.0 g of water, lowered its vapour pressure by 0.5 mm at a given temperature. The vapour pressure of water at this temperature is 25.0 mm. Calculate the molecular weight of solute.

### SOLUTION :

$\Delta P = 0.5$  mm, using the formula for lowering of vapour pressure :

$$\frac{\Delta P}{P_A^0} = \chi_B = \frac{n_B}{n_A + n_B} = \frac{g_B / M_B}{g_A / M_A + g_B / M_B}$$

$$\Rightarrow \frac{0.5}{25} = \frac{4.375 / M_B}{36 / 18 + 4.375 / M_B} \quad \Rightarrow \quad M_B = 109.38 \text{ gm/mol}$$

**Illustration - 2** Assuming ideal behaviour, calculate the vapour pressure of 1.0 molal solution of a non-volatile molecular solute in water at 50°C is 0.122 atm.

### SOLUTION :

$$P_{\text{solution}} = P_A = P_A^0 \chi_A \quad (\text{Raoult's Law})$$

By using the relation between molality and mole fraction, we have :

$$m = \frac{\chi_B}{\chi_A} \times \frac{1000}{M_A} = \frac{1 - \chi_A}{\chi_A} \times \frac{1000}{M_A}$$

$$\Rightarrow \chi_A = \frac{1000}{mM_A + 1000}$$

$$\Rightarrow \chi_A = \frac{1000}{1 \times 18 + 1000} = \frac{1000}{1018} = 0.982$$

$$\Rightarrow P_{\text{solution}} = P_A^0 \chi_A = 0.122 \times 0.982 = 0.120 \text{ atm}$$

**Illustration - 3** The vapour pressure of pure water 25°C is 23.76 torr. What is the vapour pressure of 100 gm of water to which 100 gm of  $C_6H_{12}O_6$  (glucose) has been added ?

### SOLUTION :

$$P_{\text{solution}} = P_A = P_A^0 \chi_A$$

$$\Rightarrow P_{\text{solution}} = P_A^0 \frac{n_A}{n_A + n_B} = P_A^0 \frac{\frac{g_A}{M_A}}{\frac{g_A}{M_A} + \frac{g_B}{M_B}}$$

$$\Rightarrow P_{\text{solution}} = 23.76 \times \frac{\frac{100}{18}}{\frac{100}{18} + \frac{100}{180}}$$

$$\left[ M_{\text{Glucose}} = 180 \text{ gm/mol}; P_A^0 = 23.76 \text{ torr} \right]$$

$$\Rightarrow P_{\text{solution}} = 21.6 \text{ torr}$$

**Illustration - 4** At 298 K, the vapour pressure of pure liquied n-butane is 1823 torr and vapour pressure of pure liquid n-pentane is 521 torr and form nearly and ideal solution.

- (a) Find the total vapour pressure at 298 K of a liquid sution containing 10% n-butane and 90% n-pentane by weight.
- (b) Find the mole fraction of n-butane in solution exerting a total vapour pressure of 760 torr.
- (c) What is the composition of vaporus of two components (mole fraction in vapour state) ?

**SOLUTION :**

$$(a) \quad \chi_{n-butane} = \frac{10/58}{10/58 + 90/72} = 0.122$$

$$\chi_{n-pentane} = 1 - 0.122 = 0.878$$

From Raoult's Law :

$$P_{Total} = P_A^0 \chi_A + P_B^0 \chi_B$$

$$P_{Total} = 0.122 \times 1823 + 0.878 \times 521$$

$$\Rightarrow P_{Total} = 679.84 \text{ torr}$$

$$(b) \quad \text{Let mole fraction of n-butane} = y$$

$$\Rightarrow \text{mole fraction of n-pentane} = 1 - y$$

Using Raoult's Law, we have:

$$760 = y(1823) + (1 - y) 521$$

$$\Rightarrow y = 0.183$$

$$(c) \quad \text{The mole fraction in vapour state :}$$

$$\chi_{n-butane}^v = \frac{0.122 \times 1823}{679.84} = 0.327$$

$$\chi_{n-pentane}^v = \frac{0.278 \times 521}{679.84} = 0.673$$

$\chi_{vapour}^v$  is als called as vapour fraction

### 3. Formation of Ideal Solutions :

When solute B is added to a solvent A, **an ideal solution** is formed if molecular interactions A-A and B-B are same and there is no change in the type of molecular interaction when A and B are mixed to form a solution. This means that in solution, A-B interactions are almost same as A-A and B-B interactions.

It has been observed that liquid pairs which are generally similar in size and structure form ideal solutions. For example, *bromo-ethane* and *chloro-ethane*, *n-hexane* and *n-heptane*, *benzene* and *toluene*,  $CCl_4$  and  $SiCl_4$  form nearly an ideal solution.

### Criteria for formation of Ideal Solutions :

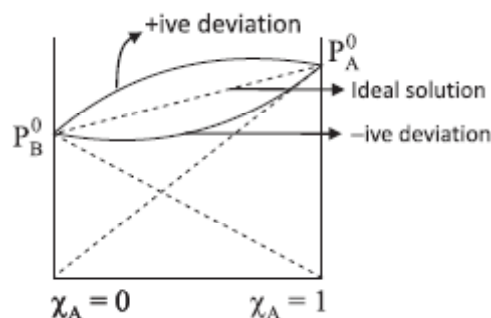
- They must obey Raoult's Law at all concentrations and at all temperatures.
- The heat of solution should be equal to zero, i.e.,  $\Delta H_{\text{solution}} = 0$ .
- There should be no change in the volume of solution on mixing, i.e., neither there is any contraction nor there is any expansion or  $\Delta V_{\text{solution}} = 0$ .

Like gases, most of the solutions deviate from ideal behaviour and are called as *Non ideal solution or Real Solutions*.

Real solutions do not obey Raoult's Law over entire range of composition. *It is observed that by progressive dilution, all solutions tend to reach a state where they behave ideally.*

### 4. Formation of Non-ideal Solutions :

- Solutions which show higher experimental values of pressure ( $P_{\text{Total}}$ ) than those calculated from Raoult's law are said to show **positive deviation** from Raoult's law e.g. solution of cyclohexane and ethonal.
- Solutions which shown lower experimental values of pressure ( $P_{\text{Total}}$ ) than those calculated from Raoult's law are said to show **negative deviation** from Raoult's law e.g. solution of chloroform and acetone.



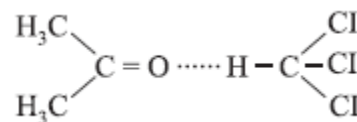
**Note :** The cause for these deviations lies in the nature of interactions at the molecular level. On mixing two dissimilar substances, their molecular environment will change.

Suppose the two components that are mixed to form a non-ideal solution are A and B.

A **positive deviation** is exhibited when interaction between A–B is weaker than that between A–A and B–B. This means that on mixing, molecules of A (or of B) will find it easier to escape than if these were as pure components. This will cause an increase in the vapour pressure resulting in a positive deviation. Molecules of ethanol and acetone are hydrogen bonded. On adding acetone to pure ethanol, these molecules get in between the host molecules (ethanol) breaking the hydrogen bonds of host molecules. This changes the intermolecular interaction pattern and becomes the cause for ethanol and acetone solution to behave non-ideally and show a positive deviation from Raoult's law.

A mixture of chloroform and acetone forms a solution with **negative deviation** from Raoult's law. This is because chloroform molecules are able to form hydrogen bond with acetone molecules as shown below :

This decreases the escaping tendency of molecules for each component and consequently, the vapour pressure decreases resulting in negative deviation from Raoult's law.



- Note :** ➤ Solutions showing positive deviations boil at relatively low temperature than calculated value as well as have  $\Delta V_{\text{mixing}} = +\text{ive}$  and  $\Delta H_{\text{mixing}} = +\text{ive}$ . On the other hand, solutions showing negative deviations boil at relatively high temperature than calculated value as well as have  $\Delta V_{\text{mixing}} = -\text{ive}$  and  $\Delta H_{\text{mixing}} = -\text{ive}$ .  
 +ive : positive ; -ive : negative.
- Raoult's law is also not valid when solute shows dissociation or association nature in given solvent.

### Some examples of Ideal solutions are :

|       |                                  |      |                                    |
|-------|----------------------------------|------|------------------------------------|
| (i)   | n-Hexane and n-heptane           | (ii) | Chlorobenzene and Bromo benzene    |
| (iii) | Ethyl Bromide and Ethyl Chloride | (iv) | $\text{CCl}_4$ and $\text{SiCl}_4$ |
| (v)   | Ethyl Bromide and Ethyl Iodide   | (vi) | Benzene and Toluene                |

### Example of solutions showing positive deviation :

|       |                                    |        |  |
|-------|------------------------------------|--------|--|
| (i)   | Benzene and Ethyl alcohol          | (ii)   | $\text{CS}_2$ and acetone                            |
| (iii) | Chloroform and ethanol             | (iv)   | n-hexane and ethanol                                 |
| (v)   | Benzene and acetone                | (vi)   | $\text{CCl}_4$ and benzene                           |
| (vii) | $\text{CCl}_4$ and $\text{CHCl}_3$ | (viii) | $\text{CCl}_4$ and $\text{C}_6\text{H}_5\text{CH}_3$ |
| (ix)  | $\text{H}_2\text{O}$ and Methanol  | (x)    | $\text{H}_2\text{O}$ and Ethanol                     |

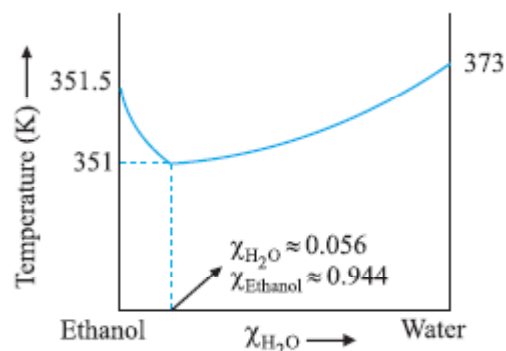
### Solutions showing negative deviation :

|       |   |      |                          |
|-------|---|------|--------------------------|
| (i)   | Chloroform and Acetone                  | (ii) | Chloroform and Benzene   |
| (iii) | Chloroform and Diethyl ether            | (iv) | Acetic acid and Pyridine |
| (v)   | $\text{H}_2\text{O}$ and $\text{HCl}$   | (vi) | Acetone and Aniline      |
| (vii) | $\text{H}_2\text{O}$ and $\text{HNO}_3$ |      |                          |



## 5. Azeotropes

Some liquids on mixing form azeotropes which are binary mixtures having same composition in liquid and vapour phase and boil at a constant temperature. There are two types of azeotropes called as *minimum boiling azeotrope* and *maximum boiling azeotrope*, respectively. Solutions of ethanol and water show such a large deviation from Raoult's law that there is a maximum in the vapour pressure curve and hence a minimum in the boiling point diagram as shown in figure (→)



There are also solutions that show large negative deviation from ideality and, therefore, have a minimum in their vapour pressure curves. This leads to a maximum on the boiling point diagram.  $HNO_3$  (68%) and  $H_2O$  (32%) form examples of this class of the azeotrope.

**Note :** Components in a Azeotrope cannot be separated by distillation as they have same composition in liquid and vapour phase, because when azeotrope is boiled, the resulting vapour has same ratio of constituents as original mixture. Also called as constant boiling mixture.

## 6. Vapour pressure of mixture of two immiscible volatile liquid :

When a volatile liquid is added to another volatile liquid, which are completely immiscible with each other, each liquid will behave independent to the other and will exert its own vapour pressure. The more dense liquid (A) will form lower layer and less dense liquid (B) will be forming upper layer. The total vapour pressure of the system will be the sum of vapour pressure of both the volatile liquids.

$$\therefore P_{\text{Total}} = P_A + P_B = P_A^\circ + P_B^\circ$$

The total vapour pressure of the system remain constant as long as both the volatile liquids are present and will not depend on the relative amounts of the two liquids.

The boiling point of a liquid system is the temperature at which its vapour pressure becomes equal to the external atmospheric pressure. Since the total vapour pressure of a mixture containing immiscible volatile liquids is greater than that of either of the pure constituents, thus the mixture will boil at a temperature, which is lower than the boiling point of either of the pure constituents. The boiling point of the liquid mixture will remain constant as long as the two layers are present, as the total vapour pressure is independent of the relative amounts of the two constituents.

**Note :** This forms the basis of steam distillation, in which one of the volatile liquids is water.

This composition of the vapour above the liquid mixture can be calculated using Dalton's law of partial pressures. Thus,

$$P_A = P_A^\circ \chi_A' = P_{\text{Total}} \chi_A' \quad \dots (i) \quad \text{and}$$

$$P_B = P_B^\circ \chi_B' = P_{\text{Total}} \chi_B' \quad \dots (ii)$$

Where  $\chi'_A$  and  $\chi'_B$  represents the mole fraction of A and B in the vapour phase. Let  $n_A$  and  $n_B$  are the mole of A and B, respectively in the vapour phase.

Dividing equation in the (ii) by (i),

$$\frac{P_{\text{Total}} \chi'_B}{P_{\text{Total}} \chi'_A} = \frac{P_B^\circ}{P_A^\circ} = \frac{\chi'_B}{\chi'_A} = \frac{\frac{n_B}{n_A + n_B}}{\frac{n_A}{n_A + n_B}} = \frac{n_B}{n_A} \quad \text{or} \quad \frac{P_B^\circ}{P_A^\circ} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$\therefore \frac{W_B}{W_A} = \frac{P_B^\circ \times M_B}{P_A^\circ \times M_A}$$

Thus, the masses of the constituents in the vapour (distillate) will be proportional to their respective molar mass and vapour pressure.

**NOW ATTEMPT IN-CHAPTER EXERCISE-A BEFORE PROCEEDING AHEAD IN THIS EBOOK**

## COLLIGATIVE PROPERTIES OF SOLUTIONS

## Section - 2

As we dilute a solution, its behaviour moves towards ideality. The properties of dilute solutions depend solely on the number of particles of the solute dissolved in the solvent and have nothing to do with the chemical behaviour of the solute. These properties in fact depend upon the nature of solvent. In our discussion, we will take solute to be non-volatile and non-associating or dissociating and solvent to be volatile.

The colligative properties that we are going to study are :

- |   |                               |
|---|-------------------------------|
| 1. Relative Lowering of Vapour Pressure | 2. Elevation in Boiling Point |
| 3. Depression in Freezing Point         | 4. Osmotic Pressure           |

**Note :** Colligative properties are the properties of only *dilute solutions* because they are supposed to behave as *ideal solutions*.

### 1. Relative Lowering of Vapour Pressure :

When a non-volatile solute (B) is dissolved in a liquid, the vapour pressure ( $P_{\text{Total}}$ ) of the solution becomes lower than the vapour pressure of pure solvent.

From Raoult's Law : Vapour pressure of the solution is given by :

$$P_{\text{Total}} = P_A \quad (P_A = \text{partial vapour pressure of the solvent in solution}) \quad [P_B = 0]$$

$$\Rightarrow P_{\text{Total}} = P_A = P_A^0 \chi_A$$

where  $P_A^0$  = vapour pressure of pure A and  $\chi_A$  = mole fraction of A.

For Binary Solution :  $\chi_A + \chi_B = 1 \Rightarrow \chi_A = 1 - \chi_B$

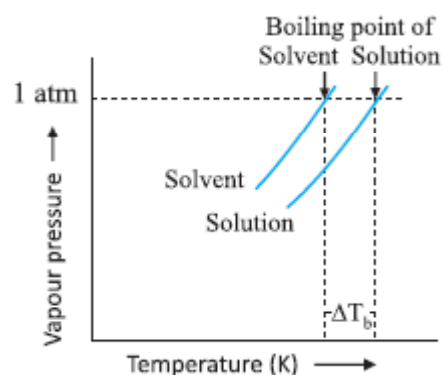
$$\Rightarrow P = P_A = P_A^0 (1 - \chi_B) \Rightarrow \frac{P_A^0 - P_A}{P_A^0} = \chi_B$$

$$\text{Relative Lowering of Vapour Pressure} = \frac{P_A^0 - P_A}{P_A^0} = \chi_B \quad \text{or} \quad \frac{\Delta P}{P_A^0} = \chi_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A}$$

For dil. solution:  $n_A + n_B = n_A$

## 2. Elevation in Boiling Point :

The vapour pressure of a solution is lower than that of pure solvent (on adding non-volatile solute). Now, the boiling point (BP) of a liquid is the temperature at which its vapour pressure becomes equal to 760 mm of Hg column (atmospheric pressure). Hence, the BP of a solution will always be higher than that of the pure solvent.



Let  $\Delta T_b$  be the elevation in boiling point, then

$$T_b = T_b^0 + \Delta T_b \quad T_b : \text{boiling point of solution} ; T_b^0 : \text{boiling point of pure solvent}$$

$K_b$  : molar boiling point elevation constant or ebullioscopic constant of solvent

$m$  : molality of the solution

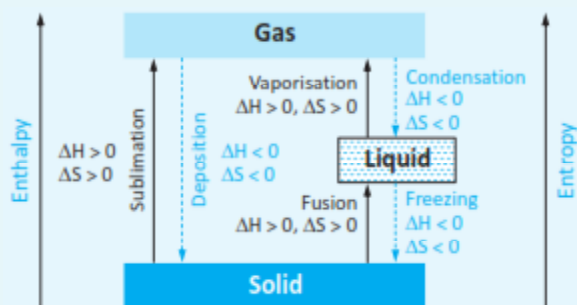
From the definition of molality, we have :

$$\Delta T_b = K_b \left( \frac{n_B}{g_A} \times 1000 \right) \quad \text{OR} \quad \Delta T_b = K_b \left( \frac{\frac{g_B}{M_B}}{g_A} \times 1000 \right)$$

**Note:** ➤ According to Trouton's rule, the ratio, of the molar heat of vaporization of a liquid to its normal boiling point (in Kelvins) is approximately the same for all the liquids :

$$\frac{\Delta H_{\text{vap}}}{T_b} = 88 \text{ J / K / mol}$$

➤ Enthalpy change and entropy change in various phase change processes.



### 3. Depression in Freezing Point :

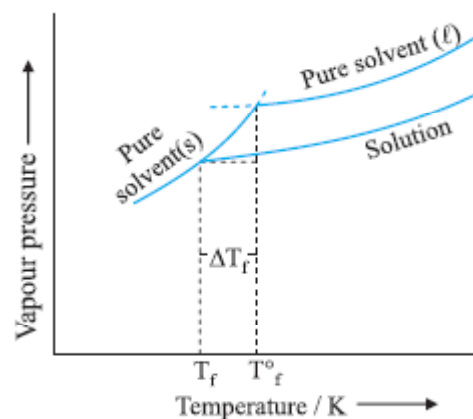
Freezing point is a temperature at which a solid and a liquid state of a substance have the same vapour pressure. Since the vapour pressure of a solution is less than that of pure solvent, the freezing point of the solution will be lower than that of pure solvent.

Let  $\Delta T_f$  be the depression in freezing point, then

$$T_f = T_f^0 - \Delta T_f \quad \begin{array}{l} T_f : \text{freezing point of solution} \\ T_f^0 : \text{freezing point of pure solvent} \end{array}$$

We have  $\Delta T_f = K_f m$

where  $K_f$  : molal freezing point depression constant  
or cryoscopic constant of solvent  
 $m$  : molality of the solution



From the definition of molality, we have :

$$\Delta T_f = K_f \left( \frac{n_B}{g_A} \times 1000 \right) \quad \text{OR} \quad \Delta T_f = K_f \left( \frac{\frac{g_B}{M_B}}{g_A} \times 1000 \right)$$

**Note:** [1] The values of  $K_b$  and  $K_f$  which are functions of the nature of the solvent can be ascertained from the

following relations :

$$K_b = \frac{R(T_b^\circ)^2}{1000\Delta H_{\text{vap}} / M_{\text{solvent}}} \quad \text{and} \quad K_f = \frac{R(T_f^\circ)^2}{1000\Delta H_{\text{fus}} / M_{\text{solvent}}}$$

[2] During freezing of solution only solvent molecules separate out from the solution.

Here the symbols  $R$  and  $M_{\text{solvent}}$  stand for universal gas constant and molar mass of the solvent, respectively.  $T_b^\circ$  and  $T_f^\circ$  denote the boiling point and freezing point of the solvent, respectively in Kelvin. Further,  $\Delta H_{\text{vap}}$  and  $\Delta H_{\text{fus}}$  represent change in enthalpies for the vaporisation of the solvent and fusion of the pure solid solvent, respectively and are to be taken per gram of the solvent.

For  $\text{H}_2\text{O}(l)$ ,  $\Delta H_{\text{vap}} = 10 \text{ kcal mol}^{-1} = \frac{10}{18} \text{ kcal gm}^{-1} = 540 \text{ cal gm}^{-1}$

For  $\text{H}_2\text{O}(s)$ ,  $\Delta H_{\text{fus}} = 1.44 \text{ kcal mol}^{-1} = \frac{1.44}{18} \text{ kcal gm}^{-1} = 80 \text{ cal gm}^{-1}$

#### 4. Osmotic Pressure :

When a semi permeable membrane (*a material with extremely small holes in it so that it allows only solvent molecules to pass through it*) separates a solvent from a solution, solvent molecules tend to pass from the solvent side into the solution.

Also, if the solutions of different concentrations are separated by semi permeable membrane, the solvent molecule pass from dilute solution into the more concentrated solution. This movement of solvent molecules through a semi permeable membrane is called as *osmosis*.

The excess pressure (external pressure) which must be applied to a solution to prevent the flow of solvent molecules into it through the semi permeable membrane (as a result of osmosis) is called as *osmotic pressure*.

#### Laws of Osmosis :

Van't Hoff studied the phenomenon of osmosis in detail and showed that the dilute solutions behave very closely to ideal gases. He studied the effects of concentration and temperature on osmotic pressure.

#### Effect of Concentration :

At constant temperature, osmotic pressure ( $P$  or  $\pi$ ) of a solution is directly proportional to the concentration of solution.

i.e.  $\pi \propto C$  ( $C$  : concentration in mol/L)

or Osmotic pressure varies inversely as the volume of solution that contains one mole of a solute at a given temperature.

i.e.  $\pi \propto \frac{1}{V}$

**Effect of Temperature :**

Osmotic pressure varies directly as the absolute temperature (T).

$$\pi \propto T$$

Combining the two expressions :

$$\pi V = n R T \quad (R : \text{gas constant and } n : \text{moles of solute})$$

$$\text{or} \quad \pi = C R T \quad (C = n/V)$$

The equation  $\pi V = nRT$  is remarkably similar to the ideal gas law ( $PV = nRT$ ).

**Isotonic Solutions**

Two or more solutions having equal osmotic pressure under given conditions are called *isotonic solutions*. For such cases :

$$\pi_1 = \pi_2$$

**Hypertonic Solutions :**

They contain a high concentration of solute relative to another solution (e.g. cell's cytoplasm). When a cell is placed in a hypertonic solution, the water diffuses out of the cell, causing the cell to shrink.

**Hypotonic solutions :**

They contain a low concentration of solute relative to another solution (e.g. the cell's cytoplasm). When a cell is placed in a hypotonic solution the water diffuses into the cell, causing the cell to swell.

**Calculation of Molecular Mass from Colligative Properties**

All of four colligative properties are used to determine the molecular masses of non-volatile solute (especially organic solutes).

**1. Vapour Pressure Lowering :**

$$\frac{\Delta P}{P_A^0} = \chi_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$$

$$\Rightarrow \frac{\Delta P}{P_A^0} = \frac{\frac{g_B}{M_B}}{\frac{g_A}{M_A}} \Rightarrow M_B = \frac{g_B M_A}{g_A} \frac{P_A^0}{\Delta P}$$

## 2. Elevation in Boiling Point :

$$\Delta T_b = K_b \left( \frac{\frac{g_B}{M_B}}{g_A} \times 1000 \right) \Rightarrow M_B = K_b \left( \frac{g_B}{g_A \Delta T_b} \times 1000 \right)$$

### Illustrating the concept :

The boiling point of a solution made by dissolving 12.0 gm of glucose in 100 gm of water is  $100.34^\circ\text{C}$ . Calculate the molecular weight of glucose.  $K_b$  for water =  $0.52^\circ\text{C/m}$ .

### SOLUTION :

Using the relation for molecular weight of a solute from elevation in boiling point, we have :

$$\begin{aligned} M_B &= K_b \left( \frac{g_B}{g_A \Delta T_b} \times 1000 \right) \\ \Rightarrow M_B &= 0.52 \left( \frac{12}{100 \times 0.34} \times 1000 \right) \\ \Rightarrow M_B &= 183.5 \text{ g/mol} \end{aligned}$$

## 3. Depression in Freezing Point :

$$\Delta T_f = K_f \left( \frac{\frac{g_B}{M_B}}{g_A} \times 1000 \right) \Rightarrow M_B = K_f \left( \frac{g_B}{g_A \Delta T_f} \times 1000 \right)$$

## 4. Osmotic Pressure :

$$\pi V = nRT = \frac{g_B}{M_B} RT \Rightarrow M_B = \frac{g_B RT}{\pi V}$$

**Illustration - 5** Blood freezes at 272.44 K and a solution of 3.0 gm of Urea in 250 gm of water freezes at 272.63 K. Calculate osmotic pressure of blood at 310 K. (Assume density of blood at 310 K to be 1 g/cc)

**SOLUTION :**

In this question, first calculate  $K_f$  of water from Urea solution.

$$\Delta T_f = K_f \left( \frac{\frac{g_B}{M_B} \times 1000}{g_A} \right)$$

$$\Rightarrow K_f = \frac{\Delta T_f}{\left( \frac{\frac{g_B}{M_B} \times 1000}{g_A} \right)} \Rightarrow K_f = \frac{0.37}{\left( \frac{\frac{3}{60} \times 1000}{250} \right)} = 1.85 \quad [\Delta T_f = 273 - 272.63 = 0.37 \text{ K}]$$

Now determine the molality of blood by using :

$$\Delta T_f = K_f m$$

$$\text{Now, } \Delta T_f = 273 - 272.44 = 0.56^\circ\text{C}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.56}{1.85} = 0.303$$

**Note :** Colligative properties are defined for dilute solutions. Assume molarity  $\approx$  molality.

$$\Rightarrow \text{Molarity} = \text{molality} = 0.303$$

$$\text{Now using : } \pi = c RT$$

$$\Rightarrow \pi = 0.303 \times 0.0821 \times 310 = 7.7 \text{ atm}$$

**Illustration - 6** Calculate the freezing point depression and boiling point elevation of a solution of 10.0 gm of urea ( $M_B = 60$ ) in 50.0 gm of water at 1 atm. pressure.  $K_b$  and  $K_f$  for water are  $0.52^\circ\text{C/m}$  and  $1.86^\circ\text{C/m}$  respectively.

**SOLUTION :**

$$\text{Depression in freezing point} = \Delta T_f \text{ and Elevation in boiling point} = \Delta T_b$$



$$\Delta T_f = K_f \left( \frac{g_B}{M_B} \times 1000 \right) = 1.86 \left( \frac{10}{60} \times 1000 \right) = 6.2^\circ\text{C}$$

$$\Delta T_b = K_b \left( \frac{g_B}{M_B} \times 1000 \right) = 0.52 \left( \frac{10}{60} \times 1000 \right) = 1.7^\circ\text{C}$$

**Note :** Freezing point ( $T_f$ ) =  $T_f^0 - \Delta T_f = 0 - 6.2 = -6.2^\circ\text{C}$   
 Boiling point ( $T_b$ ) =  $T_b^0 + \Delta T_b = 100 + 1.7 = 101.7^\circ\text{C}$

**Illustration - 7** The boiling point elevation constant for benzene is  $2.57^\circ\text{C/m}$ . The boiling point of benzene is  $80.1^\circ\text{C}$ . Determine the boiling point of a solution formed when 5.0 gm of  $\text{C}_{14}\text{H}_{12}$  is dissolved in 15 gm of benzene.

**SOLUTION :**

Using the result :

$$\Delta T_b = K_b \left( \frac{g_B}{M_B} \times 1000 \right) = 2.57 \left( \frac{5}{180} \times 1000 \right) = 4.76^\circ\text{C}$$

$$T_b = T_b^0 + \Delta T_b \quad [T_b^0 = \text{Boiling point of pure solvent}]$$

$$= 80.1 + 4.76 = 84.86^\circ\text{C}$$

**Illustration - 8** What mass of sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  ( $M_0 = 342$ ) must be dissolved in 4.0 kg of  $\text{H}_2\text{O}$  to yield a solution that will freeze at  $-3.72^\circ\text{C}$ . (Take  $K_f = 1.86^\circ\text{C/m}$ )

**SOLUTION :**

$$\Delta T_f = 3.72^\circ\text{C}, M_{\text{sugar}} = 342$$

$$\Delta T_f = K_f \left( \frac{g_B}{M_B} \times 1000 \right)$$

$$\Rightarrow g_B = \frac{\Delta T_f g_A M_B}{1000 K_f}$$

$$\Rightarrow g_B = \frac{3.72 \times 4 \times 10^3 \times 342}{1000 \times 1.86} = 2736 \text{ gm}$$

**NOW ATTEMPT IN-CHAPTER EXERCISE-B BEFORE PROCEEDING AHEAD IN THIS EBOOK**

## ABNORMAL MOLECULAR MASS (van't Hoff Factor)

## Section - 3

It has been observed that molecular masses of non-volatile solutes calculated from colligative properties (observed molecular masses) are sometimes not accurate i.e., these do not agree with actual values (normal molecular masses). This is attributed to following reasons :

1. Solution may not behave as an ideal solution. (i.e. it may not be dilute solution).
2. Association of molecules of solute.
3. Dissociation of molecules of solute.

## Association

There are certain organic molecules (like acids) which forms dimers (or trimers) in non-aqueous solutions. In solution of such solutes, there exist single, double and larger associated molecules. Hence the effective number of molecules decreases and as a result all colligative properties are less than that calculated on the basis of single molecule. So the molecular masses calculated by using colligative properties will be higher than actual. For example ; *acetic acid in benzene, benzoic acid in benzene and chloro-acetic acid in naphthalene.*

## Dissociation

Inorganic acids and ionic solutes undergo dissociation in aqueous medium. They form cation and anions in the solutions. For example when KCl is dissolved in water, it exists as  $K^+$  and  $Cl^-$  ions in solution. As a result, the number of effective solute particles increases and therefore, the colligative properties of such solutions are much higher than those calculated on the basis of undissociated single molecule. As a result, the molecular mass calculated in such case will be lower than the actual value.

Van't Hoff Factor ( $i$ ) :

$$i = \frac{\text{Observed osmotic effect}}{\text{Normal osmotic effect}}$$

The colligative property implies osmotic effect implies osmotic pressure ( $\pi$ ), vapour pressure lowering ( $\Delta P/P_{\text{Total}}$ ), elevation in B.P. ( $\Delta T_b$ ) and depression in freezing point ( $\Delta T_f$ ).

$$\text{Osmotic effect} \propto \frac{1}{\text{Molecular Weight}}$$

$$\Rightarrow i = \frac{\text{Normal Molecular Weight}}{\text{Observed Molecular Weight}} \quad \left[ \begin{array}{l} \text{Note : "Observed" means "Experimental"} \\ \text{"Normal" means "Theoretical"} \end{array} \right]$$

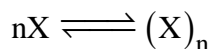
$$\text{or We can write } \left( \begin{array}{c} \text{colligative} \\ \text{property} \end{array} \right)_{\text{observed}} = i \times \left( \begin{array}{c} \text{colligative} \\ \text{property} \end{array} \right)_{\text{normal}}$$

$$\Rightarrow \Delta T_b = i (K_b m) \quad ; \quad \Delta T_f = i (K_f m) \quad ; \quad \pi = i (CRT) \quad ; \quad \frac{\Delta P}{P_A^0} = i \chi_B$$

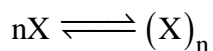
**Degree of Association :**

It is the fraction of total number of molecules of solute which combines to form bigger molecules.

Let  $n$  moles of solute (X) associate from one mole of it.



Let  $x$  be the degree of association.



Initially            1            0

In solution     $1 - x$              $x/n$

Total moles (or molecules) in the solution =  $1 - x + x/n$

As osmotic effect is proportional to the number of moles (or molecules)

$$\Rightarrow i = \frac{\text{Observed osmotic effect}}{\text{Normal osmotic effect}} = \frac{1 - x + x/n}{1}$$

$$\text{or } i = \frac{\text{Normal Molecular Weight}}{\text{Observed Molecular Weight}} = \frac{1 - x + x/n}{1}$$

**Note :** Number of solute particles decreases during complex formation.

**Illustration - 9** Acetic acid associates in benzene to form a dimer. 1.65 gm of acetic acid when dissolved in 100 gm of benzene raised the B.P. by  $0.36^\circ\text{C}$ . Calculate the Van't Hoff factor and degree of association of acetic acid.

( $K_b$  for benzene =  $2.57^\circ\text{C/m}$ )

**SOLUTION :**

Calculation of Van't Hoff factor :

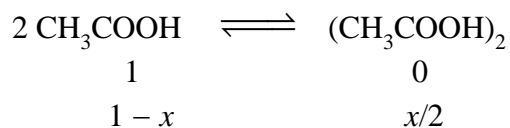
First calculate molecular mass from elevation in boiling point.

$$M_B = K_b \left( \frac{g_B}{g_A \Delta T_b} \times 1000 \right) = 2.57 \left( \frac{1.65}{100 \times 0.36} \times 1000 \right) = 117.8$$

$$\Rightarrow i = \frac{\text{Normal Molecular Weight}}{\text{Observed Molecular Weight}} = \frac{60}{117.8} = 0.509$$

Calculation of degree of association :

Let  $x$  = degree of association



Total moles =  $1 - x/2$

$$i = \frac{\text{Total Moles}}{\text{Initial Moles}} = \frac{1 - x/2}{1}$$

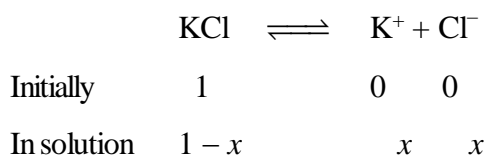
$$\Rightarrow 0.509 = \frac{1 - x/2}{1}$$

$$\Rightarrow x = 0.982$$

### Degree of Dissociation :

It is defined as the fraction of total number of molecules which dissociates into free ions.

Let us take 1 mole of KCl and  $x$  be its degree of dissociation, then we have



Total moles in solution =  $1 - x + x + x = 1 + x$

$$\Rightarrow i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{1 + x}{1}$$

$$\Rightarrow i = \frac{\text{Normal Molecular Weight}}{\text{Observed Molecular Weight}} = \frac{1 + x}{1}$$

### Illustrating the concept :

Find van't Hoff factor of :

(a)  $\text{CH}_3\text{COOH}$  in  $\text{H}_2\text{O}$ ,

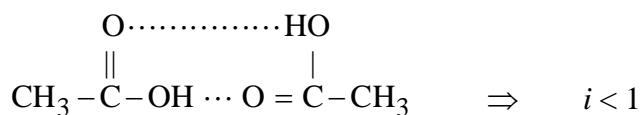
(b)  $\text{CH}_3\text{COOH}$  in benzene

### SOLUTION :

(a)  $\text{CH}_3\text{COOH}$  in water dissociates (as a weak acid) :  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$\Rightarrow i > 1$$

- (b)  $\text{CH}_3\text{COOH}$  in benzene (i.e. non-polar solvent) associates to form a Dimer.



**Illustration - 10** Van't Hoff factors of aqueous solution of X, Y, Z are 1.8, 0.8 and 2.5. Which of the following statement (s) is (are) correct ?

- (A) B.P. :  $X < Y < Z$  (B) F. P. :  $Z < X < Y$   
 (C) Osmotic Pressure :  $X = Y = Z$  (D) V.P. :  $Y < X < Z$

**SOLUTION : (B)**

Observed colligative property =  $i \times$  Normal colligative Property

- (A) Elevation in B.P. follows the order :  $Y < X < Z$  (C) Osmotic Pressure follows the order :  $Y < X < Z$   
 $\Rightarrow$  B.P. following the order :  $Y < X < Z$   
 (B) Depression in F.P. follows the order :

$$Y < X < Z \quad (T_f = T_f^0 - \Delta T_f)$$

$\Rightarrow$  F.P. Following the order :  $Z < X < Y$

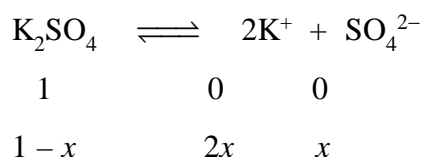
- (D) Relative lowering in the vapour pressure follows :  
 $Y < X < Z$   
 V.P. follows the order :  $Z < X < Y$

**Illustration - 11** A 0.1 M solution of potassium sulphate,  $\text{K}_2\text{SO}_4$  is dissolved to the extent of 90%. What would be its osmotic pressure at  $27^\circ\text{C}$  ?

**SOLUTION :**

Using the result :  $\pi = i C R T$

Calculation of  $i$  :



$$\text{Total moles} = 1 - x + 2x + x = 1 + 2x$$

$$i = \frac{1 + 2x}{1} = \frac{1 + 2 \times 0.9}{1} = 2.8$$

$$\pi = 2.8 \times (0.1 \times 0.0821 \times 300) = 6.90 \text{ atm}$$

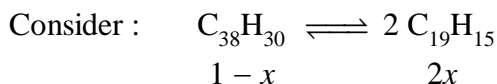
**Illustration - 12** When dissolved in benzene, a compound  $C_{38}H_{30}$  partially dissociates by the following equation :  $C_{38}H_{30} \rightleftharpoons 2 C_{19}H_{15}$ . 25.6 gm of  $C_{38}H_{30}$  is dissolved in 400 g of benzene, the freezing point is lowered by  $0.680^\circ\text{C}$ . What % age of  $C_{38}H_{30}$  molecules have dissociated ? ( $K_f = 4.9$ )

**SOLUTION :**

$$\Delta T_f = i K_f m$$

$$i = \frac{\Delta T_f}{K_f \left( \frac{g_B}{M_B} \times 1000 \right)} = \frac{0.68}{4.9 \left( \frac{25.6}{486} \times 1000 \right)}$$

$$= 1.0538$$



$$\text{Total moles} = 1 - x + 2x = 1 + x$$

$$i = \frac{\text{Total Moles}}{\text{Initial Moles}} = \frac{1+x}{1}$$

$$\Rightarrow 1.0538 = \frac{1+x}{1} \Rightarrow x = 0.0538$$

$$\Rightarrow \% \text{ age dissociation} = 5.38 \%$$

**Illustration - 13** Calculate osmotic pressure of a solution containing 0.01 moles of NaCl and 0.03 moles of Glucose in 500 ml at  $27^\circ\text{C}$ .

**SOLUTION :**

$$C_{\text{effective}} = i_{\text{NaCl}} (= 2) \times C_{\text{NaCl}} + i_{\text{Glucose}} (= 1) \times C_{\text{Glucose}}$$

$$= \left( 2 \times \frac{0.01}{500/1000} + 1 \times \frac{0.032}{500/100} \right) \text{M} = 0.1 \text{ M}$$

$$\Rightarrow \pi = C_{\text{eff.}} RT = 0.1 \times 0.082 \times 300 \text{ atm} = 2.46 \text{ atm}$$

**Illustration - 14** Dry air is passed through a solution containing 20g of an organic non-volatile solute in 250 ml of water. Then the air was passed through pure water and then through a U-tube containing anhydrous  $\text{CaCl}_2$ . The mass lost in solution is 26 g and the mass gained in the U-tube is 26.48 g. Calculate the molecular mass of the organic solute.

**SOLUTION :**

The loss in mass is due to absorption of vapours of solvent in dry air and due to absorption by anhydrous  $\text{CaCl}_2$  [ if solvent is water ]. Loss in mass  $\propto$  pressure of vapours of solvent /solution.

$$\frac{\text{Loss in mass of solvent}}{\text{Gain in mass of U-tube}} = \frac{P^0 - P}{P^0}$$

Loss in mass in solution = 26 g ; Gain in mass of U-tube = 26.48 g

Therefore, loss in mass in solvent = 0.48 g

$$\frac{0.48}{26.48} = \frac{P^0 - P}{P^0} = \text{mole fraction of solute in the solution}$$

$$\frac{0.48}{26.48} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + 250/18}$$

$$\Rightarrow n_{\text{solute}} = \frac{250 \times 0.48}{18(26)}$$

$$\Rightarrow M_{\text{solute}} = \frac{20 \times 18 \times 26}{250 \times 0.48} = 78$$

### IN-CHAPTER EXERCISE-C

1. Arrange the following solutions as directed.

- (a) (i) 0.001 m NaCl, (ii) 0.001 m urea, (iii) 0.001 m MgCl<sub>2</sub>,  
(vi) 0.001 m CH<sub>3</sub>COOH

Increasing order of boiling points

- (b) (i) 0.1 M ethanol, (ii) 0.1 M Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, (iii) 0.1 M Na<sub>2</sub>SO<sub>4</sub>  
Increasing order of freezing points

- (c) (i) 0.1 M glucose, (iii) 1% urea solution, (iii) 0.1 M common salt  
Increasing order of osmotic pressure

- (d) (i) NaNO<sub>3</sub>, (ii) BaCl<sub>2</sub>, (iii) K<sub>3</sub>[Fe(CN)<sub>6</sub>],  
(iv) C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, (v) CH<sub>3</sub>COOH  
Increasing order of van't Hoff Factor

**NOW ATTEMPT IN-CHAPTER EXERCISE-C BEFORE PROCEEDING AHEAD IN THIS EBOOK**

## SUBJECTIVE SOLVED EXAMPLES

**Example - 1** A 0.025 M solution of a monobasic acid has a freezing point of  $-0.06^{\circ}\text{C}$ . Find the value of  $K_a$  of this acid.  $K_f$  of water = 1.86 K/m. Assume that molarity is equal to molality.

**SOLUTION :**

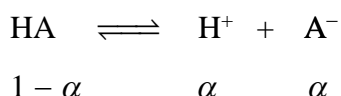
Calculate Van't Hoff factor using the relation :

$$\Delta T_f = i K_f m$$

Taking  $m \approx M$

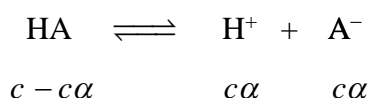
$$\Rightarrow i = \frac{\Delta T_f}{K_f m} = \frac{0.06}{1.86 \times 0.025} = 1.29$$

Van't Hoff factor is given as :



$$i = \frac{\text{Total Moles}}{\text{Initial Moles}} = \frac{1 + \alpha}{1}$$

$$\Rightarrow i = 1 + \alpha = 1.29 \quad \Rightarrow \alpha = 0.29$$



$$\begin{aligned} \Rightarrow K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(c\alpha)}{c - c\alpha} = \frac{c\alpha^2}{1 - \alpha} \\ &= \frac{0.025 \times (0.29)^2}{1 - 0.29} = 2.96 \times 10^{-3} \end{aligned}$$

**Note :** In dilute solutions of weak acids (or weak bases), do not use  $K_a \approx C\alpha^2$  as  $1 - \alpha \neq 1$ .

**Example - 2** Vapour pressure of benzene at  $30^{\circ}\text{C}$  is 164.88 mm of Hg. When in 3 moles of benzene, 6 gm of acetic acid was dissolved, the solution has a vapour pressure of 162.04 mm of Hg. Calculate :

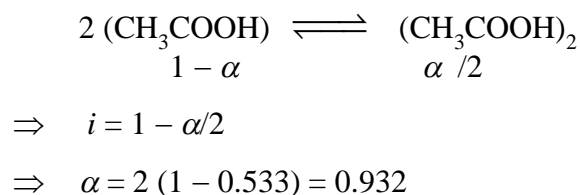
(a) Van't Hoff factor      (b) the degree of association of acetic acid in benzene at  $30^{\circ}\text{C}$ .

**SOLUTION :**

Using the relation for lowering in vapour pressure and considering the van't Hoff factor (i), we have

$$\begin{aligned} \frac{\Delta P}{P_A^0} &= i \chi_B \\ \Rightarrow \frac{(164.88 - 162.04)}{164.88} &= i \cdot \left( \frac{0.1}{0.1 + 3} \right) \\ \Rightarrow i &= 0.533 \text{ (i.e., } i < 1) \end{aligned}$$

Hence, acetic acid *associates* in benzene





**Example - 3** 1.0 gm of monobasic acid when dissolved in 100 gm of pure water lowers the freezing point by  $0.168^{\circ}\text{C}$ . 0.2 gm of the same acid when dissolved and titrated required 15.1 ml of  $N/10$  base. Determine the degree of dissociation of the acid.  $K_f$  of water is  $1.86 \text{ K/m}$ .

**SOLUTION :**

Calculate the molecular mass (observed from colligative property) using the relation :

$$M_B = K_f \left( \frac{g_B}{g_A \Delta T_f} \times 1000 \right)$$

$$= 1.86 \left( \frac{1}{100 \times 0.168} \times 1000 \right)$$

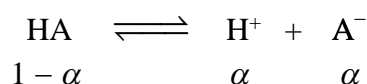
$$\Rightarrow M_B = 110.6$$

Now calculate the actual molecular mass from neutralisation experiment.

$$\frac{0.2}{M/1} = \frac{0.1 \times 15.1}{1000} \quad (\text{meq of acid} = \text{meq of base})$$

$$\Rightarrow M = 132.45$$

$$i = \frac{M_{\text{actual}}}{M_0} = \frac{132.45}{110.6} = 1.19$$



$$\Rightarrow i = 1 + \alpha = 1.19$$

$$\Rightarrow \alpha = 0.19$$

**Example - 4** The molar volume of liquid benzene (density =  $0.877 \text{ g/cc}$ ) increases by a factor of 2750 as it vapourises at  $20^{\circ}\text{C}$  and that of liquid toluene (density =  $0.867 \text{ g/cc}$ ) increases by a factor of 7720 at  $20^{\circ}\text{C}$ . A solution of benzene and toluene at  $20^{\circ}\text{C}$  has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

**SOLUTION :**

$$\text{molar volume of benzene} = \frac{78}{0.877} \text{ ml}$$

$$\text{molar volume of toluene} = \frac{92}{0.867} \text{ ml}$$

At  $20^{\circ}\text{C}$ , volume of vapour of benzene and toluene

$$V_B = \frac{78}{0.877} \times 2750 = 244.58 \text{ L}$$

$$V_T = \frac{92}{0.867} \times 7720 = 819.19 \text{ L}$$

$$P_B^0 = \frac{RT}{V_B}; P_T^0 = \frac{RT}{V_T}; P_{\text{Total}} = P_B^0 \chi_B + P_T^0 \chi_T$$

$$\Rightarrow \frac{46}{760} = \chi_B \left( \frac{RT}{V_B} \right) + \chi_T \left( \frac{RT}{V_T} \right)$$

Substitute for  $V_B$  and  $V_T$  and  $\chi_T = 1 - \chi_B$

$$\Rightarrow \chi_B = 0.452$$

Now find the vapour fraction of benzene.

$$\chi_B^V = \frac{P_B^0 \chi_B}{P_{\text{Total}}} = \frac{0.452}{46/760} \left( \frac{RT}{V_B} \right) = 0.734$$

**Example - 5** 12.2 g of benzoic acid is dissolved in (i) 1 kg acetone ( $K_b = 1.7 \text{ K kg mol}^{-1}$ )  
and (ii) 1 kg benzene ( $K_b = 2.6 \text{ K kg mol}^{-1}$ ).

The elevations of boiling points are  $0.17^\circ\text{C}$  and  $0.13^\circ\text{C}$ , respectively.

- (a) What are the molar masses of benzoic acid in the two solutions ?  
(b) What are the structures of benzoic acid in the two solutions ?

**SOLUTION :**

Let  $M$  be the molar mass of benzoic acid in the solution. The molality of the solution is

$$m = \frac{n_B}{g_A} = \frac{(12.2 \text{ g})/M}{1 \text{ kg}}$$

Since  $\Delta T_b = K_b m$ , we get :

- (a) Acetone solution

$$0.17 \text{ K} = (1.7 \text{ K kg mol}^{-1})$$

$$\left[ \frac{12.2 \text{ g} / M_{\text{Benzoic Acid}}}{1 \text{ kg}} \right]$$

$$M_{\text{Benzoic Acid}} = \frac{1.7 \times 12.2}{0.17} \text{ g mol}^{-1} \\ = 122 \text{ g mol}^{-1}$$

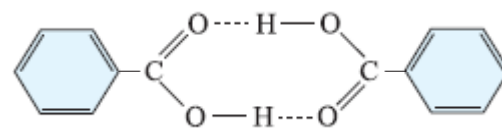
- (b) Benzene solution

$$0.13 \text{ K} = (2.6 \text{ K kg mol}^{-1})$$

$$\left[ \frac{12.2 \text{ g} / M_{\text{Benzoic Acid}}}{1 \text{ kg}} \right]$$

$$M_{\text{Benzoic Acid}} = \frac{2.6 \times 12.2}{0.13} \text{ g mol}^{-1} \\ = 244 \text{ g mol}^{-1}$$

The actual molar mass of benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) is  $122 \text{ g mol}^{-1}$ . This means benzoic acid is present as a monomer in acetone solution while it dimerises in benzene solution. The structure of dimerised benzoic acid is ( $\rightarrow$ )



**Example - 6** Match the following if the molar mass of X, Y and Z are the same.

| Solvent | $T_b / ^\circ\text{C}$ | $K_b / \text{kg K mol}^{-1}$ |
|---------|------------------------|------------------------------|
| X       | 127                    | 0.73                         |
| Y       | 27                     | 0.53                         |
| Z       | 253                    | 0.98                         |

**SOLUTION :**

Since  $K_b = \frac{RT_b^2}{1000\Delta H_{\text{vap}}/M_{\text{solvent}}}$ , we have

$$K_b = \frac{RT_b}{1000\left(\frac{\Delta H_{\text{vap}}}{T_b}\right)/M_{\text{solvent}}}$$

$$= (\text{constant}) T_b$$

$\left[\frac{\Delta H_{\text{vap}}}{T_b}\right]$  is taken to be constant as per Trouton's rule]

$$\Rightarrow K_b \propto T_b$$

Thus, we have

$$K_b(\text{X}) = 0.73 \text{ kg K mol}^{-1}; \quad K_b(\text{Y}) = 0.53 \text{ kg K mol}^{-1}; \quad K_b(\text{Z}) = 0.98 \text{ kg K mol}^{-1}$$

**Example - 7** Following are equimolal aqueous solutions :

(a) 1m urea

(b) 1m KCl

(c) 1m  $\text{MgCl}_2$

(d) 1m  $\text{Na}_3\text{PO}_4$

Arrange them in increasing (i) boiling point, (ii) freezing point, (iii) osmotic pressure, (iv) vapour pressure.

**SOLUTION :**

- ▶ While analysing the colligative properties, if the density of the solution is not given, take the Molarity of the solution same as Molality and vice-versa.
- ▶ In such type of questions, always assume 100% dissociation for the ionic solutes until and unless specified.

|     | Solute                   | Ionisation                        | <i>i</i> |
|-----|--------------------------|-----------------------------------|----------|
| (A) | Urea                     | No                                | 1        |
| (B) | KCl                      | $\text{K}^+ + \text{Cl}^-$        | 2        |
| (C) | $\text{MgCl}_2$          | $\text{Mg}^{2+} + 2\text{Cl}^-$   | 3        |
| (D) | $\text{Na}_3\text{PO}_4$ | $3\text{Na}^+ + \text{PO}_4^{3-}$ | 4        |

**(i) Boiling point of solution**

$$T_b = T_b^0 + (\Delta T_b)$$

$$\Delta T_b = i (K_b m)$$

Thus, greater the value of *i*, greater the value of  $\Delta T_b$  and boiling point of solution.

$$A < B < C < D$$

**(ii) Freezing point of solution**

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

$$\Delta T_f = i (K_f m)$$

Thus, greater the value *i*, greater the value of  $\Delta T_f$  but

Thus, greater the value *i*, greater the value of  $\Delta T_f$  but smaller the value of freezing point.

$$D < C < B$$

**(iii) Osmotic pressure ( $\pi$ )**

$$\pi = i CRT$$

Thus, greater the value *i*, larger the value of osmotic pressure.

$$A < B < C < D$$

**(iv) Vapour pressure of solution**

$$\frac{\Delta P}{P_A^0} = i\chi_B \quad \text{or} \quad \frac{\Delta P}{P_A^0} = i \frac{n_B}{n_A + n_B} \approx i \frac{n_B}{n_A}$$

$\therefore$  The greater the value of *i*, greater the value of  $\Delta P$ . Hence, smaller the value of vapour pressure of solution.

$$D < C < B < A$$

**Example - 8**

The steam distillation of chlorobenzene is observed to occur at a temperature of  $90.6^{\circ}\text{C}$ , when the total pressure is 1 atm. Assuming complete immiscibility of these liquids, calculate the mass of chlorobenzene in 0.1 kg of distillate. The vapor pressure of water at  $90.6^{\circ}\text{C}$  is 539.9 Torr.

**SOLUTION :**

For a mixture of two immiscible liquids, the total pressure is given by

$$P_{\text{Total}} = P_{\text{chlorobenzene}}^{\circ} + P_{\text{water}}^{\circ}$$

$$760 = P_{\text{chlorobenzene}}^{\circ} + 538.9$$

$$\therefore P_{\text{chlorobenzene}}^{\circ} + 221.1 \text{ Torr}$$

$$P_{\text{chlorobenzene}}^{\circ} + \chi_{\text{chlorobenzene}}^{\text{V}} \times P_{\text{Total}} \quad \dots \text{ (i)}$$

$$\text{and } P_{\text{water}}^{\circ} = \chi_{\text{water}}^{\text{(V)}} \times P_{\text{Total}} \quad \dots \text{ (ii)}$$

Dividing equation (i) by (ii) gives,

$$\frac{\chi_{\text{chlorobenzene}}^{\text{V}}}{\chi_{\text{water}}^{\text{V}}} = \frac{P_{\text{chlorobenzene}}^{\circ}}{P_{\text{water}}^{\circ}}$$

$$\text{or } \frac{P_{\text{chlorobenzene}}^{\circ}}{P_{\text{water}}^{\circ}} = \frac{\frac{n_{\text{C}}}{n_{\text{C}} + n_{\text{W}}}}{\frac{n_{\text{W}}}{n_{\text{C}} + n_{\text{W}}}}$$

where  $n_{\text{C}}$  and  $n_{\text{W}}$  represents the number of moles of chlorobenzene and water in the vapour phase, respectively.

$$\therefore \frac{P_{\text{chlorobenzene}}^{\circ}}{P_{\text{water}}^{\circ}} = \frac{n_{\text{C}}}{n_{\text{W}}} = \frac{\frac{W_{\text{C}}}{M_{\text{C}}^{\circ}}}{\frac{W_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}^{\circ}}}$$

$$\therefore \frac{P_{\text{chlorobenzene}}^{\circ}}{P_{\text{water}}^{\circ}} = \frac{W_{\text{C}} \times M_{\text{H}_2\text{O}}^{\circ}}{W_{\text{H}_2\text{O}} \times M_{\text{C}}^{\circ}}$$

Where  $M_{\text{C}}^{\circ}$  and  $M_{\text{H}_2\text{O}}^{\circ}$  represents molar mass of chlorobenzene and water respectively and  $W_{\text{C}}$  and  $W_{\text{H}_2\text{O}}$  denotes weight of chlorobenzene and water the vapour phase, respectively.

$$\therefore W_{\text{C}} = \frac{P_{\text{chlorobenzene}}^{\circ} \times W_{\text{H}_2\text{O}} \times M_{\text{C}}^{\circ}}{P_{\text{H}_2\text{O}}^{\circ} \times M_{\text{H}_2\text{O}}^{\circ}}$$

Let the mass of chlorobenzene in the distillate be  $x$  g, then mass of  $\text{H}_2\text{O}$  would be

$(100 - x)$  g.

$$\therefore x = \frac{221.1 \times (100 - x) \times 112.5}{538.9 \times 18}$$

$$x = 71.94 \text{ g}$$

**NOW ATTEMPT OBJECTIVE WORKSHEET TO COMPLETE THIS EBOOK**

## THINGS TO REMEMBER

1. **Henry's law :**  $P_{Gas} = K_H \cdot \chi_{\text{in solution}}$  Solubility of Gas  $\uparrow$  as  $T \downarrow$  and as  $P \uparrow$ .
2. **Raoult's law :** (For ideal solutions)  $P_{\text{Total}} = P_A^\circ \chi_A + P_B^\circ \chi_B$  ;  $\chi_A^v = \frac{P_A^\circ \chi_A}{P_{\text{Total}}}$  ;  $\chi_B^v = 1 - \chi_A^v$   
 where  $\chi_A$  = mole fraction of A in solution  $\chi_B$  = mole fraction of B in solution  
 $\chi_A^v$  = mole fraction of A in vapour state  $\chi_B^v$  = mole fraction of B in vapour state
  - (i) **Ideal solution :**  $\Delta V_{\text{mixing}} = 0$  ;  $\Delta H_{\text{mixing}} = 0$  ; A–B interactions are similar to A–A and B–B interactions.
  - (ii) Solution showing **+ive deviation :**  $\Delta V_{\text{mixing}} > 0$  ;  $\Delta H_{\text{mixing}} > 0$  ; A–B interactions are weaker than A–A and B–B interactions.
  - (iii) Solutions showing **–ive deviation :**  $\Delta V_{\text{mixing}} < 0$  ;  $\Delta H_{\text{mixing}} < 0$  ; A–B interactions are stronger than A–A and B–B interactions.
3. **Colligative Properties :**
  - For dilute solutions.
  - Depends only on the number of solute particles and independent of their nature.
$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} \quad \text{or} \quad i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$
  - (i)  $\frac{P_A^\circ - P_{\text{Total}}}{P_A^\circ} = \frac{\Delta P}{P_A^\circ} i \chi_B$  = Relative lowering of vapour pressure
  - (ii)  $\Delta T_b = i K_b m$  ;  $T_b = T_b^\circ + \Delta T_b$
  - (iii)  $\Delta T_f = i K_f m$  ;  $T_f = T_f^\circ + \Delta T_f$
  - (iv)  $\pi = C_{\text{eff}} RT$  [  $C_{\text{eff}} = \sum i C_i$  ]

[Osmosis : Solvent molecules move from dilute to concentrated through Semi-Permeable membrane.]

## SOLUTIONS TO IN-CHAPTER EXERCISE-C

1. (a) B.P. is higher if  $\Delta T_b$  is higher which in turn depends on  $m_{\text{effective}} (= i m_{\text{effective}})$   
 $0.001 \text{ m urea} < 0.001 \text{ m CH}_3\text{COOH} < 0.001 \text{ m NaCl} < 0.001 \text{ m MgCl}_2$
- (b) F.P. is higher if  $\Delta T_f$  is lower (depends on  $m_{\text{effective}}$ )  
 $\Rightarrow 0.1 \text{ M Ba}_3(\text{PO}_4)_2 < 0.1 \text{ M Na}_2\text{SO}_4 < 0.1 \text{ M Ethanol}$
- (c) Osmotic Pressure is higher if  $C_{\text{effective}}$  is higher.  
 $0.1 \text{ M Glucose} < 1\% \text{ urea } (\approx 0.167 \text{ M}) < 0.1 \text{ M NaCl}$
- (d)  $\text{NaNO}_3 : i = 2$     $\text{K}_3[\text{Fe}(\text{CN})_6] : i = 4$   
 $\text{CH}_3\text{COOH}$  (Weak acid) :  $1 < i < 2$ ;    $\text{BaCl}_2 : i = 3$     $\text{C}_6\text{H}_{12}\text{O}_6 : i = 1$

## My Chapter Notes







