Solutions - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- The concept of Ideal Solution and Non Ideal solution.
- Know the minimum boiling and maximum boiling azeotropes.
- The concept of colligative properties;
  - Relative lowering of vapour pressure
  - Elevation of boiling point

Contents Outline

- Introduction
- Ideal and Non Ideal Solutions
  - Ideal Solutions
  - Non Ideal Solutions
- Colligative Properties and Determination of Molar Mass
  - Relative Lowering of Vapour Pressure
  - Elevation of Boiling Point

Introduction

We are familiar with the terms "ideal gas" and "real gas". The ideal gas is one which obeys the various gas laws, expressed in the equation PV= nRT. It is found that very few gases obey this law under certain conditions i.e. at low pressure and high temperature. The gases which do not follow the ideal gas equation are called "real gases" which show deviations from ideal behaviour. In this module we shall introduce an analogous terms with reference to liquid solutions. In this module we shall be dealing with solutions containing non volatile solutes. We shall discuss the origin of ideal and non-ideal behaviour of solutions with examples. We shall also explain the colligative properties of solutions containing non volatile solute.

Ideal and Non - ideal Solutions

Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

Ideal Solutions

The solutions which obey Raoult's law (eq 1) over the entire range of concentration are known as ideal solutions. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$p_{total} = p_1^o + (p_2^o - p_1^o) x_2 \qquad (1)$$

$$\Delta_{mix}H = 0, \Delta_{mix}V = 0 \qquad (2)$$

It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of an ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

Non-ideal Solutions

When a solution does not obey Raoult's law over the entire range of concentration, then it is called a non-ideal solution. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law (eq 2). If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult's law. The plots of vapour pressure as a function of mole fractions for such solutions are shown in Fig. 1.

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

ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law [Fig. 1 (a)]. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.
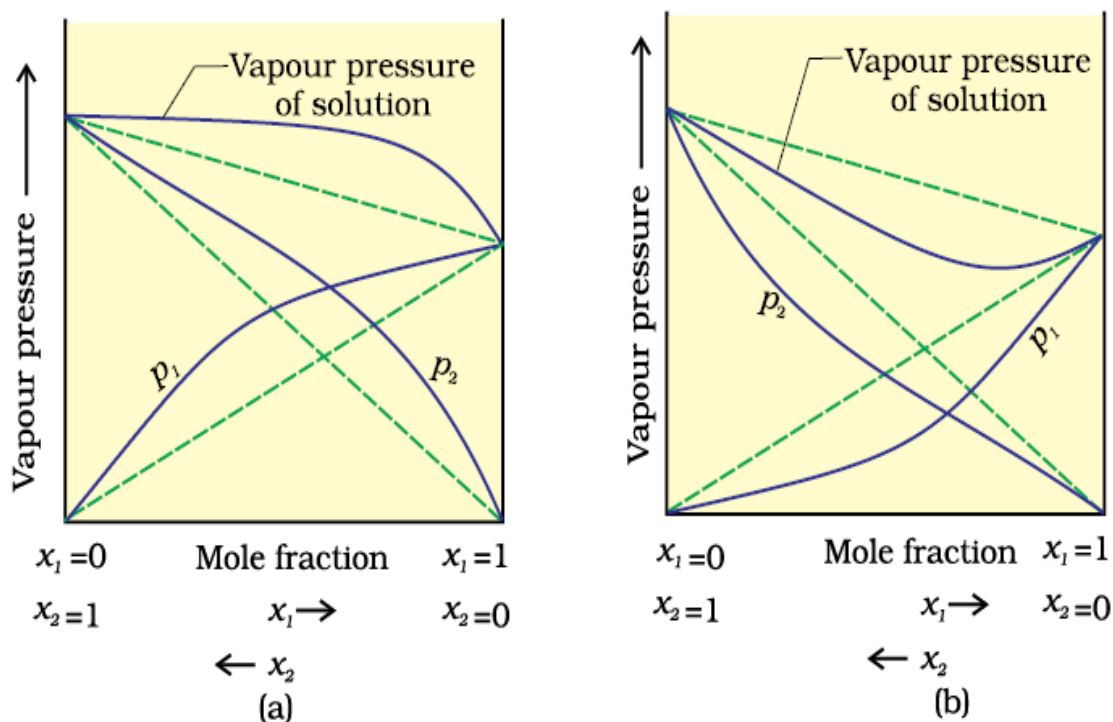

Fig. 1   The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.

In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and lead to decrease in vapour pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between the phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.
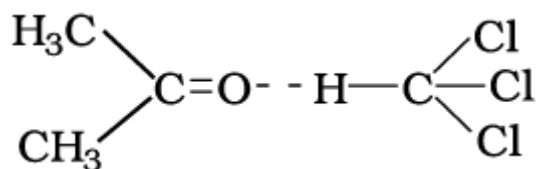
This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law [Fig. 1 (b)].

Some liquids on mixing form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition. For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

Example 1

Benzene and toluene form an ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mmHg and 32.06 mmHg, respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.

Solution

Molar mass of benzene $(C_6H_6) = 6 \times 12$ g mol$^{-1} + 6 \times 1$ g mol$^{-1} = 78$ g mol^{-1}

Molar mass of toluene $= 7 \times 12$ g mol$^{-1} + 8 \times 1$ g mol$^{-1} = 92$ g mol^{-1}

No of moles in 80 g of benzene $= \dfrac{80\ g}{78\ g\ mol^{-1}} = 1.026$ mol

No of moles in 100 g of toluene $= \dfrac{100\ g}{92\ g\ mol^{-1}} = 1.087$ mol

Mole fraction of benzene $x_{benzene} = \dfrac{1.026\ mol}{1.026\ mol + 1.087\ mol} = 0.486$

Mole fraction of toluene $x_{toluene} = 1 - 0.486 = 0.514$

We have

Vapor pressure of pure benzene $p^{o}_{benzene}$ = 50.71 mmHg

And, vapour pressure of pure toluene, $p^{o}_{toluene}$ = 32.06 mmHg

Therefore partial Vapor pressure of benzene, $p_{benzene} = x_{benzene} \times p^{o}_{benzene}$

$$= 50.71 \text{ mmHg} \times 0.486$$
$$= 24.65 \text{ mmHg}$$

And partial vapor pressure of toluene, $p_{toluene} = x_{toluene} \times p^{o}_{toluene}$

$$= 32.06 \text{ mmHg} \times 0.514$$
$$= 16.48 \text{ mmHg}$$

Total vapour pressure = 24.65 mmHg + 16.48 mmHg = 41.13 mmHg

Mole fraction of benzene in vapour phase = $\frac{24.65\ mmHg}{41.13\ mmHg}$ = 0.60

Example 2

Suggest the most important type of intermolecular attractive interaction in the following pairs.

    (i)   n-hexane and n-octane

    (ii) I_2 and CCl_4

    (iii) $NaClO_4$ and water

    (iv) Methanol and acetone

    (v)   acetonitrile (CH_3CN) and acetone (C_3H_6O)

Solution

    (i)   Both n-hexane and n-octane are nonpolar compounds and hence Weak vander Waal's intermolecular attractive interactions operate between these compounds

    (ii)   Both I_2 and CCl_4 are non polar compounds and hence Weak vander Waal's intermolecular attractive interactions operate between these compounds

    (iii) Upon dissolution in water, $NaClO_4$ ionises to give Na^+ and ClO_4^- ions in solution and since, water is a polar solvent, as a result strong ion-dipole interaction represent the intermolecular attractive interaction in this pair

    (iv) Both methanol and acetone are polar compounds and hence they have dipole- dipole interaction are intermolecular attractive interactions in this pair

(v) Both compounds are polar in nature and hence they have dipole- dipole interaction as intermolecular attractive interaction

Example 3

100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}) to result an ideal solution. The vapour pressure of pure liquid B was found to be 500 Torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

Solution

p_{total} = 475 Torr

p_B^o= 500 Torr

Molar mass of A = 140 g mol^{-1}

Molar mass of B = 180 g mol^{-1}

Moles of A = 100 g / 140 g mol^{-1} = 0.714 mol

Moles of B = 1000 g / 180 g mol^{-1} = 5.555 mol

Mole fraction of A = x_A = 0.714 mol/ (5.555 + 0.714) mol = 0.114

Mole fraction of B = x_B = 5.555 mol/ (5.555 + 0.714) mol = 0.886

we know that

$$p_{total} = p_B^o + \left(p_A^o - p_B^o\right)x_A$$

475 Torr = 500 $Torr$ + (p_A^o Torr – 500 Torr) 0.114

p_A^o= 280.7 Torr

Now $p_A = x_A p_A^o$ = 0.114 × 280.7 Torr = 32 Torr

Therefore, the vapour pressure of pure liquid A and its vapour pressure in the solution are 280.7 Torr and 32 Torr, respectively.

Example 4

Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26 g of heptane and 35 g of octane?

Solution

Molar mass of heptane = 100 g mol^{-1}

Molar mass of octane = 114 g mol^{-1}

Moles of heptanes = 26.0 g / 100 g mol^{-1} = 0.260 mol

Moles of octane = 35.0 g / 114 g mol^{-1} = 0.307 mol

Mole fraction of heptane = x_1 = 0.458

Mole fraction of octane = x_2 = 0.542

p_1^0 = 105.2 kPa : p_2^0 = 46.8 kPa

$p_{total} = x_1 p_1^0 + x_2 p_2^0$ = 0.458 × 105.2 kPa + 0.542 × 46.8 kPa = 73.52 kPa

p_{total} = 73.52 kPa

Example 5

The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

Solution

As per the data given here, we have,

p_{total} = 600 mmHg

we may consider liquid A as component 1 and liquid B as component 2

Thus, according to the data given here

p_1^o = 450 mmHg

p_2^o = 700 mmHg

Considering eq (1), we have

$p_{total} = p_1^o + (p_2^o - p_1^o) x_2$

Using the given data in the above equation, we have

600 mmHg = 450 mmHg + (700 mmHg – 450 mmHg) x_2

Thus,

$x_2 = \frac{600\,mmHg - 450\,mmHg}{700\,mmHg - 450\,mmHg} = 0.6$

$x_1 = 1 - x_2 = 1 - 0.6 = 0.4$

Thus the amount fraction of liquid A (component 1) and liquid B (component 2) in the liquid solution is 0.4 and 0.6, respectively.

According to Dalton's law of partial pressure, the amount fraction of component 1 in vapour phase; y_A is given by

$$y_1 = \frac{p_1}{p_{total}} = \frac{x_1 p_1^o}{p_{total}}$$

$$y_1 = \frac{0.4 \times 450 \, mmHg}{600 \, mm \, Hg} = 0.3$$

$y_2 = 1 - y_1 = 1 - 0.3 = 0.7$

Thus the amount fraction of chemical species A (component 1) and chemical species B (component 2) in the liquid solution is 0.3 and 0.7, respectively.

Colligative Properties and Determination of Molar Mass

We have learnt in a previous module that the vapour pressure of solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (1) relative lowering of vapour pressure of the solvent (2) depression of freezing point of the solvent (3) elevation of boiling point of the solvent and (4) osmotic pressure of the solution. All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called colligative properties (colligative: from Latin: co means together, ligare means to bind). In the following Sections we will discuss these properties one by one.

Relative Lowering of Vapour Pressure

We have learnt earlier that the vapour pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The equation (3), as described in earlier module, establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent, i.e.,

$$p_1 = x_1 \, p_1^{\circ} \tag{3}$$

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

$$\Delta p_1 = p_1^{\circ} - p_1 = p_1^{\circ} - p_1^{\circ} x_1$$

$$\Delta p_1 = p_1^{\circ}(1 - x_1) \tag{4}$$

Knowing that $x_2 = 1 - x_1$, equation (4) reduces to

$$\Delta p_1 = x_2 p_1^\circ \qquad (5)$$

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

Equation (5) can be written as

$$\frac{\Delta p_1}{p_1^\circ} = \frac{p_1^\circ - p_1}{p_1^\circ} = x_2 \qquad (6)$$

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

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1 + n_2}, \ \text{Since } x_2 = \frac{n_2}{n_1 + n_2} \qquad (7)$$

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

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1} \qquad (8)$$

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_2 \times M_1}{M_2 \times w_1} \qquad (9)$$

Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute, respectively.

From this equation (9), knowing all other quantities, the molar mass of solute (M_2) can be calculated.

Example 6

The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass of benzene is 78 g mol^{-1}). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

Solution

The various quantities known to us are as follows:

$p_1^\circ = 0.850$ bar; $p = 0.845$ bar; $M_1 = 78$ g mol^{-1}; $w_2 = 0.5$ g; $w_1 = 39$ g

Substituting these values in equation (9), we get

$$\frac{0.850 \ bar - 0.845 \ bar}{0.850 \ bar} = \frac{0.5 \ g \times 78 \ g \ mol^{-1}}{M_2 \times 39 \ g}$$

Therefore, $M_2 = 170g \ mol^-$

Example 7

Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% .

Solution

Molar mass of octane = 114 g mol^{-1}

Mass of the solute = w_2 g

Mole fraction of solute = x_2

Vapour pressure of pure octane = p^o

Lowering of vapour pressure = Δp

$$\frac{\Delta p}{p^o} = \frac{p^o - p}{p^o} = x_2$$

$$p^o - p = x_2 p^o$$

As the vapour pressure gets reduced to 80 % when non volatile solute is dissolved in it,

Thus, $p = 0.8 \ p^o$

$$p^o - 0.8p^o = x_2 p^{\circ}$$

$$0.2 \ p^o = x_2 \ p^{\circ}$$

Therefore $x_2 = 0.2$

Now considering the formula $x_2 = \dfrac{n_2}{n_1 + n_2} = \dfrac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$

Now since $x_2 = 0.2$, $M_1 = 114$ gmol^{-1}, $M_2 = 40$ g mol^{-1} and $w_1 = 114$ g

Using this data in above equation,

We get

$$0.2 = \dfrac{\frac{w_2}{40 \ g \ mol^{-1}}}{\frac{114g}{114 \ g \ mol^{-1}} + \frac{w_2}{40 \ g \ mol^{-1}}}$$

Rearranging the above equation we get

$w_2 = 10$ g

Thus, 10 g of non volatile solute must be dissolved in 114 g of octane to reduce the vapour pressure of octane to 80 %.

Elevation of Boiling Point

We have learnt earlier, that the vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. For example, water boils at 373.15 K (100° C) because at this temperature the vapour pressure of water is 1.013 bar (1 atmosphere). We have also learnt in the last section that vapour pressure of the solvent decreases in the presence of non-volatile solute. Fig. 2.7 depicts the variation of vapour pressure of the pure solvent and solution as a function of temperature. For example, the vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 2. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure.
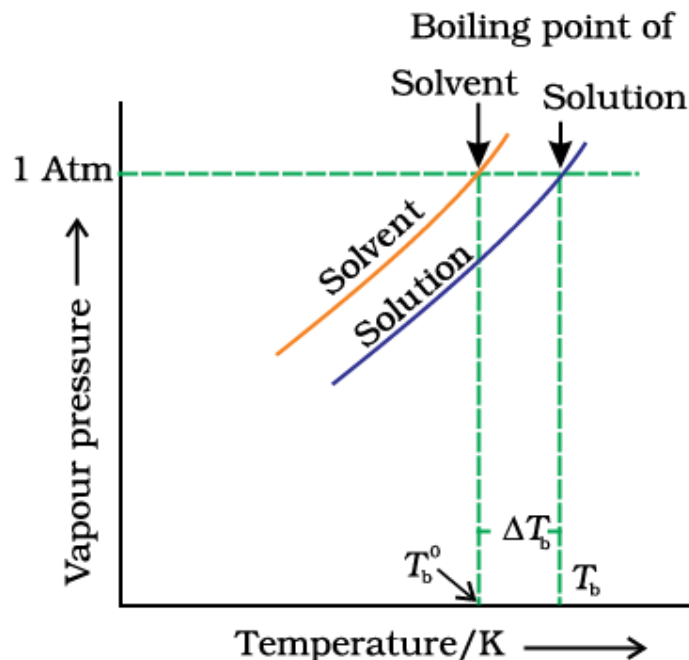

Fig. 2: The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

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

Experiments have shown that for dilute solutions the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

$\Delta T_b \propto m$ (10)

or $\Delta T_b = K_b\, m$ (11)

Here m (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, K_b is called Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant). The unit of K_b is K kg mol^{-1}. Values of K_b for some common solvents are given in Table 1. If w_2 gram of solute of molar mass M_2 is dissolved in w_1 gram of solvent, then molality, m of the solution is given by the expression:

$$m = \frac{\frac{w_2 M_2}{w_1}}{1000} = \frac{1000 \times w_2}{M_2 \times w_1} \tag{12}$$

Substituting the value of molality in equation (11) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \tag{13}$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \tag{14}$$

Thus, in order to determine M_2, the molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

Example 8

18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar? K_b for water is 0.52 K kg mol^{-1}.

Solution

Moles of glucose = 18 g/ 180 g mol^{-1} = 0.1 mol

Number of kilograms of solvent = 1 kg

Thus molality of glucose solution = 0.1 mol kg^{-1}

For water, change in boiling point

$\Delta T_b = K_b\, m = 0.52$ K kg mol^{-1} × 0.1 mol kg^{-1} = 0.052 K

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be 373.15 + 0.052 = 373.202 K.

Example 9

The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute is dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K_b for benzene is 2.53 K kg mol^{-1}.

Solution

The elevation (ΔT_b) in the boiling point = 354.11 K – 353. 23 K = 0.88 K

Substituting these values in expression (14) we get

$M_2 = \frac{1000 \times 1.8\ g \times 2.53\ K\ kg\ mol^{-1}}{0.88\ K \times 90\ g} = 0.058\ kg\ mol^{-1}$

$= 0.058\ kg\ mol^{-1} \times 1000 \frac{g}{kg}$

$= 58$ g.mol^{-1}

Note: A conversion factor of 1000 $\frac{g}{kg}$ is used to convert the kg mol^{-1} unit to g mol^{-1} unit.

Therefore, molar mass of the solute, $M_2 = 58$ g mol^{-1}.

Example 10

Boiling point of water at 750 mmHg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.

Solution

Normal boiling point of water = 100 °C

Elevation of boiling point, ΔT_b = 100 °C − 99.63 °C = 0.37 °C or 0.37 K

Mass of water w_1= 500 g

Molar mass of sucrose ($C_{12}H_{22}O_{11}$), M_2 = 11 × 12 g mol^{-1} + 22 × 1 g mol^{-1} + 11 × 16 g mol^{-1}

$$= 342 \text{ g mol}^{-1}$$

Molal elevation constant, K_b = 0.52 K kg mol^{-1}

Let us now consider the formula

$M_2 = \frac{1000\ g.kg^{-1} \times w_2\ g \times K_b\ K\ kg\ mol^{-1}}{\Delta T_b\ K \times w_1\ g}$

$M_2 = \frac{1000\ g.kg^{-1} \times w_2\ g \times 0.52\ K\ kg\ mol^{-1}}{0.37\ K \times 500\ g}$

Therefore, w_2 = 121.67 g