Chapter Five

5. Non-Electrolytic Solutions

5.1. What is a Solution?

A *solution* is a homogenous mixture of two or more than two non-reacting substance. A *homogeneous mixture* is one in which the composition is the same throughout the solution. There is also only one phase throughout the mixture. The relative amounts of various constituents of a solution can be varied within a certain limit but there is no fixed ratio for constitutes to be mixed. If we have two substances mixed, it is called a *binary solution* and if three substances are mixed the solution is termed as *ternary solution* and so on.

The substance present in large quantity is called a *solvent* and the other components of the solution are called *solutes*. *Solvent* is a substance that dissolves other material(s) to form solution. Common solvents are liquids at room temperature but it can be solid or gas.

The maximum amount of solute that can be dissolved in a given solvent at a given temperature and pressure is known as the *solubility of the solute*. At this stage the solution is termed as *saturated* where a dynamic equilibrium between the dissolved solute and the undissolved solute is established. If the quantity of a solute dissolved is more than the saturation value it is said to be *supersaturated* and if it is less than the saturation value it is known as *unsaturated* solution.

Non-electrolyte solution is a solution that does not conduct electricity when solute dissolved by solvents. For example; when sugar dissolves in water, it doesn't dissociate in the water; hence the solution of sugar is non electrolyte solution.

5.2. Solutions of gases in liquids

Gases dissolve in liquids to form true solutions. Such solutions are examples of two component systems. The solubility of a gas is usually determined by measuring the volume of the gas rather than the mass of dissolved gas using *Bunsen absorption coefficient* (α) which is defined as the volume of the gas at STP dissolved by a unit volume of the solvent at the given temperature under a partial pressure of 1 atm. If V_0 is the volume of the gas that dissolves reduced to STP, V is the volume of the solvent and P is the partial pressure of the gas in atmosphere, then the absorption coefficient α is given by

$$\alpha = \frac{V_o}{VP}$$

For example the α values of helium, hydrogen, nitrogen and oxygen in water are 0.0087, 0.0019, 0.0014 and 0.0028 atm^{-1} respectively.

When a gases dissolved in liquids to form true solutions of two component systems. The solubility of the gases depends on

- The temperature of the solution
- The pressure of the gas over the solution
- The nature of the gas
- The nature of the solvent

Effect of temperature on solubility of gases in liquids

Solubility is strongly dependent on temperature. In general, gases are less soluble at higher temperatures. This may be regarded as temperature increases, it becomes more difficult to contain the gas (solute) and the solute-solvent attraction is increasingly disrupted by thermal agitation. **T**here are certain cases where solubility of gases like hydrogen and inert gases increase with increase in temperature in non-aqueous solvents.

Effect of pressure on solubility of gases in liquids (Henry's law)

For real solution at low concentration, the English chemist William Henry experimentally found that the mole fraction of volatile solute is proportional to the vapor pressure of the solute. This is known as Henry's Law. Mathematically, the Henry's Law is written as:

$$P_B = X_B K_H$$

Where P_B is the vapor pressure of the solute, X_B is the mole fraction of the solute and K_H is the Henry's constant with the dimension of pressure.

Example

Under normal atmospheric conditions the partial pressure of oxygen is 0.20948 atm. Calculate the amount of oxygen dissolved in air saturated water at 25°C. Use K_H of 756.7 atm L mol^{-1}.

Solution

Using Henry's law, the concentration of oxygen is:

$$X_{Oxygen} = \frac{P_{oxygen}}{K_H} = \frac{0.20948\ atm}{756.7\ atm\ L\ mol^{-1}} = 2.77\ mol\ L^{-1}$$

5.3.   Solutions of gases in gases (Dalton's law of partial pressure)

Dalton's law of partial pressures states that in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases. Mathematically, the pressure of a mixture of non-reactive gases can be defined as the summation:

$$P_{total} = \sum_{i=1}^{n} p_i \qquad \text{or} \qquad P_{total} = p_1 + \cdots + p_n$$

Where $p_1, p_2, \cdots, p_n$ represent the partial pressure of each component.

$$P_i = P_{total}X_i$$

Where X_i is the mole fraction of the ith component in the total mixture of n components.

Dalton's law is not strictly followed by real gases, with deviations being considerably large at high pressures. Under such conditions the volume occupied by the molecules can become significant compared to the free space between them. In particular, the short average distances between molecules raise the intensity of intermolecular forces between gas molecules enough to substantially change the pressure exerted by them. Neither of those effects is considered by the ideal gas model.

Example

Two containers are connected by a stopcock as shown below. Gas "A" is at a pressure of 202 kPa while gas "B" is at a pressure of 140 kPa. What will the resultant pressure be when the stopcock is opened at a fixed temperature?
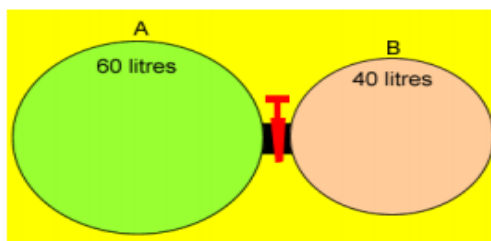
Solution

First calculate the pressure that each gas alone will exert when the stopcock is opened. Since the temperature and amount of each gas is constant we use the formula below.

$$P_1V_1 = P_2V_2$$

For gas A:

$$P_1 = 202\ kPa, V_1 = 60\ L,\ V_2 = 100\ L\ and\ P_2 = ?$$

$$P_2 = 121.2\ kPa$$

For gas B:

$$P_1 = 140\ kPa, V_1 = 40\ L,\ V_2 = 100\ L\ and\ P_2 = ?$$

$$P_2 = 56\ kPa$$

The total pressure is:

$$P_T = P(A) + P(B) = 177.2\ kPa$$

5.4. Solutions of liquids in liquids

Vapour Pressure of Ideal solutions

An ideal solution is defined as the one in which there is a complete uniformity in cohesive forces. This means the solute-solvent; solute-solute and the solvent-solvent interactions are assumed to be equal. An ideal solution would follow Raoult's Law, but ideal solutions do not exist. No heat is evolved or absorbed during Mixing. Final volume of solution is the summation of volume of each constituents. The properties of solution such as vapour pressure, surface tension, viscosity etc are the average of the two pure liquids.

Generally, an ideal solution possesses the following characteristics.

i. When two pure substances mix to form an ideal solution there is no evolution or absorption of heat, i.e., the change in heat of mixing (ΔHmix) is zero.
ii. The total volume of an ideal solution will be equal to the sum of the volumes of the components mixed, i.e., the change in the total volume due to mixing (ΔVmix) is zero.
iii. An ideal solution must obey the Raoult's law and Henry's law over the whole range of concentration

The calculation of properties of both ideal and non-ideal solution is based on the fact that the chemical potential of a species is the same in different phases when the phases are at equilibrium. When a binary liquid mixture is in equilibrium with its vapour at a constant temperature, the chemical potential of each component is the same in the gas and liquid phases:

$$\mu_i\,(g) = \mu_i\,(l)$$

$$\Longrightarrow \mu_i^0\,(g) + RT\ln\frac{P_i}{P^0} = \mu_i^0\,(l) + RT\ln a_i$$

For pure liquid, which has an activity of unity in the liquid phase the above equation is written as:

$$\mu_i^0\,(g) + RT\ln\frac{P_i^*}{P^0} = \mu_i^0\,(l)$$

Where P_i^* is the equilibrium vapour pressure of pure i at temperature T.

Substituting this equation in the second equation for $\mu^o{}_i(l)$ and after rearrangement we will arrive at:

$$a_i = \frac{P_i}{P_i^*}$$

This discussion has been quite general, but so far it has not shown us how to predict the partial pressure P_i of a component of an actual solution.

Raoult's law states that at a given temperature the partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture. Mathematically;

$$P_i = P_i^0 X_i$$

Where P_i the partial vapour pressure of component i and P_i^0 is the vapour pressure of pure component i and X_i is the mole fraction of component i.

Raoult's law assumes ideal behaviour based on the simple microscopic assumption that intermolecular forces between unlike molecules are equal to those between similar molecules: the conditions of an ideal solution. This is analogous to the ideal gas law, which is a limiting law valid when the interactive forces between molecules approach zero.

In a system, where ideal liquid and ideal vapour are assumed, a very useful equation emerges if Raoult's law is combined with Dalton's Law.

$$P_T = P_1 + P_2 = P_1^0 X_1 + P_2^0 X_2 + \ ...$$

If a non-volatile solute (zero vapor pressure, does not evaporate) is dissolved into a solvent to form an ideal solution, the vapor pressure of the final solution will be lower than that of the pure solvent.

Examples

1. A solution is composed of 1.40 mol cyclohexane (P°cy = 97.6 torr) and 2.50 mol acetone (P°ac = 229.5 torr). What is the total vapour pressure above this solution?

Solution:

$$X_{cyc} = \frac{1.4\ mol}{1.4\ mol + 2.5\ mol} = 0.36$$

$$X_{ace} = \frac{2.5\ mol}{1.4\ mol + 2.5\ mol} = 0.64$$

$$P_T = P^0_{cyc}X_{cyc} + P^0_{ace}X_{ace} = 182\ torr$$

2. Benzene and toluene form a solution which is very nearly ideal. Consider a mixture of benzene (BZ) and toluene (Tol) at 60 °C. At 60 °C the vapour pressures of pure benzene and pure toluene are 385 Torr and 139 Torr, respectively. What are the vapour pressures of benzene and toluene in a mixture with X_{Bz} = 0.400, and X_{Tol} = 0.600, and what is the composition of the vapour in equilibrium with this solution?

4. **Colligative Properties of Solutions**

A colligative property is a property which depends only up on the number of solute particles present in the solution but not up on the chemical nature of these solute particles. There is a connecting relationship between each of the colligative properties. If one property is measured the other can be calculated using exact mathematical relationships. These relations are exact only when we assume that

   i.   The added solute is nonvolatile and doesn't appear in the vapour phase

  ii.   The nonvolatile solute is insoluble in the solid solvent, that is to say, on cooling solution only the pure solvent separates as solid at the freezing point.

If there is association or dissociation of the solute particles the properties mentioned above will be affected.

  ➢ If there is association of the particles, the number of particles actually added will become less and as a result the colligative properties will be lowered

  ➢ If there is dissociation of particles, the number of particles actually added will become very high as a result the colligative properties will increased.

While discussing colligative properties it is assumed that the solutions are very dilute and ideal i.e no interaction between particles or no association and dissociation. It has been observed that any solution

containing a non-volatile solute exhibits the four properties namely; Vapour pressure lowering of the solvent, Boling point elevation, Freezing point depression and Osmotic pressure. These four properties are collectively known as colligative properties. (Means "collective")

I.   Lowering of Vapour Pressure of Solvent

Vapour pressure is the pressure exerted by a vapour when it is in dynamic equilibrium with its liquid at a fixed temperature. At any given temperature, the vapor pressure of a solution containing a nonvolatile solute is less than that of the pure solvent. This effect is called vapor pressure lowering. A pure solvent vaporizes because particles moving randomly in a vapor phase are more disorder than when huddled near each other in the liquid. But a solution is already more disordered than a pure liquid, The solute reduces the escaping tendency of the solvent, and, on the basis of Raoult's law, the vapor pressure is lowered proportional to the relative number (rather than the weight concentration) of the solute molecules.

Consider any solution containing some non-volatile solute and let X_1 and X_2 are the mole fractions of the solvent and the solute respectively and if P^0 is the vapor pressure of the pure solvent and P is the vapour pressure of the solvent above the solution then according to Raoult's low.

$$P = P^0 X_1 \quad \ldots\ldots\ldots\ldots\ldots 4.1$$

Since the mole fraction of the solvent (X_1) is always less than 1, $P_{solvent}$ is always less than $P^0{}_{solvent}$. Hence it can be said that whenever a non voltaile solute is added to a solvent, the effect is the lowering of the vapour pressure of the solvent.

How does the amount of solute affect the magnitude of vapour pressure lowering ΔP?

$$X_1 + X_2 = 1 \text{ Thus } X_1 = 1 - X_2$$

From Raout's low $P = X_1 P^0 = (1 - X_2)P^0$

$$P = P^0 - (X_2 . P^0)$$
$$P - P^0 = -X_2 P^0$$

$$\Delta P = P^0 - P = X_2 . P^0 \quad \ldots\ldots\ldots\ldots 4.2$$

The magnitude of ΔP equals the mole fraction of the solute times the vapour pressure of the pure solvent.

Example 4.1. Calculate the vapour pressure lowering ΔP, when 10.0 ml glycerol ($C_3H_8O_3$) is added to 500.0 ml of water at 50^0C. At this temperature the vapour pressure of pure water is 92.5 torr and its density is 0.988g/ml, the density of glycerol is 1.26g/ml.

Solution

$$\Delta P = X_{gly} \times P^0 = \frac{n_{gly}}{n_w + n_{gly}} \times P^0$$

$$n_{gly} = \frac{V_{gly} \times \rho_{gly}}{M_{gly}} = \frac{10.0ml \times 1.26gml^{-1}}{92gmol^{-1}} = 0.137mol$$

$$n_{wat} = \frac{V_{wat} \times \rho_{wat}}{M_{wat}} = \frac{500.0ml \times 0.988gml^{-1}}{18gmol^{-1}} = 27.4mol$$

$$\Delta P = X_{gly} \times P^0 = \frac{0.137mol}{27.4mol + 0.137mol} \times 92.5Torr = \frac{0.137mol \times 92.5Torr}{27.537mol} = 0.46Torr$$

Example 4.2. What is the vapor pressure of the pure solvent if the vapor pressure of a solution of 10 g of sucrose ($C_6H_{12}O_6$) in 100 g of ethanol (C_2H_6O) is 55 mmHg?

Solution

$$P = X_{eth} \times P^0 = \frac{n_{eth}}{n_{eth} + n_{suc}} \times P^0$$

$$n_{eth} = \frac{w_{eth}}{M_{eth}} = \frac{100.0g}{46gmol^{-1}} = 2.17mol \text{ and } n_{suc} = \frac{w_{suc}}{M_{suc}} = \frac{10.0g}{180gmol^{-1}} = 0.055mol$$

$$P^0 = \frac{P}{X_{eth}}, X_{eth} = \frac{2.17mol}{2.17mol + 0.055mol} = 0.975 \Rightarrow P^0 = \frac{55mmHg}{0.975} = 56.41mmHg$$

Determination of molecular mass from ΔP

Equation (4.2) can be utilized to calculate the molecular weight of the solute if the vapour pressure of the pure solvent and the solution are known as follows.

Since the mole fraction of the solute $X_2 = \frac{n_2}{n_1 + n_2}$, Where $n_2 = \frac{W_2}{M_2}$ and $n_1 = \frac{W_1}{M_1}$

Therefore equation (4.2) becomes $\dfrac{P^0 - P}{P} = \dfrac{n_2}{n_1 + n_2} = \dfrac{W_2/m_2}{W_1/m_1 + W_2/M_2}$

Since the solution under consideration is very dilute $n_\partial < n_1$ and $n_1 + n_\partial \; \square$

Thus $\dfrac{P^0}{P^0} = \dfrac{W_2 M_1}{W_1 M_2}$ $\Rightarrow$ $\boxed{M_2 = \dfrac{P^0}{P^0 - P}\left(\dfrac{W_2}{W_1}\right)M_1}$ -------------------------------- 4.11

where M_2 is the molecular weight of the solute

Example 4.3. When 2 g of a non-volatile hydrocarbon is dissolved in 100 g of benzene the vapour pressure of benzene at 20 ^{0}C is lowered from 77.66mm Hg to 74.01 mmHg. Calculate the molecular mass of the hydrocarbon

Solution
$$M_2 = \frac{P^0}{P^0 - P}\left(\frac{W_2}{W_1}\right)M_1$$

$$M_2 = \frac{74.66\ mmHg}{74.66\ mmHg - 74.01\ mmHgP}\left(\frac{2g}{100g}\right)78\ gmol^{-1} = 179\ gmol^{-1}$$

Example 4.4. The vapour pressure of water at 293K is 17.540 mm Hg and the vapour pressure of solution of 0.10824 kg of a non-volatile solute in 1kg of water at the same temperature is 7.354mmHg. Calculate the molar masses of the solute.

Solution
$$M_2 = \frac{P^0}{P^0 - P}\left(\frac{W_2}{W_1}\right)M_1$$

$$M_2 = \frac{17.540\ mmHg}{17.540\ mmHg - 17.354\ mmHgP}\left(\frac{108.24g}{1000g}\right)18\ gmol^{-1} = 183.7\ gmol^{-1}$$

Exercises 4.1. At 25 ^{0}C, the vapor pressure of pure benzene ($C_6\ H_6$) is 0.1252 atm. Suppose 6.4 g of naphthalene ($C_{10}H_8$) is dissolved in 78.0 g of benzene. What is the vapor pressure of benzene above the solution assuming ideal behavior?

II.   Elevation of Boiling point

Boiling point is defined as the temperature at which the vapour pressure of the liquid becomes equal to the external pressure (usually 1 atmosphere).The addition of a non-volatile solute to the solvent lowers its vapour pressure and there by elevates the boiling point of the solution. The difference between the boiling point of the solution (*T*) containing a non-volatile solute and the boiling point of pure solvent (*T$_b$*) is known as the ***Elevation of boiling point*** (ΔT_b).

$$\Delta T_b = (T - T_b) \quad \text{..........4.12}$$

The elevation of boiling point depends on the nature of the solvent and the concentration of the solute. Boiling point elevation can be readily understood in terms of lowering of vapour pressure as show in figure 4.1.
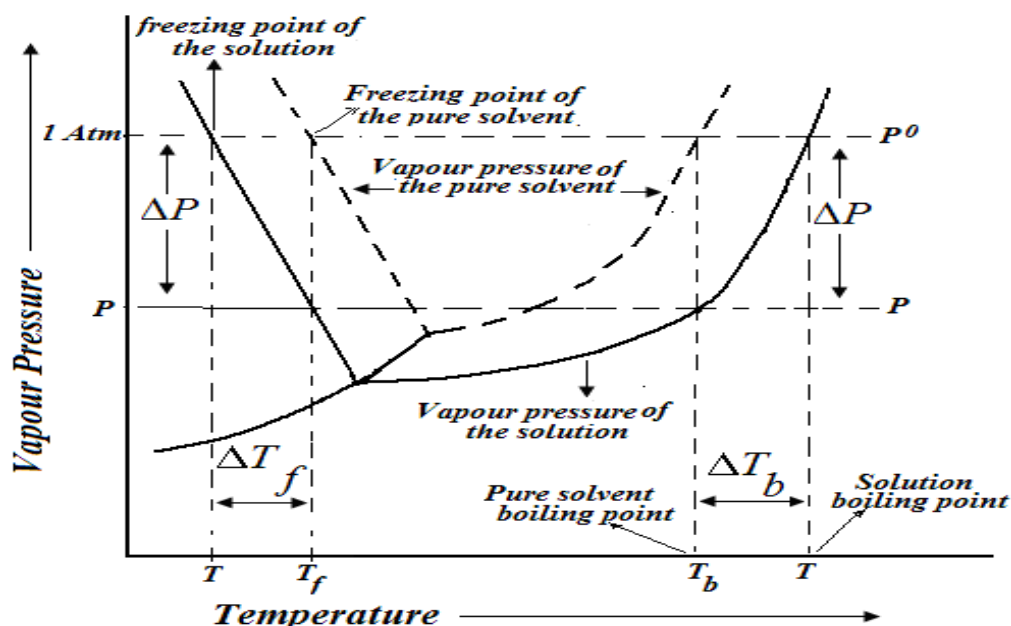
Figure 5.1. A phase diagram for the vapour pressure lowering, boiling point elevation, and freezing point depression of the solvent (water) when a non-volatile solute is dissolved in it.

Let T_b be the boiling temperature of the pure solvent at *1* atmosphere. At this temperature, the solution has lower vapour pressure than 1 atmosphere and hence it couldn't boil with an increase of temperature to *T* the vapour pressure of the solution rises to 1 atmosphere and the solution boils. This means that the solution has a higher boiling point than that of the pure solvent. Thus, $\Delta T_b = (T - T_b)$ (elevation in the boiling point of the solution). Points P^0 at 1 atm and *P* represents the vapour pressure of the solvent and the solution respectively .This the lowering of the vapur pressure $\Delta P = P^0 - P$.

The boiling point elevation (ΔT_b) is given by

$$\Delta T_b = (T - T_b) = K_b m \quad \text{--- 4.13}$$

Where m = molality of the solution and K_b= molal boiling point elevation constant. K_b values of common liquids are given in table 4.1.

Determination of molecular mass from ΔT_b

It is possible to calculate the molar mass of the solute as

$$\Delta T_b = K_b m = K_b \times n_2 \frac{1000}{w_1} = \frac{1000 K_b w_2}{M_2 w_1}$$

$$\Rightarrow \quad \boxed{M_2 = \frac{1000 \, K_b w_2}{\Delta T_b w_1}} \quad \text{-------------------------------------- 4.14}$$

Example 4.5. When 5.50 g of biphenyl ($C_{12}H_{10}$) is dissolved in 100.0 g of benzene, the boiling point increases by 0.903 ^{0}C. When 6.3 g of an unknown hydrocarbon is dissolved in 150.0 g of benzene, the boiling point of the solution increases by 0.597 ^{0}C. What is the molar mass of the solute?

$$M_2 = \frac{1000\,K_b w_2}{\Delta T_b w_1} \qquad n_{biph} = \frac{5.5g}{154.2g/mol} = 0.357mol$$

$$m = \frac{moles\ of\ solute}{Kg\ of\ solvent} = \frac{0.357mol}{0.1Kg} = 0.357mol/Kg$$

Therefore, we can determine the constant: K_b $\quad K_b = \dfrac{\Delta T_b}{m} = \dfrac{0.903K}{0.357mol/Kg} = 2.53K.Kg.mol^{-1}$

Now that we know the value of K_b for benzene, we can use it to determine the molar mass of the unknown solute. Given the increase in the boiling temperature, we solve for the molality of the unknown solution:

$$m = \frac{\Delta T_b}{K_b} = \frac{0.597K}{2.53K.Kg.mol^{-1}} = 0.236mol/Kg$$

From this, we can determine the number of moles of the solute (n):

$$n = m \times Kg\ of\ the\ solvent\ = 0.236mol/Kg \times 0.150Kg = 0.0354mol$$

Then, given the number of grams of solute, the molar mass is calculated as

$$M = \frac{6.3g}{0.0354mol} = 178g/mol$$

Example 4.6. The boiling point of chloroform was raised by 0.325 K when 5.145 x 10^{-4} kg of anthracene was dissolved in 35x10^{-3} kg of chloroform. Calculate the molar mass of the solute. (K_b for chloroform is 3.9 K.kg mol^{-1}).

Solution

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

$$M_2 = \frac{(3.9K.Kgmol^{-1})(5.14 \times 10^{-4}Kg) \times 1000g/Kg}{(0.325K)(35 \times 10^{-3}Kg)} = 176.26g/mol$$

Exercise 4.2. When 5.50 g of biphenyl ($C_{12}H_{10}$) is dissolved in 100.0 g of benzene, the boiling point increases by 0.903 ^{0}C. When 6.3 g of an unknown hydrocarbon is dissolved in 150.0 g of benzene, the boiling point of the solution increases by 0.597 ^{0}C. What is the molar mass of the solute?

Exercise 4.3. Calculate the molecular weight of sulfur if 35.5 grams of sulfur dissolve in 100.0 g of CS_2 to produce a solution that has a boiling point of 49.48^{o}C. Boiling point of sulfur is 46.23^{o}C

III. Freezing point depression

The freezing point of a liquid is the temperature at which the solid phase begins to separate out from the liquid. At this temperature solid and liquid phases are in equilibrium and have equal vapour pressure. A solution freezes at a temperature lower than that of the pure solvent. This is due to the lowering of the vapour pressure of a solution as a result of addition of a small amount of non-volatile solute.

Figure 5.1 shows the phase diagram of the solution and the pure solvent showing the freezing point depression. T_f corresponding to the vapour pressure P^0 is the freezing point of the pure solvent. The vapour pressure curve of the solution of a non-volatile solute will be lower than that of the pure solvent. At the sublimation curve the vapour pressure of the solution is equal to the vapour pressure of the pure solid solvent. Hence T is the freezing point of the solution and is lower than T_f.

$$\Delta T_f = T_f - T \quad \text{............................ 4.16}$$

The magnitude of ΔT_f depends on the nature of the solvent and the amount of the solute.

$$\Delta T_f = T_f - T = K_f m \quad \text{............ 4.17}$$

Where, m = molality and K_f= molal freezing point depression constant. K_f values of common liquids are given in table 4.1.

Table 4.1. Freezing Point Depression and Boiling Point Elevation of some liquids

Solvent	Formula	Melting Point (°C)	Boiling Point (°C)	K_f(°C/m)	K_b (°C/m)
Water	H_2O	0.000	100.0	1.858	0.521
Acetic acid	$HC_2H_3O_2$	16.60	118.5	3.59	3.08
Benzene	C_6H_6	5.455	80.2	5.065	2.61
Camphor	$C_{10}H_{16}O$	179.5	...	40	...
Carbon disulfide	CS_2	...	46.3	...	2.40
Cyclohexane	C_6H_{12}	6.55	80.74	20.0	2.79
Ethanol	C_2H_5OH	...	78.3	...	1.07

Determination of molecular mass from ΔT_f

It is possible to calculate molar masses of the solute from freezing point depression as

$$\Delta T_f = K_f m = K_f \times n_2 \frac{1000}{w_1} = \frac{1000 K_f w_2}{M_2 w_1}$$

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

Example 4.7. A solution of urea in water has a boiling point of 100.13 ^{0}C. Calculate the freezing point of the same solution.

Solution

$$\Delta T_b = T - T_b = K_b m \,, \Delta T_b = 100.13\,^0C - 100\,^0C = 0.521\,^0C / m \times molality$$

$$molality = \frac{0.13\,^0C}{0.521\,^0C / m} = 0.25$$

Once we know the molality we can determine the freezing point depression.

$$\Delta T_f = T_f - T = K_f m$$

$$\Delta T_f = 1.86\,^0C / m \times 0.25m = 0.465\,^0C$$

$$\Delta T_f = T - T_f \quad \Rightarrow \quad 0.465\,^0C = 0\,^0C - T \quad \Rightarrow \quad T = -0.465\,^0C$$

The freezing point of the solution is -0.465 ^0C

Example 4.8. A hydrocarbon $H_2(CH_2)_n$ is dissolved in a solvent S which freezes at 9.0 ^{0}C. A solution which contains 0.90 g of hydrocarbon per 180 g of solvent freezes at 4.48 ^{0}C. Calculate the molecular weight of the hydrocarbon. (K_f =12 K/m)

Solution

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

$$M_2 = \frac{1000 \times 12K/m \times 0.9g}{0.52K \times 180g} = 115.4 gmol^{-1}$$

IV.   Osmotic Pressure

Abbe' Nollet in 1748 observed an important colligative property known as osmotic pressure. He observed that when a solution is separated from a pure solvent by a semi permeable membrane (which allows the flow of solvent molecules only through it), there is a spontaneous flow of solvent in to a solution. By applying certain pressure to the solution osmosis can be prevented. The minimum pressure required to prevent osmosis is known as the *osmotic pressure*.

As can be seen in figure 4.2 below we have a liquid partitioned in two volumes. The two volumes are separated by a membrane that will let the solvent through, but not the solute (could have done it the other way around as well). To one side we add some solute; the other side is pure solvent. The side with the solute has a lower chemical potential. Thus, solvent from the pure solvent side will migrate through the membrane towards the side that has a lower chemical potential. The osmotic pressure is defined as the amount of pressure (in addition to atmospheric pressure) that one would have to apply to the side that has the solute in it in order to keep more solvent from going over to that side. Again, by balancing the chemical potentials, one can derive the equation as follows.
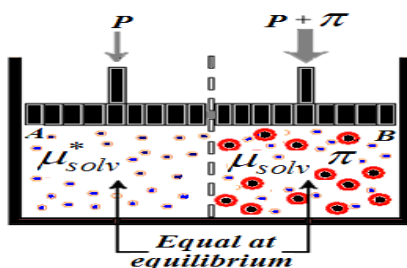
Figure 4.2. The osmotic pressure of a solution partitioned by a membrane from the pure solvent.

Osmotic Pressure is the pressure that would be applied to a solution to stop the passage through a semi permeable membrane of solvent molecules from the pure solvent. When a solution containing n (moles) of solute in a volume V (L) is in contact with the pure solvent at a temperature of T (K) and gas constant R (0.082 atm L K-1 mol-1), the osmotic pressure is given by:

$$\pi V = nRT \qquad \text{and} \qquad \pi = \frac{nRT}{V} \qquad \text{where n/v = Molarity}$$

$$\pi = MRT$$

Determination of molecular mass from π

It is possible to calculate molar masses of the solute from freezing point depression as

$$\pi = C_2 RT = \frac{n_2}{V} RT = \frac{w_2}{M_2 V} RT$$

$$M_2 = \frac{w_2}{V\pi} RT$$

Example 4.9. An aqueous solution contains $20 \times 10^{-3} kg$ of glucose per dm^3. Assuming the solution to be ideal, calculate its osmotic pressure at 298k.

$$\pi v = nRT$$

$$\pi = \frac{n}{V} RT \qquad \text{and} \qquad n = \frac{20 \times 10^{-3} Kg}{180 \times 10^{-3} \, Kg/_{mol}} = 1/9 \, mol$$

$$\text{Hence } \pi = \frac{1/9 \, mol}{1 \, dm^3} (0.0821 \, dm^3 atm.K^{-1} mol^{-1})(298K) = 2.718 \, atm$$

Example 4.10. 20 g of a substance were dissolved in 500 ml of water and the osmotic pressure of the solution was found to be 600 mm Hg at 15 ^{0}C. Determine the molecular weight of the substance

$$M_2 = \frac{w_2}{V\pi} RT$$

$$M_2 = \frac{20g}{0.5 \, lit \times 600 \, mmHg} (0.0821 \, lit.atm.K^{-1} mol^{-1})(288K) \times (760 \, mmHg / 1 \, atm)$$

$$= 1198 \, g / mol$$