9 DILUTE SOLUTIONS : COLLIGATIVE PROPERTIES

In the previous chapter we discussed the properties of solutions in general. If the concentration of the solute in a solution is very low, the solution is called a dilute solution. Four properties of dilute solutions are so intimately connected with each other that they are grouped together and are commonly known as the *'colligative properties'* (*colligative* means "tied together"). These four properties are:

(i) Lowering of vapour pressure,

(ii) Elevation of boiling point,

(iii) Depression of freezing point and

(iv) Osmotic pressure.

All the four properties depend *only on the number of particles* (*molecules or ions*) in a solution, but they are independent of molecular structure. A litre of solution containing one mole of sodium chloride contains twice the number of particles if one mole of sugar molecules dissolved in the same volume of solution. This is because each sodium chloride unit gives two particles, one Na^+ ion and one Cl^- ion, and the above solution will contain two moles of particles. The property of the sodium chloride solution will, therefore, be twice the value of the same property of a solution of sugar of the same concentration. A solution of urea (RMM = 60) has the same value of the properties as that of a solution of sucrose (RMM = 342) of the same concentration in mol L^{-1}. Pressure exerted by a gas is also independent of molecular structure and so the gas pressure or volume should be termed as colligative properties. However, colligative properties have almost universally been associated with dilute solutions.

The properties are quantitatively expressed in the form of certain laws, the validity of which is restricted to dilute solutions. One use of the study of these properties is that the molecular mass of solutes may be determined from measurements of any one of them with the help of these laws.

9.1 Lowering of Vapour Pressure

If a non-volatile and non-electrolyte solute like sucrose, glucose or urea is dissolved in a solvent like water the vapour pressure of the solution is found to be lower than that of pure water. The magnitude of the lowering of vapour pressure is dependent on the concentration of the solute in solution. Although attempts had been made to relate vapour pressure lowering quantitatively to concentration since the days of Berthollet and

Faraday, the credit for stating the correct relationship goes to F.M. Raoult (1837-1888). He stated that *the relative lowering of vapour pressure of a solvent due to the addition of a non-volatile and non-electrolyte solute is equal to the mole fraction of the solute in the solution.* This statement, which is known as *Raoult's law*, is an important generalization in Physical Chemistry and is fundamental to the study of solutions.

Relative lowering is defined as the ratio of the difference of vapour pressures of the pure solvent and the solution to the vapour pressure of the pure solvent. The mole fraction of the solute on the other hand is the ratio of the number of moles of the solute to the total number of moles in solution. If p^0 and p are vapour pressures of the solvent and the solution respectively, the lowering of vapour pressure is $(p^0 - p)$, and relative lowering of vapour pressure is $(p^0 - p) / p^0$. In a solution containing, n moles of solute in N moles of solvent the mole fraction of the solute is $n/(N + n)$. Then according to Raoult's law,

$$\frac{p^0 - p}{p^0} = \frac{n}{N + n} = x_2 \tag{9.1}$$

where x_2 is the mole fraction of the solute. Experimental supports in favour of the law have been obtained by various investigators. The law is, however, valid only for dilute solutions of solutes which do not undergo association or dissociation in the dissolved state.

Equation (9.1) may be written in the form

$$1 - \frac{p^0 - p}{p^0} = 1 - x_2 \tag{9.2}$$

which reduces to $\frac{p}{p^0} = x_1$, or $p = p^0 . x_1$ (9.3)

where x_1 is the mole fraction of the solvent. Thus the vapour pressure of the solution is directly proportional to the mole fraction of the solvent. This is considered as an alternative way of stating Raoult's law. When both the components of a binary ideal solution are volatile, Raoult's law is applicable to both the components. If p_A and p_B are the partial vapour pressures of the components A and B in a solution, then according to Raoult's law

$$p_A = x_A p_A^0 \quad \text{and} \quad p_B = x_B p_B^0$$

where x_A and x_B are the mole fractions of A and B respectively in the solution and p_A^0 *and* p_B^0 are the vapour pressures of pure liquids A and B. The total vapour pressure p of the ideal solution containing components A and B is equal to

$$p = p_A + p_B = x_A p_A^0 + x_B p_B^0 \tag{9.4}$$

9.2 Ideal Solution

As mentioned in *Section 8.2 a solution is said to be ideal when it obeys Raoult's law over all compositions and at all temperatures.* Such a solution is formed from its components without heat being given out or absorbed ($\Delta H=0$) and the solution process is not accompanied by any volume change ($\Delta V=0$). It follows from Raoult's law that if the solution is ideal the escaping tendency of each component will be proportional to the mole fraction of that component in the solution. From the molecular point of view one can say that in an ideal solution of *A* and *B* the intermolecular forces between *A* and *A* molecules, *A* and *B* molecules, and *B* and *B* molecules are the same and the escaping tendency of the *A* molecules will be the same whether these are surrounded by other *A* molecules, or *B* molecules or partly by *A* and partly by *B* molecules. If there is interaction the solution will deviate from ideal behaviour. In reality there are very few solutions which obey Raoult's law strictly, i.e., behave ideally; but the more dilute a solution is, the more nearly does it approach ideality. When the solution is infinitely dilute it is expected to be ideal.

9.3 Molecular Mass from Lowering of Vapour Pressure

For a dilute solution $n/(N + n)$ in equation (9.1) may be replaced by n/N as n is negligible in comparison to N. Equation (9.1) may, therefore, be written as

$$\frac{p^0 - p}{p^0} = \frac{n}{N} \tag{9.5}$$

If w_2 *g* of a solute of molecular mass M_2 be present in w_1 *g* of solvent of molecular mass M_1, then

$$\frac{n}{N} = \frac{w_2/M_2}{w_1/M_1} \tag{9.6}$$

and equation (9.5) becomes

$$\frac{p^0 - p}{p^0} = \frac{w_2/M_2}{w_1/M_1} \tag{9.7}$$

By measuring p^0 and p for a solution of known concentration M_2 may be obtained.

Example 9.1: What will be the vapour pressure exerted by an aqueous solution containing 0.5 mole of a substance in 1000 *g* of water at 20.0°C if the vapour pressure of water at the working temperature is 17.574 mm Hg ?

Solution: From equation (9.1) $\dfrac{p^0 - p}{p^0} = x_2$

Or $p^0 - p = (17.574)\dfrac{0.5}{0.5 + 1000/18}$

and $p = 17.574 - 0.157 = 17.417$ mm Hg

(RMM of H_2O = 18)

Since the concentration of the solution is known the molecular mass of the solute is easily calculated. If temperature control is good and this experiment is carried out carefully, the method is capable of giving results of high accuracy. The method is simple and inexpensive. If water is used as the solvent, the absorption tube may be filled with fused anhydrous calcium chloride. The last tube should be guarded against moisture absorption from the atmosphere. If organic solvents are used, as often is the case, the absorption tubes are dispensed with and the results can be obtained by weighing the tubes, *A* and *B*. The current of gas should be passed slowly otherwise fine stream of liquid drops may escape with the gas. The total volume of the gas passed should be large so that appreciable loss in mass in the two bulbs may occur.

Example 9: Dry air was passed first through a set of bulbs containing a solution of 3.458 *g* of a substance in 100 *g* of ethanol and then through a series of bulbs containing pure ethanol. The first set of the bulbs underwent a loss of 0.9675 *g* and the latter series a loss of 0.0255 *g*. Calculate the molecular mass of the solute.

Solution: Total loss of solvent = 0.9675 + 0.0255 = 0.9930 *g*. From equation (9.10) we get,

$$\frac{p^0 - p}{p^0} = \frac{0.0255}{0.9930}$$

Now $$\frac{p^0 - p}{p^0} = \frac{w_2/M_2}{w_1/M_1}$$ [from equation (9.7)]

Or $$\frac{0.0255}{0.9930} = \frac{3.458 \times 46}{M_2 \times 100}$$

And $$M_2 = \frac{3.458 \times 46 \times 0.9930}{100 \times 0.0255} = 62$$

(RMM of ethanol = 46)

9.6 Elevation of Boiling Point

The boiling point of a liquid is defined as *the temperature at which the vapour pressure is equal to the atmospheric pressure*. As the vapour pressure of a solution is less than that of the solvent, the vapour pressure of the solution will become equal to the atmospheric pressure at a higher temperature. In other words, the boiling point of the solution will be higher than that of the solvent. The vapour pressure-temperature diagrams of pure solvent and solution (Figure 9.3) clearly explain the elevation of boiling point of the solution as compared with that of the pure solvent.

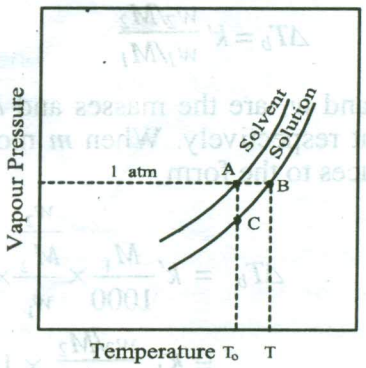

Figure 9.3 Vapour pressure vs temperature curves

The dotted horizontal line corresponds to 1.0 atm pressure. It intersects the vapour pressure curves at points corresponding to temperatures, T_o and T. It is seen that the boiling point, T, of the solution is higher (elevated) than the boiling point, T_o, of the solvent. Thus the elevation of boiling point of a solution is a direct consequence of the lowering of vapour pressure on addition of solute.

Experimental results on the elevation of boiling point by solutes were summarized in the form of the following laws which are generally called Raoult's laws of elevation of boiling point:

(i) *The elevation of the boiling point of solution is proportional to its molal concentration, i.e., to its molality, m.*

Or $\Delta T_b = K_b \cdot m$ [where $\Delta T_b = (T - T_o)$] (9.11)

(ii) *Equimolecular quantities of different substances dissolved in the same quantity of a particular solvent raise its boiling point to the same extent.*

The relation between ΔT_b and m may be easily deduced with the help of Figure 9.3. The distance AB corresponds to ΔT_b. Since the solution is assumed to be dilute the decrease in vapour pressure and boiling point elevation will be very small. The vapour pressure curves for the solution and solvent may be considered to be parallel near the boiling temperature. The ratio AB/AC may, therefore, be taken to be constant for such solutions. Now AC is equivalent to the lowering of vapour pressure, $p^o - p$, at temperature, T_o. Hence one may write,

$$\frac{AB}{AC} = \frac{\Delta T_b}{p^0 - p} = constant,\ k \tag{9.12}$$

Using equation (9.3) and remembering that p^0 is constant and $1 - x_1 = x_2$ one obtains,

$$\begin{aligned} \Delta T_b = (p^o - p)k &= (p^o - p^o . x_1)k \\ &= p^o (1 - x_1)k \\ &= k'.x_2 \end{aligned} \tag{9.13}$$

The constant of proportionality $k'(= p^0 . k)$ does not depend in any way on the nature of the solute. For a dilute solution the approximate form of x_2, as in equation (9.5), may be used and one obtains,

$$\Delta T_b = k' \frac{w_2/M_2}{w_1/M_1} \tag{9.14}$$

where w_2 and w_1 are the masses and M_2 and M_1 are the molecular masses of the solute and solvent respectively. When m moles are present in 1000 g of the solvent equation (9.14) reduces to the form

$$\Delta T_b = k' \frac{M_1}{1000} \times \frac{\frac{w_2}{M_2}}{w_1} \times 1000 \tag{9.15}$$

$$= K_b . \frac{w_2/M_2}{w_1} \times 1000 \tag{9.16}$$

$$= K_b . m$$

where $K_b = k'\dfrac{M_1}{1000}$ is a constant for a given solvent and is known as the *molal boiling point elevation constant* or the *molal ebullioscopic constant*. For a solution of unit molality $K_b = \Delta T_b$. The molal boiling point elevation of a liquid may then be defined *'as the elevation of boiling point when the concentration of the solution is 1 molal.*

9.7 Thermodynamic Derivation of Boiling Point Elevation

Equation (9.16) may be derived thermodynamically which will allow independent calculation of K_b from the known properties of the solvent. The Clapeyron-Clausius equation in the integrated form is written as,

$$ln\ \frac{p}{p^0} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{9.17}$$

Equation (9.17) may be used for the calculation of K_b. In applying this relation to the vapour pressures of solution between the boiling point T_o of solvent and T of solution it should be noted (Figure 9.3) that the vapour pressure of the solution is p at T_o and p^o at T, where p and p^o are the vapour pressures of the solvent and solution respectively at T_o. Hence from equation (9.17)

$$ln\frac{p}{p^0} = -\frac{\Delta H_{ev}}{R}\left[\frac{1}{T_0} - \frac{1}{T}\right] \tag{9.18}$$

$$= -\frac{\Delta H_{ev}}{R}\left[\frac{T - T_0}{TT_0}\right] = -\frac{\Delta H_{ev}}{R} \times \frac{\Delta T_b}{T_0^2} \tag{9.19}$$

since T and T_o are not very different and ΔH may be taken as constant over this temperature range. Again, $p/p_o = x_1$ according to Raoult's law where x_1 is the mole fraction of the solvent; but $x_1 = (1 - x_2)$, where x_2 is the mole fraction of the solute. Hence equation (9.19) takes the form

$$ln\,(1 - x_2) = -\frac{\Delta H_{ev}}{R} \times \frac{\Delta T_b}{T_0^2} \tag{9.20}$$

For a dilute solution x_2 is small compared to unity and

$$ln\,(1 - x_2) \approx -x_2$$

so that

$$\frac{\Delta H_{ev}}{R} \times \frac{\Delta T_b}{T_0^2} = x_2 \tag{9.21}$$

or

$$\Delta T_b = \frac{RT_o^2}{\Delta H_{ev}} \cdot x_2 \tag{9.22}$$

On further simplification equation (9.22) reduces to

$$\Delta T_b = \left(\frac{RT_0^2}{\frac{\Delta H_{ev}}{M_1} \times 1000}\right) \times \frac{w_2 / M_2}{w_1} \times 1000 \quad (9.23)$$

$$= K_b . \frac{w_2/M_2}{w_1} \times 1000 \quad (9.24)$$

$$= K_b . m \quad (9.25)$$

where $K_b = \dfrac{RT_0^2}{\frac{\Delta H_{ev}}{M_1} \times 1000}$

Since all the quantities within the bracket on the right hand side of equation (9.23) are constants for a particular solvent, K_b is independent of the nature of the solute. This is the Raoult's law of boiling point elevation.

In the case of water as solvent,

$T_o = 373.16$ K, $\Delta H_{ev} = 2255.18$ J g^{-1},

R = 8.314 J K^{-1}mol^{-1} and hence

$$K_b = \frac{8.314 \times (373.16)^2}{2255.18 \times 1000} = 0.513 \text{ K kg mol}^{-1}$$

Thus K_b may be calculated for a given solvent from its latent heat of vaporization and boiling point.

The observed and calculated values of K_b of some solvents are given in Table 9.1. The agreement between the values is satisfactory in most cases.

Table 9.1 Ebullioscopic and cryoscopic constants

Solvent	K_b (K kg mol^{-1})	K_f (K kg mol^{-1})
Acetic acid	3.09	3.90
Benzene	2.53	5.12
CCl_4	5.02	30.00
Cyclohexane	----	20.20
CS_2	2.37	3.80
Naphthalene	5.80	6.94
Phenol	3.04	7.27
Water	0.513	1.86

Since the boiling point of a liquid changes with atmospheric pressure and ΔH_{ev} may also change, the value of K_b is likely to be different at different atmospheric pressures. For concentrated solutions the derivations are not valid as the assumptions made are not justified

Substituting these data in equation (9.16) we get,

$$0.40 = 5.02 \times \frac{0.35}{40 \times M_2} \times 1000$$

$$M_2 = \frac{5.02 \times 0.35 \times 1000}{0.40 \times 40}$$

Or $M_2 = 111.0$

9.9 Depression of Freezing Point

The freezing point of a liquid is *defined as the temperature at which the liquid and solid forms are in equilibrium* and the *freezing point of a* ***solution*** *is the temperature at which the solution is in equilibrium with the pure crystalline solvent.* The depression of freezing point of a liquid by the addition of a non-volatile and non-electrolytic solute may be discussed more conveniently with the help of vapour pressure-temperature curves as in Figure 9.7. The vapour pressure curves of liquid solvent and solid solvent meet at *A*. Hence this corresponds to the freezing point T_o of the solvent. *D* corresponds to the freezing point *T* of the solution as this is the temperature at which the solution and solid solvent have the same vapour pressure. It is clear that *T* is lower than T_o and the freezing points of solutions will always be lower than those of pure solvent as the vapour pressure curves for the former lie below that for the latter.

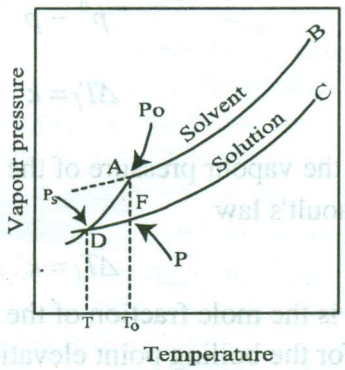

Figure 9.7 Depression of freezing point

A quantitative relationship between the concentration of solute in solution and the depression of freezing point was given by F.M. Raoult (1878–86) in the form of two laws which are generally known as Raoult's laws of depression of freezing point.

(i) *The depression of freezing point of a solvent due to the addition of a solute is proportional to the molality, m, of the solution.* Expressed mathematically

$$\Delta T_f = K_f . m \qquad (9.25)$$

where K_f is a constant known as the *molal depression of freezing point constant* or *cryoscopic constant.*

(ii) *Equimolecular quantities of different substances dissolved in the same quantity of the same solvent lower the freezing point to the same extent.*

It may be noted that these laws are similar to the laws of boiling point elevation and have the same limitations as those, *i.e.*, these are applicable to dilute solutions of non-volatile non-electrolytes, which do not undergo association or dissociation in solution. An additional condition is that during freezing only pure solvent should separate as the solid phase.

Substituting these data in equation (9.16) we get,

$$0.40 = 5.02 \times \frac{0.35}{40 \times M_2} \times 1000$$

$$M_2 = \frac{5.02 \times 0.35 \times 1000}{0.40 \times 40}$$

Or $M_2 = 111.0$

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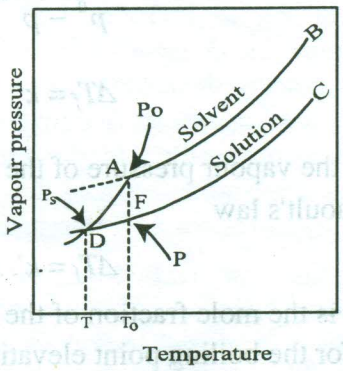

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Solution: 20 *mL* of benzene has mass = (20 × 0.877) *g* = 17.57 *g*

Then from equation (9.29) we get,

Or $$M = \frac{5.12 \times 0.565 \times 1000}{17.57 \times 0.355}$$

$$= 46.3$$

Example 9.6: Calculate the freezing point of a 0.050 molal solution of a non-volatile compound that does not associate or dissociate in cyclohexane. T_f^0 (cyclohexane) = 6.5°C and K_f = 20.0 K kg mol^{-1}.

Solution: We know from equation (9.38) that,

$$\Delta T_f = K_f.m = 20.0 \times 0.050 = 1.0\ ^\circ C$$

Or, $$T_f = T_f^0 - \Delta T_f = 5.5\ ^\circ C.$$

9.12 Osmosis and Osmotic Pressure

We know that a gas or vapour spreads out from a region of high pressure to a region of low pressure. Similarly, if a concentrated solution and a dilute solution of the same solute are placed together in the same container the solute particles move from the concentrated solution into the dilute solution. These spreading out of gases or solutes in solution is spontaneous, and continue till the mixtures are homogeneous. The process is known as *diffusion (Section 2.10)*. This migration of the gas molecules or solute particles is caused by translational motion of the molecules/particles. If, however, a solution is separated from the solvent (or a dilute solution is separated from a concentrated solution) by a *semi-permeable membrane* a reverse process will take place in which only the solvent molecules migrate through the membrane but not the solute molecules. This is shown in Figure 9.10.

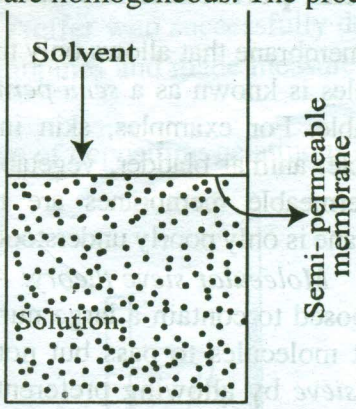

Figure 9.10 Osmosis

Due to difference in concentration the solvent molecules will go on migrating through the semi-permeable membrane unless it is prevented by external forces to do so. *This phenomenon of selective migration of the solvent molecules through the separating semi-permeable membrane to the solution is called osmosis.* As a result of osmosis the solute concentration on either side of the membrane becomes equal at equilibrium. Due to spontaneous inflow of the solvent through the membrane to the solution side, a pressure is developed in the solution side. This continues to increase as long as the solvent flows. However, the inflow of the solvent can be stopped from the beginning by application of

an appropriate external pressure to the solution side. For equilibrium the external pressure must be equal to the pressure developed by osmosis. This external pressure is denoted by P, as in Figure 9.11.

defn *The osmotic pressure may, therefore, be defined as the external pressure that must be applied on the solution side to just prevent the inflow of the solvent through the semi-permeable membrane which separates the solvent and solution.* In this case the pressure,

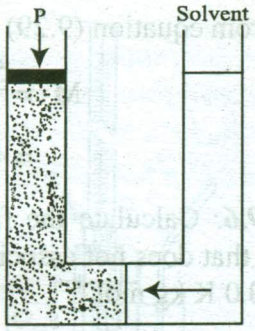

Figure 9.11 Osmotic pressure

P, shall be equal to the osmotic pressure. If the semi-permeable membrane separates two solutions of different concentrations then also the solvent from the lower concentration side will flow to the higher concentration side. Thus concentration difference is the cause of osmotic pressure. Osmotic pressure is a colligative property.

It must be clearly understood that during diffusion migration of solvent molecules take place in both directions. But in osmosis the solvent molecules migrate in one direction only.

9.13 Semi-permeable Membrane

A membrane that allows only the solvent molecules to pass through it, but not the solute molecules is known as a *semi-permeable membrane*. Natural membranes are mostly semi-permeable. For examples, skin inside the egg shell, membranes around the red blood corpuscle, animal bladder, vegetable tissue are all semi-permeable. A variety of synthetic semi-permeable membranes are now available. The mechanism of the action of the membrane is only poorly understood. A brief discussion of the existing concept follows.

(i) *Molecular sieve theory:* According to this theory the semi-permeable membrane is supposed to contain a large number of extremely minute pores which allow the small solvent molecules to pass but not the solute molecules. The membrane, therefore, acts like a *sieve* by allowing preferential migration of the solvent. However, the *molecular sieve theory* is not satisfactory, because cases are known where the solute molecules are smaller than the solvent molecules and yet only the solvent molecules pass through the membrane.

(ii) Membrane solution theory: Membrane solution theory envisages that the membrane contains protein bearing functional groups such as, –COOH, –OH, –NH etc., which 'dissolves' water molecules by hydrogen bonding or chemical interaction. As a result the solvent molecules pass on to the solution side. Since solute particles are not dissolved in the membrane these cannot pass through. This theory can explain a number of facts but again is found to be unsatisfactory in many cases.

(ii) *Dynamic osmometer:* In this case the flow of solvent through the membrane is prevented by the application of appropriate pressure to the solution side.

A simple form of *static osmometer* is illustrated in Figure 9.14. The solution under investigation is taken in the inner bulb which carries at one end the semi permeable membrane like cellophane. The other end of the bulb is attached to a graduated capillary tube. This bulb is placed inside a wider vessel which contains the solvent. The solvent passes into the solution and causes the liquid to rise until an equilibrium height, *h*, is attained. After incorporating necessary corrections the osmotic pressure is calculated.

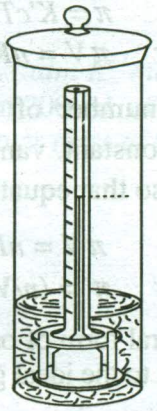

Figure 9.14 A modern osmometer

Dynamic osmometer, like vapour phase osmometer, is particularly used for the determination of molar mass of high molecular mass polymers or macromolecules.

9.15 Van't Hoff's Laws of Osmotic Pressure

Quantitative relations between the concentration of the solution and the osmotic pressure were first derived by van't Hoff in1886. These are known as *van't Hoff's laws of osmotic pressure.*

First law: *The osmotic pressure (π) of a solution is directly proportional to the molar concentration of the solute at constant temperature.* Mathematically,

$$\pi \propto c \qquad (T = \text{constant}) \tag{9.39}$$

$$\text{or} \quad \pi \propto \frac{1}{V} \quad (\text{since } c = \frac{1}{V}) \tag{9.39a}$$

$$\text{and} \quad \pi V = constant \tag{9.40}$$

where c is the concentration of the solution in mol L^{-1} and V is the volume containing one mole of the solute. Equation (9.40) is similar to Boyle's law for gas pressure.

Second law: *The osmotic pressure of a solution of given concentration varies directly as the temperature in Kelvin (K).* Expressed mathematically,

$$\pi \propto T \qquad (c = \text{constant}) \tag{9.41}$$

$$\text{or} \quad \pi = KT \tag{9.42}$$

Equation (9.42) is similar to Charles' law for gas pressure.

Third law: *Equimolecular quantities of different solutes dissolved in such volumes of the solvent as to give the same volume of the solution have the same osmotic pressure at the same temperature.*

Laws of variation are used to combine of equations (9.39) and (9.41) to give equation (9.43).

$$\pi = K'cT$$

$$\text{or} \quad \pi V = nK'T \tag{9.43}$$

where n is the number of moles of the solute in V L of the solution and K' is the proportionality constant. van't Hoff also found that K' has the same value as the universal gas constant, R, so that equation (9.43) may be written as

$$\pi V = nRT \tag{9.44}$$

$$\text{or} \quad \pi = (n/V)RT = cRT \tag{9.44a}$$

which is the general form of osmotic pressure equation. Thus, the osmotic pressure equation is exactly analogous to the ideal gas equation including the numerical value of the constant R.

Example 9.7: What will be the osmotic pressure exerted by 100 mL of an aqueous solution containing 1.00 g of glucose at 27°C?

Solution: 1.00 g glucose is present in 100 mL solution.

So, the molar concentration, $c = \dfrac{1.00 \times 1000}{180 \times 100}$, (molar mass of glucose is 180)

Substituting the values in the equation $\pi = cRT$ we get,

$$\pi = \frac{1000 \times 0.082 \times 300}{180 \times 100} = 1.36 \text{ atm (unit of } R \text{ is } L\text{-}atm\ K^{-1}mol^{-1})$$

9.16 Determination of Molecular Mass from Osmotic Pressure Measurements

Like the other colligative properties, osmotic pressure measurements are extensively used for the determination of molecular masses of substances. If the number of moles in a solution of volume V litres is n then equation (9.44) takes the form

$$\pi V = n\,RT = \frac{w}{M}RT \tag{9.45}$$

where w is the mass of the solute and M its molecular mass. This equation readily gives a method of calculating molecular masses of solutes in solution. Equation (9.45) may also be written as,

$$\pi = cRT \tag{9.46}$$

where c is the molar concentration. This is the same as equation (9.44a).

Example 9.8: The molecular mass of an enzyme is 25,000. How much of the substance is present in 100 mL of a solution which has an osmotic pressure of 157.0 mm of H_2O at 25°C?

Solution: From (9.45), $\pi V = \dfrac{w}{M}RT$, or $w = \dfrac{M\pi V}{RT}$

Now 157.0 mm of H_2O is equivalent to 157.0/13.6 = 11.55 mm Hg since the density of mercury is = 13.6 g $(mL)^{-1}$