

15

Theory of Dilute Solutions

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COLLIGATIVE PROPERTIES OF ELECTROLYTES

ABNORMAL MOLECULAR MASSES OF ELECTROLYTES



In this chapter we will restrict our discussion to solutions in which a solid is dissolved in a liquid. The solid is referred to as the **solute** and the liquid as the **solvent**.

COLLIGATIVE PROPERTIES

Dilute solutions containing non-volatile solute exhibit the following properties :

- (1) Lowering of the Vapour Pressure
- (2) Elevation of the Boiling Point
- (3) Depression of the Freezing Point
- (4) Osmotic Pressure

The essential feature of these properties is that they depend *only* on the number of solute particles present in solution. Being closely related to each other through a common explanation, these have been grouped together under the class name **Colligative Properties** (Greek *colligatus* = Collected together).

A colligative property may be defined as one which depends on the number of particles in solution and not in any way on the size or chemical nature of the particles.

Consequent to the above definition, each colligative property is exactly related to any other. Thus if one property is

measured, the other can be calculated. The colligative properties of dilute solutions are particularly important as these provide valuable methods for finding the molecular weights of the dissolved substances.

LOWERING OF VAPOUR PRESSURE : RAOULT'S LAW

The vapour pressure of a pure solvent is decreased when a non-volatile solute is dissolved in it. If p is the vapour pressure of the solvent and p_s that of the solution, the lowering of vapour pressure is $(p - p_s)$. This lowering of vapour pressure relative to the vapour pressure of the pure solvent is termed the **Relative lowering of Vapour pressure**. Thus,

$$\text{Relative Lowering of Vapour Pressure} = \frac{p - p_s}{p}$$

As a result of extensive experimentation, Raoult (1886) gave an empirical relation connecting the relative lowering of vapour pressure and the concentration of the solute in solution. This is now referred to as the **Raoult's Law**. It states that : **the relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution.**

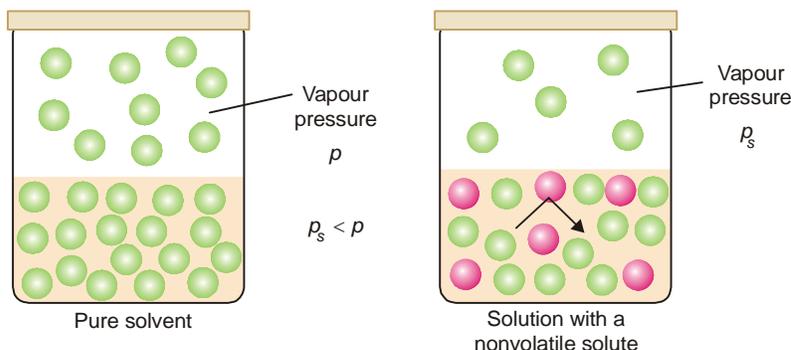
Raoult's Law can be expressed mathematically in the form :

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

where n = number of moles or molecules of solute
 N = number of moles or molecules of solvent.

Derivation of Raoult's Law

The vapour pressure of the pure solvent is caused by the number of molecules evaporating from its surface. When a nonvolatile solute is dissolved in solution, the presence of solute molecules in the surface blocks a fraction of the surface where no evaporation can take place.



■ **Figure 15.1**

Lowering of vapour pressure by a nonvolatile solute. The particles of the solute block the escape of solvent molecules from the surface of the solution.

This causes the lowering of the vapour pressure. The vapour pressure of the solution is, therefore, determined by the number of molecules of the solvent present at any time in the surface which is proportional to the mole fraction. That is,

$$p_s \propto \frac{N}{n + N}$$

where N = moles of solvent and n = moles of solute.

$$\text{or } p_s = k \frac{N}{n + N} \quad \dots(1)$$

k being proportionality factor.

In case of pure solvent $n = 0$ and hence

$$\text{Mole fraction of solvent} = \frac{N}{n + N} = \frac{N}{0 + N} = 1$$

Now from equation (1), the vapour pressure $p = k$

Therefore the equation (1) assumes the form

$$p_s = p \frac{N}{n + N}$$

or

$$\frac{p_s}{p} = \frac{N}{n + N}$$

$$1 - \frac{p_s}{p} = 1 - \frac{N}{n + N}$$

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

This is Raoult's Law.

SOLVED PROBLEM. Calculate the vapour pressure lowering caused by the addition of 100 g of sucrose (mol mass = 342) to 1000 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

SOLUTION

Using Raoult's Law Equation

$$\frac{p - p_s}{p} = \frac{\Delta p}{p} = \frac{n}{n + N} \quad \dots(1)$$

where

Δp = lowering of vapour pressure

p = vapour pressure of water = 23.8 mm Hg

n = moles of sucrose = $\frac{100}{342} = 0.292$ mole

N = moles of water = $\frac{1000}{18} = 55.5$ moles

Substituting values in equation (1)

$$\frac{\Delta p}{23.8} = \frac{0.292}{0.292 + 55.5}$$

$$\Delta p = 23.8 \times \frac{0.292}{55.792} = \mathbf{0.125 \text{ mm}}$$

Thus the lowering of vapour pressure = **0.125 mm Hg**

Ideal Solutions and Deviations from Raoult's Law

A solution which obeys Raoult's law strictly is called an **Ideal solution**. A solution which shows deviations from Raoult's law is called a **Nonideal** or **Real solution**.

Suppose the molecules of the solvent and solute are represented by A and B respectively. Now let γ_{AB} be the attractive force between A and B, and γ_{AA} between A and A. If

$$\gamma_{AB} = \gamma_{AA}$$

the solution will show the same vapour pressure as predicted by Raoult's law and it is an ideal

solution. However, if

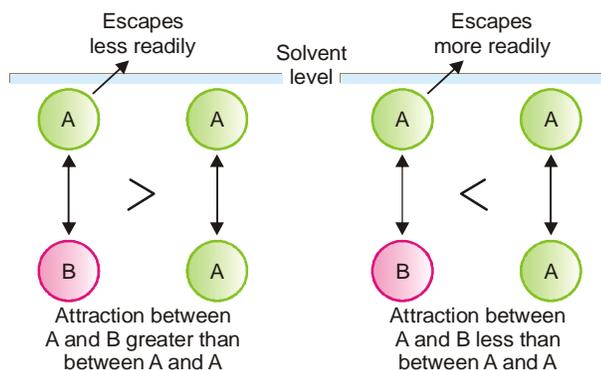
$$\gamma_{AB} > \gamma_{AA}$$

molecule A will escape less readily and the vapour pressure will be less than that predicted by Raoult's law (**Negative deviation**). On the other hand, if

$$\gamma_{AB} < \gamma_{AA}$$

A molecule will escape from the solution surface more readily and the vapour pressure of the solution will be higher than predicted by Raoult's law (**Positive deviation**).

In very dilute solutions of nonelectrolytes, the solvent and solute molecules are very much alike in both molecular size and molecular attractions. Thus such solutions tend to approach the ideal behaviour and obey Raoult's law fairly accurately.



■ **Figure 15.2**
Negative deviation and Positive deviation.

Determination of Molecular Mass from Vapour Pressure Lowering

The molecular mass of a nonvolatile solute can be determined by measuring the lowering of vapour pressure ($p - p_s$) produced by dissolving a known weight of it in a known weight of the solvent.

If in a determination w grams of solute is dissolved in W grams of the solvent, m and M are molecular masses of the solute and solvent respectively, we have :

$$\text{No. of Moles of solute } (n) = \frac{w}{m}$$

$$\text{No. of Moles of solvent } (N) = \frac{W}{M}$$

Substituting these values in the Raoult's law Equation,

$$\frac{p - p_s}{P} = \frac{n}{n + N} \quad \dots(\text{Raoult's Law Eq.})$$

$$\frac{p - p_s}{P} = \frac{w/m}{w/m + W/M} \quad \dots(1)$$

Since for very dilute solution, the number of moles (molecules) of solute (w/m), is very small, it can be neglected in the denominator. The equation (1) can now be written as

$$\frac{p - p_s}{P} = \frac{wM}{mW} \quad \dots(2)$$

Knowing the experimental value of $p - p_s/p$, and the molecular mass of the solvent (M), the molecular weight of solute (m) can be calculated from (1) or (2).

SOLVED PROBLEM 1. The vapour pressure of ether (mol mass = 74) is 442 mm Hg at 293 K. If 3g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426 mm Hg. Calculate the molecular mass of A. Assume that the solution of A in ether is very dilute.

SOLUTION

Here the approximate form of the Raoult's law Equation will be used.

$$\frac{p - p_s}{p} = \frac{w}{m} = \frac{wM}{mW} \quad \dots(1)$$

In this case :

w , the mass of solute (A)	= 3 g
W , the mass of solvent (ether)	= 50 g
m , the mol mass of solute A	= ?
M , the mol mass of solvent (ether)	= 74
p , the vapour pressure of solvent (ether)	= 442 mm
p_s , the vapour pressure of solution	= 426 mm

Substituting the values in equation (1),

$$\frac{442 - 426}{442} = \frac{3 \times 74}{m \times 50} \text{ or } m = \frac{3 \times 74 \times 442}{50 \times 16}$$

Hence $m = 122.6$

Thus **the molecular weight of A is 123**

SOLVED PROBLEM 2. 18.2 g of urea is dissolved in 100 g of water at 50°C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50°C is 92 mm Hg.

SOLUTION

Since the solution is not very dilute, the complete Raoult's Law Equation applied is

$$\frac{p - p_s}{p} = \frac{w/m}{W/M + w/m} \quad \dots(1)$$

In this case :

w , the mass of solute (urea)	= 18.2 g
W , the mass of solvent (water)	= 100 g
m , the mol mass of solute (urea)	= ?
M , the mol mass of solvent (water)	= 18
$p - p_s$, the lowering of vapour pressure	= 5 mm
p , the vapour pressure of solvent (water)	= 92 mm

Substituting these values in equation (1),

$$\frac{5}{92} = \frac{18.2/m}{18.2/m + 100/18}$$

Hence m , the molecular mass of urea = **57.05**

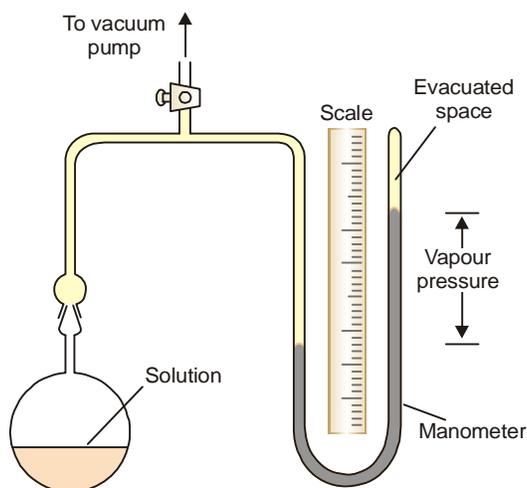
MEASUREMENT OF LOWERING OF VAPOUR PRESSURE

(1) Barometric Method

Raoult measured the individual vapour pressure of a liquid and then the solution by this method. He introduced the liquid or the solution into Toricellian vacuum of a barometer tube and measured the depression of the mercury level. This method is neither practicable nor accurate as the lowering of vapour pressure is too small.

(2) Manometric Method

The vapour pressure of a liquid or solution can be conveniently measured with the help of a manometer (see Fig. 15.3). The bulb *B* is charged with the liquid or solution. The air in the connecting tube is then removed with a vacuum pump. When the stopcock is closed, the pressure inside is due only to the vapour evaporating from the solution or liquid. This method is generally used for aqueous solutions. The manometric liquid can be mercury or *n*-butyl phthalate which has low density and low volatility.



■ **Figure 15.3**
Measurement of vapour pressure of aqueous solutions with a manometer.

(3) Ostwald and Walker's Dynamic Method (*Gas Saturation Method*)

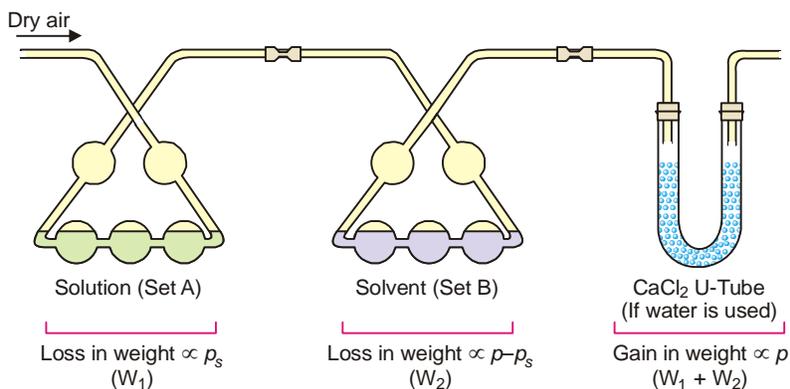
In this method the relative lowering of vapour pressure can be determined straightway. The measurement of the individual vapour pressures of a solution and solvent is thus eliminated.

Procedure. The apparatus used by Ostwald and Walker is shown in Fig. 15.4. It consists of two sets of bulbs :

- (a) Set *A* containing the solution
- (b) Set *B* containing the solvent

Each set is weighed separately. A slow stream of dry air is then drawn by suction pump through the two sets of bulbs. At the end of the operation, these sets are reweighed. From the loss of weight in each of the two sets, the lowering of vapour pressure is calculated. The temperature of the air, the solution and the solvent must be kept constant throughout.

Calculations. As the air bubbles through set *A* it is saturated up to the vapour pressure p_s of solution and then up to vapour pressure p of solvent in set *B*. Thus the amount of solvent taken up in set *A* is proportional to p_s and the amount taken up in set *B* is proportional to $(p - p_s)$.



■ **Figure 15.4**
Ostwald-Walker method of measuring the relative lowering of vapour pressure.

If w_1 and w_2 be the loss of weight in set A and B respectively,

$$w_1 \propto p_s \quad \dots(1)$$

$$w_2 \propto p - p_s \quad \dots(2)$$

Adding (1) and (2), we have

$$\begin{aligned} w_1 + w_2 &\propto p_s + p - p_s \\ &\propto p \end{aligned} \quad \dots(3)$$

Dividing (2) by (3), we can write

$$\frac{p - p_s}{p} = \frac{w_2}{w_1 + w_2} \quad \dots(4)$$

Knowing the loss of mass in set B (w_2) and the total loss of mass in the two sets ($w_1 + w_2$), we can find the relative lowering of vapour pressure from equation (4).

If water is the solvent used, a set of calcium chloride tubes (or a set of bulbs containing conc. H_2SO_4) is attached to the end of the apparatus to catch the escaping water vapour. Thus the gain in mass of the CaCl_2 -tubes is equal to ($w_1 + w_2$), the total loss of mass in sets A and B.

SOLVED PROBLEM 1. A current of dry air was passed through a solution of 2.64 g of benzoic acid in 30.0 g of ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$) and then through pure ether. The loss in weight of the solution was 0.645 g and the ether 0.0345 g. What is the molecular mass of benzoic acid?

SOLUTION

According to the theory of Ostwald-Walker method,

$$\frac{p - p_s}{p} = \frac{w_2}{w_1 + w_2} \quad \dots(1)$$

In this case,

$$w_1, \text{ loss of mass of solution} = 0.645 \text{ g}$$

$$w_2, \text{ loss of mass of solvent} = 0.0345 \text{ g}$$

Substituting values in equation (1)

$$\begin{aligned} \frac{p - p_s}{p} &= \frac{0.0345}{0.645 + 0.0345} \\ &= \frac{0.0345}{0.6795} = 0.0507 \end{aligned}$$

From Raoult's Law, we have

$$\frac{p - p_s}{p} = \frac{w/m}{w/m + W/M} \quad \dots(2)$$

M the molecular mass of ether, $(C_2H_5)_2O = 48 + 10 + 16 = 74$

Substituting values in (2)

$$0.0507 = \frac{2.64/m}{2.64/m + 30/74} \quad \text{or } m = 122$$

Hence, m , the molecular mass of benzoic acid = 122

SOLVED PROBLEM 2. A stream of dry air was passed through a bulb containing a solution of 7.50 g of an aromatic compound in 75.0 g of water and through another globe containing pure water. The loss in mass in the first globe was 2.810 g and in the second globe it was 0.054 g. Calculate the molecular mass of the aromatic compound. (Mol mass of water = 18)

SOLUTION

According to the theory of Ostwald-Walker method,

$$\frac{p - p_s}{p} = \frac{w_2}{w_1 + w_2} \quad \dots(1)$$

In the present case,

w_1 , loss of mass of solution = 2.810 g

w_2 , loss mass of solvent (water) = 0.054 g

Substituting values in (1)

$$\frac{p - p_s}{p} = \frac{0.054}{2.810 + 0.054} = \frac{0.054}{2.864} = 0.0188 \quad \dots(2)$$

From Raoult's Law,

$$\frac{p - p_s}{p} = \frac{w/m}{w/m + W/M}$$

Substituting values

$$0.0188 = \frac{7.50/m}{7.50/m + 75.0/18} \quad \text{or } m = 93.6$$

Hence m , mol mass of solute = 93.6

SOLVED PROBLEM 3. In an experiment air was drawn successively through a solution of sugar (38.89 g per 100 g water) and distilled water, and then through anhydrous calcium chloride. It was found that the water lost was 0.0921 g and calcium chloride tubes gained 5.163 g. Find the molecular mass of the sugar. (Mol mass of $H_2O = 18$)

SOLUTION

According to the theory of Ostwald-Walker method,

$$\frac{p - p_s}{p} = \frac{w_2}{w_1 + w_2} \quad \dots(1)$$

In this case,

w_2 , the loss of mass of water = 0.0921 g

$(w_1 + w_2)$, the total loss of solution and solvent = 5.163 g

Substituting values in equation (1)

$$\frac{p - p_s}{p} = \frac{0.0921}{5.163} = 0.0164$$

From Raoult's Law,

$$\frac{p - p_s}{p} = \frac{w/m}{w/m + W/M}$$

Substituting values

$$0.0164 = \frac{38.89/m}{38.89/m + 100/18}$$

Hence m , mol mass of sugar = **385**

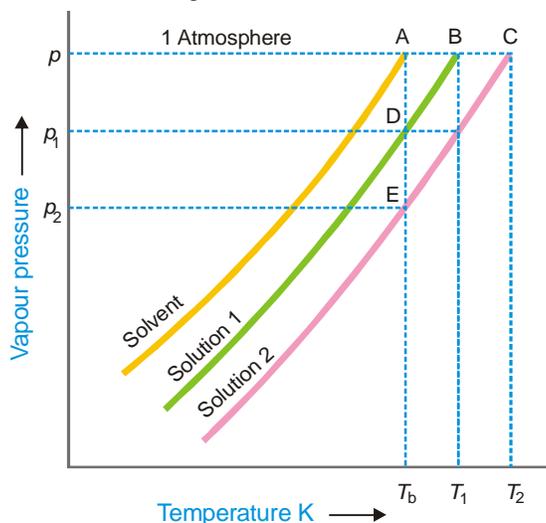
ELEVATION OF BOILING POINT

Relation between Elevation of Boiling Point and Lowering of Vapour-pressure

When a liquid is heated, its vapour pressure rises and when it equals the atmospheric pressure, the liquid boils. The addition of a non volatile solute lowers the vapour pressure and consequently elevates the boiling point as the solution has to be heated to a higher temperature to make its vapour pressure become equal to atmospheric pressure. If T_b is the boiling point of the solvent and T is the boiling point of the solution, the difference in the boiling points (ΔT) is called the **elevation of boiling point**.

$$T - T_b = \Delta T$$

The vapour pressure curves of the pure solvent, and solutions (1) and (2) with different concentrations of solute are shown in Fig.15.5.



■ **Figure 15.5**

Ostwald-Walker method of measuring the relative lowering of vapour pressure.

For dilute solutions, the curves BD and CE are parallel and straight lines approximately. Therefore for similar triangles ACE and ABD , we have

$$\frac{AB}{AC} = \frac{AD}{AE}$$

or

$$\frac{T_1 - T_b}{T_2 - T_b} = \frac{p - p_1}{p - p_2}$$

where $p - p_1$ and $p - p_2$ are lowering of vapour pressure for solution 1 and solution 2 respectively. Hence **the elevation of boiling point is directly proportional to the lowering of vapour pressure.**

$$\text{or} \quad \Delta T \propto p - p_s \quad \dots(1)$$

Determination of Molecular Mass from Elevation of Boiling Point

Since p is constant for the same solvent at a fixed temperature, from (1) we can write

$$\Delta T \propto \frac{p - p_s}{p} \quad \dots(2)$$

But from Raoult's Law for dilute solutions,

$$\frac{p - p_s}{p} \propto \frac{wM}{Wm} \quad \dots(3)$$

Since M (mol mass of solvent) is constant, from (3)

$$\frac{p - p_s}{p} \propto \frac{w}{Wm} \quad \dots(4)$$

From (2) and (4)

$$\Delta T \propto \frac{w}{m} \times \frac{1}{W}$$

$$\text{or} \quad \Delta T = K_b \times \frac{w}{m} \times \frac{1}{W} \quad \dots(5)$$

where K_b is a constant called **Boiling point constant or Ebullioscopic constant of molal elevation constant.** If $w/m = 1$, $W = 1$, $K_b = \Delta T$. Thus,

Molal elevation constant may be defined as the boiling-point elevation produced when 1 mole of solute is dissolved in one kg (1000 g) of the solvent.

If the mass of the solvent (W) is given in grams, it has to be converted into kilograms. Thus the expression (5) assumes the form

$$\Delta T = K_b \times \frac{w}{m} \times \frac{1}{W/1000} \quad \dots(6)$$

$$\text{Hence} \quad m = \frac{1000 \times K_b \times w}{\Delta T \times W} \quad \dots(7)$$

where ΔT = elevation of boiling point; K_b = molal elevation constant; w = mass of solute in grams; m = mol mass of solute; and W = mass of solvent in grams.

Sometimes the value of K_b is given in K per 0.1 kg (100 g). In that case, the expression (6) becomes

$$m = \frac{100 \times K_b \times w}{\Delta T \times W}$$

The value of K_b . The value of K_b can be determined by measurement of ΔT by taking a solute of known molecular mass (m) and substituting the values in expression (7).

Units of K_b . From equation (6), we have

$$K_b = \frac{\Delta T \times W/1000}{w/m} = \frac{\Delta T \times \text{kg-solvent}}{\text{mol-solute}}$$

Thus the units of K_b are

$$\frac{^\circ\text{C kg-solvent}}{\text{mol-solute}}$$

The constant K_b , which is characteristic of a particular solvent used, can also be calculated from thermodynamically derived relationship

$$K_b = \frac{RT_b^2}{1000 \times L_v}$$

where R = gas constant; T_b = boiling point of solvent; L_v = molar latent heat of vaporization. Thus for water $R = 8.134 \text{ J mol}^{-1}$; $T = 373 \text{ K}$; $L_v = 2260 \text{ J g}^{-1}$

Therefore,

$$K_b = \frac{8.314 \times 373 \times 373}{1000 \times 2260} = 0.52 \text{ K Kg}^{-1}$$

The molal boiling point constant for some common solvents are listed in Table 15.1

TABLE 15.1. MOLAL BOILING-POINT CONSTANTS		
Solvent	K_b per kg (1000 g)	K_b per 0.1 kg (100 g)
Water	0.52	5.2
Propanone (acetone)	1.70	17.0
Ethoxyethane (ether)	2.16	21.6
Ethanoic acid (acetic acid)	3.07	30.7
Ethanol	1.75	11.5
Benzene	2.70	27.0
Trichloromethane (chloroform)	3.67	36.7

SOLVED PROBLEM 1. The boiling point of a solution containing 0.20 g of a substance X in 20.00 g of ether is 0.17 K higher than that of pure ether. Calculate the molecular mass of X. Boiling point constant of ether per 1 Kg is 2.16 K.

SOLUTION

Applying the expression $m = \frac{1000 \times K_b \times w}{\Delta T \times W}$

In this case, we have

$$\begin{aligned} \Delta T &= 0.17 \text{ K} \\ K_b &= 2.16 \\ w &= 0.20 \text{ g} \\ W &= 20.00 \text{ g} \end{aligned}$$

Substituting values

$$\begin{aligned} m &= \frac{1000 \times 2.16 \times 0.20}{0.17 \times 20.00} \\ m &= \mathbf{127.81} \end{aligned}$$

SOLVED PROBLEM 2. Acetone boils at 56.38°C and a solution of 1.41 grams of an organic solid in 20 grams of acetone boils at 56.88°C. If K for acetone per 100 g is 16.7, calculate the mass of one mole of the organic solid.

SOLUTION

Applying the expression

$$m = \frac{1000 \times K_b \times w}{\Delta T \times W}$$

In this case, we have

$$\Delta T = 56.88 - 56.38 = 0.50$$

$$K = 16.7$$

$$w = 1.41$$

$$W = 20$$

Substituting the values

$$m = \frac{1000 \times 16.7 \times 1.41}{0.50 \times 20}$$

Hence $m = 235$ or molar mass = **235 g**

SOLVED PROBLEM 3. In a Cottrell determination, 22 g of benzene was used as solvent. The readings on the differential thermometer before and after adding 0.586 g of naphthalene (mol mass = 128), were 1.262 and 1.799 respectively. In a separate experiment, using the same amount of benzene but this time adding 0.627 g of an organic compound X, the temperature readings were 1.269 and 1.963. Calculate the molecular mass of X.

SOLUTION

Calculation of K_b

The value of K_b is found from the results of the first experiment.

$$\Delta T = 1000 K_b \frac{w}{m \times W}$$

$$\Delta T = 1.799 - 1.262 = 0.537$$

$$w = 0.586$$

$$m = 128$$

$$W = 22.0$$

Hence,
$$0.537 = 1000 \times K_b \times \frac{0.586}{128 \times 22}$$

$$\therefore K_b = \frac{0.537 \times 128 \times 22}{1000 \times 0.586} = 2.58$$

Molecular weight of X

Knowing the value of K_b , m , the molecular mass can be found from the expression

$$m = \frac{1000 \times K_b \times w}{\Delta T \times W}$$

In this case,

$$\Delta T = 1.963 - 1.269 = 0.694$$

$$w = 0.627$$

$$W = 22$$

Substituting these values,

$$m = \frac{1000 \times 2.58 \times 0.627}{0.694 \times 22}$$

Hence $m = 106$

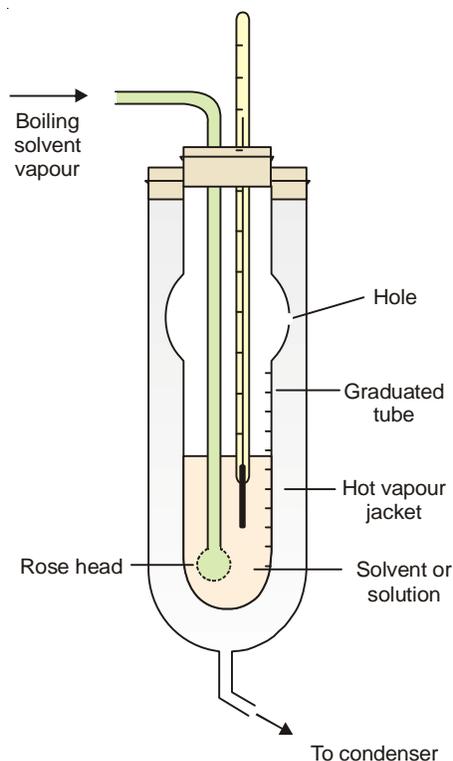
MEASUREMENT OF BOILING-POINT ELEVATION

There are several methods available for the measurement of the elevation of boiling point. Some of these are outlined below :

(1) Landsberger-Walker Method

This method was introduced by Landsberger and modified by Walker.

Apparatus. The apparatus used in this method is shown in Fig. 15.6 and consists of : (i) An *inner tube* with a hole in its side and graduated in ml; (ii) A *boiling flask* which sends solvent vapour in to the graduated tube through a 'rosehead' (a bulb with several holes); (iii) An *outer tube* which receives hot solvent vapour issuing from the side-hole of the inner tube; (iv) A *thermometer* reading to 0.01 K, dipping in solvent or solution in the inner tube.



■ **Figure 15.6**
Landsberger-Walker apparatus.

Procedure. Pure solvent is placed in the graduated tube and vapour of the same solvent boiling in a separate flask is passed into it. The vapour causes the solvent in the tube to boil by its latent heat of condensation. When the solvent starts boiling and temperature becomes constant, its boiling point is recorded.

Now the supply of vapour is temporarily cut off and a weighed pellet of the solute is dropped into the solvent in the inner tube. The solvent vapour is again passed through until the boiling point of the solution is reached and this is recorded. The solvent vapour is then cut off, thermometer and rosehead raised out of the solution, and the volume of the solution read.

From a difference in the boiling points of solvent and solution, we can find the molecular weight of the solute by using the expression

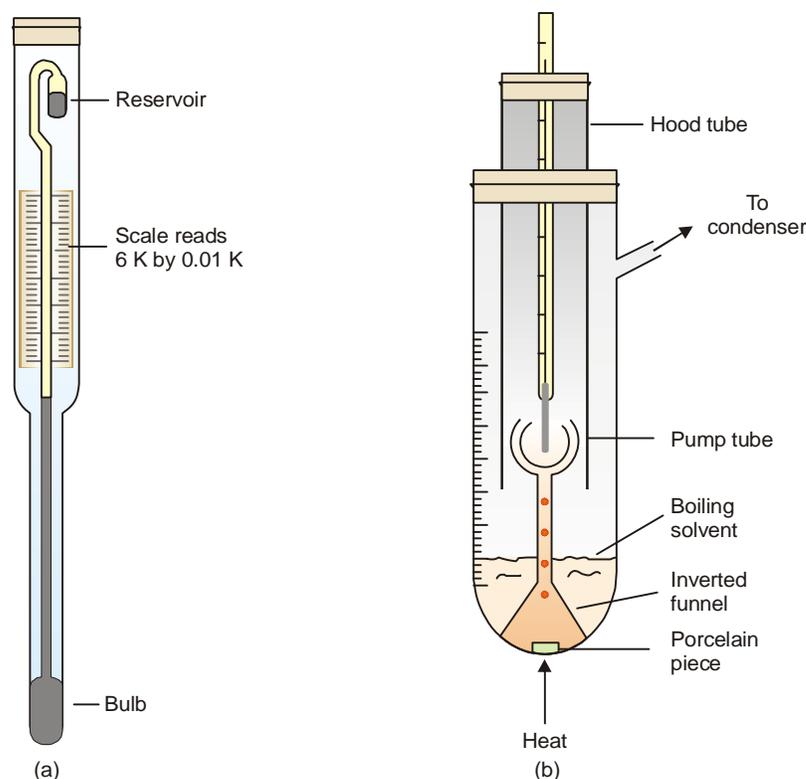
$$m = \frac{1000 \times K_b \times w}{\Delta T \times W}$$

where w = weight of solute taken, W = weight of solvent which is given by the volume of solvent (or solution) measured in ml multiplied by the density of the solvent at its boiling point.

(2) Cottrell's Method

A method better than Landsberger-Walker method was devised by Cottrell (1910).

Apparatus. It consists of : (i) a graduated *boiling tube* containing solvent or solution; (ii) a reflux condenser which returns the vapourised solvent to the boiling tube; (iii) a thermometer reading to 0.01 K, enclosed in a glass hood; (iv) A small inverted funnel with a narrow stem which branches into three jets projecting at the thermometer bulb.



■ **Figure 15.7**

(a) Beckmann thermometer reading to 0.01 K. (b) Cottrell's Apparatus.

Beckmann Thermometer (Fig. 15.7a). It is *differential thermometer*. It is designed to measure small changes in temperature and not the temperature itself. It has a large bulb at the bottom of a fine capillary tube. The scale is calibrated from 0 to 6 K and subdivided into 0.01 K. The unique feature of this thermometer, however, is the small reservoir of mercury at the top. The amount of mercury in this reservoir can be decreased or increased by tapping the thermometer gently. In this way the thermometer is adjusted so that the level of mercury thread will rest at any desired point on the scale when the instrument is placed in the boiling (or freezing) solvent.

Procedure. The apparatus is fitted up as shown in Fig. 15.7 (b). Solvent is placed in the boiling tube with a porcelain piece lying in it. It is heated on a small flame (micro burner). As the solution starts boiling, solvent vapour arising from the porcelain piece pump the boiling liquid into the narrow stem. Thus a mixture of solvent vapour and boiling liquid is continuously sprayed around the thermometer bulb. The temperature soon becomes constant and the boiling point of the pure solvent is recorded.

Now a weighed pellet of the solute is added to the solvent and the boiling point of the solution noted as the temperature becomes steady. Also, the volume of the solution in the boiling tube is noted. The difference of the boiling temperatures of the solvent and solute gives the elevation of

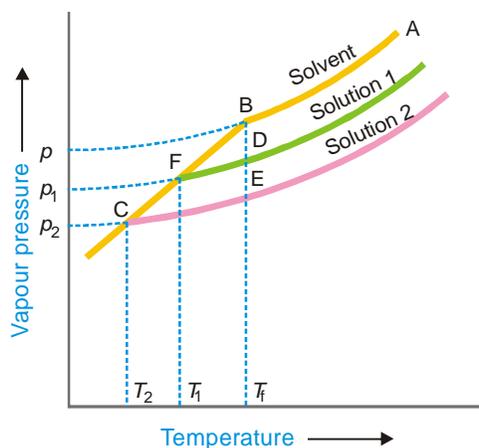
boiling point. While calculating the molecular weight of solute the volume of solution is converted into mass by multiplying with density of solvent at its boiling point.

FREEZING-POINT DEPRESSION

Relation between Depression of Freezing-point and Lowering of Vapour-pressure

The vapour pressure of a pure liquid changes with temperature as shown by the curve ABC , in Fig. 15.8. There is a sharp break at B where, in fact, the freezing-point curve commences. Thus the point B corresponds to the freezing point of pure solvent, T_f . The vapour pressure curve of a solution (*solution 1*) of a nonvolatile solute in the same solvent is also shown in Fig. 15.8. It is similar to the vapour pressure curve of the pure solvent and meets the freezing point curve at F , indicating that T_1 is the freezing point of the solution. The difference of the freezing point of the pure solvent and the solution is referred to as the **Depression of freezing point**. It is represented by the symbol ΔT or ΔT_f .

$$T_f - T_1 = \Delta T$$



■ **Figure 15.8**
Relation between lowering of vapour-pressure and depression of freezing point.

When more of the solute is added to the solution 1, we get a more concentrated solution (*solution 2*.) The vapour pressure of *solution 2* meets the freezing-point at C , indicating a further lowering of freezing point to T_2 .

For dilute solutions FD and CE are approximately parallel straight lines and BC is also a straight line. Since the triangles BDF and BEC are similar,

$$\frac{DF}{EC} = \frac{BD}{BE}$$

$$\text{or} \quad \frac{T_f - T_1}{T_f - T_2} = \frac{p - p_1}{p - p_2}$$

where p_1 and p_2 are vapour pressure of *solution 1* and *solution 2* respectively. **Hence depression of freezing point is directly proportional to the lowering of vapour pressure.**

$$\text{or} \quad \Delta T \propto p - p_s \quad \dots(1)$$

Determination of Molecular Weight from Depression of Freezing point

Since p is constant for the same solvent at a fixed temperature, from (1) we can write

$$\Delta T \propto \frac{p - p_s}{p} \quad \dots(2)$$

But from Raoult's Law for dilute solutions,

$$\frac{p - p_s}{p} = \frac{wM}{Wm} \quad \dots(3)$$

Since M (mol wt) of solvent is constant, from (3)

$$\frac{p - p_s}{p} = \frac{w}{Wm} \quad \dots(4)$$

from (2) and (4)

$$\Delta T \propto K_f \times \frac{w}{m} \times \frac{1}{W}$$

$$\text{or} \quad \Delta T = K_f \times \frac{w}{m} \times \frac{1}{W} \quad \dots(5)$$

where K_f is a constant called **Freezing-point constant or Cryoscopic constant or Molal depression constant**. If $w/m = 1$ and $W = 1$, $K_f = \Delta T$. Thus,

Molal depression constant may be defined as the freezing-point depression produced when 1 mole of solute is dissolved in one kg (1000 g) of the solvent.

If the mass of solvent (W) is given in grams, it has to be converted into kilograms. Thus the expression (5) assumes the form

$$\Delta T = K_f \times \frac{w}{m} \times \frac{1}{W/1000}$$

$$\text{or} \quad \Delta T = K_f \times \frac{w}{m} \times \frac{1000}{W}$$

$$\text{Hence} \quad m = \frac{1000 \times K_f \times w}{\Delta T \times w} \quad \dots(6)$$

where m = molecular mass of solute ; K_f = molal depression constant ; w = mass of solute ; ΔT = depression of freezing point ; W = mass of solvent.

Given the value of K_f , the molecular mass of solute can be calculated.

Sometimes the value of K_f is given in K per 0.1 kg. (100 g.) In that case, the expression (6) becomes

$$m = \frac{100 \times K_f \times w}{\Delta T \times w}$$

The value of K_f . The value of K_f can be determined by measurement of ΔT by taking a solute of known molecular mass (m) and substituting the values in expression (6). The constant K_f , which is characteristic of a particular solvent, can also be calculated from the relation

$$K_f = \frac{RT_f^2}{1000 L_f}$$

where T_f = freezing point of solvent in K; L_f = molar latent heat of fusion; R = gas constant. Hence for water, $T_f = 273$ K and $L_f = 336$ J g⁻¹. Therefore,

$$K_f = \frac{8.32 \times 273 \times 273}{1000 \times 336} = 1.86 \text{ K kg}^{-1}$$

The molal depression constant for some common solvents are given in Table 15.2

TABLE 15.2. MOLAL FREEZING-POINT CONSTANTS

Solvent	K_f per kg (1000 g)	K_f per 0.1 kg (100 g)
Water	1.86	18.6
Ethanoic acid (acetic acid)	3.90	39.0
Benzene	5.10	51.0
Camphor	40.0	400.0

SOLVED PROBLEM 1. 0.440 g of a substance dissolved in 22.2 g of benzene lowered the freezing point of benzene by 0.567°C . Calculate the molecular mass of the substance. ($K_f = 5.12^\circ\text{C mol}^{-1}$)

SOLUTION

We can find the molecular mass by applying the expression

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

In this case :

$$w = 0.440 \text{ g}$$

$$\Delta T = 0.567^\circ\text{C}$$

$$W = 22.2 \text{ g}$$

$$K_f = 5.12^\circ\text{C mol}^{-1}$$

Substituting the values,
$$m = \frac{1000 \times 5.12 \times 0.440}{0.567 \times 22.2} = 178.9$$

\therefore Molecular mass of substance = **178.9**

SOLVED PROBLEM 2. 1.250 g of naphthalene was dissolved in 60 cm^3 of benzene and freezing point of the solution was found to be 277.515 K , while that of benzene 278.495 K . Density of benzene $= 0.880 \text{ g cm}^{-3}$, $K_f = 5.1 \text{ K per } 1000 \text{ g benzene}$. Calculate the molecular mass of naphthalene.

SOLUTION

Let us apply the expression

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

In this case

$$K_f = 5.1 \text{ K}$$

$$w = 1.250 \text{ g}$$

$$W = 60 \times 0.880 \text{ g}$$

$$\Delta T = 278.495 - 277.515 = 0.980 \text{ K}$$

Substituting the values,

$$m = \frac{1000 \times 5.1 \times 1.250}{0.980 \times 60 \times 0.880} = 123$$

Thus the molecular weight of naphthalene is **123**.

SOLVED PROBLEM 3. A solution of 0.124 g of a substance, X, in 25.0 l of ethanoic acid (acetic acid) has a freezing point 0.324°C below that of the pure acid 16.6°C. Calculate the molecular mass (relative molecular mass) of X, given that the specific latent heat of fusion of ethanoic acid is 180.75 J g⁻¹.

SOLUTION

Calculation of Molal depression Constant

We know that

$$K_f = \frac{RT_f^2}{L_f \times 1000} \quad \dots(1)$$

Here, freezing point of benzene, $T_f = 273.2 + 16.6 = 289.8$ K

Specific latent heat of fusion $L_f = 180.75$ J g⁻¹

Substituting in the equation (1)

$$K_f = \frac{8.314 \times (289.8)^2}{180.75 \times 1000} = 3.86^\circ$$

Calculation of Molecular weight

Applying the expression

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

We have

$$m = \frac{1000 \times 3.86 \times 0.124}{0.324 \times 25} = 59.09$$

Thus the molecular weight (or relative molecular) mass of X is **59.09**.

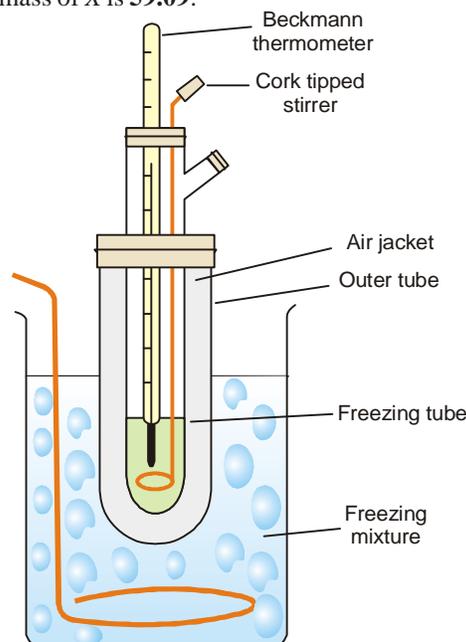
MEASUREMENT OF FREEZING-POINT DEPRESSION

The depression of freezing point can be measured more correctly and with less difficulty. Two simple methods commonly used are outlined below.

(1) Beckmann's Method (1903)

Apparatus. It consists of (i) A *freezing tube* with a side-arm to contain the solvent or solution, while the solute can be introduced through the side-arm; (ii) An outer larger tube into which is fixed the freezing tube, the space in between providing an air jacket which ensures a slower and more uniform rate of cooling; (iii) A *large jar* containing a freezing mixture *e.g.*, ice and salt, and having a stirrer.

Procedure. 15 to 20 g of the solvent is taken in the freezing point of the solvent by directly coding the freezing point tube and the apparatus set up as shown in Fig. 15.9 so that the bulb of the thermometer is completely



■ **Figure 15.9**
Relation between lowering of vapour-pressure and depression of freezing point.

immersed in the solvent. First determine the approximate freezing point of the solvent by directly cooling the freezing point tube in the cooling bath. When this has been done, melt the solvent and place the freezing-point tube again in the freezing bath and allow the temperature to fall.

When it has come down to within about a degree of the approximate freezing point determined above, dry the tube and place it cautiously in the air jacket. Let the temperature fall slowly and when it has come down again to about 0.5° below the freezing point, stir vigorously. This will cause the solid to separate and the temperature will rise owing to the latent heat set free. Note the highest temperature reached and repeat the process to get concordant value of freezing point.

The freezing point of the solvent having been accurately determined, the solvent is remelted by removing the tube from the bath, and a weighed amount (0.1–0.2 g) of the solute is introduced through the side tube. Now the freezing point of the solution is determined in the same way as that of the solvent. A further quantity of solute may then be added and another reading taken. Knowing the depression of the freezing point, the molecular weight of the solute can be determined by using the expression

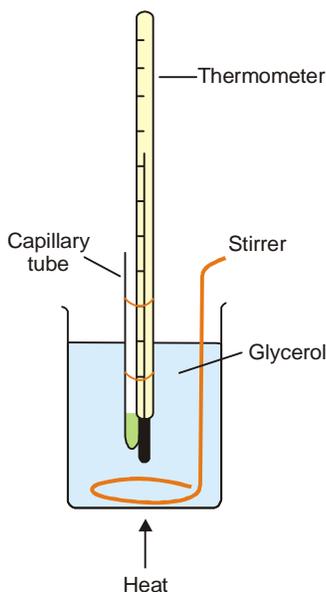
$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

This method gives accurate results, if the following precautions are observed :

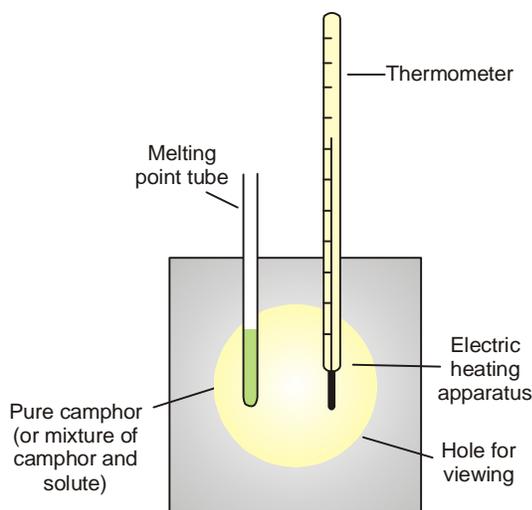
- The supercooling should not exceed 0.5°C .
- The stirring should be uniform at the rate of about one movement per second.
- The temperature of the cooling bath should not be 4° to 5° below the freezing point of the liquid.

(2) Rast's Camphor Method

This method due to Rast (1922) is used for determination of molecular weights of solutes which are soluble in molten camphor. The freezing point depressions are so large that an ordinary thermometer can be used.



■ **Figure 15.10**
Determination of depression of melting point by capillary method.



■ **Figure 15.11**
Determination of depression of melting point by electrical apparatus.

Pure camphor is powdered and introduced into a capillary tube which is sealed at the upper end. This is tied along a thermometer and heated in a glycerol bath (see Fig. 15.10). The melting point of camphor is recorded. Then a weighed amount of solute and camphor (about 10 times as much) are melted in test-tube with the open end sealed. The solution of solute in camphor is cooled in air. After solidification, the mixture is powdered and introduced into a capillary tube which is sealed. Its melting point is recorded as before. The difference of the melting point of pure camphor and the mixture, gives the depression of freezing point. In modern practice, electrical heating apparatus is used for a quick determination of melting points of camphor as also the mixture.

The molal depression constant of pure camphor is 40°C . But since the laboratory camphor may not be very pure, it is necessary to find the depression constant for the particular sample of camphor used by a preliminary experiment with a solute of known molecular weight.

SOLVED PROBLEM. A sample of camphor used in the Rast method of determining molecular masses had a melting point of 176.5°C . The melting point of a solution containing 0.522 g camphor and 0.0386 g of an unknown substance was 158.8°C . Find the molecular mass of the substance. K_f of camphor per kg is 37.7.

SOLUTION

Applying the expression

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

to the present case, we have

$$\Delta T = 176.5 - 158.8 = 17.7$$

$$K_f = 37.7$$

$$w = 0.0386 \text{ g}$$

$$W = 0.522 \text{ g}$$

Substituting these values

$$m = \frac{1000 \times 37.7 \times 0.0386}{17.7 \times 0.522} = 157$$

COLLIGATIVE PROPERTIES OF ELECTROLYTES

The colligative properties of solutions *viz.*, vapour-pressure lowering, boiling-point elevation, freezing-point depression and osmotic pressure, all depend solely on the total number of solute particles present in solution. The various electrolytes ionize and yield more than one particle per formula unit in solution. Therefore, **the colligative effect of an electrolyte solution is always greater than that of a nonelectrolyte of the same molal concentration.**

To represent the colligative properties of electrolytes by means of the same relations as for nonelectrolytes, van't Hoff (1880) suggested the use of a factor i . This is now known as **van't Hoff factor** and is defined as : **the ratio of the colligative effect produced by an electrolyte solution to the corresponding effect for the same concentration of a nonelectrolyte solution.**

Applying this definition of i to the freezing-point depression, we have

$$i = \frac{\Delta T_f}{[\Delta T_f]_0} \quad \dots(1)$$

where ΔT_f is the freezing-point depression for the electrolyte measured experimentally and $[\Delta T_f]_0$ is the corresponding value calculated for a nonelectrolyte of the equal concentration. In other words, $[\Delta T_f]_0$ is the value of depression of freezing-point of the electrolyte solution assuming no ionization.

From (1)

$$\Delta T_f = i [\Delta T_f]_0$$

We know that

$$[\Delta T_f]_0 = \frac{1000 K_f w}{mW} \quad \dots(2)$$

$$\therefore \Delta T_f = i \times \frac{1000 K_f w}{mW} \quad \dots(3)$$

A similar relation will hold for the observed elevation of boiling point of an electrolyte solution *i.e.*,

$$\Delta T_b = i \times \frac{1000 K_b w}{mW} \quad \dots(4)$$

The value of i can, therefore, be calculated from the experimental data as mentioned in (4).

It has been found that once i is known for a particular concentration of an electrolyte for one colligative property, the same value of i is essentially valid for other properties at the same concentration. That is,

$$\begin{aligned} i &= \frac{\Delta T_f}{[\Delta T_f]_0} = \frac{\Delta T_b}{[\Delta T_b]_0} = \frac{\Delta p}{[\Delta p]_0} \\ &= \frac{\pi}{[\pi]_0} \end{aligned}$$

where the subscript zero refers in each case to the effect produced by a solute that is a nonelectrolyte.

ABNORMAL MOLECULAR MASSES OF ELECTROLYTES

Dividing (2) by (3), it is evident that

$$\frac{\Delta T_f}{[\Delta T_f]_0} = \frac{m_0}{m} = i \quad \text{or} \quad m = i \times m_0$$

where

m_0 = molecular mass calculated from formula

m = molecular mass from observed data

Since the value of i is always greater than 1 **the experimental molecular weight will always be less than the theoretical value calculated from the formula.**

Relation Between van't Hoff Factor and Degree of Dissociation

Since colligative properties depend on the number of particles in solution, the van't Hoff factor may be interpreted as the ratio of the **number of particles present in solution to the number obtained assuming no ionization.** That is,

$$i = \frac{\text{Actual number of particles}}{\text{Number of particles for no ionization}}$$

The **degree of dissociation** is the fraction of an electrolyte which is dissociated into ions in aqueous solution. If an electrolyte is 50 per cent dissociated, its degree of dissociation is 0.5. The degree of dissociations is usually represented by α .

Suppose 1 mole of an electrolyte is capable of forming ν ('nu') ions on complete dissociation. If the degree of dissociation be α , the total number of particles in solution are :

$$\text{Number of undissociated molecules} = 1 - \alpha$$

$$\text{Number of ions produced} = \alpha \nu$$

$$\therefore \text{Total number of particles} = 1 - \alpha + \alpha \nu$$

Hence
$$i = \frac{1 - \alpha + \alpha v}{1}$$

or
$$i - 1 = \alpha(v - 1)$$

$$\alpha = \frac{i - 1}{v - 1}$$

This expression states the relationship between van't Hoff factor and the degree of dissociation. Knowing the value of i from colligative property measurements, α can be calculated.

SOLVED PROBLEM 1. A solution containing 1.5 g of barium nitrate in 0.1 kg of water freezes at 272.720 K. Calculate the apparent degree of dissociation of the salt.

$$K_b = 1.86$$

$$\text{Molecular mass of Ba(NO}_3)_2 = 261$$

SOLUTION

Calculation of Depression of Freezing point $[\Delta T]_0$ for no ionization :

$$\begin{aligned} \Delta T &= \frac{1000 K_f w}{mW} = \frac{1000 \times 1.5 \times 1.86}{261 \times 0.1 \times 1000} \\ &= 0.1068^\circ\text{C} \end{aligned}$$

Calculation of van't Hoff Factor

$$i = \frac{\Delta T}{[\Delta T]_0} = \frac{1 - 0.720}{0.1068} = \frac{0.280}{0.1068}$$

Calculation of Degree of dissociation :

$$\alpha = \frac{i - 1}{v - 1}$$

Here $\text{Ba(NO}_3)_2 \longrightarrow \text{Ba}^{2+} + 2\text{NO}_3^-$
and 1 formula unit yields 3 particles on dissociation.

$$\therefore v = 3$$

$$\text{and } \alpha = \frac{\frac{0.280}{0.1068} - 1}{3 - 1} = 0.81 \text{ or } \mathbf{81\%}$$

SOLVED PROBLEM 2. Find the degree of ionization for HF (hydrofluoric acid) in 0.100 m aqueous solution if the freezing point of the solution is -0.197°C . (K_f for water = 1.86°C)

SOLUTION

Calculation of Freezing-point depression, $[\Delta T_f]_0$ for no ionization

$$[\Delta T_f]_0 = K_f \times m$$

where m = molal concentration (moles of solute/kg solvent)

$$\therefore (\Delta T_f) = 1.86 \times 0.100$$

Calculation of i

$$i = \frac{\Delta T}{[\Delta T]_0}$$

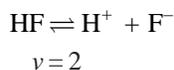
Substituting values

$$i = \frac{0.197}{1.86 \times 0.100} = 1.06$$

Calculation of Degree of dissociation

$$\alpha = \frac{i - 1}{v - 1}$$

Since HF dissociates as



Substituting values

$$\alpha = \frac{1.06 - 1}{2 - 1} = 0.06$$

Therefore, the degree of dissociation of 0.100 *m* HF is 0.06, or it is 6% ionized.

SOLVED PROBLEM 3. Phenol ($\text{C}_6\text{H}_5\text{OH}$) associates in water to double molecules. When 0.6677 g of phenol is dissolved in 35.5 g of water; it depresses the freezing point by 0.215°C . Calculate the van't Hoff factor and the degree of association of phenol. Molal depression constant of water = $1.85^\circ\text{C mole}^{-1}$.

SOLUTION**Calculation of van't Hoff Factor**

Normal molecules weight calculated from formula = $6 \times 12 + 5 + 16 + 1 = 94$

$$\text{Observed molecular mass} = \frac{1000 K_f w}{\Delta T W} = \frac{1000 \times 1.85 \times 0.6677}{0.215 \times 35.5}$$

$$= 161.84$$

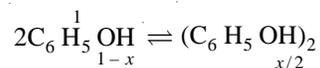
$$\text{van't Hoff factor } (i) = \frac{\text{normal mol. mass}}{\text{observed mol. mass}}$$

$$= \frac{94}{161.84}$$

Calculation of Degree of association

$$i = \frac{\text{Number of particles after association}}{\text{Number of particles for no association}}$$

If x be the degree of association, we have



\therefore Number of particles on association = $1 - x + x/2 = 1 - x/2$

Number of particles for no association = 1

$$\therefore i = \frac{94}{161.84} = \frac{1 - x/2}{1}$$

Hence $x = 0.838$ or **Phenol is 83.8% associated**

CONCEPT OF ACTIVITY AND ACTIVITY COEFFICIENT

From the studies of solutions, G.N. Lewis discovered that **the experimentally determined value of concentration whether of molecules or ions in solution is less than the actual concentration.**

The apparent value of concentration is termed 'activity'. It may be defined as : **the effective concentration of a molecule or ion in a solution.**

The activity coefficient ' γ ' is defined as : the ratio between the activity, denoted by a , or effective concentration and actual concentration of the molecule or ion in solution. That is,

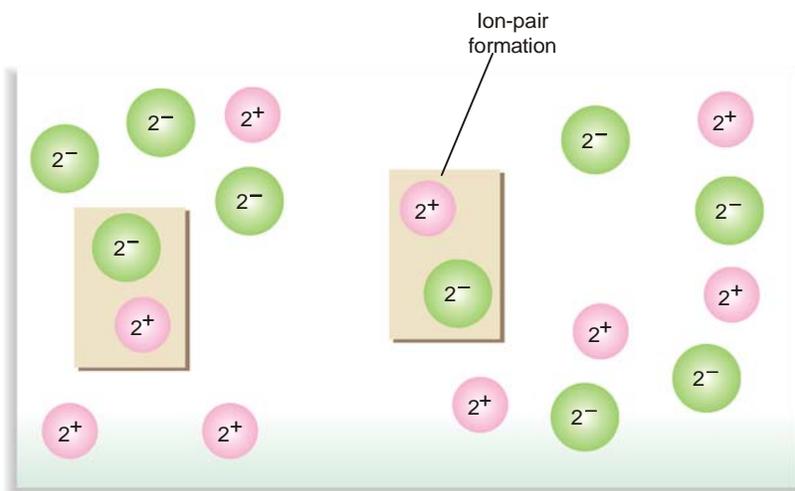
$$\gamma = \frac{\text{effective concentration}}{\text{actual concentration}} = \frac{a}{c}$$

or $a = \gamma c$

γ can be determined experimentally and is given in Tables. Thus the value of activity can be calculated by applying the above relation.

Explanation

The effective number of cations and anions in solution becomes less as these tend to form ion-pairs (Fig. 15.12) because of strong electrostatic attractions. Thus the effective concentration of the ions becomes less than the actual concentration.



■ **Figure 15.12**
Ion-pair formation of a 2^+ cation and a 2^- anion in a solution reduces the effective concentration of ions compared to actual concentration.

SOLVED PROBLEM. Calculate the effective concentration of a 0.0992 M solution of NaCl at 25°C for which activity coefficient is 0.782.

SOLUTION

We know that : $a = \gamma c$

Substituting the values, we have

$$\begin{aligned} a &= (0.782)(0.0992 \text{ M}) \\ &= 0.0776 \text{ M} \end{aligned}$$

CONCLUSIONS

- (1) The activity coefficient, γ of strong electrolytes is always less than 1.
- (2) The value of γ decreases with dilution at the same temperature, and at infinite dilution it approaches 1.
- (3) In the mathematical expressions of the various laws of physical chemistry such as Raoult's law, Henry's law, law of Mass action and Ostwald's law the actual concentration (C) has to be replaced with effective concentration (γC) for accurate experimental work.

EXAMINATION QUESTIONS

- Define or explain the following terms :

(a) Colligative properties	(b) Raoult's law
(c) Molecular mass	(d) Boiling point elevation
(e) Boiling point constant	(f) Molal Elevation constant
(g) Freezing point depression	(h) Electrolytes
- (a) State Raoult's law.
 (b) A solution of 8.585 g of sodium nitrate in 100 g of water freezes at -3.04°C . Calculate the molecular mass of sodium nitrate and account for the abnormal value. (K_f for water = 1.86 K mol^{-1})
Answer. (b) 52.52
- A 0.1 molar solution of urea at room temperature freezes at -0.25°C at normal pressure. What would be approximate freezing point of 0.1 molar aqueous solution of aluminium chloride at room temperature assuming complete ionization? What is the principle underlying the calculation?
Answer. -0.25°C
- (a) Discuss van't Hoff theory of dilute solutions. What is van't Hoff factor?
 (b) The values of molal elevation constant and molal depression constant for water are 0.52 and $1.86^{\circ}\text{C kg mol}^{-1}$ respectively. If the elevation in boiling point by dissolving a solute is -0.2°C , what will be the depression in freezing point of this solution?
Answer. (b) 0.71°C
- When a certain amount of solute is added to 100 g of water at 25°C , the vapour pressure reduces to one-half of that for pure water. The vapour pressure of water is 23.76 mm Hg. Find the amount of salt added.
Answer. 2.78 moles
- 0.3×10^{-3} kg of camphor (molar mass $154.4 \times 10^{-3}\text{ kg mol}^{-1}$) when added to 25.2×10^{-3} kg of chloroform raised the boiling point of the solvent by 0.299 K. Calculate the molar elevation constant of chloroform.
Answer. 3.88°C
- (a) How is the molecular mass of a solute determined from elevation of boiling point?
 (b) Calculate the value of K_b for water, given that pure water boils at 100°C and the latent heat of its vaporization is 540 cal g^{-1} .
Answer. (b) 0.512°C
- (a) Derive a relationship between the elevation in boiling point of a solution and the mole fraction of the solute from thermodynamic consideration.
 (b) The molal elevation constant (K_b) and the boiling point for carbon tetra chloride are 5.02 deg/molal and 76.8°C respectively. Calculate the boiling point of 1.0 molal solution of naphthalene in carbon tetrachloride.
Answer. (b) 81.82°C
- When 0.946 g of a sugar is dissolved in 150 g of water, the resulting solution is observed to have a freezing point of -0.0651°C . What is the molecular mass of the sugar? K_f for water is 1.86° .
Answer. 180
- A freezing point depression of $1/200$ molal solution of sodium sulphate in water was found to be 0.0265 K. Calculate the degree of dissociation of the salt at this concentration (K_f for water is 1.86 K mole^{-1})
Answer. 0.404
- Why the boiling point 0.1 m BaCl_2 solution is more than 0.1 m NaCl solution?
- Show that Raoult's law is a special case of Henry's law. (Delhi BSc, 2000)

13. Why benzoic acid dissolved in benzene shows a lesser value of osmotic pressure than expected one, but 0.1 molar HCl shows greater depression in freezing point than 0.1 molar acetic acid.
(Goa BSc, 2000)
14. Explain the following :
(a) Vapour pressure of a liquid does not depend upon the size of the container.
(b) Boiling point of a liquid increases on adding non-volatile solute in it.
(c) Vapour pressure of a liquid varies with temperature. (Kathmandu BSc, 2001)
15. (a) Define Raoult's law. Derive Henry's law thermodynamically.
(b) Give physical significance of chemical potential. (Jamia Millia BSc, 2002)
16. Osmotic pressure and freezing point depression have the same origin. Explain.
(Vidyasagar BSc, 2002)
17. (a) What are isotonic solutions? Explain
(b) Write a note on van't Hoff factor. (Punjabi BSc, 2002)
18. (a) Explain the term lowering of vapour pressure and relative lowering of vapour pressure.
(b) What are the colligative properties? Explain. Why electrolytes have abnormally high values of colligative properties? (Arunachal BSc, 2002)
19. State and explain Raoult's law and Henry's law. Show that in any solution if the solvent obeys Raoult's law, the solute obeys Henry's law. (Lucknow BSc, 2002)
20. State and explain Raoult's law. (Purvanchal BSc, 2002)
21. Describe a method for determining the molar mass of a non-volatile solute by the relative lowering in vapour pressure of the solvent. (Arunachal BSc, 2003)
22. What is molal depression constant? How is it related to the latent heat of fusion.
(Punjabi BSc, 2003)
23. Draw a vapour pressure composition diagram showing positive deviations from Raoult's law. Why do positive deviations occur? (Guru Nanak Dev BSc, 2003)
24. (a) Derive a relation for the depression of freezing point of a solution with its molality.
(b) Derive a relation for the elevation in boiling point of a solution with its molality.
(Sambalpur BSc, 2003)
25. State Raoult's law for ideal solutions. Draw a vapour pressure composition diagram for an ideal binary solution obeying this law and compare this with similar diagram showing deviation from Raoult's law. Why do these deviations occur? (Panjab BSc, 2003)
26. Write a short note on 'Elevation in boiling point'. (Arunachal BSc, 2003)
27. Give the defining equations of van't Hoff factor ' i ' in terms of molecular weight of solutes and freezing point depression in solutions. (Guru Nanak Dev BSc, 2003)
28. What do you understand by depression of freezing point? Derive an expression relating the freezing point depression of a solution with the mole fraction of the dissolved solute. (Arunachal BSc, 2003)
29. Explain giving reasons :
(a) Addition of non-volatile solute lowers the freezing point and elevates the boiling point of a solvent.
(b) Equimolar solutions of sucrose and sodium chloride in water are not isotonic.
(Arunachal BSc, 2003)
30. What do you mean by van't Hoff factor? Explain it when solute is associated in solution.
(Arunachal BSc, 2003)
31. "If a solute obeys Raoult's law over a concentration range then the solvent must obey Henry's law over the same range". Prove it thermodynamically. (Panjab BSc, 2003)

32. 53.94 g of a substance of molecular mass 182 is dissolved in 1000 g of water at 20°C. At this temperature the vapour pressure of water is 17.5 mm Hg. Calculate the vapour pressure of this dilute solution.
Answer. 17.4 mm Hg (Andhra BSc, 2002)
33. What will be the boiling point of solution containing 0.6 g of urea (molecular mass = 60) in 2.5 g of water? (Boiling point of water = 373 K; $K_b = 0.52 \text{ K mol}^{-1} \text{ kg}^{-1}$)
Answer. 0.208 K
34. (a) Describe the determination of molecular weight of a solute from relative lowering of vapour pressure.
 (b) Calculate the molecular weight of a non-volatile solute, if $1.2 \times 10^{-3} \text{ kg}$ of it is dissolved in 0.1 kg of acetone at 292 K. Vapour pressure of the solution = 182.5 mm and vapour pressure of acetone = 185 mm.
Answer. 50.80 (Nagpur BSc, 2002)
35. Acetic acid associates in benzene to form double molecule. $1.65 \times 10^{-3} \text{ kg}$ of acetic acid when dissolved in $100 \times 10^{-3} \text{ kg}$ of benzene raised the boiling point by 0.36 K. Calculate the van't Hoff's factor and degree of association of acetic acid in benzene (K for benzene = 2.57 K kg^{-1})
Answer. 0.984; 0.509 (Delhi BSc, 2003)
36. A solution containing $2.44 \times 10^{-3} \text{ kg}$ of a solute dissolved in $75 \times 10^{-3} \text{ kg}$ of water boiled at 373.413 K. Calculate the molar mass of the solute. (K_b for water = $0.52 \text{ K kg mol}^{-1}$)
Answer. $40.96 \times 10^{-3} \text{ kg mol}^{-1}$ (Nagpur BSc, 2003)
37. When 1.2 g of an organic compound X was dissolved in 51 g of benzene, the freezing point depression was found to be 0.001°C. Calculate the molar mass of the compound.
Answer. $195.8 \times 10^{-3} \text{ kg mol}^{-1}$ (Delhi BSc, 2003)
38. (a) Describe a method for determining the molar mass of a non-volatile solute by the relative lowering of vapour pressure of solvent.
 (b) The vapour pressure of water at 293 K is $2.337 \times 10^3 \text{ Nm}^{-2}$ and the vapour pressure of a solution of 0.108 kg of a non-volatile solute in 1 kg of water at the same temperature is $2.313 \times 10^3 \text{ Nm}^{-2}$. Calculate the molar mass of the solute.
Answer. $0.187 \text{ kg mol}^{-1}$ (Arunachal BSc (H), 2003)
39. An aqueous sucrose solution freezes at -0.31°C . Calculate the molality of the solution and also its boiling point. Given that $K_f = 1.86^\circ$ and $K_b = 0.51^\circ$ for water.
Answer. 0.1666 molal; 100.085°C (Guru Nanak Dev BSc, 2003)
40. (a) State and derive Raoult's law for lowering of vapour pressure. How is this law used for the determination of molecular mass of a non-volatile solute?
 (b) Calculate the freezing point of the solution that contains 7.2 g of glucose in 200 g of water. Normal freezing point of water is 0°C and cryoscopic constant for water is $1.86^\circ\text{C kg}^{-1}$.
Answer. -0.0372°C (Sambalpur BSc, 2003)
41. (a) Give the thermodynamic derivation of the expression for boiling point elevation ΔT_b in the form

$$\Delta T_b = K_b m$$
 where m is the solute molality and K_b the ebullioscopic constant.
 (b) Calculate the boiling point elevation resulting from dissolution of 2.0 g of C_6Cl_6 (mol. mass = 285) in 50.0 g of CCl_4 . (Ebullioscopic constant for solution in CCl_4 is $5.22 \text{ K kg mol}^{-1}$)
Answer. 0.732 K (Guru Nanak Dev BSc, 2004)
42. (a) What is molal elevation constant? How is it related to mole fraction of a non-volatile solute?
 (b) A solution containing 5.0 g of KCl per litre of water boils at 100.065°C at 760 mm pressure. Determine the degree of dissociation of KCl (K_b for water is 0.54°C)
Answer. (b) 0.7935 (Kalyani BSc, 2004)

43. (a) Define the term colligative properties.
 (b) A solution of 12.5 g of an unknown solute in 170 g of water gave a boiling point elevation of 0.63 K. Calculate the molar mass of the solute. ($K_b = 0.52 \text{ K m}^{-1}$)
Answer. (b) 60.69 (Nagpur BSc, 2004)
44. The molal depression constant for benzene is 5.12 K mol^{-1} . A solution containing 1 g solute per 100 g benzene freezes at 5.1°C . What is the molar mass of the solute. (Freezing point of pure benzene is 5.5°C)
Answer. 128 (Gulbarga BSc, 2004)
45. (a) Derive an expression for the elevation of boiling point of a liquid when a solute is dissolved in it and explain as to how the molecular mass of solute can be evaluated by the boiling point method.
 (b) The molecular mass of a water soluble non-electrolyte is 58.0. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water at atmospheric pressure (K_{1000} for water = 0.573)
Answer. (b) 100.395°C (Osmania BSc, 2004)
46. The boiling point of a solution containing 2.56 g of substance A per 100 g of water is higher by 0.052°C than the boiling point of pure water. Calculate the molar mass of the substance if molar elevation constant of water is $0.512 \text{ K kg m}^{-1}$.
Answer. 252 g mol^{-1} (Agra BSc, 2005)
47. The vapour pressure of methyl alcohol at 298 K is 96 torr. Its mole fraction in a solution with ethyl alcohol is 0.305, what is its vapour pressure if it obeys Raoult's law.
Answer. 29.28 torr (Baroda BSc, 2005)
48. Calculate the amount of CS_2 present as an impurity in 50 g of Chloroform which raises the boiling point of Chloroform by 0.3°C .
Answer. 3.14 g (Aligarh BSc, 2005)
49. The vapour pressure of a dilute solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 750 mm of Hg at 373 K. Calculate the molality and mole fraction of the solute ?
Answer. 0.7404 m ; 0.132 (Madurai BSc, 2006)
50. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2K.
Answer. 80.1 g (Andhra BSc, 2006)
51. An aqueous solution contains 30 % by weight of a liquid A (molecular mass 120) has a vapour pressure of 160 mm at 310 K. Find the vapour pressure of pure liquid A (the vapour pressure of water at 310 K is 150 mm)
Answer. 1715 mm (Dibrugarh BSc, 2006)

MULTIPLE CHOICE QUESTIONS

1. A colligative property depends upon
 (a) chemical nature of the particles (b) size of the particles
 (c) number of particles (d) temperature of the solution
Answer. (c)
2. When a non-volatile solute is dissolved in a pure solvent, the vapour pressure of the pure solvent
 (a) increases (b) decreases
 (c) remains the same (d) none of these
Answer. (b)

3. The relative lowering of vapour pressure is represented by

- (a) $\frac{p - p_s}{p}$ (b) $\frac{p_s - p}{p}$
 (c) $\frac{p_s + p}{p}$ (d) $\frac{p}{p_s + p}$

Answer. (a)

4. Mathematically, Raoult's law can be expressed as

- (a) $\frac{p_s - p}{p} = \frac{n}{n + N}$ (b) $\frac{p_s - p}{p} = \frac{N}{n + N}$
 (c) $\frac{p_s + p}{p} = \frac{n}{n + N}$ (d) $\frac{p - p_s}{p} = \frac{n}{n + N}$

Answer. (d)

5. A real solution is that which

- (a) obeys Raoult's law (b) does not obey Raoult's law
 (c) obeys Henry's law (d) does not obey Henry's law

Answer. (b)

6. The molecular mass of the solute (m) can be calculated by measuring the lowering of vapour pressure using the formula

- (a) $\frac{wM}{mW} = \frac{p - p_s}{p}$ (b) $\frac{wM}{mW} = \frac{p_s - p}{p}$
 (c) $\frac{wM}{mW} = \frac{p + p_s}{p}$ (d) $\frac{wM}{mW} = \frac{p_s}{p - p_s}$

Answer. (a)

7. A liquid boils when its vapour pressure becomes equal to

- (a) one atmospheric pressure (b) zero
 (c) very high (d) very low

Answer. (a)

8. The addition of a non-volatile solute _____ the vapour pressure

- (a) enhances (b) lowers
 (c) diminishes (d) none of these

Answer. (b)

9. The elevation in boiling point is given by the formula

$$\Delta T = K_b \times \frac{w}{m} \times \frac{1}{W}$$

where K_b is called

- (a) boiling point constant (b) ebullioscopic constant
 (c) molal elevation constant (d) all of these

Answer. (d)

10. Molal elevation constant is the boiling point elevation when _____ of the solute is dissolved in one kg of the solvent

- (a) one gram (b) one kg
 (c) one mole (d) none of these

Answer. (c)

11. When a non-volatile solute is added to a solvent, the freezing point of the solvent _____.

- (a) increases (b) remains the same

- (c) decreases (d) none of these

Answer. (c)

12. The depression in freezing point is measured by using the formula

$$\Delta T = K_f \times \frac{w}{m} \times \frac{1}{W}$$

where K_f is called

- (a) molal depression constant (b) freezing point depression constant
(c) cryoscopic constant (d) all of these

Answer. (d)

13. Freezing point depression is measured by

- (a) Beckmann's method (b) Rast's camphor method
(c) both (d) none of these

Answer. (c)

14. The colligative effect of an electrolyte is always _____ that of a non-electrolyte of the same molal concentration.

- (a) greater (b) smaller
(c) equal to (d) none of these

Answer. (a)

15. The ratio of the colligative effect produced by an electrolyte solution to the corresponding effect for the same concentration of a non-electrolyte solution is known as

- (a) degree of dissociation (b) degree of association
(c) activity coefficient (d) van't Hoff factor

Answer. (d)

16. Abnormal molecular masses are obtained when there exists

- (a) dissociation of molecules (b) association of molecules
(c) either of the two (d) none of these

Answer. (c)

17. The degree of dissociation is the fraction of an electrolyte which

- (a) is associated to form bigger molecules (b) is dissociated into ions
(c) does not pass into solution (d) none of these

Answer. (b)

18. The law of the relative lowering of vapour pressure was given by

- (a) van't Hoff (b) Ostwald
(c) Raoult (d) Henry

Answer. (c)

19. The vapour pressure of a dilute aqueous solution of glucose is 740 mm of mercury at 373 K. The mole fraction of the solute is

- (a) $\frac{1}{20}$ (b) $\frac{1}{38}$
(c) $\frac{1}{76}$ (d) $\frac{1}{740}$

Answer. (b)

20. Which of the following is a colligative property?

- (a) molar refractivity (b) optical rotation
(c) depression in freezing point (d) viscosity

Answer. (c)

21. Which of the following is not a colligative property?
 (a) relative lowering of vapour pressure (b) surface tension
 (c) elevation in boiling point (d) depression in freezing point
Answer. (b)
22. The mole fraction of the solvent in a solution of non-volatile solute is 0.950. The relative lowering of vapour pressure is
 (a) 0.050 (b) 0.020
 (c) 0.010 (d) 0.095
Answer. (a)
23. An aqueous solution of Sodium chloride in water has vapour pressure
 (a) equal to that of water (b) more than that of water
 (c) less than that of water (d) none of these
Answer. (c)
24. Which of the following is a colligative property?
 (a) K_b (b) K_f
 (c) ΔT_f (d) degree of ionisation
Answer. (c)
25. The ratio of the value of colligative property for K_2SO_4 solution to that of KCl solution at the same concentration is nearly
 (a) 1.25 (b) 1.5
 (c) 2.0 (d) 2.5
Answer. (b)
26. The freezing point of 1 molal K_2SO_4 solution assuming K_2SO_4 to be 100% ionised in water is
 (a) $-1.86^\circ C$ (b) $-3.72^\circ C$
 (c) $-5.58^\circ C$ (d) $+5.58^\circ C$
Answer. (c)
27. Which of the following 0.05 M aqueous solution will have the highest boiling point?
 (a) glucose (b) NaCl
 (c) K_2SO_4 (d) $Al(NO_3)_3$
Answer. (d)
28. The depression in freezing point of an unknown solution is equal to the depression in freezing point of 0.1 molal aqueous solution of urea. The concentration of the unknown solution is
 (a) 0.1 M (b) 0.2 M
 (c) 0.5 M (d) 1.0 M
Answer. (a)
29. The study of depression in freezing point of a solution is called
 (a) osmotic pressure (b) ebullioscopy
 (c) cryoscopy (d) none of these
Answer. (c)
30. The freezing point of 2% aqueous solution of Potassium nitrate is
 (a) equal to $0^\circ C$ (b) less than $0^\circ C$
 (c) higher than $0^\circ C$ (d) none of these
Answer. (b)
31. The molal depression constant is given by the expression
 (a) $\Delta T_f \times M$ (b) $\Delta T_f \times m$
 (c) $\Delta T_f \div m$ (d) $\Delta T_f \div M$
Answer. (c)

32. Ebullioscopy deals with study of
 (a) osmotic pressure and membranes (b) depression in freezing point
 (c) relative lowering of vapour pressure (d) elevation in boiling point
Answer. (d)
33. The depression in freezing point for 1 M urea, 1 M glucose and 1 M NaCl are in the ratio
 (a) 1:2:2 (b) 1:2:1
 (c) 1:1:1 (d) 1:1:2
Answer. (d)
34. One mole of sugar is dissolved in three moles of water. The relative lowering of vapour pressure is
 (a) 1/2 (b) 1/3
 (c) 1/4 (d) 1/5
Answer. (c)
35. Which one of the following salts would have the same value of the van't Hoff factor as that of $\text{Al}(\text{NO}_3)_3$?
 (a) KCl (b) K_2SO_4
 (c) $\text{Al}_2(\text{SO}_4)_3$ (d) $\text{K}_3[\text{Fe}(\text{CN})_6]$
Answer. (d)
36. Which one of the following is true for the van't Hoff factor, i ?
 (a) $i = \Delta T_f / [\Delta T_f]_o$ (b) $i = \Delta T_b / [\Delta T_b]_o$
 (c) $i = \Delta p / [\Delta p]_o$ (d) all of these
Answer. (d)
37. The colligative effect of an electrolyte solution is always _____ that of a non-electrolyte of the same molal concentration.
 (a) equal to (b) lesser than
 (c) greater than (d) none of these
Answer. (c)
38. The degree of dissociation is related to the van't Hoff factor by the expression (v is the no. of ions on complete dissociation of the electrolyte)
 (a) $\alpha = \frac{i+1}{v+1}$ (b) $\alpha = \frac{i-1}{v+1}$
 (c) $\alpha = \frac{i+1}{v-1}$ (d) $\alpha = \frac{i-1}{v-1}$
Answer. (d)
39. Which one of the following solutions would produce maximum elevation in boiling point?
 (a) 0.1 M glucose (b) 0.2 M sucrose
 (c) 0.1 M $\text{Ba}(\text{NO}_3)_2$ (d) 0.1 M MgSO_4
Answer. (c)
40. Which one of the following solutions will boil at highest temperature?
 (a) 1% glucose (b) 1% urea
 (c) 1% KCl (d) 1% K_2SO_4
Answer. (d)
41. At high altitudes, water boils at a temperature which is
 (a) higher than the normal boiling point (b) lower than the normal boiling point
 (c) is equal to normal boiling point (d) none of these
Answer. (b)
42. The value of van't Hoff factor is _____ for an electrolyte

- (a) greater than one (b) less than one
(c) equal to one (d) equal to zero

Answer. (a)

43. The ratio of the value of elevation in boiling point for NaCl solution to that of urea solution is nearly
(a) 0.5 (b) 1.0
(c) 1.5 (d) 2.0

Answer. (d)

44. On dissolving common salt in water it is observed that
(a) boiling point of the solution increases (b) boiling point of the solution decreases
(c) vapour pressure is increased (d) freezing point is raised

Answer. (a)

45. The highest boiling point will be observed in 1% solution of which of the following substances?
(a) $\text{NH}_2\text{-CO-NH}_2$ (b) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
(c) NaCl (d) Na_2SO_4

Answer. (d)

46. Benzoic acid when dissolved in benzene undergoes
(a) dissociation (b) association
(c) no change (d) none of these

Answer. (b)

47. The value of van't Hoff factor ' i ' in case of dimerisation of benzoic acid in benzene is given by the expression
(a) $i = 1 - \alpha$ (b) $i = 1 + \alpha$
(c) $i = 1 - \alpha/2$ (d) $i = 1 + \alpha/2$

Answer. (c)

48. The ratio between the effective concentration and the actual concentration of the molecule or ions in a solution is called
(a) van't Hoff factor (b) colligative property
(c) active concentration (d) activity coefficient

Answer. (d)

49. The activity coefficient of strong electrolytes is
(a) always equal to zero (b) always equal to one
(c) always less than one (d) always greater than one

Answer. (c)