Solutions - Part 4

Objectives

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

- The concept of colligative properties;
    - Depression of freezing point
    - Osmosis and osmotic pressure
- Van't Hoff Factor

Contents Outline

- Introduction
- Depression of Freezing Point
- Osmosis and Osmotic Pressure
- Reverse Osmosis and Water Purification
- Abnormal Molar Masses

Introduction

The term colligative is derived from latin words co (which means together) and ligare (which means to bind). Thus colligative properties are those set of properties which have common origin. There are many properties of liquid solutions which have common origin i.e. a decrease of vapour pressure of volatile liquid solvent due to dissolution of non volatile solute in it. This depend s on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Thus colligative properties depend only on the number of particles and not on their nature. We have already discussed two colligative properties in the previous module. In this module we shall discuss the Depression in Freezing Point and Osmotic pressure as two important colligative properties. The study of these colligative properties helps to calculate the molar mass of a non volatile solute. We shall also discuss the van't Hoff Factor which accounts for abnormal molar mass of a solute.

Depression of Freezing Point

The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig. 1). We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent as is clear from Fig. 1. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

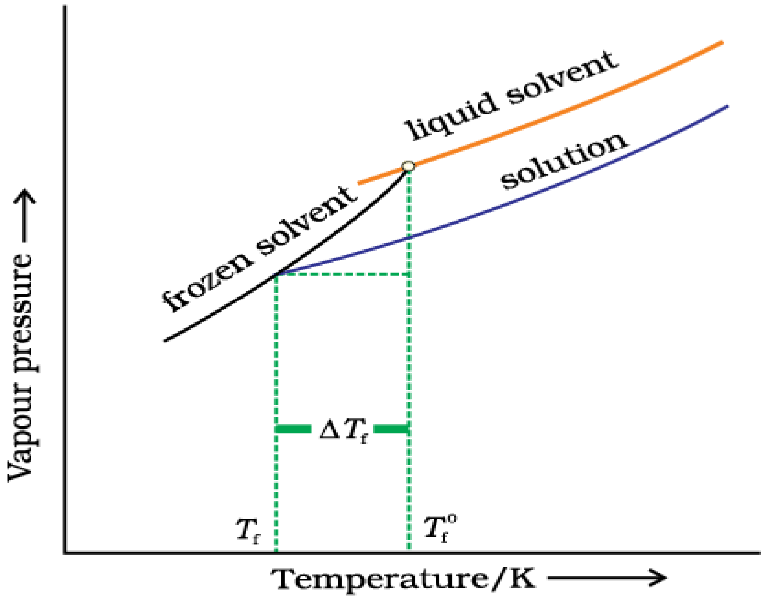


Fig 1: Diagram showing ΔT_f depression of the freezing point of a solvent in a solution

Let T_f° be the freezing point of pure solvent and T_f be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.

$\Delta T_f = T_f^{\circ} - T_f$ is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point (ΔT_f) for dilute solution (ideal solution) is directly proportional to molality, m of the solution. Thus,

$\Delta T_f \propto$ m

or $\Delta T_f = K_f.$m (1)

The proportionality constant, K_f, which depends on the nature of the solvent is known as Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant. The unit of K_f is K kg mol^{-1}. Values of K_f for some common solvents are listed in Table 1.

If w_2 gram of the solute having molar mass as M_2, present in w_1 gram of solvent, produces the depression in freezing point ΔT_f of the solvent then molality of the solute is given by the equation (2).

$$m = \frac{w_2 M_2}{\frac{w_1}{1000}} = \frac{1000\times w_2}{M_2\times w_1} \tag{2}$$

Substituting this value of molality in equation (1) we get:

$$\Delta T_f = \frac{K_f \times 1000 \times w_2}{M_2\times w_1} \tag{3}$$

$$M_2 = \frac{K_f \times 1000 \times w_2}{\Delta T_f \times w_1} \tag{4}$$

Thus for determining the molar mass of the solute we should know the quantities w_1, w_2, ΔT_f, along with the molal freezing point depression constant.

The values of K_f and K_b, which depend upon the nature of the solvent, can be ascertained from the following relations.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H} \tag{5}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H} \tag{6}$$

Here the symbols R and M_1 stand for the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further, $\Delta_{fus}H$ and $\Delta_{vap}H$ represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

Table 1: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

Solvent	**b.p./K**	**K_b/K kg mol^{-1}**	**f. p./K**	**K_f /K kg mol^{-1}**
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.79
Carbon tetrachloride	350.0	5.03	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83

Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

Example 1

45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

Solution

Depression in freezing point is related to the molality, therefore, the molality

Of the solution with respect to ethylene glycol = $\frac{moles\ of\ ethylene\ glycol}{mass\ of\ water \in kilogram}$

Moles of ethylene glycol = $\frac{45g}{62\ g\ mol^{-1}} = 0.73\ mol$

Mass of water in kg = $\frac{600g}{1000\ g\ kg^{-1}} = 0.6\ Kg$

Hence molality of ethylene glycol = $\frac{0.73mol}{0.60\ kg} = 1.2\ mol\ kg^{-1}$

Therefore freezing point depression,

$\Delta T_f = 1.86\ K\ kg\ mol^{-1} \times 1.2\ mol\ kg^{-1} = 2.2\ K$

Freezing point of aqueous solution = 273.15 K – 2.2 K = 270.95 K

Example 2

1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant

of benzene is 5.12 K kg mol^{1-}. Find the molar mass of the solute.

Solution

Substituting the values of various terms involved in equation (4) we get,

$M_2 = \frac{5.12\ K\ kg\ mol^{-1} \times 1.00\ g \times 1000\ g\ kg^{-1}}{0.40 \times 50g} = 256\ g\ mol^{-1}$

Thus, molar mass of the solute = 256 g mol^{-1}

Osmosis and Osmotic Pressure

There are many phenomena which we observe in nature or at home. For example, raw mangoes shrivel when pickled in brine (salt water); wilted flowers revive when placed in fresh water, blood cells collapse when suspended in saline water, etc. If we look into these processes we find one thing common in all, that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. Small solvent molecules, like water, can pass through these holes but the passage of bigger molecules like solute is hindered. Membranes having this kind of properties are known as semipermeable membranes (SPM).

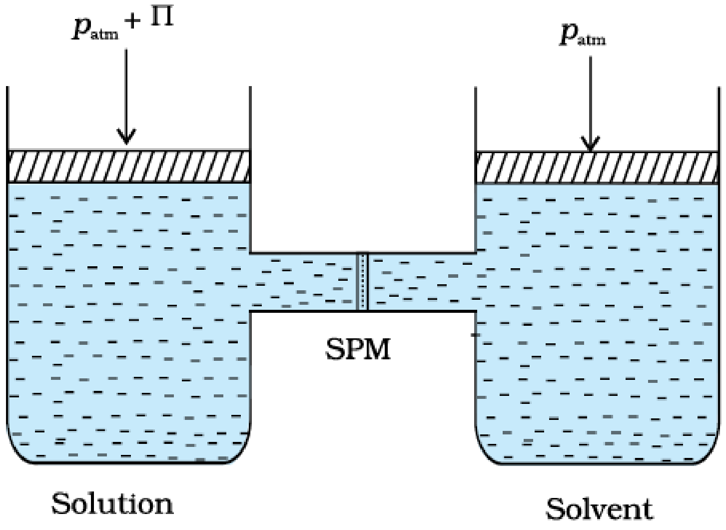


Fig. 3: The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.

Assume that only solvent molecules can pass through these semi-permeable membranes. If this membrane is placed between the solvent and solution as shown in Fig. 2, the solvent molecules will flow through the membrane from pure solvent to the solution. This process of flow of the solvent is called osmosis.

The flow will continue till the equilibrium is attained. The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. This pressure that just stops the flow of solvent is called osmotic pressure of the solution. The flow of solvent from dilute solution to the concentrated solution across a semipermeable membrane is due to osmosis. The important point to be kept in mind is that solvent molecules always flow from lower concentration to higher concentration of solution. The osmotic pressure has been found to depend on the concentration of the solution.

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution. This is illustrated in Fig. 3. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T. Thus:

$$\pi = C\,R\,T \tag{7}$$

Here π is the osmotic pressure and R is the gas constant.

$$\pi = (n_2/V)\,R\,T \tag{8}$$

Here V is the volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2 / M_2$ and we can write,

$$\pi V = \frac{w_2 RT}{M_2} \tag{9}$$

$$\text{or } M_2 = \frac{w_2 RT}{\pi V} \tag{10}$$

Thus, knowing the quantities w_2, T, π and V we can calculate the molar mass of the solute. Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

Two solutions having the same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called hypertonic. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be hypotonic. In this case, water will flow into the cells if placed in this solution and they would swell.

Example 3

200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57 10^{-3} bar. Calculate the molar mass of the protein.

Solution

The various quantities known to us are as follows: $\pi = 2.57\ 10^{-3}$ bar,

$V = 200\ \text{cm}^3 = 0.200$ litre

$T = 300$ K

$R = 0.083$ L bar $\text{mol}^{-1}\ \text{K}^{-1}$

Substituting these values in equation (10) we get

$$M_2 = \frac{1.26\ g \times 0.0083\ L\ K^{-1} mol^{-1} \times 300\ K}{2.57 \times 10^{-3} \times {}^{-}0.200\ L} = 61,022\ g\ mol^{-1}$$

The phenomena mentioned in the beginning of this section can be explained on the basis of osmosis. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickles. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into them through osmosis. When placed in water containing less than 0.9% (mass/volume) salt, blood cells collapse due to loss of water by osmosis. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called edema. Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis. The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis and is of great practical utility. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Fig. 4. When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.

The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.

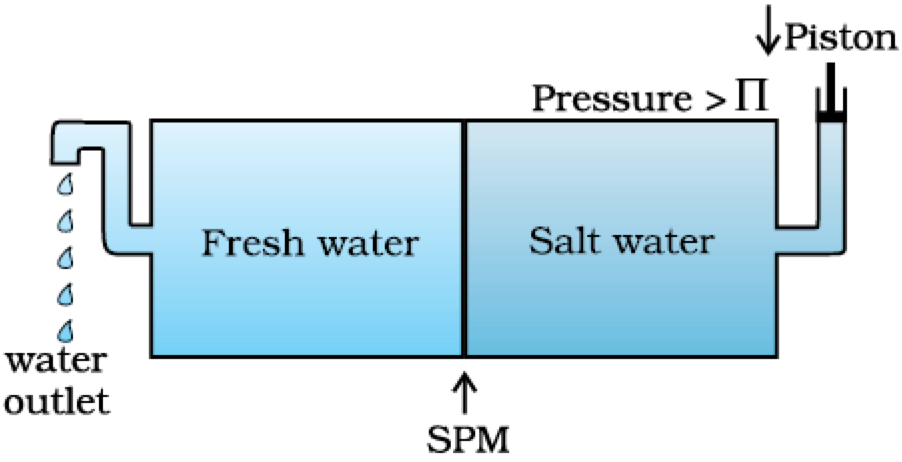


Fig. 4: Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

Example 4

Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Solution

Mass of polymer = 1.0 g

Molar mass of polymer = 185,000 g mol^{-1}

Volume of water, $V = 450\ \text{mL} = 450\ \text{mL} \times 10^{-3} \frac{L}{mL} = 0.45\ \text{L}$ (1 liter = 1000 mL)

Temperature, $T = (37 + 273.15)\ \text{K} = 310.15\ \text{K}$

Moles of polymer solute added = $\frac{mass\ of\ polymer}{molar\ mass\ of\ polymer} = \frac{1\ g}{185000\ g\ mol^{-1}}$

$$= 5.405 \times 10^{-6}\ \text{mol}$$

Now considering the formula

$\pi = cRT = \frac{n}{V}RT$

$\pi = 5.405 \times 10^{-6}\ \text{mol} \times \frac{1}{0.45\ L} \times 8.314\ kPa\ L\ K^{-1} mol^{-1} \times 310.15\ K$

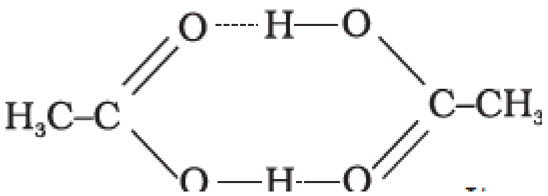
$= 5.405 \times 10^{-6}\ \text{mol} \times \frac{1}{0.45\ L} \times 8.314 \times 1000 \times Pa\ L\ K^{-1} mol^{-1} \times 310.15\ KPa$

$= 30.97\ \text{Pa}$

Abnormal Molar Masses

We know that ionic compounds when dissolved in water dissociate into cations and anions. For example, if we dissolve one mole of KCl (74.5 g) in water, we expect one mole each of K^+ and Cl^- ions to be released in the solution. If this happens, there would be two moles of particles in the solution. If we ignore interionic attractions, one mole of KCl in one kg of water would be expected to increase the boiling point by 2 × 0.52 K = 1.04 K. Now if we did not know about the degree of dissociation, we could be led to conclude that the mass of 2 mol particles is 74.5 g and the mass of one mole of KCl would be 37.25 g. This brings into light the rule that, when there is dissociation of solute into ions, the experimentally determined molar mass is always lower than the true value.

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



Molecules of ethanoic acid (acetic acid) dimerise in benzene due to hydrogen bonding. This normally happens in solvents of low dielectric constant. In this case the number of particles is reduced due to dimerisation. Association of molecules is depicted as follows:

It can be undoubtedly stated here that if all the molecules of ethanoic acid associate in benzene, then ΔT_b or ΔT_f for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this ΔT_b or ΔT_f will, therefore, be twice the expected value. Such a molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

In 1880 van't Hoff introduced a factor i, known as the van't Hoff factor, to account for the extent of dissociation or association. This factor i is defined as:

$$i = \frac{Normal\ molar\ mass}{Abnormal\ molar\ mass}$$

$$= \frac{Observed\ colligative\ property}{Calculate\ colligative\ property}$$

$$i = \frac{Total\ number\ of\ moles\ of\ particles\ after\ \frac{association}{dissociation}}{Number\ of\ moles\ of\ particles\ before\ \frac{association}{dissociation}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated. In case of association, value of i is less than unity while for dissociation it is greater than unity. For example, the value of i for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$\frac{\overset{\circ}{p_1}-p_1}{\overset{\circ}{p_1}} = i.\frac{n_2}{n_1}$$

Elevation of Boiling point, $\Delta T_b = i\, K_{\bar{\imath}}\, m$

Depression of Freezing point, $\Delta T_f = i\, K_f\, m$

Osmotic pressure of solution, $\pi = i\, n_2\, R\, T / V$

Table 2 depicts values of the factor, i for several strong electrolytes. For KCl, NaCl and $MgSO_4$, I approach 2 as the solution becomes very dilute. As expected, the value of i gets close to 3 for K_2SO_4.

Table 2: Values of van't Hoff factor, i, at Various Concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4.

Salt	Values of i			van't Hoff Factor ***i*** for complete dissociation of solute
	0.1 m	0.01m	0.001m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
$MgSO_4$	1.21	1.53	1.82	3.00
K_2SO_4	2.32	2.70	2.84	3.00

Example 5

2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution?

Solution

The given quantities are: $w_2 = 2$ g; $K_f = 4.9$ K kg mol^{-1}; $w_1 = 25$ g, $\Delta T_f = 1.62$ K

Substituting these values in equation (4) we get:

$$M_2 = \frac{4.9 Kg\ mol^{-1} \times 2\ g \times 1000\ g\ kg^{-1}}{1.62\ K \times 25\ g} = 241.98\ \ g\ mol^{-1}$$

Thus, experimental molar mass of benzoic acid in benzene is = 241.98 g mol^{-1}

Now consider the following equilibrium for the acid: 2 $C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$

If x represents the degree of association of the solute then we would have $(1 - x)$ mol of benzoic acid left in unassociated form and correspondingly $x/2$ as associated moles of benzoic acid at equilibrium. Therefore, total number of moles of particles at equilibrium is:

$$1 - x + \frac{x}{2} = 1 - \frac{x}{2}$$

Thus, the total number of moles of particles at equilibrium equals van't Hoff factor.

But $i = \frac{Normal\ molar\ mass}{Abnormal\ molar\ mass}$

$$= \frac{122\ g\ mol^{-1}}{241.98\ g\ mol^{-1}}$$

Or

$$\frac{x}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$$

or x = 2 × 0.496 = 0.992

Therefore, the degree of association of benzoic acid in benzene is 99.2 %.

Example 6

Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10–3$, $K_f = 1.86$ K kg mol^{-1}.

Solution

Molar mass of $CH_3CH_2CHClCOOH$ = (12 + 3 + 12 + 2 + 12 + 1 + 35.5 + 12 + 16 + 16 + 1) g mol^{-1}

$$= 122.5\ g\ mol^{-1}$$

Number of moles present in 10 g of $CH_3CH_2CHClCOOH = \frac{10g}{122.5\ g\ mol^{-1}}$

$$= 8.16 \times 10^{-2}\ mol$$

Since the density of water ρ_{water} is 1 g cm^{-3}, thus the volume of 250 g of water is given by

Since Volume of water = $\frac{mass\ of\ water}{density\ of\ water}$

Volume of 250 g of water= $\frac{250\ g}{1g\ cm^{-3}} = 250\ cm^3 = 250\ cm^3 \times 10^{-3} \frac{dm^3}{cm^3} = 0.25\ dm^3$

Now,

Molarity of solution = $\frac{moles\ of\ solute}{Volume\ Of\ Solution\ in\ dm^3\ liter} = \frac{8.16 \times 10^{-2}\ mol}{0.25\ dm^3} = 0.326\ M$

Now Mass of solvent = 250 g = $250\ g \times 10^{-3} \frac{kg}{g} = 0.25\ kg$

Molality of solution = $\frac{moles\ of\ solute}{mass\ of\ solvent \in Kg} = \frac{8.16\times10^{-2} mol}{0.25\ kg}$=0.3264 m

Let us consider the equilibrium

$$CH_3CH_2CHClCOOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3CH_2CHClCOO^-\ (aq)$$

Initial conc:	c	0 mol	0 mol
Equilibrium conc:	c (1 – α)	c.α	c.α

Now $K_a = \frac{[CH_3CH_2CHClCOO^-][H^+]}{[CH_3CH_2CHClCOOH]} = \frac{c.\alpha\times c.\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \approx c\alpha^2$

Solving the above equation for the degree of dissociation; α, we get

degree of dissociation of acid = $\sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.4\times10^{-3}}{0.3264}} = 0.065$

Thus total moles of particles are c (1 – α + α + α) = c (1 +x)

i = $\frac{conc.at\ equilibrium}{initial\ conc.} = \frac{c(1+\alpha)}{c} = 1 + \alpha = 1.065$

$\Delta T_f = i K_f m$

= 1.065 × 1.86 K kg Mol^{-1} × 0.3264 mol kg^{-1}

= 0.654 K

Example 7

0.6 mL of acetic acid (CH_3COOH), having density 1.06 g mL^{-1}, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.020°C. Calculate the van't Hoff factor and the dissociation constant of acid.

Solution

Number of moles of acetic acid = $\frac{0.6\ mL\times1.06\ g\ mol^{-1}}{60\ gmol^{-1}}$

= 0.00106 mol = n

Molality = $\frac{0.0106\ mol}{1000\ mL \times 1\ g\ mL^{-1}} = 0.0106\ mol\ kg^{-1}$

Using eq (3)

ΔT_f = 1.86 k Kg $mol^{-1\times\ 0.0106mo\ l\ Kg^{-1}}$ = 0.0197 K

Van’t Hoff Factor i= $\frac{Observed\ Freezing\ point}{Calculate\ Freezing\ point} = \frac{0.0205\ K}{0.0106\ K}$=1.041

Acetic acid is a weak electrolyte and will dissociate into two ions: acetate and hydrogen ions per molecule of acetic acid. If x is the degree of dissociation of acetic acid, then we would have n (1 – x) moles of undissociated acetic acid, nx moles of CH_3COO^- and nx moles of H^+ ions,

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

n mol 0 0

n (1 – α) mol n α mol n α mol

Thus total moles of particles are n (1 – x + x +x) = n (1 +x)

$i = \frac{n(1+\alpha)}{n} = 1 + \alpha = 1.041$

Thus degree of dissociation of acetic acid = x = 1.041 – 1.000 = 0.041

Then $[CH_3COOH]$ = n (1 – α) = 0.0106 (1 – 0.041),

$[CH_3COO^-]$ = n α = 0.0106 × 0.041

$[H^+]$ = n α = 0.0106 × 0.041

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]}$$

$$= 1.86 \times 10^{-5}$$