SOLUTIONS

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Introduction

A "solution" is defined as a homogeneous mixture of two or more substances (called as components), the relative proportion or composition of which may vary between certain limits.

Types of Solutions

Following types of solutions are generally considered

(a) gas in gas
(b) liquid in liquid
(c) gas in liquid
(d) solid in liquid

The component of a particular type of solution which is present in the greater quantity is called **solvent** while the other component(s) is called the **solute.** However, in the case of a solution formed from a solid and a liquid, the liquid is always referred to as the solvent even though there may be the cases when the solid is present in the larger quantity.

A solution is **unsaturated** if it can still dissolve more solute at the same temperature; when it can dissolve no more of the solute at the same temperature it is said to be **saturated.**

It is possible to obtain **supersaturated solution,** i.e., solutions which contain more dissolved solute than they should at a particular temperature, by cooling a hot concentrated solution of a solid in a liquid in the absence of traces of solids (even dust). In order to ensure that a particular solution is saturated but not supersaturated there must be a small amount of excess solute present.

- Supersaturated solutions are not in equilibrium with the solid substance. Thus, if a small crystal of solute (say sodium thiosulphate) is added to its supersaturated solution, the excess immediately crystallises out, which is usually quite fast.

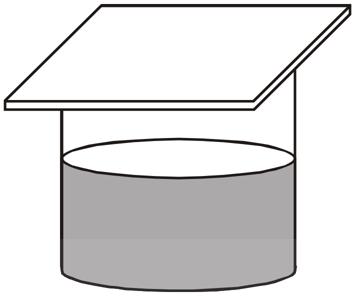
Kind of solution	Example
1. Gas in gas	Air (O_2, N_2, Ar and other gases)
2. Gas in liquid	Carbonated water
3. Gas in solid	H_2 in platinum metal (adsorption)
4. Liquid in liquid	Mixture of hydrocarbons (gasoline)
5. Liquid in solid	Dental amalgam (Hg in Ag)
6. Solid in liquid	Sea water (NaCl and other salts in water)
7. Solid in solid	Metal alloys such as 14–carat gold (Au and Ag)

Note : Closely related to weight percent and particularly useful for dilute solutions are the concentration units parts per million (ppm) and parts per billion (ppb).

$$\text{Parts per million (ppm)} = \frac{\text{mass of solute component}}{\text{total mass of solution}} \times 10^6$$

$$\text{Parts per billion (ppb)} = \frac{\text{mass of solute component}}{\text{total mass of solution}} \times 10^9$$

VAPOUR PRESSURE



When a liquid is placed in a closed container, it evaporates and converts to vapour. After some time, the liquid and the vapour reaches equilibrium, i.e., the rate of evaporation becomes equal to the rate of condensation. At this point of time the pressure exerted by the vapours of the liquid on the surface of the liquid and on the walls of the container is called the vapour pressure of the liquid.

Does the vapour pressure of a liquid depend on the volume of the vessel, shape of the vessel or the amount of liquid taken in the container ?

These questions can be answered by invoking the concept of equilibrium constant. For the equilibrium, liquid $\rightleftharpoons$ vapour, the K_p for the equilibrium would be = P_{vap}, since this is the pressure exerted by the vapours at equilibrium (by definition). We know K_p depends only on temperature and the nature of substance. This means that vapour pressure of a liquid will also be constant at a given temperature and will depend on temperature and the nature of liquid.

Therefore, it should be noted that whatever be the volume or shape of the vessel, or the amount of liquid in it (assuming it to be more than the minimum amount required), the vapour pressure of a liquid is constant at a given temperature and changes only with the change of temperature of the liquid.

Moreover, on addition of any substance to the liquid, as long as the substance does not dissolve in the liquid and completely covers the surface, the vapour pressure of a liquid remains constant.

Addition of a Non-Volatile Solute to a Volatile Solvent

When a non-volatile solute is added to a liquid (solvent), it is found that the vapour pressure of the solution is less than the vapor pressure of the pure liquid. This is because of the following two reasons

1. Attraction between the solute and solvent molecules
2. Reduction in the number of solvent molecules per unit area of the surface.

Let us understand these two reasons.

Solute–solvent attraction : When the solute is non-volatile, it is always invariably a solid. The reason a solid would dissolve in a liquid is the attraction that the solvent has for the molecules/

ions of the solute. Therefore, there is a strong solute-solvent attraction present in the solution. Moreover, this attraction would be dependent on the nature of solute, as different solutes will have different extent of attraction with the same solvent. To do away with the dependency on the nature of solute, we would like this attraction to have negligible impact on the vapour pressure of a solution.

Reduction in the number of solvent molecules : When a non-volatile solute is dissolved in a liquid, it distributes itself homogenously throughout the solution. Therefore, it occupies the surface of the liquid also. This reduces the number of solvent molecules present per unit area on the surface. This further diminishes the number of vapour molecules that are in equilibrium with the molecules of the liquid present per unit area on the surface. Thus, the vapour pressure gets reduced.

The first cause would be dependent on the nature of solute and the second cause is independent of the nature of solute. To eliminate the first cause, we propose that those solutions in which the solvent content is very high and the solute content is very low (highly dilute solutions) are the ones in which the nature of solute plays an insignificant role towards lowering the vapour pressure of a solution. This is because the solute amount being very small, the change in the vapour pressure on changing the nature of the solute would also be small. Such infinitely dilute solutions are called ideal solutions. In these solutions, the lowering of vapour pressure depends only on the amount of solute and not on its nature.

RAOULT'S LAW

The partial vapour pressure of a component in such type of solution is given by **Raoult's Law.** It states that the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

Let χ_A and χ_B be the mole fractions of solvent (A) and solute (B) molecules in the solution and P_A and P_B be the partial pressures of A and B respectively. Then according to Raoult's Law :

$P_A \propto \chi_A$ and

$P_B \propto \chi_B$

From the results of various experiments, it has been observed that :

$P_A = P_{A} \chi_A$ and

$P_B = P_{B} \chi_B$

P_{A} and P_{B} are vapour pressures of pure A and B.

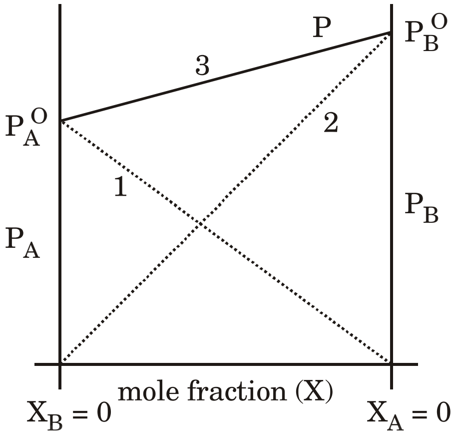
Now the total vapour pressure (P) of the solution is given by Dalton's Law of partial pressures as follows:

$$P = P_A + P_B$$

$$\Rightarrow \quad P = P_{A} \chi_A + P_{B} \chi_B$$

For a solution of different compositions made from A and B, the plot of P_A, P_B against χ_A and χ_B is shown as follows :

In the graph



Two dotted lines 1 and 2 show variations in partial pressure with increasing mole fraction and the solid line 3 gives the total vapour pressure P exerted by the solution as a whole at any composition.

Note : The solutions which obey Raoult's Law at all compositions of solute in solvent are called as **Ideal Solutions**. The plot of partial pressure Vs mole fraction of such solution is typical and in general like the graph shown here.

When solute is non-volatile : In such a solutions, the surface molecules of only solvent will escape and contribute to the vapour phase i.e., there is no contribution from solute in the vapour phase. The vapour pressure of such a solution is equal to the partial vapour pressure of solvent molecules (= P_A).

$$P = P_A = P_A \chi_A \qquad \text{(from Raoult's law)}$$

For binary solution : $\chi_A + \chi_B = 1 \quad \Rightarrow \quad \chi_A = 1 - \chi_B$

$$\Rightarrow \quad \frac{P_A^0 - P_A}{P_A^0} = \chi_B$$

The expression $\dfrac{P_A^0 - P_A}{P_A^0}$ is called as Relative Lowering of Vapour Pressure for a solution.

Another form of Raoult's Law can now be stated as :

Relative Lowering of vapour pressure for a solution containing non-volatile solute is equal to the mole fraction of the solute.

Ideal Solution

- An ideal solution consisting of two components A and B is one in which the intermolecular attraction A ... A, B ... B and A ... B are equal. For such cases,

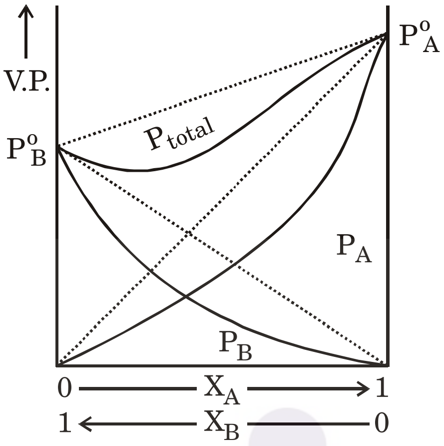
  $\Delta H_m = 0$, $\Delta V_m = 0$ (m stands for mixture)

  In such cases there is **no deviation** from **Raoult's law**
- If attraction A ... B are greater than average of A ... A and B ... B attraction then vapour pressure of the mixture is less than the expected value. In such cases, $\Delta V_m = -$ ve,

ΔH_m = –ve,and there is – ve deviation from Raoult's law. Boiling point in such cases is larger than expected.

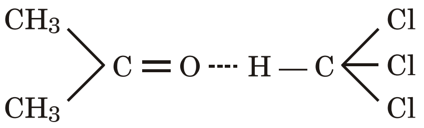
- If A ... B attractions are smaller than the average of A ... A and B ... B attractions then vapour pressure of the mixture is larger than the expected value. For such cases, ΔV_m = + ve, ΔH_m = + ve, and there is **+ ve deviation** from **Raoult's law.**

  Boiling point in such cases is smaller than expected.



Vapour pressure diagram for real solutions of two liquids A and B that exhibit a negative deviation from Raoult's law. The vapour pressure of both A and B are less than predicted by Raoult's law. The dashed lines represent the plots for ideal solutions.

A mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. Chloroform ($CHCl_3$) molecule is hydrogen-bonded to acetone (CH_3COCH_3) as shown :

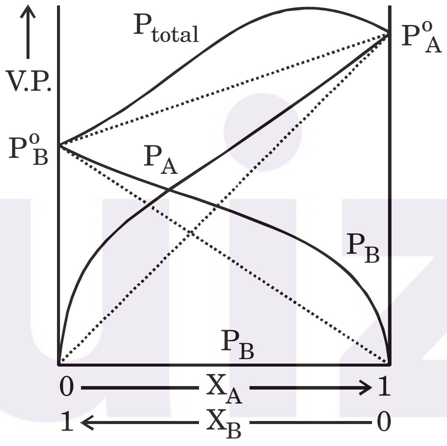


This results in decrease of escaping tendency of molecules for each component and thus vapour pressure decreases–a case of negative deviation.

Mixture of ethanol and acetone forms a solution with positive deviation. Ethanol molecules are H-bonded. If acetone is added, these molecules get in between ethanol molecules and thus H-bonding breaks. This changes the intermolecular pattern and escaping tendency of ethanol and acetone molecules increases and thus vapour pressure increases–a case of positive deviation.

Deviation from Raoult's Law

Positive deviation (ΔH = + ve)		Negative deviation (ΔH = – ve)		Zero deviation (ΔH = 0)	
(i)	ethanol + cyclohexane	(i)	acetone + chloroform	(i)	benzene + toluene
(ii)	acetone + carbon disulphide	(ii)	benzene + chloroform	(ii)	n-hexane + n-heptane
(iii)	acetone + benzene	(iii)	nitric acid + chloroform	(iii)	ethyl bromide + ethyl iodide
(iv)	ethanol + acetone	(iv)	acetone + aniline	(iv)	chlorobenzene + bromo benzene
(v)	ethanol + water	(v)	water + nitric acid		
(vi)	carbon tetrachloride + chloroform	(vi)	diethyl ether + chloroform		



Vapour pressure diagram for real solutions of two liquids A and B that exhibit a positive deviation from Raoult's law. The vapour pressure of both A and B are greater than predicted by Raoult's law.

The dashed lines represented the plots for ideal solutions.

- In case of + ve and – ve deviations the boiling point composition curves have minima or maxima. The separation of such solutions into their component can't be obtained by simple or fractional distillation and these are called **azeotrope mixture.** An azeotropic mixture boils at a constant temperature and distills over without undergoing any change in its composition.

  There are two types of azeotropes called as **minimum boiling azeotrope** and maximum boiling azeotrope, respectively. Solutions of ethanol and water show such a large deviation from Raoult's law that there is a maximum in the vapour pressure curve and hence a minimum in the boiling point curve.

Example 1

How many grams of sucrose must be added to 360 g of water to lower the vapour pressure by 1.19 mm Hg at a temperature at which vapour pressure of pure water is 25 mm Hg ?

Solution :

Given $\Delta P = 1.19$ mm Hg

$P_{solvent} = 25$ mm Hg

By Raoult's law

$$\frac{\Delta P}{P_{solvent}} = X_{solute}$$

$$\therefore \quad X_{solute} = \frac{1.19}{25} = 0.0476$$

$$\therefore \quad X_{solvent} = 1 - 0.0476 = 0.9524$$

$$\frac{n_{solvent}}{n_{total}} = 0.9524$$

$$n_{solvent} = \frac{360}{18} = 20$$

$$\therefore \quad n_{total} = \frac{n_{solvent}}{0.9524} = \frac{20}{0.9524} = 21$$

$$\therefore \quad n_{solute} = 21 - 20 = 1 = 1 \quad 342 \text{ g}$$

$$= 342 \text{ g}$$

Example 2

The vapour pressure of pure liquid A at 300 K is 575 Torr and that of pure liquid B is 390 Torr. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.35. Calculate the total pressure of the vapour and the composition of the liquid mixture.

Solution :

A and B are volatile liquids, given

$$P_A^\circ = 575 \text{ Torr}, \; P_B^\circ = 390 \text{ Torr}$$

let mole fraction of A in solution = X_A

hence, $$P_{Total} = P_A^\circ X_A + P_B^\circ (1 - X_A)$$

also X'_A = mole fraction of A in the vapour = 0.35

$$X'_A = \frac{P_A^\circ X_A}{P_A^\circ X_A + P_B^\circ (1 - X_A)} = 0.35$$

$$= \frac{575\, X_A}{575 X_A + 390(1 - X_A)}$$

this gives $X_A = 0.27$

hence, total pressure

$$P_{total} = 575 \quad 0.27 + 390 \quad 0.73$$

$$= 440 \text{ Torr}$$

Composition of liquid mixture,

∴ A = 27 mol %, B = 73 mol %

Total pressure = 440 Torr

Example 3

At a certain temperature, the vapour pressure of pure ether is 646 mm and that of pure acetone is 283 mm. Calculate the mole fraction of each component in the vapour state if the mole fraction of ether in the solution is 0.50.

Solution :

In the given solution, both ether and acetone are volatile, so from Raoult's Law, we can have vapour pressure of solution (P).

Let A : ether and B : acetone

$$P = P_A + P_B = P_A^0 \chi_A + P_B^0 \chi_B$$

$$\Rightarrow \quad P = 646 \quad 0.5 + 283 \quad 0.5 = 464.5 \text{ mm}$$

Now mole fraction in vapour state is given as follows :

$$\chi_A \text{ (vapour)} = \frac{P_A}{P} = \frac{P_A^0 \chi_A}{P} = \frac{646 \times 0.5}{464.5} = 0.695$$

$$\chi_B \text{ (vapour)} = \frac{P_B}{P} = \frac{P_B^0 \chi_B}{P} = \frac{283 \times 0.5}{464.5} = 0.305$$

Colligative Properties

Certain properties of solutions depend only on the number of particles of the solute (molecular or ions) present in definite volume of the solution and do not depend on the nature of solute. Such properties are called colligative properties.

A few colligative properties are :

(i) Relative lowering of vapour pressure

(ii) Elevation of boiling point

(iii) Depression in freezing point

(iv) Osmotic pressure

(i) Relative lowering of vapour pressure :

The relative lowering of vapour pressure is a colligative property as it depends only on the concentration of the solute and it is independent of its nature.

Consider a binary solution consisting of non volatile solute in a volatile solvent. The vapour pressure of the solution (P) is equal to vapor pressure of solvent (P_A) in the solution, which in turn is directly proportional to its mole fraction in solution.

$$P = P_A$$

$$= P_A^0 \chi_A \qquad \ldots (i)$$

where χ_A = mole fraction of solvent

If mole fraction of solute is χ_B then

$$\chi_A + \chi_B = 1 \text{ or } \chi_A = 1 - \chi_B \ \ldots (ii)$$

From eq. (i) and (ii) $P_A = P_A^0 (1 - \chi_B) = P_A^0 - P_A^0 \chi_B$

$$P_A^0 - P_A = P_A^0 \chi_B$$

$$\frac{P_A^0 - P_A}{P_A^0} = \chi_B$$

$$\frac{P_A^0 - P_A}{P_A^0} = \chi_B$$

is called the relative lowering of vapor pressure and is equal to the mole fraction of the solute.

Now, $\dfrac{\Delta P}{P_A^0} = \chi_B = \dfrac{n_B}{n_A + n_B} = \dfrac{n_B}{n_A}$ {for dilute solutions : $n_A + n_B \approx n_A$}

Calculation of molecular mass from relative lowering of vapor pressure

A known mass W_B of the non-volatile solute is dissolved in a known mass (W_A) of the volatile solvent to prepare a dilute solution and relative lowering of vapor pressure is determined experimentally. Knowing the molecular mass (M_A) of the solvent, molecular mass (M_B) of the solute can be determined as follows :

$$n_A = \frac{W_A}{M_A},\ n_B = \frac{W_B}{M_B}$$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{W_B / M_B}{W_A / M_A + W_B / M_B}$$

Relative lowering of vapor pressure is given by

$$\frac{\Delta P}{P_A^0} = \frac{P_A^0 - P_A}{P_A^0} = X_B = \frac{W_B / M_B}{W_A / M_A + W_B / M_B}$$

For dilute solutions $W_B/M_B << W_A/M_A$ and hence in the above expression W_B/M_B may be neglected in the denominator as compared with W_A/M_A.

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B M_B}{M_B W_A}$$

$$M_B = \frac{W_B M_A}{W_A} \times \left(\frac{P_A^0}{P_A^0 - P_A} \right)$$

In this expression all the parameters are known except M_B and hence M_B can be calculated.

Example 4

Dry air was passed through a container having a solution of a non-volatile solute in water. The solute weighed 26.66 g and the solvent weighed 200 g. The air then went into a solvent container and then finally through a tube containing fused calcium chloride. The loss in weight of water container is 0.087 g and gain in weight of $CaCl_2$ tube is 2.036 g. Calculate the molecular weight of the non-volatile solute present in the solution.

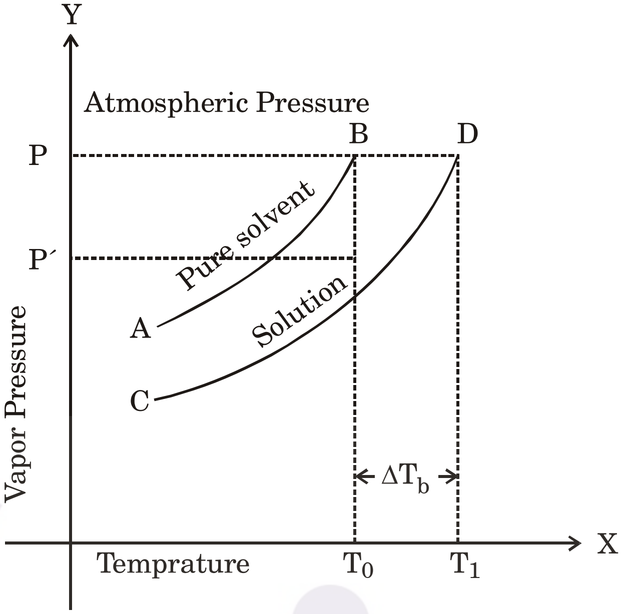
Solution : We can use the relation

$$\frac{P^0 - P_s}{P_s} = \frac{n}{N} = \frac{\text{loss in weight of solvent}}{\text{loss in weight of solution}}$$

$$\frac{0.087}{2.036 - 0.087} = \frac{\frac{26.66}{M}}{\frac{200}{18}} = \frac{26.66 \times 18}{200 \times M};\quad M = \frac{26.66 \times 18 \times 1.949}{200 \times 0.087} = 53.75$$

ELEVATION OF BOILING POINT

The boiling point of a liquid may be defined as the temperature at which the vapor pressure of the liquid becomes equal to the atmospheric pressure.



The vapor pressure curves for the pure solvent and solution consisting of a non-volatile solute is represented diagrammatically. AB is the vapor pressure curve for pure solvent and CD is vapor pressure curve for the solution. T_0 represents the boiling point of pure solvent and T_1 represents the boiling point of solution. In the presence of a non-volatile solute the solution has to be heated to a slightly higher temperature so that the vapor of the solution becomes equal to atmospheric pressure and solution begins to boil. The differences in the boiling points are represented as ΔT_b, which is the elevation in boiling point.

$$\Delta T_b = K_b\ m$$

K_b : molal boiling point elevation constant or ebullioscopic constant of solvent

m : molality of the solution

Hence, $\Delta T_b = K_b \left(\frac{n_B}{g_A} \times 1000 \right)$

$$\Rightarrow \quad \boxed{\Delta T_b = \frac{1000\ K_b\ g_B}{g_A\ M_B}}$$

Boiling Point Elevation Constant (K_b) : It is the elevation in point achieved when a solution of a non-volatile solute of concentration 1 molal is boiled. Its boiling units are K kg mol^{-1}. K_b is related to molar enthalpy of vaporization as

$$K_b = \frac{M\,RT_b^2}{\Delta H_{vap} \times 1000}$$

where M = molar mass of solvent,

R = Universal gas constant,

T_b = boiling point of pure solvent and

ΔH_{vap} = enthalpy of vaporization of solvent.

Example 5

A solution containing 0.512 g of naphthalene (molar mass 128.2 g mol^{-1}) in 50 g CCl_4 yields a boiling point elevation of 0.402 K, while a solution of 0.6216 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.647 K. Find the molar mass of the unknown solute.

Solution :

$$T_{b,\ naphthalene} - T_{b,CCl_4} = \Delta T_{b,\ naphthalene} = K_b\ m_{naphthalene}$$

$$T_{b,\ unknown\ solute} - T_{b,CCl_4} = \Delta T_{b,\ unknown\ solute} = K_b\ m_{unknown\ solute}$$

$$\therefore\ T_{b',\ unknown\ solute} - T_{b,\ naphthalene} = \Delta T_{b,\ unknown\ solute} - \Delta T_{b,\ naphthalene} = K_b\ (m_{unknown\ solute} - m_{naphthalene})$$

$$K_b = \frac{\Delta T_{b,\ naphthalene}}{m_{naphthalene}} = \frac{0.402\,K}{\left(\dfrac{\dfrac{0.512\ g}{128.2\ g\,mol^{-1}}}{50\ g}\right) \times 1000\ kg^{-1}}$$

$$K_b = \frac{0.402 \times 50 \times 128.2}{0.512 \times 1000} = 5.03\ K\ kg\ mol^{-1}$$

$$0.647\ K - 0.402\ K = 5.03\ K\ kg\ mol^{-1}\left(\frac{0.6216\ g \times 1000\ g\ kg^{-1}}{M\,g\,mol^{-1} \times 50\,g} - \frac{0.512\ g \times 1000\ kg^{-1}}{128.2\,g\ mol^{-1} \times 50\ g}\right)$$

Solving for M we get,

$M = 96.68\ g\ mol^{-1}$.

DEPRESSION IN FREEZING POINT

Freezing point of a substance is defined as the temperature at which the vapor pressure of the solid form is in equilibrium with liquid form of the substance. In other words, solid and liquid forms of the substance has same vapor pressure. Since the vapour pressure of a solution is less than that of pure solvent, the freezing point of the solution will be lower than that of pure solvent.

Let ΔT_f be the depression in freezing point, then

$\Delta T_f = T_f - T_0$

T_f : freezing point of solution

T_0 : freezing point of pure solvent

$\Delta T_f = K_f\ m$

K_f : molal boiling point elevation constant or cryoscopic constant of solvent.

m : molality of solution

$$\boxed{\Delta T_f = \frac{1000\ K_f\ g_B}{g_A\ M_B}}$$

Final point Depression Constant (Kf) : It is the depression in freezing point achieved when a solution of a non-volatile solute of concentration 1 molal is frozen. Its units are K kg mol^{-1}. K_f is related to the molar enthalpy of fusion as

$$K_f = \frac{MRT_1^2}{\Delta H_{fusion} \times 1000}$$

where M = molar mass of solvent,

R = universal gas constant,

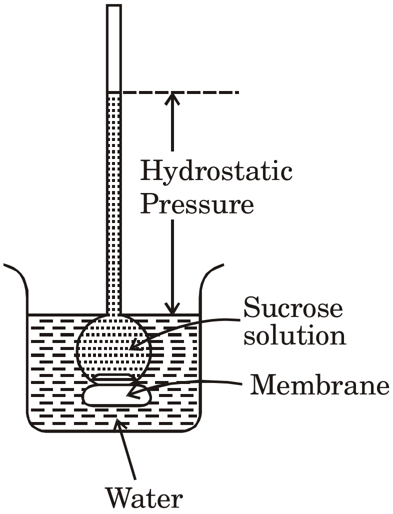
T_f = freezing point of pure solvent and

ΔH_{fusion} = enthalpy of fusion of solid solvent

4. OSMOTIC PRESSURE

Osmosis is defined as the spontaneous flow of solvent into solution or from a more dilute to a more concentrated solution, when the two solutions are separated by a suitable membrane. The membrane allows the free passage of the solvent but not of the dissolved substances. Membranes possessing this property are said to be semipermeable.

The phenomenon of osmosis may be illustrated in a simple manner by tying an animal membrane, e.g., bladder, over the end of an inverted thistle tube, which is then partly filled with a concentrated solution of sucrose (cane sugar) and dipped into a beaker of water, as shown in the given figure. The level of the liquid will rise in the tube until the hydrostatic pressure so produced is sufficient to stop the flow of water. It is seen, therefore, that as a result of osmosis, a pressure is developed which opposes the tendency for the solvent to pass through the semipermeable membrane into the solution. This pressure is called the **osmotic pressure** of the solution. It is defined as **"the excess pressure that must be applied to a solution to prevent the passage into of solvent when the liquids are separated by a perfectly semipermeable membrane".**



There has been some tendency to think pressure as a pressure produced by the solution, but this point of view is misleading. The osmotic pressure is brought into existence only when the solution is separated from the solvent by a semipermeable membrane. The resulting osmosis or tendency for osmosis to occur then produces an excess pressure in the solution. When this excess pressure attains the value of the osmosis pressure, the tendency for solvent to enter the solution is exactly counterbalanced by the reverse tendency and a condition of equilibrium results.

For the accurate measurement of osmotic pressure, it is necessary to have a membrane that is perfectly semipermeable. Artificial membranes made of copper ferrocyanide, $Cu_2Fe(CN)_6$, is the best material for osmosis.

The osmotic pressure of a dilute solution of a non-volatile solute is given by $\pi V = nRT$

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

$$\pi = \frac{w}{M} \frac{RT}{V}$$

where π is the osmotic pressure in atmospheres, n = number of moles of solute $\left(\frac{w}{M}\right)$ in V litres of solution at temperature T (Kelvin), R = 0.0821 Lit atm K^{-1} mol^{-1}. C is the molarity of the solution. Measurement of osmotic pressure provides a method of determining molecular weights of proteins, polymer and other macromolecules.

If two solutions are of equal concentrations at the same temperature, they have the same osmotic pressure and they are said to be isotonic. If two solutions have unequal osmotic pressures, the more concentrated solution is said to be hypertonic and the more dilute solution is described as hypo tonic. To study the contents of red blood cells, which are protected by a semipermeable membrane, a technique called haemolysis is used. The red blood cells are placed in a hypo tonic solution, when water moves into the cells. The cells swell and eventually burst releasing the haemoglobin and other molecules.

When a bacterial cell is placed in a hypertonic solution (high concentration), the intracellular water tends to move out of the cell by osmosis. This causes the cell to shrink.

Example 6

Find the molecular weight of the polymer having the concentration of 9.6 g/l and exerting an osmotic pressure of 2.56 torr at a temperature of 298 K.

Solution :

$$\pi = CRT$$

$$\frac{2.56}{760} = \frac{9.6 \times 0.0821 \times 298}{M}$$

or $M = 69727.5$ g/mol.

Example 7

A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene ?

Solution :

$$\frac{P^{\circ} - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W} \qquad \therefore \quad \frac{100 - 98.88}{98.88} = \frac{w \times 78 \times 1000}{m \times W \quad 1000}$$

or $$\text{molality}\left(\frac{w \times 1000}{m \times W}\right) = \frac{1.12 \times 1000}{78 \times 98.88} = 0.1452$$

Also $\Delta T = K'_f \quad \text{molality}$

$0.73 = K'_f \quad 0.1452 \qquad \therefore \qquad K'_f = 5.028 \text{ K molality}^{-1}$

Example 8

An aqueous solution containing 5% by weight of urea and 10% by weight of glucose. What will be its freezing point ? K'_f for H_2O is 1.86 mol^{-1} kg.

Solution : $\therefore$ Solution has 5% by weight urea and 10% by weight glucose

$$\therefore \quad \% \text{ By weight} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 100$$

$$\therefore \quad \text{Wt. of water} = 85 \text{ g}; \qquad \text{wt. of urea} = 5 \text{ g}; \qquad \text{wt. of glucose} = 10 \text{ g}$$

$$\Delta T = \Delta T_{\text{Urea}} + \Delta T_{\text{Glucose}}$$

$$\Delta T = \frac{1000 \times 1.86 \times 5}{60 \times 85} + \frac{1000 \times 1.86 \times 10}{180 \times 85}$$

$$= 1.824 + 1.216 = 3.04$$

$$\therefore \quad \text{Freezing point} = 0 - 3.04 = -3.04 \text{ C}$$

Example 9

1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of a solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molecular weight of (A).

Solution :

For acetone + Benzene mixture :

$$\Delta T = \frac{K_f' \times 1000 \times w}{m \times W}$$

$$(278.40 - 277.12) = \frac{1000 \times K_f \times 1.4}{100 \times 58}$$

$$\text{or} \qquad 1.28 = \frac{1000 \times K_f \times 1.4}{100 \times m} \qquad \text{...(1)}$$

For solute (A) + Benzene mixture (Let m be the mol. weight of A)

$$(278.40 - 277.76) = \frac{1000 \times K_f \times 2.8}{100 \times m}$$

$$\text{or} \qquad 0.64 = \frac{1000 \times K_f \times 2.8}{100 \times m} \qquad \text{...(2)}$$

By Eqs. (1) and (2), $m = 232$

Example 10

If boiling point of an aqueous solution is 100.1 C. What is its freezing point ? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

Solution :

For a given aqueous solution

$$\Delta T_b = K_b' \quad \text{molality}$$

$$\Delta T_f = K_f' \quad \text{molality}$$

$$\therefore \quad \frac{\Delta T_b}{\Delta T_f} = \frac{K_b'}{K_f'} = \frac{RT_b^2}{1000 l_v} \times \frac{1000 l_f}{RT_f^2}$$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{T_b^2 \times l_f}{T_f^2 \times l_v}$$

$$\therefore \quad T_b = 100 + 273 = 373 \text{ K}$$

$$T_f = 0 + 273 = 273 \text{ K}$$

$$l_f = 80 \text{ cal g}^{-1}$$

$$l_v = 540 \text{ cal g}^{-1}$$

Example 11

Two solutions of non-volatile solutes A and B having molar mass ratio of A and B (M_A/M_B) as 1/3 are prepared by dissolving 5% (wt./vol.) of each in water. Calculate the ratio of freezing point depression. If the two solutions are mixed to prepare a new solution (S_1) by mixing in the ratio 2 : 3 by volume and another new solution (S_2) is obtained by mixing in the ratio 3 : 2, find out $\frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}}$. Assume density of solution A and B equal to one.

Solution :

For 5% solution of A :

$$(\Delta T_f)_A = \frac{K_f \times 5 \times 1000}{m_A \times 95} \quad \ldots (1)$$

For 5% solution of B :

$$(\Delta T_f)_B = \frac{K_f \times 5 \times 1000}{m_B \times 95} \quad \ldots (2)$$

By Eqs. (1) and (2),

$$\therefore \qquad \frac{(\Delta T_f)_A}{(\Delta T_f)_B} = \frac{m_B}{m_A} = \frac{3}{1} \qquad \left(\because \frac{m_A}{m_B} = \frac{1}{3}\right)$$

For solution S_1 : Let 2V mL solution of A is mixed with 3V mL solution of B.

$$\text{Weight of A in 2V mL or 2V g} = \frac{5 \times 2V}{100} g = \frac{10V}{100} g$$

$$\text{Weight of B in 3V mL or 3V g} = \frac{5 \times 3V}{100} g = \frac{15V}{100} g$$

Total weight of solution $= 5V$

$$(\Delta T_f)_{S_1} = \frac{K_f \times 1000 \times \left[\frac{0.1V}{m_A} + \frac{0.15V}{m_B}\right]}{\left[5V - \frac{10V}{100}\right]} = \frac{1000K_f\left[0.1m_B + 0.15m_A\right]}{4.9 \times m_A \times m_B}$$

For solution S_2 : Similarly, have

$$(\Delta T_f)_{S_2} = \frac{1000 \times K_f\left[0.15m_B + 0.10m_A\right] \times 0.9898}{4.85 \times m_A \times m_B}$$

$$\text{Thus,} \qquad \frac{(\Delta T_f)_{S_1}}{(\Delta T_f)_{S_2}} = \frac{(0.1m_B + 0.15m_A) \times 0.9898}{(0.10m_A + 0.15m_B)}$$

$$= \frac{(0.1\ \ 3m_A + 0.15m_A) \times 0.9898}{(0.10m_A + 0.15 \times 3m_A)}$$

$$= \frac{0.45 \times 0.9898}{0.55} = 0.81$$

VAN'T HOFF FACTOR (*i*)

Since colligative properties depend on the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results for colligative properties are obtained.

Dissociation : Let us consider the case of acetic acid dissolved in water. Let the number of mole of acetic acid dissolved be ‘n’.

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

Initial no. of mole	n	0	0
After dissociation	$n(1 - \alpha)$	$n\alpha$	$n\alpha$
Total mole of solute =	$n(1 + \alpha)$		

Theroctical colligative property (for example ΔT_b) based on the number of mole of CH_3COOH added)

$$\Delta T_b = K_b\, m = K_b \frac{n}{W} \times 1000$$, where W is the mass of solvent in gm.

Experimental colligative property would be given by

$$\Delta T'_b = K_b\, m' = K_b \frac{n(1+\alpha)}{W} \times 1000$$

$$\frac{\text{Experiment colligative property}}{\text{Theoretical colligative property}} = \frac{n(1+\alpha)}{n} = (1+\alpha) = i, \text{ Van't Hoff factor}$$

Association : Let us consider the case of acetic acid dissolved in benzene. Let the number of mole of acetic acid dissolved be ‘n’ it forms dimer in benzene.

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

Initial no. of mole	n	0
After dissociation	$n(1 - \alpha)$	$n\alpha/2$
Total mole of solute =	$n(1 - \alpha/2)$	

Theoretical colligative property (for example ΔT_b) (based on the no. of mole of CH_3COOH added)

$$\Delta T_b = K_b\, m = K_b \frac{n}{W} \times 1000$$, where W is the mass of solvent in gm.

Experimental colligative property would be given by

$$\Delta T'_b = K_b\, m' = K_b \frac{n\left(1 - \frac{\alpha}{2}\right)}{W} \times 1000$$

$$\frac{\text{Experimental colligative property}}{\text{Theoretical colligative property}} = \frac{n\left(1 - \frac{\alpha}{2}\right)}{n} = 1 - \frac{\alpha}{2} = i, \text{ Van't Hoff factor}$$

Therefore, for dissociation i > 1 and for association i < 1. When a solute neither dissociates nor associates, the Van't Hoff factor is equal to 1.

Example 12

Acetic acid associates in benzene to form a dimer. 1.65 gm of acetic acid when dissolved in 100 gm of benzene raised the B.P. by 0.36 C. Calculate the Van't Hoff factor and degree of association of acetic acid. (k_b **for benzene = 2.57 C**/m**)**

Solution :

Calculation of Van't Hoff factor :

First calculate molecular mass from elevation in boiling point

$$M_B = \frac{1000\ k_b\ g_B}{g_A\ \Delta\ T_b}$$

$$= \frac{1000 \times 2.57 \times 1.65}{100 \times 0.36} = 117.8$$

$$\Rightarrow \qquad i = \frac{\text{Normal molecular mass}}{\text{observed molecular mass}}$$

$$= \frac{60}{117.8} = 0.509$$

Calculation of degree of dissociation

Let x = degree of dissociation

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

$$1 \qquad\qquad 0$$

$$1 - x \qquad\qquad x/2$$

$$\text{Total mass} = 1 - x/2$$

$$i = \frac{\text{total mass}}{\text{initial mass}} = \frac{1 - \frac{x}{2}}{1}$$

$$\Rightarrow \qquad 0.509 = \frac{1 - \frac{x}{2}}{1} \qquad \Rightarrow \qquad x = 0.982$$

Example 13

When dissolved in benzene, a compound $C_{38}H_{30}$ partially dissociates by the following equation : $C_{38}H_{30} \rightleftharpoons 2\ C_{19}H_{15}$. 25.6 gm of $C_{38}H_{30}$ is dissolved in 400 gm of benzene, the freezing point is lowered by 0.680 C. What % age of $C_{38}H_{30}$ molecules have dissociated ? (k_f = 4.9)

Solution :

Calculate observed molecular mass (due to dissociation) as done in above example and then by calculating i, find x.

OR Use the following approach.

$\Delta T_b = i\ k_b\ m$

$$i = \frac{\Delta T_b \times g_A}{k_b\ (g_B / M_B) \times 1000} = \frac{0.68 \times 400}{4.9 \times \dfrac{25.6}{486} \times 1000}$$

$\Rightarrow$ $i = 1.0538$

$$\begin{array}{ccc} C_{38}H_{30} & \rightleftharpoons & 2\ C_{19}H_{15} \\ 1 - x & & 2x \end{array}$$

Total mass = $1 - x + 2x = 1 + x$

$$i = \frac{\text{total moles}}{\text{initial moles}}$$

$\Rightarrow$ $1.0538 = \dfrac{1 + x}{1}$

$\Rightarrow$ $x = 0.0538$

$\Rightarrow$ % age of dissociation = 5.38%

Example 14

Acetic acid (CH_3COOH) associates in benzene to form double molecules. 1.65 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36 C. Calculate the Van't Hoff factor and the degree of association of acetic acid in benzene (Molal elevation constant of benzene is 2.57).

Solution :

Normal molar mass of acetic acid = 60

Observed molar mass of acetic acid

$$M = K_b \frac{w_{solute}}{W_{solvent}\,(\text{in gms})\,\Delta T} \times 1000 = \frac{2.57 \times 1.65 \times 1000}{100 \times 0.36} = 118$$

$$\text{Van't Hoff factor} = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{60\text{g mol}^{-1}}{118\text{g mol}^{-1}}$$

$$= 0.508 = 1 - \left[\alpha\left(1 - \frac{1}{n}\right)\right] = 1 - \left[\alpha\left(1 - \frac{1}{2}\right)\right] = 1 - \alpha/2$$

$$\alpha/2 = 1 - 0.508 = 0.492$$

$$\therefore \qquad \alpha = \quad 0.492 = 0.984$$

Thus acetic acid is 98.3% associated in benzene.

Now, if we include Van't Hoff factor in the formular for colligative properties we obtain the normal results.

1. Relative lowering of vapour pressure, $\frac{P_1^o - P_1}{P_1^o} = iX_2 = i\frac{n}{n+N}$
2. Osmotic pressure, $\pi = iCRT$
3. Elevation in boiling point, $\Delta T_b = i.\ 1000 \quad K_b \quad \text{molality}$
4. Depression in freezing point, $\Delta T_f = i\ 1000 \quad K_f \quad \text{molality}$

Note : The value of i is taken as one when solute is non electrolyte.

Example 15

A 0.5 percent aqueous solution of Potassium Chloride was found to freeze at 0.24 C. Calculate the Van't Hoff factor and degree of dissociation of the solute at this concentration (K_f for water is 1.86).

Solution :

$$\Delta T_f = \frac{i \times 1000\ K_f\ w}{W.\ M}$$

$$0.24 = \frac{i \times 1000 \times 0.5 \times 1.86}{100 \times 74.5}$$

$$i = \frac{0.24 \times 100 \times 74.5}{1000 \times 0.5 \times 1.86} = 1.923$$

$$i = 1 + (n - 1)\alpha$$

$$1.923 = 1 + (2 - 1)\alpha$$

$$1.923 = 1 + \alpha$$

$$\alpha = 1.923 - 1 = 0.923$$

or $\alpha = 0.923$ or 92.3%

SOLVED EXAMPLES

Example 1

If the apparent degree of ionization of KCl (KCl = 74.5 gm mol^{-1}) in water at 290 K is 0.86. Calculate the mass of KCl which must be made up to 1 dm^3 of aqueous solution so as to produce the same osmotic pressure as the 4.0% solution of glucose at that temperature.

Solution :

Due to ionization of KCl

	KCl	$\longrightarrow$	K^+	$+ Cl^-$
Initial moles	1		0	0
Moles after dissociation	$1 - \alpha$		α	α

$$\therefore \quad i = \frac{(1-\alpha) + \alpha + \alpha}{1} = 1 + \alpha$$

From question, degree of ionization = $\alpha = 0.86$

$\therefore \quad i = 1 + 0.86 = 1.86$

For Osmotic pressure of glucose,

For 4% glucose solution, Weight of glucose = 40 gm,

Volume of solution = V = 1 L = 1 dm^3

Molecular weight of glucose $C_6H_{12}O_6$ = m = 180

$$\therefore \quad \pi_{glucose} = n \times \frac{1}{V} \times RT, \text{ where } \pi_{glucose} = \text{osmotic pressure of glucose}$$

$$= \frac{w}{m} \times \frac{1}{V} R \times T = \frac{40}{180} \times \frac{1}{1} \times RT$$

Similarly,

$$\pi_{KCl} = i \times n \times \frac{1}{V} RT = 1.86 \times n \times \frac{1}{V} \times RT$$

$$= 1.86 \times \frac{w_1}{m_1} \times \frac{1}{V} \times RT$$

$$= 1.86 \times \frac{w_1}{74.5} \times \frac{1}{1} \times RT$$

As both solutions are isotonic,

$$\therefore \qquad \pi_{KCl} = \pi_{glucose}$$

$$1.86 \times \frac{w_1}{74.5} \times RT = \frac{40}{180} \times RT$$

$$\therefore \qquad W_1 = \frac{40}{180} \times \frac{74.5}{1.86}$$

$$= 8.9 \text{ gm}$$

Example 2

1 kg of an aqueous solution of Sucrose is cooled and maintained at – 4 C. How much ice will be separated out if the initial molality of the solution is 0.75 ?

Solution :

Sucrose is a non-electrolyte, hence i = 1

Molecular weight of sucrose ($C_{12}H_2O_{11}$) = m = 342 gm mol^{-1}

Molality of the solution = 0.75 m

= 0.75 mol kg^{-1} solvent

= 0.75   342 gm Sucrose per kg solvent

= 256.5 gm Sucrose per kg solvent

Hence, weight of 1 molal solution = 1000 + 256.5 = 1256.5 gm

Sucrose present in 1 kg solution $= \frac{256.5}{1256.5} \times 1000 = 204.14$ gm

Weight of solvent (H_2O) present in 1 kg solution = 1000 – 204.14 = 795.86 gm

Since depression in freezing point

$$\Delta T_f = K_f \quad i \quad \frac{w}{m} \quad \frac{1000}{W}$$

Where W = weight of solvent

w = weight of the solute

or, $4 = 1.86 \quad 1 \quad \frac{204.14}{342} \times \frac{1000}{W}$

$\therefore$ W = 277.55 gm

i.e., weight of solvent required to maintain this solution at – 4 C is W = 277.55

Hence rest weight of H_2O will convert into ice.

Hence amount of ice formed = 795.86 – 277.55 = 518.31 gm

Example 3

The osmotic pressure of an aqueous solution of sucrose is 2.47 atm at 303 K and the molar volume of the water present is 18.10 cm^3. Calculate the elevation in boiling point of the solution. Given ΔH_{vap} = 540 cal/g. Assume volume of solvent equal to volume of solution.

Solution :

$$\pi = CST$$

$$2.47 = C \quad 0.0821 \quad 303$$

$$\therefore \qquad C = 9.93 \quad 10^{-2}\ M$$

Thus, 1 litre solution of sucrose contains 9.93 10^{-2} mole of sucrose or 9.93 10^{-2} 342 g of sucrose.

$$\therefore \qquad \text{Volume of solution} = \text{Volume of solvent} = 1000\ \text{mL}$$

$$\therefore \qquad \text{Mole of water} = \frac{1000}{18.10}$$

$$\therefore \qquad \text{Weight of water} = \frac{1000}{18.10} \times 18 = 994.475\ g$$

$$\text{Thus, molality of solution} = \frac{9.93 \times 10^{-2}}{994.475 \times 10^{-3}} = 9.985 \times 10^{-2}\ M$$

$$\Delta T_b = K_b \quad \text{molality} = \frac{RT_b^2}{1000l} \times \text{molality}$$

$$= \frac{2 \times 373 \times 373}{1000 \times 540} \times 9.985 \times 10^{-2}$$

$$= 5.145 \quad 10^{-2}$$

Example 4

The molecular weight of an organic compound is 58 g/mol. 24 g of this dissolved in 600 g of water, calculate its boiling point when vapour pressure of water becomes 760 mm at 99.725 C. K_b of H_2O is 0.513 K kg mol^{-1}.

Solution :

$$\text{B. pt. of } H_2O = 99.725\ C$$

Given $w_{\text{organic compound}} = 24\ g, \qquad w_{H_2O} = 600\ g,$

$m_{\text{organic compound}} = 58$

Also, $$\Delta T_b = \frac{1000 \times K_b \times w}{W \times m}$$

$$= \frac{1000 \times 0.513 \times 24}{600 \times 58} = 0.354$$

$\therefore$ B. pt. of solution $= 99.725 + 0.354$

$= 100.079$ C

Example 5

A 0.025 M solution of a monobasic acid has a freezing point of – 0.06 C. Find the value of K_a of this acid. K_f of water = 1.86 K/m. Assume that molarity is equal to molality.

Solution :

Calculate Van't Hoff factor using the relation :

$$\Delta T_f = i\ K_f\ m \qquad \text{Taking } m \approx M$$

$$\Rightarrow \qquad i = \frac{\Delta T_f}{K_f\ m} = \frac{0.06}{1.86 \times 0.025} = 1.29$$

Van't Hoff factor is given as :

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^- \\ 1-\alpha & & \alpha & & \alpha \end{array}$$

$$i = \frac{\text{total moles}}{\text{initial moles}} = \frac{1+\alpha}{1}$$

$$\Rightarrow \qquad i = 1 + \alpha = 1.29 \qquad \Rightarrow \qquad \alpha = 0.29$$

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A \\ c - c\alpha & & c\alpha & & c\alpha \end{array}$$

$$\Rightarrow \qquad K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.29)^2}{1-0.29} = 2.96 \times 10^{-3}$$

Example 6

1.0 gm of monobasic acid when dissolved in 100 gm of pure waters lowers the freezing point by 0.168 C. 0.2 gm of the same acid when dissolved and titrated required 15.1 ml of N/10 base. Determine the degree of dissociation of the acid. K_f of water is 1.86 K/m.

Solution :

Calculate the molecular mass (observed from colligative property) using the relation :

$$M_0 = \frac{K_f \times g_B \times 1000}{\Delta T_f \times g_A} = \frac{1.86 \times 1 \times 1000}{0.168 \times 100} = 110.6$$

Now calculate the actual molecular mass from neutralisation experiment

$$\frac{0.2}{M/1} \times 1000 = 0.1 \times 15.1 \qquad \text{(meq of acid = meq of base)}$$

$\Rightarrow$ $M = 132.45$

$$i = \frac{M_{actual}}{M_0} = \frac{132.45}{110.6} = 1.19$$

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^- \\ 1-\alpha & & \alpha & & \alpha \end{array}$$

$\Rightarrow$ $i = 1 + \alpha = 1.19$

$\Rightarrow$ $\alpha = 0.19$

Example 7

30 ml of CH_3OH (d = 0.7980 gm cm^{-3}) and 70 ml of H_2O (d = 9984 gm cm^{-3}) are mixed at 25 C to form a solution of density 0.9575 gm cm^{-3}. Calculate the freezing point of the solution K_f (H_2O) is 1.86 Kg mol^{-1} K. Also calculate its molarity.

Solution :

Weight of CH_3OH (w_1) = 30 cm^3 0.7980 gm cm^{-3} = 23.94 gm

Weight of solvent (H_2O) (w_2) = 70 cm^3 0.9984 gm cm^{-3} = 69.888 gm

$\therefore$ Molality of solution = $\frac{w_1}{m_1} \times \frac{1000}{w_2}$

Where m_1 = molecular weight of CH_3OH = 32

$$m = \frac{23.94}{32} \times \frac{1000}{69.88} = 10.7046 \text{ m}$$

As we know that

Depression in freezing point, $\Delta T_f = K_f$ i   molality,

For CH_3OH, i = 1

ΔT_f = 1.86   10.7046 C = 19.91 C

Freezing point of the solution = 0 – 19.91 C = – 19.91 C

Weight of solution = weight of solute + weight of solvent = 23.94 + 69.888 = 93.828 gm

$$\text{Volume of the solution} = \frac{\text{wt. of the solution}}{\text{density of the solution}} = \frac{93.828}{0.95751} = 97.99 \text{ ml}$$

$$\text{Molarity of solution} = \frac{w_1}{m_1} \times \frac{1000}{V(\text{in ml})} = \frac{23.94}{32} \times \frac{1000}{97.99} \text{ mol lit}^{-1} = 7.63 \text{ M}$$

Example 8

The freezing point of an aqueous solution of KCN containing 0.1892 mol kg^{-1} of solvent was found to be – 0.704 C. On adding 0.095 mol of Hg $(CN)_2$, the freezing point of the solution was found to be – 0.530 C. If the complex – formation takes place according to the following equation.

$$\mathbf{Hg(CN)_2 + nKCN \rightleftharpoons K_n[Hg(CN)_{n+2}]\ (K_f = 10^{23})}$$

What is the formula of the complex ? $K_f(H_2O)$ is 1.86 kg mol^{-1} K.

Solution :

ΔT_f (KCN solution) = 0.704 C

Molality of KCN solution = 0.1892

$i = (1 + x)$

$\Delta T_f = K_f \quad m \quad i$

$$i = (1 + x) = \frac{\Delta T_f}{K_f \times m} = \frac{0.704}{1.86 \times 0.1892} = 2.0$$

This gives x = 1, indicating 100% ionization of KCN

ΔT_f of the complex = 0.530

Molality of Hg $(CN)_2$ = 0.095 mol kg^{-1}

$$\begin{array}{ccccc} K_n[Hg(CN)_{n+2}] & \rightleftharpoons & nK^+ & + & [Hg(CN)_{n+2}]^- \\ 1 & & 0 & & 0 \\ 1-\alpha & & n\alpha & & \alpha \end{array}$$

here $i = (1 - \alpha) + n\alpha + \alpha = 1 + n\alpha$

$\therefore \quad \alpha = 1$

$\therefore \quad i = 1 + n$

$$\Delta T_f = K_f \quad i \quad \text{molality}$$

$$0.503 = 1.86 \quad 1 \quad 0.095$$

$$i = \frac{0.503}{1.86 \times 0.095} \approx 3$$

$$1 + n = 3$$

or $$n = 2$$

Hence, the complex is $\mathbf{K_2[Hg(CN)_4]}$

Example 9

The freezing point of a solution of acetic acid (mole fraction is 0.02) in benzene 277.4 K. Acetic acid exists partly as a dimer $2A \rightleftharpoons A_2$. Calculate equilibrium constant for dimerisation. Freezing point of benzene is 278.4 k and (K_f for benzene is 5).

Solution :

Let acetic acid = A

Benzene = B

Assume, α part of A forms dimer

$$\begin{array}{ll} 2A & \rightleftharpoons \; A_2 \\ 1 & \quad\;\; 0 \\ 1-\alpha & \quad\;\; \alpha/2 \end{array}$$

$$\therefore \quad i = \frac{(1-\alpha) + \alpha/2}{1}$$

$$= 1 - \alpha/2$$

$$\text{Mol. fraction of A} = x_A = 0.02$$

$$\text{Mol. fraction of B} = x_B = 0.98$$

$$\text{Molarity of A in B} = \frac{x_A}{m_B} \times \frac{1000}{X_B}$$

$$= \frac{0.02}{78} \times \frac{1000}{0.98}$$

$$= 0.262 \text{ mol kg}^{-1} \text{ of Benzene}$$

$$\text{Since } \Delta T_f = K_f \quad i \quad \text{molality}$$

$$278.4 - 277.4 = 5 \quad i \quad 0.262$$

or

$$1 = 5 \quad i \quad 0.262$$

$$i = \frac{1}{5} \times 0.262$$

$$= 0.763$$

$$1 - \alpha/2 = 0.763$$

$$\Rightarrow \quad \alpha = 0.47$$

Hence the molality of A after dimer is formed = $(1 - \alpha)$ initial molality

$= (1 - 0.48)$ initial molality

$= 0.52 \quad 0.262$

Molality of A_2 after dimer is formed $= \frac{\alpha}{2} \times$ molality

$$= \frac{0.48}{2} \times 0.262$$

$$= 0.24 \quad 0.26$$

$$= 0.06288$$

The equation constant

$$\text{Keq} = \frac{[A_2]}{[A]^2} = \frac{0.06288}{(0.13624)^2}$$

$$= 3.39 \text{ kg mol}^{-1}$$

Example 10

Find K_a, the ionization constant of tartaric acid if a 0.100 molal aqueous solution of tartaric acid freezes at – 0.205 C. Assume that only the first ionization is of importance and that 0.1 m = 0.1 M. K_f = 1.86 kg mol^{-1} K.

Solution :

Assuming that the tartaric acid be a monobasic as AH. It ionizes as

$$AH \rightleftharpoons A + H^+$$

	AH	A	H⁺
Initially conc.	C	0	
Conc. after dissociation	$C(1 - \alpha)$	$C\alpha$	$C\alpha$

Here, $$i = \frac{C(1-\alpha) + C\alpha + C\alpha}{C}$$, where α = degree of dissociation

$$= \frac{C(1+\alpha)}{C} = 1 + \alpha$$

Molal concentration = 0.1

$$\Delta T_f = K_f \quad C_m \quad 1$$

$\therefore$ $\alpha = 0.1$

$$K_a = \frac{\left[A^-\right]\left[H^+\right]}{[AH]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{\alpha^2 C}{1-\alpha}$$

$$K_a = \frac{(0.1)^2 \times 0.1}{1 - 0.1} = 1.11 \times 10^{-3}$$

$\therefore$ $K_a = 1.11 \quad 10^{-3}$.