

Physical Chemistry

For

Second Year Students

In

Chemistry Department

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Second Course

Chapter One: ((Theory of Dilute Solutions))

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.

1- Lowering of Vapour Pressure: RAOULT'S LAW

The vapor 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:

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

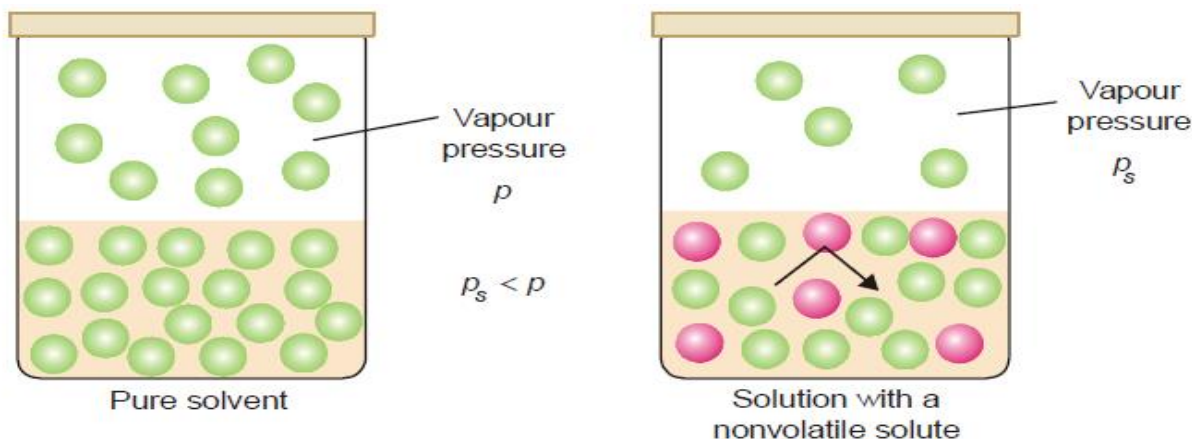
Or
$$\frac{\Delta p}{p} = \frac{n}{n + N}$$

n = Number of moles or molecules of solute

N = Number of moles or molecules of solvent.

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.

This causes the lowering of the vapour pressure.



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.

Q1: Calculate the vapour pressure lowering caused by the addition of 100g 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:

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

Δp = lowering of vapour pressure

p = vapour pressure of water = 23.8 mm Hg

$$n = \text{mole of sucrose} = \frac{100}{342} = 0.2924 \text{ mole}$$

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

$$\frac{\Delta p}{23.8} = \frac{0.2924}{0.2924+55.5} \quad \therefore \Delta p = 0.125 \text{ mm.Hg}$$

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

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

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

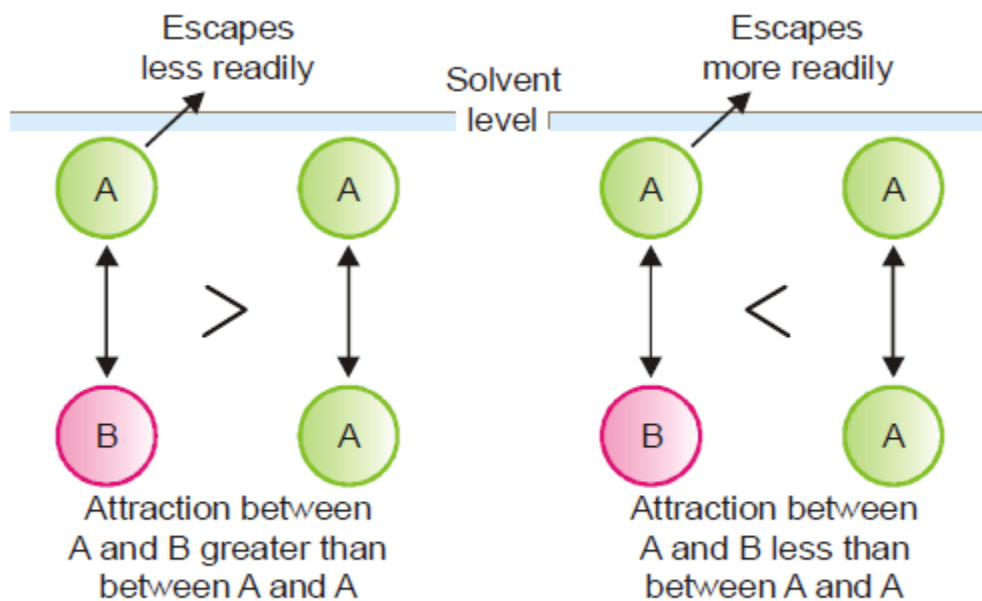
molecule A will escape less readily and the vapour pressure will be less than that predicted by Raoult's law (Negative deviation).

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.



Negative deviation and Positive deviation.

***Determination of Molecular Mass from Vapor Pressure Lowering:**

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

Q2: The vapor 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 vapor pressure falls to 426 mm Hg. Calculate the molecular mass of A. Assume that the solution of A in ether is very dilute.

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

$$\frac{442 - 426}{442} = \frac{\frac{3}{M.wt}}{\frac{3}{M.wt} + \frac{50}{74}}$$

M. wt of compound A = 118.22 g/mol

Q3: 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.

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

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

$$M.wt \text{ of urea} = ? \frac{g}{mol}, \text{ wt of urea} = 18.2 \text{ g}$$

$$M.wt \text{ of water} = 18 \frac{g}{mol}, \text{ wt of water} = 100 \text{ g}$$

$$\frac{\Delta p}{p} = \frac{5}{92} = \frac{\frac{18.2}{M.wt \text{ of urea}}}{\frac{18.2}{M.wt \text{ of urea}} + \frac{100}{18}}$$

$$M.wt \text{ of urea} = 57 \frac{g}{mol}$$

Raoult's Law:

The French chemist François Marie Raoult (1830–1901) found that for some solutions, the ratio (P_1/P_1^o) is equal to the mole fraction of component 1, that is:

$$\frac{P_1}{P_1^o} = x_1 \quad \text{or} \quad P_1 = P_1^o x_1$$

P_1 : Partial vapor pressure or partial pressure.

P_1^o : Vapor pressure.

This equation is known as Raoult's law, which states that the vapor pressure of a component of a solution is equal to the product of its mole fraction and the vapor pressure of the pure liquid.

Solutions that obey Raoult's law are called ideal solutions. An example of a nearly ideal solution is the benzene–toluene system.

If we have two volatile solvents

$$P_T = P_1 + P_2$$

$$P_1 = P_1^o x_1 \quad \text{and} \quad P_2 = P_2^o x_2$$

$$x_1 + x_2 = 1 \quad \text{then} \quad x_2 = 1 - x_1$$

$$P_T = P_1^o x_1 + P_2^o x_2 = P_1^o x_1 + P_2^o (1 - x_1)$$

$$P_T = P_1^o x_1 + P_2^o - P_2^o x_1 = P_2^o + (P_1^o - P_2^o)x_1$$

$$\therefore P_T = P_2^o + (P_1^o - P_2^o)x_1$$

Or

$$P_T = P_1^o + (P_2^o - P_1^o)x_2$$

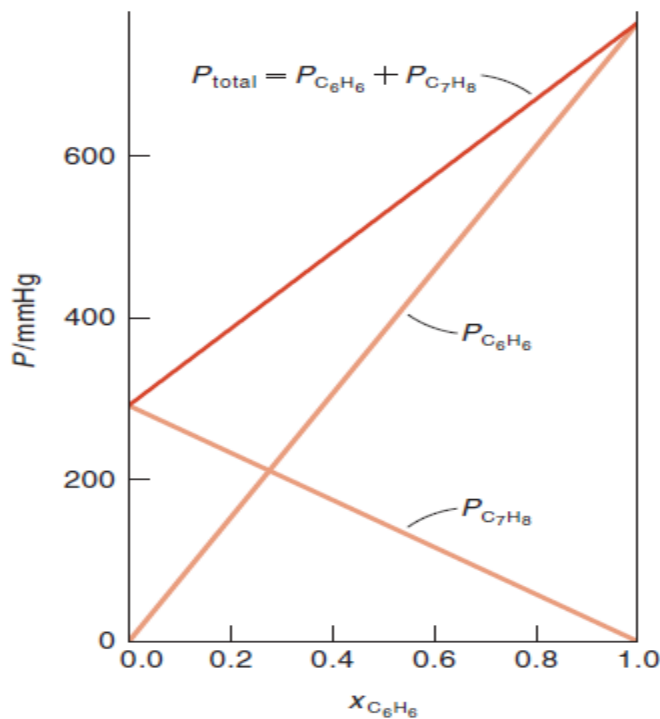
According to Daltons law

$$P_1 = x_1^v P_T \quad \text{and} \quad x_1^v = \frac{P_1}{P_T}$$

$$x_1^v = \frac{P_1^o x_1}{P_2^o + (P_1^o - P_2^o)x_1}$$

And

$$x_1 = \frac{x_1^v P_2^o}{P_1^o - (P_1^o - P_2^o)x_1^v} \quad \text{?????? H.W}$$



Total vapor pressure of the benzene–toluene mixture as a function of the benzene mole fraction at 80.1°C.

Example: Liquids A and B form an ideal solution. At 45°C, the vapor pressures of pure A and pure B are 66 torr and 88 torr, respectively. Calculate the composition of the vapor in equilibrium with a solution containing 36 mole percent A at this temperature.

Answer: $x_A = 0.36 \quad \therefore \quad x_B = 0.64$

According to Raoult's law $P_1 = P_1^o x_1$

$$\therefore P_A = P_A^o x_A = 66 \times 0.36 = 23.8 \text{ torr}$$

$$P_B = P_B^o x_B = 88 \times 0.64 = 56.3 \text{ torr}$$

The total vapor pressure, P_T , is given by:

$$P_T = P_A + P_B = 23.8 + 56.3 = 80.1 \text{ torr}$$

Finally, the mole fractions of A and B in the vapor phase, x_A^v and x_B^v , are given by:

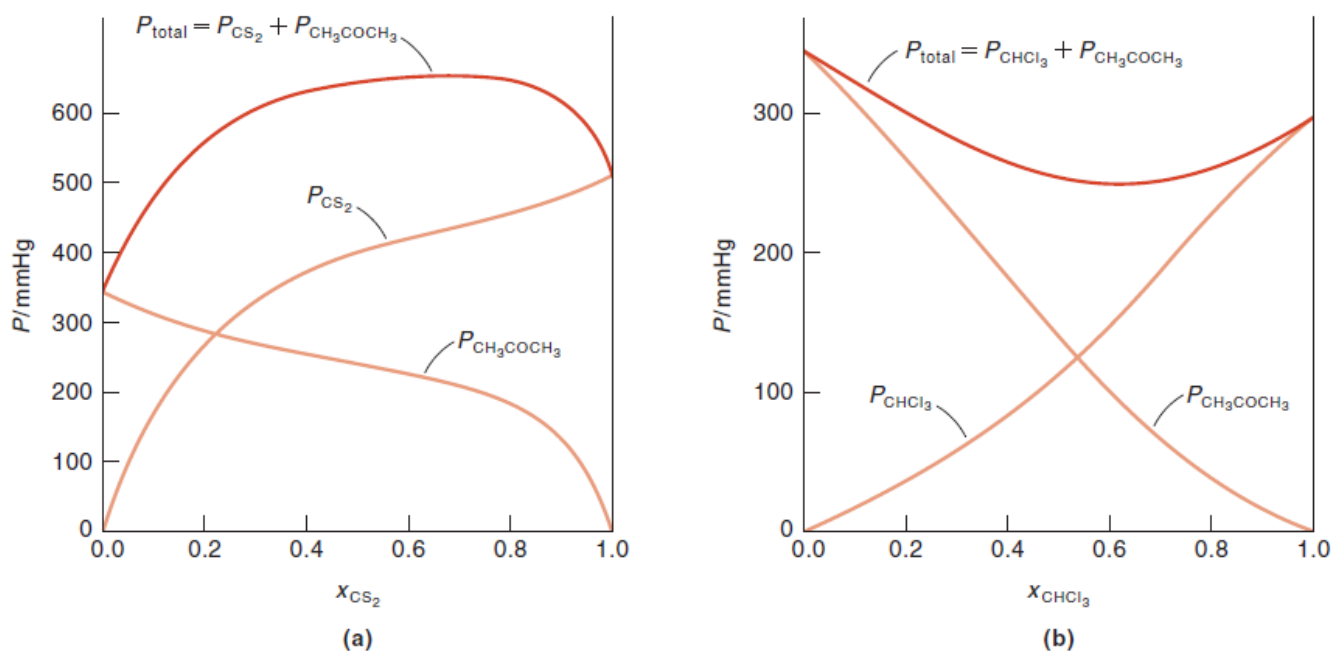
$$x_A^v = \frac{P_A}{P_T} = \frac{23.8}{80.1} = 0.3$$

And

$$x_B^v = \frac{P_B}{P_T} = \frac{56.3}{80.1} = 0.7$$

In an ideal solution, all intermolecular forces are equal, whether the molecules are alike or not. The benzene–toluene system approximates this requirement because benzene and toluene molecules have similar shapes and electronic structures.

Most solutions do not behave ideally, however. The figure below shows the positive and negative deviations from Raoult's law. The positive deviation (a) corresponds to the case in which the intermolecular forces between unlike molecules are weaker than those between like molecules, and there is a greater tendency for these molecules to leave the solution than in the case of an ideal solution. Consequently, the vapor pressure of the solution is greater than the sum of the vapor pressures for an ideal solution. Just the opposite holds for a negative deviation (b) from Raoult's law. In this case, unlike molecules attract each other more strongly than they do their own kind, and the vapor pressure of the solution is less than the sum of the vapor pressures for an ideal solution.



2- 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_b) is called the **elevation of boiling point**.

$$\Delta T_b = T - T_b$$

$$\Delta T_b = m \cdot K_b$$

K_b is a constant called **Boiling point constant** or **Ebulioscopic constant of molal elevation constant**.

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.

$$m = \text{molality of the solution}$$

$$m = \frac{\text{wt of solute (g)} \times 1000}{M.\text{wt of solute} \times \text{wt of solvent (g)}}$$

$$\therefore \Delta T_b = \frac{w \times 1000 \times k_b}{M \times W}$$

$$\therefore M = \frac{w \times 1000 \times k_b}{\Delta T_b \times W} \dots \dots \dots (1)$$

Where ΔT_b = 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.

The value of k_b . The value of k_b can be determined by measurement of ΔT_b by taking a solute of known molecular mass (M) and substituting the values in expression (1).

Units of k_b

$$\frac{^{\circ}\text{C} \cdot \text{Kg (solvent)}}{\text{mol (solute)}} = \frac{\text{K} \cdot \text{Kg (solvent)}}{\text{mol (solute)}} = \frac{\text{K}}{\text{molal}}$$

MOLAL BOILING-POINT CONSTANTS

Solvent	K_b per kg (1000 g)
Water	0.52
Propanone (acetone)	1.70
Ethoxyethane (ether)	2.16
Ethanoic acid (acetic acid)	3.07
Ethanol	1.75
Benzene	2.70
Trichloromethane (chloroform)	3.67

SOLVED PROBLEM 4 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

$$\Delta T = 0.17 \text{ K}$$

$$K_b = 2.16$$

$$w = 0.20 \text{ g}$$

$$W = 20.00 \text{ g}$$

Substituting values

$$M = \frac{1000 \times 2.16 \times 0.20}{0.17 \times 20.00}$$

$$M = 127.81 \text{ g/mol}$$

3- Freezing Point Depression

$$\Delta T_f = \frac{w \times 1000 \times k_f}{M \times W}$$

$$M = \frac{w \times 1000 \times k_f}{\Delta T_f \times W}$$

Where k_f is a constant called Freezing-point constant or Cryoscopic constant or **Molal depression constant**.

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.

MOLAL FREEZING-POINT CONSTANTS

Solvent	K_f per kg (1000 g)
Water	1.86
Ethanoic acid (acetic acid)	3.90
Benzene	5.10
Camphor	40.0

SOLVED PROBLEM 5. 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 g/mol**

SOLVED PROBLEM 6. 1.250 g of naphthalene was dissolved in 60 cm³ 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 g cm⁻³, $K_f = 5.1$ K per 1000 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**.

The constant K_f , which is characteristic of a particular solvent, can also be calculated from the relation

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

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

Therefore,

$$K_f = \frac{8.314 \times (273)^2}{1000 \times 336} = 1.85 \text{ K.Kg/mol}$$

And for K_b

$$K_b = \frac{RT_b^2}{1000H_v}$$

Where R = gas constant; T_b = boiling point of solvent; H_v = molar latent heat of vaporization. Thus for water R = 8.314 J mol⁻¹; T = 373 K : H_v = 2260 J g⁻¹.

$$K_b = \frac{8.314 \times 373^2}{1000 \times 2260} = 0.512 \text{ K.Kg/mol}$$

Solved problem 7:

A solution of 0.124 g of a substance, X, in 25.0 g 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.

$$K_f = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86 \text{ K.Kg/mol}$$

$$\begin{aligned} M &= \frac{w \times 1000 \times k_f}{\Delta T_f \times W} \\ &= \frac{0.124 \times 1000 \times 3.86}{0.324 \times 25} \\ &= 59.1 \frac{\text{g}}{\text{mol}} \end{aligned}$$

Thus the molecular weight of X is 59.1 $\frac{\text{g}}{\text{mol}}$

COLLIGATIVE PROPERTIES OF ELECTROLYTES

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

$$i = \frac{\Delta T_f}{[\Delta T_f]_o}$$

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

$$i = \frac{\Delta T_f}{[\Delta T_f]_o} = \frac{\Delta T_b}{[\Delta T_b]_o} = \frac{\Delta p}{[\Delta p]_o} = \frac{\pi}{\pi_o} = \frac{M_o}{M}$$

ΔT_f = Depression in freezing point.

ΔT_b = Elevation in boiling point.

Δp = Lowering of vapor pressure.

π = Osmotic pressure.

M = Molecular weight.

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 dissociation 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 :

Number of undissociated molecules = $1 - \alpha$

Number of ions produced = $\alpha\nu$

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

$$i = \frac{1 - \alpha + \alpha\nu}{1}$$

$$i - 1 = \alpha(\nu - 1)$$

$$\therefore \alpha = \frac{i - 1}{\nu - 1}$$

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 8:

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.

$K_b = 1.86 \text{ K.Kg/mol}$.

$$\text{molecular mass of } Ba(NO_3)_2 = 261 \frac{g}{mol}$$

SOLUTION

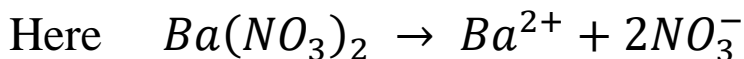
Calculation of Depression of Freezing point $[\Delta T_f]_o$ for no ionization:

$$\Delta T_f = \frac{w \times 1000 \times k_f}{M \times W} = \frac{1.5 \times 1000 \times 1.86}{261 \times 100} = 0.1069 \text{ K}$$

Calculation of van't Hoff Factor

$$i = \frac{\Delta T_f}{[\Delta T_f]_o} = \frac{273 - 272.72}{0.1069} = 2.62$$

Calculation of Degree of dissociation:



and 1 formula unit yields 3 particles on dissociation.

$$\alpha = \frac{i - 1}{v - 1} = \frac{2.62 - 1}{3 - 1} = 0.81 = 81\%$$

Solved Problem 9. Find the degree of ionization for HF (hydrofluoric acid) in 0.1m aqueous solution if the freezing point of the solution is $-0.197^\circ C$. (k_f for water = 1.86 K.Kg/mol).

Solution:

Calculation of freezing point depression for no ionization $[\Delta T_f]_o$.

$$[\Delta T_f]_o = k_f \times m$$

Where $m = \text{molal concentration } \left(\frac{\text{moles of solute}}{\text{Kg solvent}} \right)$

$$\therefore [\Delta T_f]_o = 1.86 \times 0.1 = 0.186^\circ C$$

Calculation of i :

$$i = \frac{\Delta T_f}{[\Delta T_f]_o}$$

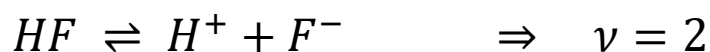
Substituting value

$$i = \frac{0.197}{0.186} = 1.06$$

Calculation degree of dissociation

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

Since HF dissociates as



Substituting values

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

Therefore. The degree of dissociation of 0.1m HF is 0.06 or it is 6% ionized.

SOLVED PROBLEM 10. Phenol (C_6H_5OH) 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 $0.215^\circ C$. Calculate the van't Hoff factor and the degree of association of phenol. Molal depression constant of water = $1.85^\circ C \text{ mole}^{-1}$.

SOLUTION

Calculation of van't Hoff Factor

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

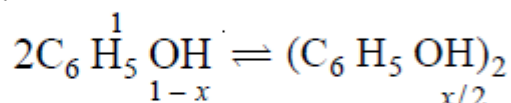
$$\begin{aligned} \text{Observed molecular mass} &= \frac{1000 K_f w}{\Delta T W} = \frac{1000 \times 1.85 \times 0.6677}{0.215 \times 35.5} \\ &= 161.84 \end{aligned}$$

$$\begin{aligned} \text{van't Hoff factor } (i) &= \frac{\text{normal mol. mass}}{\text{observed mol. mass}} \\ &= \frac{94}{161.84} \end{aligned}$$

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



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

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**

Chapter Two: ((Osmosis and Osmotic Pressure))

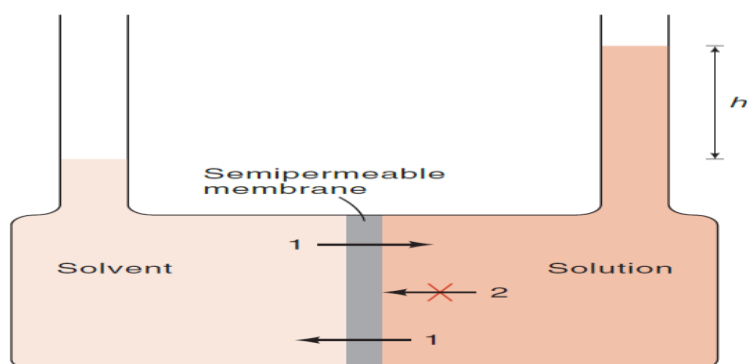
WHAT IS OSMOSIS?

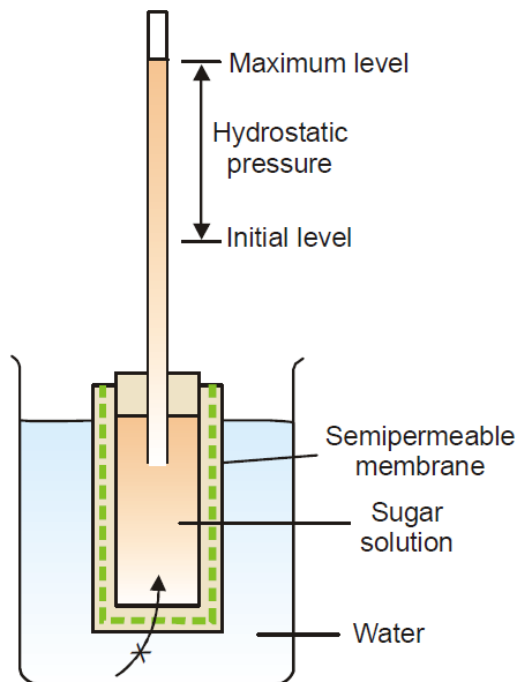
Let us consider a pure solvent and solution separated by a membrane which permits the passage to solvent molecules but not to solute molecules. Only the solvent will diffuse through the membrane into solution. **A membrane which is permeable to solvent and not to solute is called a semipermeable membrane.**

The flow of the solvent through a semipermeable membrane from pure solvent to solution, or from a dilute solution to concentrated solution, is termed Osmosis (Greek Osmos = to push).

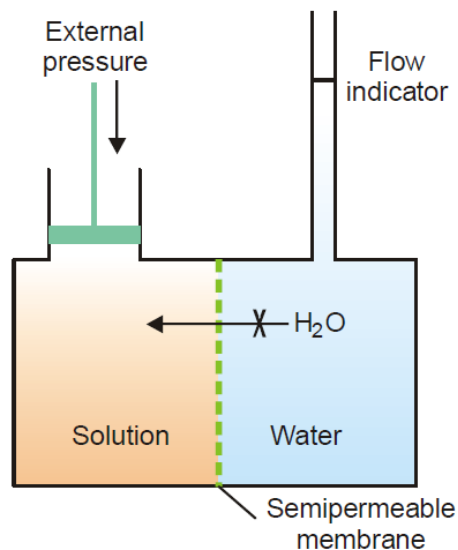
The hydrostatic pressure built up on the solution which just stops the osmosis of pure solvent into the solution through a semipermeable membrane, is called **Osmotic Pressure**.

Osmotic pressure may be defined as the external pressure applied to the solution in order to stop the osmosis of solvent into solution separated by a semipermeable membrane.





■ **Figure 16.9**
Hydrostatic pressure necessary to stop osmosis is equal to osmotic pressure.



■ **Figure 16.10**
The external pressure applied on solution to stop osmosis is equal to osmotic pressure.

LAWS OF OSMOTIC PRESSURE

Van't Hoff Equation for Solutions

$$\pi V = nRT$$

If π is the osmotic pressure.

Q1: - A solution of sugar (mol. Mass= 342 g/mol) containing 34.2 g/l, has an osmotic pressure of 2.4 atm at 20°C. Calculate the value of R in litre-atmospheres.

Solution:- From van't Hoff equation

$$R = \frac{\pi V}{T}$$

Where π = osmotic pressure, V = volume of solution in litres containing 1 mole of solute, T = absolute temperature.

In the present case,

$$\pi = 2.4 \text{ atm} \quad V = \frac{1}{34.2} \times 342 = 10 \text{ l/mol}$$

$$T = 20 + 273 = 293 \text{ K}$$

$$\therefore R = \frac{2.4 \times 10}{293} = 0.0819 \text{ l. atm. K}^{-1} \text{ mol}^{-1}$$

Q2: Calculate the osmotic pressure of a 5% solution of glucose (mol wt = 180) at 18°C.

SOLUTION

$$\pi V = nRT$$

$$\pi = ?, V = 100 \text{ ml} = 0.1 \text{ l}$$

$$R = 0.0821 \text{ l. atm. mol}^{-1} \text{ K}^{-1}$$

$$T = 273 + 18 = 291 \text{ K}$$

$$n = \frac{5}{180} = 0.0278 \text{ mol}$$

Substituting the values in van't Hoff Equation

$$\pi = \frac{0.0278 \times 0.0821 \times 291}{0.1} = 6.64 \text{ atm}$$

Q3:- Calculate the osmotic pressure of solution obtained by mixing (a) 100 ml of 3.4 per cent solution of urea (mol mass = 60) and (b) 100 ml of 1.6 per cent solution of sugar (mol mass = 342) at 20°C.

SOLUTION

1-Osmotic pressure of urea

$$\pi V = nRT$$

$$V = \frac{200}{1000} = 0.2 \text{ l}$$

$$n = \frac{3.4}{60} = 0.0567 \text{ mol}$$

R = 0.0821 litre-atmosphere

T = 20 + 273 = 293 K

Substituting values in van't Hoff equation $\pi = 6.82 \text{ atm}$

Osmotic pressure of sugar $\pi = 0.563 \text{ atm}$

According to the van't Hoff theory of dilute solutions, dissolved substances behave like gases.

Thus they obey Dalton's Law of Partial Pressures. Hence the total osmotic pressure of the mixture = 6.82 + 0.563 = 7.383 atm

DETERMINATION OF MOLECULAR WEIGHT FROM OSMOTIC PRESSURE

$$\pi V = nRT$$

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

$$M = \frac{wRT}{\pi V}$$

SOLVED PROBLEM 1. Morse and Frazer observed that a solution of glucose containing 18 grams per litre had an osmotic pressure of 2.39 atmospheres at 23°C. Find the molecular weight of glucose.

SOLUTION

We know that:

$$M = \frac{wRT}{\pi V}$$

Here,

$$w = 18 \text{ g}$$

$$R = 0.0821 \text{ litre-atmosphere}$$

$$T = 23 + 273 = 296 \text{ K}$$

$$\pi = 2.39 \text{ atmospheres}$$

$$V = 1 \text{ litre}$$

Substituting these values in relation (1)

$$\begin{aligned} M &= \frac{18 \times 0.0821 \times 296}{2.39 \times 1} \\ &= 183.0 \end{aligned}$$

OSMOTIC PRESSURE OF ELECTROLYTES

Like other colligative properties, observed osmotic pressure of electrolytes (π) in aqueous solutions is higher than the value calculated using van't Hoff equation, $\pi_0 V = nRT$. Expressing in terms of van't Hoff factor i ,

$$\frac{\pi}{\pi_0} = i$$

Consequently, the van't Hoff equation for solutions of electrolytes assumes the form

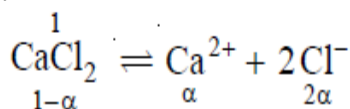
$$\pi V = inRT$$

SOLVED PROBLEM 1. The osmotic pressure of a 0.01 m solution of CaCl_2 and sucrose at 298.15 K are 0.605 atm and 0.224 atm respectively. Calculate the van't Hoff factor and degree of dissociation of CaCl_2 .

SOLUTION

$$i = \frac{\pi}{\pi_0} = \frac{0.605}{0.224} = 2.70$$

If α is the degree of dissociation,



$$\therefore \frac{1 + 2\alpha}{1} = 2.70$$

and $\alpha = 0.85$

As shown above the van't Hoff factor $i = 2.70$ and the degree of dissociation (α) = 0.85

SOLVED PROBLEM 2. Find the osmotic pressure of an aqueous solution of BaCl_2 at 288 K containing 0.39 g per 60 ml. The salt is 60% dissociated. (Ba = 137; Cl = 35.5)

SOLUTION

For an electrolyte solution, van't Hoff equation assumes the form

$$\pi V = inRT, \text{ where } i \text{ is van't Hoff factor}$$

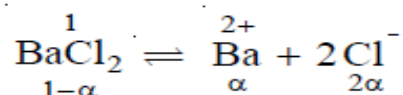
In this case,

$$V = \frac{60}{1000} = \frac{6}{100} \text{ litre}$$

$$n = \frac{0.39}{208}$$

$$T = 288 \text{ K}$$

Calculation of i



$$\therefore i = \frac{1 - \alpha + \alpha + 2\alpha}{1} = \frac{1 + 2\alpha}{1}$$

But $\alpha = 0.60$

$$\therefore i = \frac{1 + 2 \times 0.60}{1} = 2.2$$

Substituting values in equation (1)

$$\begin{aligned} \pi &= 2.2 \times \frac{0.39}{208} \times 0.0821 \times 288 \times \frac{100}{60} \\ &= \mathbf{1.6256 \text{ atm}} \end{aligned}$$

A mixture of liquids A and B exhibits ideal behavior. At 84°C , the total vapor pressure of a solution containing 1.2 moles of A and 2.3 moles of B is 331 mmHg. Upon the addition of another mole of B to the solution, the vapor pressure increases to 347 mmHg. Calculate the vapor pressures of pure A and B at 84°C .