

## SOLUTIONS

### Topic-3

#### COLLIGATIVE PROPERTIES, APPLICATIONS, DERIVATIONS AND NUMERICALS

##### VERY SHORT ANSWER QUESTIONS

**1. Define colligative property?**

**Ans:** Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as colligative properties. The colligative properties are:

- Lowering in the vapour pressure,
- Elevation in the boiling point,
- Depression in the freezing point, and
- Osmotic pressure

**2. What is molal elevation constant?**

**Ans: Molal elevation constant:** Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship. The elevation in boiling point observed in one molal solution of a non-volatile solute is known as molal elevation constant ( $K_b$ )

$$K_b = (RT_b^2) / (1000L_v)$$

Where, R is molar gas constant,

$T_b$  is the boiling point of the solvent on Kelvin scale

$L_v$  the latent heat of vaporization of solvent in calories per gram.

For water  $K_b = 2 \times (373)^2 / 1000 \times 540 = 0.515$

**3. What is molal depression constant?**

**Ans:** Molal depression constant : Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship. The depression in freezing point observed in one molal solution of a non-volatile solute is known as molal depression constant ( $K_f$ )

$$K_f = (RT_f^2) / (1000L_f)$$

Where, R is molar gas constant,

$T_f$  is the freezing point of the solvent on Kelvin scale

$L_f$  the latent heat of fusion of solvent in calories per gram

**4. Define Osmotic Pressure?**

**Ans: Osmotic pressure:** The pressure required to be applied to just stop the inflow of solvent into the solution, when solution is separated from the solvent by a semi permeable membrane

Osmosis pressure = hydrostatic pressure

$$\pi = h d g$$

**5. Explain Osmosis.?**

**Ans:** The process of solvent flowing in to the solution when the solvent and the solution are separated by a semi permeable membrane is called **Osmosis**.

**6. What is meant by abnormal behaviour of electrolytes in colligative properties?**

**Ans:** The colligative properties of solutions depend on the number of solute particles present in solution. Various relations derived for colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case the total number of particles of the solute changes in solution, due to **dissociation or Association** the number of particles will increase or decrease and consequently the value of colligative property changes. This is called the abnormal behaviour.

**7. Will the molecular weight determined for an ionizing solute be greater or lesser than that calculated by elevation of boiling point method?**

**Ans:** In case of solute which dissociate in solution, exhibit higher colligative property than expected. Molecular weight of solute is inversely proportional to the colligative property. From this one concludes that the observed molecular weight will be less than the normal molecular weight.

**8. What are isotonic solutions?**

**Ans:** Isotonic solutions are the solutions having same osmotic pressures at a given temperature. Isotonic solutions will have same concentrations.

Exaple: Blood and saline have same molar concentrations.

**9. One formula weight of each NaCl and Glucose is dissolved in 1000 ml of water separately in two different solutions are prepared. In which solution, you expect higher colligative property and why?**

**Ans:** In NaCl we observe higher colligative property. This is because dissociation of each formula unit of NaCl will give two particles due to ionisation whereas glucose on the other hand gives only one particle for each formula unit.

**10. In which of the following solutions of same molality one can expect higher elevation in boiling point? Why? A) NaCl b) BaCl<sub>2</sub>?**

**Ans:** The elevation in boiling point is more in BaCl<sub>2</sub> as each formula unit will give three particles where as each formula unit of NaCl will give only two particles on complete ionisation .

**11. A person involved in accident, when admitted to hospital is administered with saline. Why?**

**Ans:** The patient loses blood. Therefore osmotic pressure of blood falls. Therefore to maintain the osmotic pressure of blood at normal value, saline is given to the patient. Saline is isotonic with blood.

**12. A dilute solution of A of concentration C showed on osmotic pressure which is higher in value than that calculated from  $\Pi = CRT$  at 25°C. What does this indicate about the nature of solute?**

**Ans:** This indicates that the solute dissociates into its ions. This shows that the solute is ionic compound.

**13. Between NaCl and BaCl<sub>2</sub> of same concentration the (i) factor is more for which compound and why?**

**Ans:** For NaCl the (i) factor is more.

$$\text{We know that } i = 1 + (n-1)\alpha$$

$$\text{For NaCl, } i = 1 + (2 - 1) \alpha = 1 + 2 \alpha$$

$$\text{For BaCl}_2 \quad i = 1 + (3 - 1) \alpha = 1 + 2 \alpha$$

14. A solute 'x' is trimerised in a solvent. What about the experimental molar mass of solute when compared to calculated mass?

**Ans:** The association of solute molecules leads to decrease in colligative property. Molar mass is inversely proportional to colligative property. Therefore molar mass is high.

15. An aqueous solution contained 6g of urea (mol. Wt. 60). Its osmotic pressure is found equal to a solution of glucose. (mol. Wt. 180). How much weight of glucose is present in one litre of the solutions?

**Ans:** Since osmotic pressures are the same the mole fractions are the same

Mole fractions of Urea = Mole fraction of Glucose

$$(6 / 60) = (\text{wt. of glucose} / 180)$$

$$\text{St. of glucose} = 0.1 \times 180 = 18 \text{ g}$$

### SHORT ANSWER QUESTIONS

1. What is colligative property? Give two examples?

#### **COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS**

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behavior as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as colligative properties. The colligative properties are:

- Lowering in the vapour pressure,
- Elevation in the boiling point,
- Depression in the freezing point, and
- Osmotic pressure

2. What is meant by an ideal solution?

**Ans: Ideal solutions:** An ideal solution one in which the molecules attract one another with equal force irrespective of their nature. Thus, a solution composed of two components A and B will be an ideal one if the forces between A and A, B and B should be the same. An ideal solution possesses the following characteristics:

(i) Volume change of mixing should be zero.

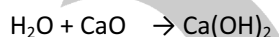
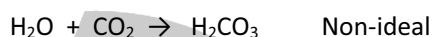
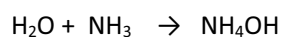
$$V_{\text{mix}} = 0; V_{\text{solvent}} + V_{\text{solute}} = V_{\text{solution}}$$

(ii) Heat change on mixing should be zero.

$$H_{\text{mix}} = 0 \text{ (Heat is neither absorbed nor evolved).}$$

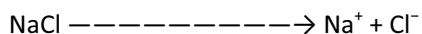
(iii) There should be no chemical reaction between solvent and solute.

Solvent + solute  $\rightarrow$  solution



(iv) Solute molecules should be not dissociated in the ideal solution.

Aqueous medium



Non-ideal

(v) Solute molecules should not associate in ideal solution.

(vi) Ideal solutions must obey Raoult's law at all concentrations.

The following are some of the examples are;

(a) Benzene and toluene.

(b) Carbon tetrachloride, and silicon tetrachloride,

(c) N-Hexane and n-heptane,

**3 Write equation relating depression in freezing point of a solution and the molar s of the solute. Explain the terms?**

**DEPRESSION OF FREEZING POINT (CRYOSCOPY):** Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. Since the addition of a non-volatile solute always lowers the vapour pressure of solvent, therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of the pure solvent and its solution is called depression of freezing point.

Depression of freezing point

$$(\Delta T) = \text{Freezing point of the solvent} - \text{Freezing point of the solution}$$

$$\Delta T_f = K_f \times \frac{a \times 1000}{M \times b}$$

$$\Rightarrow M = \frac{K_f \times a \times 1000}{\Delta T_f \times B}$$

Where, a = weight of solvent

b = weight of solvent

M = Mol. Wt of solute

$K_f$  = Molal depression constant

$\Delta T_f$  = depression in freezing point

#### 4. What are Van't Hoff laws of osmotic pressure?

### VAN'T HOFF THEORY OF DILUTE SOLUTIONS

van't Hoff realized that an analogy exists between gases and solutions provided osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for dilute solutions of non-electrolysis the following laws hold good.

#### 1. Boyle-van't Hoff law:

The osmotic pressure ( $\Pi$  or  $\alpha$ ) of a solution is directly proportional to its concentration (C) when the temperature is kept constant. The concentration of the solution containing one gram mole in V litres is equal to  $1/V$  ( $C = 1/V$ )

Thus  $\Pi \propto C$  (when temperature is constant)

Or  $\Pi \propto 1/V$

or  $\Pi V = \text{constant}$

van't Hoff presumed that the osmotic pressure is due to the bombardment of solute molecules against the semipermeable membrane as the gas pressure is due to hits recorded by gas molecules against the walls of its container.

#### 2. Pressure-Temperature law (Gay-Lussac-van't Hoff law):

Concentration remaining same; the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), i.e.,

$$\Pi \propto T$$

or  $\Pi/T = \text{constant}$  or  $\Pi = KT$  where, K is constant

**5. Derive the equation  $\Pi = CRT$ .**

Ans

According to Boyle-van't Hoff law,

$$\Pi \propto C \quad (\text{when temperature is constant}) \text{-----(1)}$$

According to Gay-Lussac-van't Hoff law

$$\Pi \propto T \text{-----(2)}$$

Combining the two equations, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by:

$$\Pi \propto CT$$

Or  $\Pi = SCT$  where S = proportionality constant

$$\Pi = CST$$

Hence derived.

**6. What is Van't Hoffs factor (i) and how is it related to 'α' in case of a binary electrolyte .? (1:1).**

**Ans: Van't Hoff Factor (i):** It is defined as the ration of the observed value of colligative property of the theoretical value of colligative property.

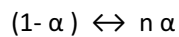
Experimental values of colligative property



$$i = \frac{\text{Calculated value of colligative property}}{\dots}$$

Calculated value of colligative property

**Solute dissociation or ionisation process :** If a solute on ionisation gives 'n' ions and 'α' is the degree of dissociation at the given concentration, we will have [1 + (n-1) α] particles.



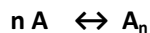
The total number of ions =  $1 - \alpha + n \alpha = [1 + (n - 1) \alpha]$

$$i = \frac{[1 + (n - 1) \alpha]}{1}$$

From this ,  $\alpha = \frac{i - 1}{n - 1}$

Therefore, **α ionisation** =  $\frac{i - 1}{n - 1}$

**For solute association process:** If nA molecules combine to A<sub>n</sub> , we have



If 'α' is the degree of association at a given concentration

$$1 - \alpha \leftrightarrow \frac{\alpha}{N} \Rightarrow \text{total no. of particles} = 1 - \alpha + (\alpha/n)$$

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

From this the value of  $\alpha$  can be obtained.

$$\alpha = \frac{1 - i}{1 - (1/n)}$$

### LONG ANSWER QUESTIONS

1. What are colligative properties? Explain each of them with necessary examples?

Ans:

#### COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behavior as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as colligative properties. The colligative properties are:

- Lowering in the vapour pressure,
- Elevation in the boiling point,
- Depression in the freezing point, and
- Osmotic pressure

Colligative properties are the properties of dilute solutions, that is why these are termed as colligative properties of dilute solutions. These properties are related to one another. Thus, if one is

measured, the other can be calculated. The importance of these properties lies in the fact that they provide methods for the determination of molecular masses of dissolved solutes. The results are excellent if the following three conditions are satisfied.

- The solution should be very dilute.
- The solute should be non-volatile
- The solute does not dissociate or associate in solution

**a) LOWERING IN THE VAPOUR PRESSURE:** When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons:

- Percentage surface area occupied by the solvent decreases. Thus the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the per cent surface area occupied by the solvent decreases.
- According to Graham's law of evaporation,  
Rate of evaporation  $\propto 1/\sqrt{\text{density}}$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus both rate of evaporation and vapour pressure are lowered.

If  $p_0$  is the vapour pressure of pure solvent and  $p_s$  is the vapour pressure of the solution, the difference ( $p_0 - p_s$ ) is termed lowering in vapour pressure

**b) ELEVATION OF BOILING POINT (EBULLIOSCOPY):**

The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Hence, the temperature of the solution when its vapour pressure will be equal to atmospheric pressure will be higher than the temperature of the pure solvent. In other words, the boiling point of the solvent is elevated by the addition of non-volatile solute. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed elevation of boiling point.

Elevation of boiling point,

$$\Delta T = \text{Boiling point of the solution} - \text{Boiling point of pure solvent}$$

**c) DEPRESSION OF FREEZING POINT (CRYOSCOPY):**

Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. Since the addition of a non-

volatile solute always lowers the vapour pressure of solvent, therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of the pure solvent and its solution is called depression of freezing point.

Depression of freezing point is given by

$$\Delta T = \text{Freezing point of the solvent} - \text{Freezing point of the solution}$$

**D) OSMOTIC PRESSURE:** A porous pot is taken and a semi permeable membrane of copper ferrocyanide is deposited in its walls. It is fitted with a long glass with the help of a rubber stopper. It is filled with concentrated aqueous sugar solution and placed in distilled water. Osmosis occurs and the level of the solution in glass tube rises over a period of time. After a few days, the level becomes stationary. At this equilibrium state the hydrostatic pressure of the liquid column exactly balances the tendency which enables the water molecules to pass through semi permeable membrane.

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution. Osmotic pressure is also defined as the hydrostatic pressure built up on the solution which just stops the osmosis.

Osmosis pressure = hydrostatic pressure

$$\pi = hdg$$

where,  $h$  = increase in level in the tube of unit cross section,  $d$  = density of solution and

$g$  = acceleration due to gravity.

## 2. Define osmosis and osmotic pressure. Describe Berkeley – Hartly method of determining osmotic pressure?

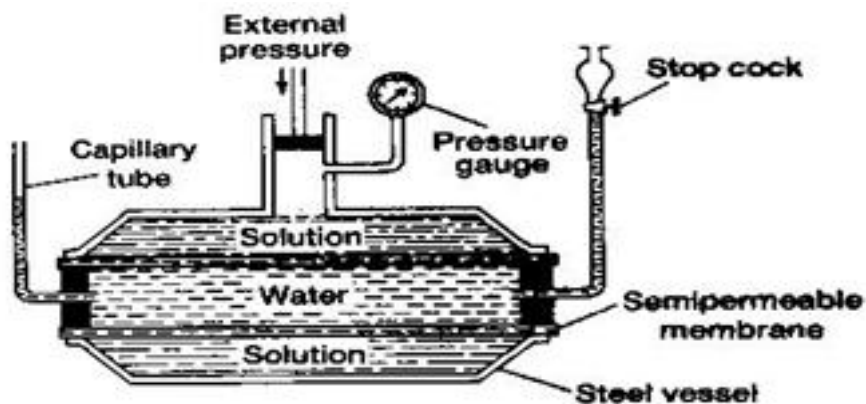
**Osmosis:** Osmosis is defined as the spontaneous flow of solvent molecules through semi permeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

Osmotic pressure Osmotic pressure is also defined as the pressure required to be applied on the solution to just stop the inflow of solvent into the solution, when solution and solvent are separated by a semi permeable membrane.

### Determination of osmotic pressure: Berkeley and Hartley's method

Various methods are employed for the measurement of osmotic pressure but the best known method was suggested by Berkeley and Hartley. The apparatus used is shown in Fig.. A porcelain tube having copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. The porcelain tube is fitted with a reservoir of pure solvent at one end and a capillary tube at the other end. In a metallic jacket is an arrangement for applying external pressure which is measured with the help of pressure eggs.

**Procedure:** The porcelain tube is filled with pure solvent and the metallic jacket with solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.



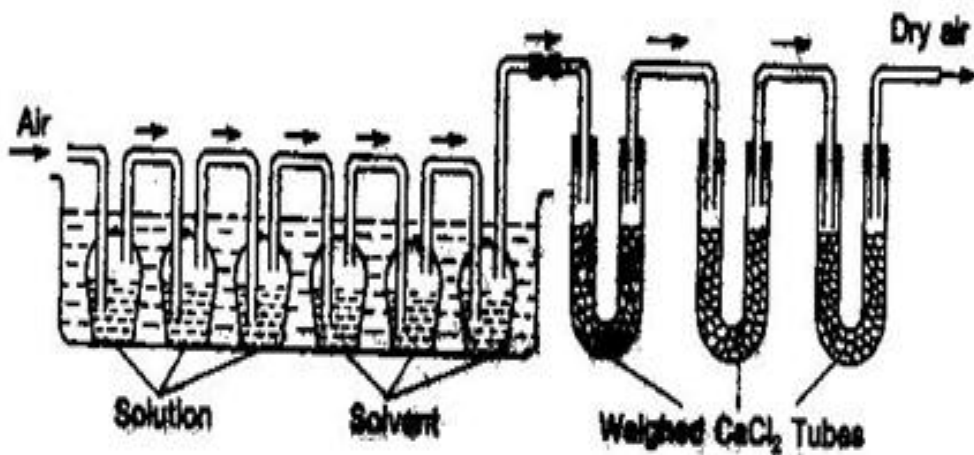
**Advantages:**

- It is a quick and accurate method.
- The concentration of the solution does not change because flow of solvent is not permitted into solution; so the results obtained by this method are reliable.
- As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated. So, this method can be used to measure high osmotic pressure also.

**3. How is molecular weight of solute determined by Ostwald's dynamic method?**

**Ostwald and Walker method:** The apparatus used is shown in Fig. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent. Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like  $P_2O_5$ , conc.  $H_2SO_4$  etc. The bulbs of solution and pure solvent are kept in a thermostat

maintained at a constant temperature.



A current of pure dry air is bubbled through. The air gets saturated with the vapours in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, i.e.  $p_0 - p_s$ . The two sets of bulbs are weighed again. The guard tubes are also weighed.

$$\begin{aligned} \text{Loss in mass}(x) \text{ in the solution bulbs} &\propto p_s \\ \text{Loss in mass}(y) \text{ in the solvent bulbs} &\propto (p_0 - p_s) \\ \text{Total loss}(x+y) \text{ in both sets of bulb} &\propto [p_s + (p_0 - p_s)] \\ &\propto p_0 \end{aligned}$$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

Thus,

$$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$

Loss in mass in solvents bulbs

$$= \frac{\text{Gain in mass of guard tubes}}{\dots}$$

Further we know from Raoult's law;

$$\frac{P_0 - p_s}{P_0} = \frac{n_s}{n_0} = \frac{y}{x + y} = X_s \dots \dots \dots (1)$$

where,  $n_s$  = No. of moles of solute

$n_0$  = No. of moles of solvent

Using equation (1) the molecular weight of solute can be found out using the following equation.

$$\frac{y}{x + y} = \frac{a \times W}{M \times b}$$

$$M = \frac{a \times W \times (x+y)}{B \times y} \dots \dots \dots (2)$$

Where,

a = wt. of solute

b = wt. of solvent

M = molecular wt. of solute

W = molecular wt. of solvent

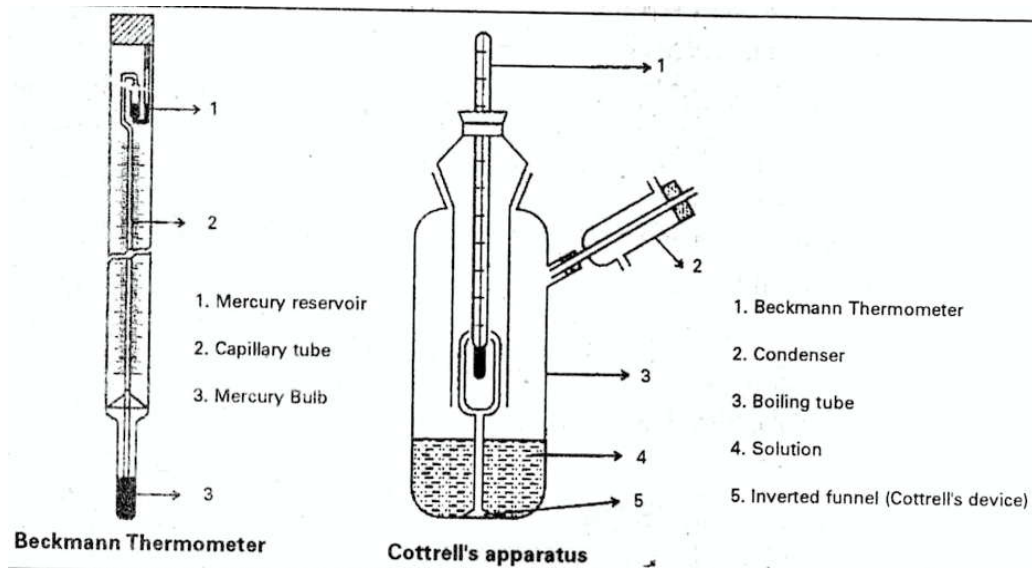
#### 4. Describe Cortell's method of determining the molecular weight of non-volatile solute?

##### Cottrell's method of determining molar mass of solute using elevation of boiling point

The methods of determination of molar mass by elevation in B.P. or depression in F.P. require (1) an accurate method of determining the elevation or depression respectively. The magnitudes of these values are small. Hence conventional thermometers are not useful.

So Beckman designed a thermometer which measures only the elevation or depression in temperature ( $\Delta T$ ) but not absolute values of B.P. and F.P. this thermometer contains a reservoir of Hg at one end of the capillary and as usual a bulb at the other end. These are internally connected through the capillary. At any level of temperature ( $-6^{\circ}$  to  $300^{\circ}$  C) the elevation or depression can be measured by adjusting the amount of Hg in the bulb unlike in conventional thermometer. This adjustment is done with the help of the reservoir. (2) The second requirement is elimination of super heating during boiling. For this Cottrell used a special device (pumping device) which resembles an inverted funnel, whose stem is split into three symmetrically placed tubes as shown in the following figure.





The apparatus consists of a tube provided with a side tube. The tube contains another tube through which the thermometer is inserted. At the bottom of the outer tube a platinum wire is fused which is heated during boiling. The funnel like device is placed in the solution in the tube. This pumps the bubbles of the solution along with the vapour on to the thermometer bulb point. This reduces super heating.

A known weight (b) of solvent (mol.wt.W) is taken in the cottrell tube and the boiling point of solution ( $T_0$ ). Then a known weight (ag) of the solute (mol.wt.M) is introduced into the tube through the side tube in the form of a tablet. This dissolves completely and the boiling point of solution (T) is measured. Molar mass is calculated as follows:

Wt. of solvent = b g

Wt. of solute = a g

B.P. of solvent =  $T_0$

B. P. of solution = T

Elevation =  $T - T_0 = \Delta T$

$$\Delta T_b = K_b \times \frac{a}{b} \times \frac{1000}{M} \Rightarrow M = \frac{K_b \times a \times 1000}{\Delta T_b \times b}$$

$$\Delta T_b = K_b \times \frac{b}{M}$$

$K_b$  = molal elevation constant of solvent.

$M$  = molar mass of solute

### 5. How molecular weight of solid hydrocarbon is determined by Rast's method?

**Rast's method:** This method was developed by Rast for camphor as a solvent. This method is thus generally used for solid solutions i.e., a solid solute in a solid solvent.

A known weight of camphor ( $b$ ) is taken and powdered finely in a dry mortar. To this a known weight ( $a$ ) of solid solute is added. The mixture is mixed thoroughly, the mixture is melted to form a homogeneous solution, cooled, and powdered dry. The mixture is taken in a capillary tube whose one end is sealed. Its melting point is determined carefully by the conventional melting point determination method. The melting point of the pure sample of camphor is determined separately using another capillary tube. The difference in the melting points gives  $\Delta T_f$ .

From the values  $a$ ,  $b$  &  $\Delta T_f$   $M$  is calculated ( $K_f$  for camphor = 40 K kg mol.)

Wt of camphor -  $b$  g

Wt of solute -  $a$  g

Mol Wt. of solute -  $M$

$$\Delta T_f = K_f \times \frac{a}{M} \times \frac{1000}{b} \Rightarrow M = \frac{K_f \times a \times 1000}{\Delta T_f \times b}$$

From this relation molecular weight is determined.

**6. What is meant by abnormal molar mass of solute? Explain with suitable examples, giving reasons for abnormal values?**

Colligative properties of dilute solutions depend upon the number of solute particles present in the dilute solutions. When the solute undergoes dissociation or association in solution, they behave differently while showing colligative property and hence in molar masses of solutes dissolved. (i.e.,) we obtain abnormal molar masses. This is called **abnormal molar mass of solute**.

**Ex:** Salts such as NaCl undergo ionization in aq. Solution, then the no. of ions increases. Hence magnitude of colligative properties increases. But colligative property and molar mass of solute are inversely proportional. Therefore the molar mass of solute determined for such solutions by colligative property method is less than the true value.

To explain the abnormal behavior, Van't Hoff introduced a factor called Van't Hoff's factor(i).

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal mol. wt}}{\text{Observed mol. wt}}$$

**Relation between Van't Hoff factor (i) and degree of Association ( $\alpha$ )**

$$\alpha = \frac{1 - i}{1 - 1/n}$$

$\alpha$  = degree of association

n = no.of molecules (associated) combined to form an associated molecule.

i = Van't Hoff factor

Using the above relation, 'i' is calculated and substituted in the following relation to get normal mol. wt.

$$i = \frac{\text{Normal mol.wt}}{\text{Observed mol.wt}}$$

**Relation between Van't Hoff factor (i) and degree of Association ( $\alpha$ )**

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

Knowing the values of n and  $\alpha$  we calculate 'i' from the above relation.

Normal mol. wt of the solute is calculated using the following equation.

$$i = \frac{\text{normal mol.wt}}{\text{observed mol.wt}}$$

**NUMERICALS**

**Example: 1**

Phenol associated in benzene to a certain extent for a dimer. A solution containing  $20 \times 10^{-3}$  kg of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. Calculate the fraction of the phenol that has dimerised. ( $K_f$  of benzene is  $5.12^\circ\text{K kg mol}^{-1}$ )

**Solution:**

Observed mol. mass

$$= 1000 \times K_f \times w / W \times T$$

$$= 1000 \times 5.12 \times 20 \times 10^{-3} / 1 \times 0.69 = 148.4$$

Normal mol. mass of phenol ( $C_6H_5OH$ ) = 94

So Normal mol. mass/Observed mol. mass =  $94/148.4$

$$= 1 + (1/n + 1)\alpha = 1 + (1/2 - 1)\alpha$$

$$94/148.4 = 1 - \alpha/2$$

$$\text{or } \alpha = 0.733 \text{ or } 73.3 \%$$

### Example: 2

The molal depression of the freezing point in 1000 g of water is 1.86. Calculate what would be the depression of freezing point of water when (a) 120 g of urea, (b) 117 g of sodium chloride, (c) 488.74 g of  $BaCl_2 \cdot 2H_2O$  have been dissolved in 1000 g of water. It is assumed that sodium chloride and barium chloride are fully ionized.

#### Solution:

(a) Urea is a non-electrolyte. The number of particles does not change in solution.

$$\text{Thus, } \Delta T = 1000 \times K_f \times w / W \times m = 1000 \times 1.86 \times 120 / 1000 \times 60 = 3.72^\circ C$$

$$\text{No. of moles of urea} = 120/60 = 2$$

(b) No. of moles of NaCl =  $117/58.5 = 2$

NaCl is an electrolyte. It ionizes completely.

One molecule of NaCl furnishes 2 ions (one  $Na^+$  and one  $Cl^-$ ).

Hence, the number of particles will be double as compared to urea solution.

$$\text{So } \Delta T_{NaCl} = 2 \times \Delta T_{urea} = 2 \times 3.72 = 6.44^\circ C$$

(c) One molecule of  $BaCl_2 \cdot 2H_2O$  furnishes three ions (one  $Ba^{2+}$  and two  $Cl^-$ )

No. of moles of  $\text{BaCl}_2 \cdot \text{H}_2\text{O} = 488.74/244.37 = 2$

Hence, the number of particles will be three times as compared to the urea solution.

$$\text{So } \Delta T_{\text{BaCl}_2} = 3 \cdot \Delta T_{\text{urea}} = 3 \times 3.72 = 11.16^\circ\text{C}$$

**Example: 3**

On dissolving 10.8 glucose (m.w. = 180) in 240 g of water, its boiling point increases by  $0.13^\circ\text{C}$ . Calculate the molecular elevation constant of water.

**Solution:**  $\Delta T = 100K' \times w/W \times m$

$$\text{or } K' = \frac{\Delta T \times W \times m}{100 \times w}$$

Given,  $\Delta T = 0.13^\circ\text{C}$ ,  $W = 240 \text{ g}$ ,  $m = 180$  and  $w = 10.8 \text{ g}$

$$K' = \frac{0.13 \times 240 \times 180}{100 \times 10.8} = 5.2^\circ$$

**Example: 4**

A solution of 2.5 g of a non-volatile solid in 100 g benzene boiled at  $0.42^\circ\text{C}$  higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is  $2.67 \text{ K kg mol}^{-1}$ .

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

Given,  $K_b = 2.67$ ,  $w = 2.5 \text{ g}$ ,  $W = 100 \text{ g}$ ,  $\Delta T = 0.42$

$$m = \frac{1000 \times 2.67 \times 2.5}{100 \times 0.42} = 158.9$$

The molecular mass of substance is 158.9.

**Example: 5**

The molal elevation constant for water is  $0.56 \text{ K kg mol}^{-1}$ . Calculate the boiling point of a solution made by dissolving 6.0 g of urea ( $\text{NH}_2\text{CONH}_2$ ) in 200 g of water.

**Solution:**  $\Delta T = 1000K_b \times w/m \times W$

Given,  $K_b = 0.56 \text{ K kg mol}^{-1}$ ,  $w = 6.0 \text{ g}$ ,  $W = 200 \text{ g}$ ,  $m=60$

$$\Delta T = 1000 \times 0.56 \times 6.0 / 200 \times 60 = 0.28^\circ\text{C}$$

Thus, The boiling point of solution = boiling point of water +  $\Delta T = (100^\circ\text{C} + 0.28^\circ\text{C}) = 100.28^\circ\text{C}$

**Example: 6**

By dissolving 13.6 g of a substance in 20 g of water, the freezing point decreased by  $3.7^\circ\text{C}$ . Calculate the molecular mass of the substance. [Molal depression constant for water =  $1.863 \text{ K kg mol}^{-1}$ ]

Solution:  $m = 1000K_f \times w/W \times \Delta T$

Given,  $K_f = 1.863 \text{ K kg mol}^{-1}$ .

$$w = 13.6 \text{ g}, W = 20 \text{ g}, \Delta T = 3.7^\circ\text{C}$$

$$m = 1000 \times 1.863 \times 13.6 / 20 \times 3.7 = 243.39$$

**Example: 7**

On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density  $0.8 \text{ g/mL}$ ), its freezing point decreases by  $0.40^\circ\text{C}$ . Calculate the molecular mass of non-volatile substance ( $K_f = 5.12 \text{ K kg mol}^{-1}$ ).

**Solution:** Mass of benzene,  $W = \text{volume} \times \text{density}$

$$= 30 \times 0.8 = 24 \text{ g}$$

Given,  $K_f = 5.12 \text{ K kg mol}^{-1}$ ,  $w = 0.25 \text{ g}$ ,  $\Delta T = 0.40^\circ\text{C}$ .

We know that

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

$$= \frac{1000 \times 5.12 \times 0.25}{24 \times 0.40} = 133.33$$

**Example: 8**

A solution of 1.25 g of a certain non-volatile substance in 20 g of water freezes at 271.94 K. Calculate the molecular mass of the solute. [ $K_f = 1.86 \text{ K kg mol}^{-1}$ ]

**Solution:** Freezing point of water = 273.0 K

$$\Delta T = (273 - 271.94) = 1.06 \text{ K}$$

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

Given  $K_f = 1.86 \text{ K kg mol}^{-1}$ ,  $w = 1.25 \text{ g}$ ,  $W = 20 \text{ g}$  and  $\Delta T = 1.06 \text{ K}$ .

$$m = \frac{1000 \times 1.86 \times 1.25}{20 \times 1.06} = 109.66$$

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

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

Given,  $\Delta T = 0.13^\circ\text{C}$ ,  $W = 240 \text{ g}$ ,  $m = 180$  and  $w = 10.8 \text{ g}$



$$K' = 0.13 \times 240 \times 180 / 100 \times 10.8 = 5.2^\circ$$

**Example: 9**

A solution of 2.5 g of a non-volatile solid in 100 g benzene boiled at 0.42°C higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is 2.67 K kg mol<sup>-1</sup>.

**Solution:**  $m = 1000K_b \times w / W \times \Delta T$

Given,  $K_b = 2.67$ ,  $w = 2.5$  g,  $W = 100$  g,  $\Delta T = 0.42$

$$m = 1000 \times 2.67 \times 2.5 / 100 \times 0.42 = 158.9$$

The molecular mass of substance is 158.9.

**Example: 10**

The molal elevation constant for water is 0.56 K kg mol<sup>-1</sup>. Calculate the boiling point of a solution made by dissolving 6.0 g of urea (NH<sub>2</sub>CONH<sub>2</sub>) in 200 g of water.

**Solution:**  $\Delta T = 1000K_b \times w / m \times W$

Given,  $K_b = 0.56$  K kg mol<sup>-1</sup>,  $w = 6.0$  g,  $W = 200$  g,  $m = 60$

$$\Delta T = 1000 \times 0.56 \times 6.0 / 200 \times 60 = 0.28^\circ\text{C}$$

Thus, The boiling point of solution = b.pt. of water +  $\Delta T = (100^\circ\text{C} + 0.28^\circ\text{C}) = 100.28^\circ\text{C}$

**Example: 11**

By dissolving 13.6 g of a substance in 20 g of water, the freezing point decreased by 3.7°C. Calculate the molecular mass of the substance. [Molal depression constant for water = 1.863 K kg mol<sup>-1</sup>]

Solution:  $m = 1000K_f \times w / W \times \Delta T$

Given,  $K_f = 1.863 \text{ K kg mol}^{-1}$ .

$w = 13.6 \text{ g}$ ,  $W = 20 \text{ g}$ ,  $\Delta T = 3.7^\circ\text{C}$

$$m = 1000 \times 1.863 \times 13.6 / 20 \times 3.7 = 243.39$$

**Example: 12**

On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density 0.8 g/mL), its freezing point decreases by  $0.40^\circ\text{C}$ . Calculate the molecular mass of non-volatile substance ( $K_f = 5.12 \text{ K kg mol}^{-1}$ ).

**Solution:** Mass of benzene,  $W = \text{volume} \times \text{density}$

$$= 30 \times 0.8 = 24 \text{ g}$$

Given,  $K_f = 5.12 \text{ K kg mol}^{-1}$ ,  $w = 0.25 \text{ g}$ ,  $\Delta T = 0.40^\circ\text{C}$ .

We know that

$$m = 1000K_f \times w / W \times \Delta T$$

$$= 1000 \times 5.12 \times 0.25 / 24 \times 0.40 = 133.33$$

**Example: 13**

A solution of 1.25 g of a certain non-volatile substance in 20 g of water freezes at 271.94 K. Calculate the molecular mass of the solute. [ $K_f = 1.86 \text{ K kg mol}^{-1}$ ]

**Solution:** Freezing point of water = 273.0 K

$$\Delta T = (273 - 271.94) = 1.06 \text{ K}$$

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

Given  $K_f = 1.86 \text{ K kg mol}^{-1}$ ,  $w = 1.25 \text{ g}$ ,  $W = 20 \text{ g}$  and  $\Delta T = 1.06 \text{ K}$ .

$$m = \frac{1000 \times 1.86 \times 1.25}{20 \times 1.06} = 109.66$$

## IMPORTANT QUESTIONS IN SOLUTIONS

### I. Long answer questions.

1. What do you mean by vapor pressure of liquid? Describe the vapourisation and condensation processes in a closed vessel. How does vapour pressure change with temperature?
2. What are colligative properties? Explain each of them with necessary examples?
3. Define Osmosis. Define Osmotic pressure. Describe Berkeley-?
4. Hartley method of determining osmotic pressure?
5. How is molecular weight of solid hydrocarbon determined by Rast's method?

### II. Short answer questions

1. Define molarity and molality?
2. State and explain Raoult's law?
3. What is vapour pressure? How does it vary with temperature?
4. What is an ideal solution?
5. Derive the relation between relative lowering of vapour pressure and molar mass of solute.
6. Derive the equation  $\Pi = CRT$ .
7. What is Van't Hoff's factor (i) and how is it related to  $\alpha$  in the case of a binary electrolyte.(1:1).

**III. Very short answer questions**

1. What is Osmosis? Define Osmotic pressure?
2. What is molal elevation constant?
3. What is molal depression constant?
4. Define Osmotic pressure?
5. Explain osmosis?
6. What is meant by abnormal behaviour of electrolyte in colligative properties?
7. What are isotonic solutions give one example?

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