2. SOLUTIONS AND COLLAGIVATIVE PROPERTIES

**Introduction:**- A solution contains one or more solutes in a solvent. In a solution, the particles of the solute are of molecular size 100-1000 pm in diameter. A solution containing two components is called a binary solution. The solutions prepared in water are called aqueous solutions. The solutions prepared in organic solvents are called non-aqueous solutions.

**Q.1** Define - Solution, Solute, and Solvent.

**Ans.**

**Solution:** A solution is defined as a homogeneous mixture of two or more substances whose composition can be varied within certain limits.

**Solute:** The component that dissolves and constitutes smaller portion of a solution is called solute.

**Solvent:** The component in which solution formation takes place and which constitutes larger proportion of a solution is called as solvent.

**Q.2** Classify the solution mixtures depending upon the size of the component.

**Ans:**

Depending upon the size of the components, the mixtures are classified into three types:

**(a) A coarse mixture:**
It is formed when size of the constituent components are relatively bigger.
E.g. Mixture of sugar and salt or mixture of silica and soil etc.

**(b) A colloidal dispersion:**
It is formed when the size of the particles dispersed in solvent are in the range of 10^{-7} cm to 10^{-4} cm.
E.g. Ferric hydroxide solution. Milk.
They are heterogeneous and can be easily separated.

**(c) A true solution:**
It’s a solution which is formed, when soluble substances are dissolved in the solvent. The sizes of the particles dissolved are very small of the order of 10^{-8} cm. The true solutions are homogeneous and cannot be separated into components by simple mechanical method.

**Q.3** Classify the different types of Solutions.

**Ans.**

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Solute</th>
<th>Solvent</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gas</td>
<td>Gas</td>
<td>Air , mixture of non-reacting gases</td>
</tr>
<tr>
<td>2</td>
<td>Liquid</td>
<td>Gas</td>
<td>Water Vapours in air</td>
</tr>
<tr>
<td>3</td>
<td>Solid</td>
<td>Gas</td>
<td>Sublimation of iodine</td>
</tr>
<tr>
<td>4</td>
<td>Gas</td>
<td>Liquid</td>
<td>Aerated drinks</td>
</tr>
<tr>
<td>5</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Alcohol in water</td>
</tr>
<tr>
<td>6</td>
<td>Solid</td>
<td>Liquid</td>
<td>Aqueous solution of sugar</td>
</tr>
<tr>
<td>7</td>
<td>Gas</td>
<td>Solid</td>
<td>Adsorption of a gas on metal surface</td>
</tr>
<tr>
<td>8</td>
<td>Liquid</td>
<td>Solid</td>
<td>Amalgam of Hg with Na</td>
</tr>
<tr>
<td>9</td>
<td>Solid</td>
<td>Solid</td>
<td>Alloys , Coloured gemstones</td>
</tr>
</tbody>
</table>
Q.4 Explain the ways of expressing the concentration of a Solution.

Ans. **Concentration:** The Concentration of a solution may be defined as the amount of solute present in the given quantity of the solution or solvent.

The Concentration of a Solution can be expressed in the following ways:

(i) **Percentage:**

(a) **Mass Percentage:** It is defined as the mass of solute present in 100g of the solution it is expressed as (w/w).

\[
\text{Mass Percentage of (A)} = \frac{m(A)}{m(A) + m(B)} \times 100
\]

(b) **Volume Percentage:** It is the number of parts by volume of solute per 100 parts by volume of the solution. It is expressed as (v/v).

\[
\text{Volume Percentage of (A)} = \frac{v(A)}{v(A) + v(B)} \times 100
\]

(ii) **Normality (N):** Normality of a solution may be defined as the number of gram equivalents of the solute present in one liter of the solution.

\[
\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{volume of solution in litres}}
\]

Gram equivalent of a solute = \( \frac{\text{Mass of solute}}{\text{Equivalent mass of solute}} \)

Normality of a solution changes with temperature.

(iii) **Molarity (M):** Molarity of a solution may be defined as the number of moles of solute present per liter of solution.

\[
\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{volume of solution in litres}}
\]

Number of moles of solute = \( \frac{\text{Mass of solute in grams}}{\text{Molar mass of solute}} \)

The unit of molarity is mol dm\(^{-3}\).

(iv) **Molality (m):** It is defined as the number of moles of the solute dissolved in 1 kg of the solvent.

\[
\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}
\]

The unit of molality is moles / kg.

**Why is molality independent of temperature?** (march 2016)

(v) **Mole Fraction (X):** The mole fraction of a component of the solution is defined as the ratio of the number of moles of that component to the total number of moles of all the component present in the solution.

\[
X_1 = \frac{n_1}{n_1 + n_2}; \quad X_2 = \frac{n_2}{n_1 + n_2}; \quad X_1 + X_2 = 1
\]
Q.5 How is molarity related to normality?

Ans: Normality = \[\frac{\text{Molar Mass}}{\text{Equivalent mass}} \times \text{Molarity}\]

For acids, Normality = Molarity \times \text{Basicity}

(Basicity is the number of H\(^+\) ions obtained from an acid in the solution).

For bases, Normality = Molarity \times \text{Acidity}

(Acidity is the number of OH\(^-\) ions obtained from a base in the solution).

Q.6 How are the solutions classified depending on the amount of the solute present in the solution?

Ans: Depending upon the amount of solute present in the given volume of a solution, the solutions can be classified into three types as follows:

a) Saturated solution:
   Its defined as the solution that contains just the amount of dissolved solute required for establishing equilibrium between dissolved solute and undissolved solute

b) Unsaturated solution:
   A solution containing less amount of solute required to form a saturated solution is called unsaturated solution.
   In this case, there is no equilibrium between dissolution and crystallization.

c) Supersaturated solution:
   A containing excess amount of a solute than required to form saturated solution is called supersaturated solution.
   It represents an unstable system.

Q.7 Define solubility.

Ans: The maximum amount of a solute required to be dissolved in a given amount of a solvent (generally 100cm\(^3\)) to form a saturated solution at a constant temperature is called the solubility of the solute.

Solubility is expressed in grams of solute per 100cm\(^3\) of a solvent or mol dm\(^{-3}\).

Q.8 Explain the effect of temperature on the solubility of solids.

Ans: The solubility of solids depends upon the temperature.

a) Generally the rise in temperature increases the solubility. This is due to the expansion of the holes or empty spaces in the liquid solvent. Generally 10\(^\circ\)C rise in temperature increases the solubility of solids two folds.

b) Dissolution process may be endothermic or exothermic.

c) The solubility of the substances like NaBr, NaCl, KCl etc. changes slightly with the temperature.

d) The solubility of the salts like NaNO\(_3\), KNO\(_3\), KBr etc. increases appreciably with increase in temperature.

e) The solubility of the Na\(_2\)SO\(_4\) first increases and after 30\(^\circ\)C decreases with increase in temperature. This variation in the solubility with the temperature can be used to separate the salts from the mixture by fractional crystallization.
Q.9: How can the following constituents from the mixture be separated by fractional crystallization: (i) NaNO\(_3\) and KNO\(_3\); (ii) NaCl and NaBr
Ans:- (a) As the temperature decreases solubility of the substance decreases. The solubility of KNO\(_3\) at 0°C is less than that of NaNO\(_3\). Hence when a solution containing NaNO\(_3\) and KNO\(_3\) is cooled to 0°C, when KNO\(_3\) is crystallised nearly 90% leaving NaNO\(_3\) in the solution.
(b) The solubility of NaCl at 0°C is very less than that of NaBr. Hence when solution containing a mixture of NaCl and NaBr is cooled at 0°C when NaCl crystallizes out leaving NaBr in the solution.

Q.10: Why does the solubility of a solid not depend upon pressure?
Ans:- Since the solids are incompressible, the change in pressure has no effect on the solubility of solids in liquids.

Q.11: Explain the solubility of gases in liquids.
Ans:- (a) Gases are soluble in water and other liquids and their solubility depends upon the nature of the gas.
(b) The non-polar gases like O\(_2\) have less solubility in polar solvent.
(c) Polar gases like CO\(_2\), NH\(_3\) and HCl etc are more soluble in polar solvent like water. CO\(_2\) forms H\(_2\)CO\(_3\) and NH\(_3\) forms NH\(_4\)OH in aqueous solutions.
(d) The solubility of gases in liquids increases with increase in pressure and decrease temperature.

Q.12: Why does the solubility of a gas decreases with increase in temperature?
Ans:- (a) The gases are soluble in water and other liquids.
(b) According to Charles’s Law, the volume of the given mass of a gas increases with increase in temperature at a constant pressure. Hence the volume of dissolved gas increases with increase in temperature.
(c) This enormous increase in volume of the gases cannot be accommodated by the solvent molecules and therefore excess of the gases escape out in the form of bubbles.

Q.13: Explain the effect of changes of pressure on the solubility of gases. Or Explain Henry’s Law (October 2013)
Ans:- (a) Solubility of gases is greatly influenced by the external pressure and it increases with increase in temperature.
(b) Henry’s law relates the solubility of a gas with external pressure.
(c) According to Henry, the solubility of a gas in a liquid at constant temperature is proportional to the pressure of that gas above the solution.
Consider S is the solubility of the gas in mol dm\(^{-3}\) then according to Henry’s Law
\[
S \propto P \quad \text{i.e.} \quad S = KP
\]
Where P is the pressure of the gas in atm and K is the constant of proportionality and has the unit of mol dm\(^{-3}\) atm\(^{-1}\).
(d) If P = 1 atm then S=K
(e) If several gases are present then solubility of any gas may be evaluated by using P as partial pressure of that gas in the mixture.
Illustration of Henry’s law:

(a) In case of aerated or carbonated drink beverage, the bottle is filled by dissolving CO₂ gas at high pressure and then sealed.
(b) Above the liquid surface there is air and undissolved CO₂. Due to high pressure, the amount of dissolved CO₂ is large.
(c) When the cap of bottle is removed, the pressure on the solution is lowered, hence excess of CO₂ and air escape out in the form of effervescence. Thus by decreasing the pressure, solubility of CO₂ is decreased.

Q.14 Obtain the units of Henry’s law constant.
Ans: By Henry’s law, \( S = K \times P \)
Where \( S \) is solubility of the gas in mol dm\(^{-3}\), \( P \) is the pressure of the gas in atm and \( K \) is the constant of proportionality.

\[
K = \frac{S(\text{mol dm}^{-3})}{P(\text{atm})}
\]

\[
K = \text{mol dm}^{-3}/ \text{atm}
\]

Q.15 Explain solid solution or an alloy.
Ans: (a) Solid solutions of two or more metals or metal with two or more non-metals is called a solid solution or an alloy.
(b) Only in case of mercury, alloy may or may not be in the solid state.
(c) In the solid solution or alloy form, the properties of the metals are improved.
(d) Solid solutions are necessarily alloy.
(e) For example, duralium is a strong, light and steel like hard alloy used in making aircraft.

Q.16 What is amalgam?
Ans: (a) An alloy of a metal or metal with mercury is called as amalgam. Amalgam may be in the liquid and solid depending upon the content of mercury in the alloy. The property of forming amalgam is used in the extraction of metals like silver, gold. These metals are then extracted by distillation of amalgam.

Q.17 Define colligative properties.
Ans: The colligative properties of a dilute solution may be defined as the properties of the solution of non-volatile solutes, which depend only upon the number of solute particles in the solution and not upon the nature of solute particles.
The important colligative properties are –

(i) Relative lowering of vapour pressure.
(ii) Elevation of boiling point
(iii) Depression of freezing point
(iv) Osmotic pressure

Q.18 Define vapour pressure. State the factors affecting vapour pressure.

Ans. Vapour pressure of the liquid is defined as the pressure exerted by the vapours of a liquid above the liquid surface in equilibrium with the liquid at a given temperature.

The factors affecting vapour pressure are

(i) Temperature: Vapour pressure increases with increase in temperature.
(ii) Nature of liquid: The vapour pressure of volatile liquids is higher.
(iii) Presence of impurities: The Vapour Pressure of a solution decreases due to presence of non-volatile impurities in it.

Q.19 Explain relative lowering of vapour pressure.

Ans. The relative lowering of a vapour pressure of a solution containing the non-volatile solute in is defined as the ratio of lowering of vapour pressure of the solution to the vapour pressure of the pure solvent at a given temperature. Thus,

Relative lowering of vapour pressure \[ \frac{p^0 - p}{p^0} \]

Where \( p^0 \) = vapour pressure of pure solvent, \( p \) = vapour pressure of the solution

Q.20 State and explain Raoult’s Law.

Ans. (i) For a solution of two (or more) miscible volatile liquids, Raoult’s law states that, at a particular temperature, the partial vapour pressure of each component of the solution is equal to the product of the vapour pressure of the pure liquid component and its mole fraction

\[ p_1 = p_1^0 \times X_1 \quad ; \quad p_2 = p_2^0 \times X_1 \]

\( p_1 \) = partial vapour pressure of component 1
\( p_1^0 \) = vapour pressure of pure component 1
\( X_1 \) = mole fraction of component 1

(ii) For a solution containing a non-volatile solute in a volatile solvent, Raoult’s law states that, at a particular temperature, the vapour pressure of a solution is directly proportional to the mole fraction of the solvent.

**Vapour pressure of solution = vapour pressure of pure solvent \times Mole fraction of solvent.**

\[ p = p^0 \times X_1 \]

Q.21 Derive relative lowering of vapour pressure using Raoult’s law.

Ans. According to Raoult’s law, the vapour pressure of the solution is directly proportional to the mole fraction of the solvent.

\[ p \propto X_1 \]

\[ p = p^0 \times X_1 \quad …. (i) \]

For a binary solution, \( X_1 + X_2 = 1 \)
Where \( X_2 \) = mole fraction of solute.

Therefore, \( X_1 = 1 - X_2 \)

Substituting the value in eqn (1).

\[
p = p^o (1 - X_2) \quad \text{Or,} \quad p = p^o - p^o X_2 \quad \text{Or,} \quad X_2 = \frac{p^o - p}{p^o}
\]

Thus, Raoult’s law can also be stated as –The relative lowering in vapour pressure of an ideal solution, containing non – volatile solute is equal to the mole fraction of the solute at a given temperature.

**The limitations of Raoult’s law:**

(i) Raoult’s law can be applied to dilute solution only.

(ii) This law is applicable to those solutions, in which the solute is non – volatile.

(iii) This law is applicable to those solutions in which the solute does not dissociate or associate.

**Q.22 How is the molar mass of a solute calculated from relative lowering of vapour pressure?**

(2 marks) (March 2013)

Ans

Let, \( M_1 \) and \( M_2 \) be the molar masses of the solvent and solute respectively.

Let \( n_1 \) and \( n_2 \) be the number of moles of the solvent and the solute.

Then, mole fraction of solute, \( x_2 = \frac{n_2}{n_1 + n_2} \) \( \ldots \) (i)

Now, number of moles of solvent (\( n_1 \)) = \( \frac{W_1}{M_1} \) \( \ldots \) (ii)

Number of moles of solute (\( n_2 \)) = \( \frac{W_2}{M_2} \) \( \ldots \) (iii)

Substituting the values in (1), we get, we get,

\[
X_2 = \frac{W_2 / M_2}{W_1 / M_1 + W_2 / M_2} \quad \ldots \text{(iv)}
\]

The concentration of solute is very small, it can be neglected, and eqn (4) can now be written as:

\[
X_2 = \frac{W_2 / M_2}{W_1 / M_1} \quad \Rightarrow \quad \frac{W_2}{W_1} \frac{M_1}{M_2} \quad \text{------------------------ (5)}
\]

But, from Raoult’s law

\[
X_2 = \frac{p^o - p}{p^o}
\]

Substituting the value of \( x_2 \)

\[
\frac{\Delta p}{p_1^o} = \frac{p^o - p}{p^o} = \frac{W_2 / M_2}{W_1 / M_1} \quad \therefore \quad M_2 = \frac{W_2}{W_1} \frac{M_1}{M_2} \times \frac{p^o}{p^o - p}
\]
Q.23 Define boiling point of a liquid. (March 2013)
Ans. The boiling point of a liquid may be defined as the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.

Q.24 Define molal boiling point elevation constant or ebullioscopic constant
And write its unit (2 marks) (Oct 2015)
Ans. Experimentally, it has been found that,
\[ \Delta T_b \propto m. \]
\[ \Delta T_b = K_b m. \]
If m = 1, then, \( \Delta T_b = K_b \).
Thus molal boiling point elevation constant may be defined as the elevation in boiling point for one molal solution. It is also known as ebullioscopic constant.

Q.26 Explain the determination of molecular weight of a non-volatile solute from elevation in boiling point.
Ans. Experimentally, it has been found that, \( \Delta T_b \propto m \)
where, \( K_b \) is molal boiling point elevation constant.

Molality of a solution is expressed as.
\[ \text{Molality (m)} = \frac{\text{Number of moles of solute} \times 1000}{\text{Mass of solvent in gram}} \]

The number of moles of solute \( n = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} = \frac{W_2}{M} \)

\[ \therefore m = \frac{W_2}{M} \times 1000 = \frac{1000W_2}{M_2W_1} \]

But \( \Delta T_b = K_b \times m \)

\[ \therefore \Delta T_b = \frac{K_b \times 1000 \times W_2}{M_2W_1} \]

\[ \therefore M_2 = \frac{1000 \times K_b \times W_2}{\Delta T_b \times W_1} \]

This method is also called ebullioscopic method for calculating the molar mass of a solute.

Q.27 Define – freezing point, molal depression constant. (Cryoscopic constant) (October 2014)
Ans. **Freezing point:** The freezing point of a substance may be defined as the temperature at which the solid and liquid states of the substance have the same vapour pressure.

**Molal depression constant:** Molal depression constant of a solvent may be defined as the depression in freezing point produced by dissolving one mole of a solute in one kilogram of the solvent. It is also called as cryoscopic constant.

Q.28 Explain depression in freezing point.
Ans. The depression in freezing point may be defined as the difference between the freezing point of the pure solvent and that of the solution.

It is denoted as \( \Delta T_f \)
\[ \Delta T_f = T_f^o - T_f. \]

Where, \( T_f^o \) is the freezing temperature of the pure solvent,
\( T_f \) is the freezing temperature of the solution.
Q.29 Derive a relationship between depression in freezing point and molar mass of solute.

Derive \( M_2 = \frac{1000 \times k_f \times W_2}{\Delta T_f \times W_1} \)  

(March 2016) (2 marks)

Ans. Consider \( W_2 \) g of a non-volatile solute is dissolved in \( W_1 \) g of the solvent. Let \( M_2 \) be the molar mass of the solute.

\[ \because \text{ Molality (m)} = \frac{\text{number of moles of solute}}{\text{Mass of solvent in grams}} \times 1000 \]

And No. of moles of solute = \( \frac{\text{Mass of solute}}{\text{Molar mass of solute}} = \frac{W_2}{M_2} \)

\[ \therefore m = \frac{W_2 / M_2 \times 1000}{W_1} = \frac{1000 \times W_2}{M_2 \times W_1} \]

But, \( \Delta T_f \propto m \) or

\[ \Delta T_f = K_f m \]

\[ \Delta T_f = \frac{K_f \times 1000 \times W_2}{M_2 \times W_1} \]

\[ \therefore M_2 = \frac{1000 \times K_f \times W_2}{\Delta T_f \times W_1} \]

Q.30 Define the terms

(i) Osmosis (March 2013)  
(ii) Semipermeable membrane  
(iii) Osmotic pressure

Ans.  
(i) Osmosis: It may be defined as the phenomenon of spontaneous unidirectional flow of solvent through a semi-permeable membrane from pure solvent to the solution or from a less concentrated solution to a more concentrated solution.

(ii) Semipermeable membrane: It is a kind of membrane, which allows the free passage to the solvent molecules, but not to the solute molecules.

(iii) Osmotic pressure: It may be defined as the equilibrium hydrostatic pressure, which is exerted on the solution due to osmosis of the pure solvent into it.

Q.31 Give short note on osmotic pressure.

Ans: The excess of the pressure on the side of a solution that stops the net flow of solvent into solution through semipermeable membrane is called as osmotic pressure. This concept can be explained by simple experiment.

(a) The apparatus consists of a long stem thistle funnel. The mouth of the thistle funnel is closed by semipermeable membrane like pig’s bladder.

(b) Take a sucrose solution of some concentration and filled in the thistle funnel.

(c) The thistle funnel is then placed in beaker containing water in inverted position. The solvent and solution are separated from each other by a semi permeable membrane.

(d) There occurs a net flow of solvent molecules into the solution through the semi permeable membrane.

(e) As a result, the original volume of the solution increases and the liquid level of solution rises.

(f) Hydrostatic pressure is developed due to the liquid column in thistle funnel.

(g) The liquid level in the thistle funnel tube rises until the excess pressure so produced is sufficient to stop the flow of solvent molecules.

(h) The equilibrium is reached when the hydrostatic pressure of the column matches the osmotic pressure.

(i) It should be noted that the osmotic pressure is not the pressure produced by solution. It exists only when the solution is separated from the solvent by the semi permeable membrane. The resulting osmosis produces an excess pressure (osmotic pressure) in the solution.
Q.32 Define the terms: (i) Isotonic solution (October 2013) (ii) Hypertonic solutions (iii) Hypotonic solution:
Ans: (i) Isotonic solution: The solutions of equimolar concentration, at the same temperature, having same osmotic pressure are called isotonic solutions.
(ii) Hypertonic solutions: A solution having more osmotic pressure than some other solutions is called hypertonic solution.
(iii) Hypotonic solution: A solution having less osmotic pressure than the other solutions is called hypotonic solution.

Q.33 State the laws of Osmotic pressure.
Ans. According to van’t Hoff, the solute molecules in a dilute solution play the same role similar to the gaseous molecules in a gas.

(i) Van’t Hoff – Boyle’s law:
Statement: This law states that, at constant temperature the osmotic pressure (\( \pi \)) of a dilute solution is directly proportional to its molar concentration or inversely proportional to the volume of the solution.

Thus, \( \pi \propto C \) (constant temperature)
\( \pi \propto \frac{1}{v} \) (constant temperature)

Or \( \frac{\pi}{C} = \text{constant} \)
\( \pi v = \text{constant} \)

(ii) Van’t Hoff – Charle’s law:
Statement: This law states that at constant volume (or concentration) the osmotic pressure of a dilute solution is directly proportional to the absolute temperature

\( \pi \propto T \) (at constant concentration or volume)
\( \frac{\pi}{T} = \text{constant} \)

Q.34 Derive van’t Hoff equation for dilute solutions. (March 2015) (2 marks)
Ans. From van’t Hoff – Boyle’s law:

\( \pi \propto \frac{1}{v} \) ....(i)

From van’t Hoff-charle’s law: \( \pi \propto T \) ...(ii)
Combining (i) & (ii) we get
\( \pi \propto \frac{T}{v} \) or \( \pi v = RT \)
Where \( R \) is gas constant (8.314 JK\(^{-1}\) mol\(^{-1}\))
If \( V \) is the volume of solution containing \( n \) moles of solute then
\( \pi v = nRT \) Or \( \frac{\pi}{v} = \frac{nRT}{v} = CRT \)

Where concentration \( C = \frac{n}{v} \), is the no. of solute per litre of solution.
Q.35  How is molecular weight determined from Osmotic pressure? Explain.
Ans  According to van’t Hoff, osmotic pressure is directly proportional to concentration of the solution and its temperature.

Thus,
\[ \pi \propto CT \]  

Or
\[ \pi = CRT \]

Where, \( R \) = Solution constant

\[ \pi = \frac{nRT}{V} \left( \therefore c = \frac{n}{V} \right) \]

But  \[ n = \frac{W_2}{M_2} = \frac{\text{mass of solute}}{\text{Molecular mass of solute}} \]

\[ \therefore \pi = \frac{m_2 \times RT}{M_2 \times V} \]

Or \[ M_2 = \frac{W_2RT}{\pi v} \]

Substituting the values of \( W_2 \), \( R \), \( T \), \( \pi \), \( v \) the molar mass of the solute can be determined.

Q.36  State and explain van’t Hoff-Avagadro’s law.
Ans:-  At a given temperature equal volumes of the solutions having the same osmotic pressure containing equal number of solute particles or the equal volumes of solution containing an equimolar amount of the solutes exert the same osmotic pressure at a given temperature.

**Explanation** One mole of the substance contains Avagadro’s number of molecules (i.e. \( 6.02 \times 10^{23} \) molecules). Therefore the equal number of moles of the substance will contain equal number of molecules.

The osmotic pressure, \( \pi \), is given by
\[ \pi = CRT \]

where \( C \) is the concentration of a solution in mol dm\(^{-3}\)

\[ \pi = \frac{n}{V} \times RT \]

therefore \( \pi \) is proportional to \( \frac{n}{V} \) at constant temperature.

If two solutions contain \( n_A \) and \( n_B \) moles of two solutes in the equal volumes \( (V) \) of the solutions A and B at the same temperature, then
\[ \pi_A \propto n_{A/V} \]

and \[ \pi_B \propto n_{B/V} \]

therefore \( \frac{n_B}{n_A} = \frac{\pi_A}{\pi_B} \)

If \( \pi_A = \pi_B \), then  \( n_A = n_B \).

Thus, two solutions having equal osmotic pressure will contain equal number of moles and hence equal number of the molecules of the substances (solute).
Q.37 What is abnormal colligative property? Explain the reasons.

Ans. When the experimentally measured colligative property of a solution is different from that calculated theoretically by the Van’t Hoff equation or by the laws of osmosis, then the solution is said to have abnormal colligative property.

Explanation: The colligative property depends upon the number of solute particles in the solution but it is independent of their nature. Abnormal values of them arise when the dissolved solute undergoes dissociation or association in the solution.

1) Dissociation of the solute molecules:

When a solute like an electrolyte is dissolved in a polar solvent like water, it undergoes dissociation, which results in the increase in the number of particles in the solution.

Hence the observed value of the colligative property becomes higher than the theoretical value e.g., when one mole of KCl is dissolved in the solution due to dissociation,

\[ \text{KCl} \rightarrow \text{K}^+ + \text{Cl}^- \]

the number of particles increases, hence the colligative properties like osmotic pressure elevation in the boiling point, etc. increases.

2) Association of the solute molecules:

When a solute like a nonelectrolyte is dissolved in a nonpolar solvent like benzene, it undergoes association forming molecules of higher molecular mass. Hence, the number of the particles in the solution decreases. Therefore the colligative properties like osmotic pressure, elevation in the boiling point etc., are lower than theoretical value

E.g. nA \rightarrow A_n

Like.. \[ 2\text{CH}_3\text{COOH} \rightarrow (\text{CH}_3\text{COOH})_2 \]

Q.38 Explain abnormal molecular masses.

Ans:- When the observed molecular masses obtained from their colligative properties of the substances are different than the theoretical or normal values calculated from their molecular formulae, then they called abnormal molecular masses.

Q.39 Define and explain Van’t Hoff Factor, i.

Define Van’t Hoff factor? How is it related to degree of dissociation?(2 marks)

(October 2014)

Ans:- It is defined as the ratio of observed colligative property produced by a given concentration of electrolyte solution to the property observed for the same concentration of non-electrolyte solution. Therefore,

\[ i = \frac{\text{observed colligative property of electrolyte solution}}{\text{observed colligative property of non-electrolyte of the same concentration}} \]

The observed colligative property of non-electrolyte of the same concentration is called the theoretical colligative property, as non-electrolytes in the solution remain in the molecular state and is neither association nor dissociation of solute.
Hence in terms of different colligative properties,

\[ i = \frac{\text{observed lowering of vapour pressure}}{\text{theoretical lowering of vapour pressure}} \]
\[ i = \frac{\text{observed elevation of boiling point}}{\text{elevation of boiling point}} \]
\[ i = \frac{\text{observed depression of freezing point}}{\text{theoretical depression of freezing point}} \]
\[ i = \frac{\text{observed osmotic pressure}}{\text{theoretical osmotic pressure}} \]

Therefore, In short

\[ i = \frac{(\Delta P \text{ Observed})}{(\Delta P \text{ Theoretical})} = \frac{(\Delta T_b) \text{ Observed}}{(\Delta T_b) \text{ Theoretical}} = \frac{(\Delta T_f) \text{ Observed}}{(\Delta T_f) \text{ Theoretical}} = \frac{\pi \text{ Observed}}{\pi \text{ Theoretical}} \]

But colligative property \( \propto \) Number of solute particles present in the solution

Hence,

\[ i = \frac{\text{Number of solute particles present in the solution (N observed)}}{\text{theoretical number of solute particles due to solution of non electrolyte (N theoretical)}} \]

i.e.

\[ i = \frac{(N \text{ observed})}{(N \text{ theoretical})} \]

Similarly, colligative property \( \propto \) \( \frac{1}{\text{Molecular mass (M)}} \)

Hence, \( i = \frac{\text{theoretical molecular mass (M theoretical)}}{\text{Observed molecular mass (M observed)}} \)

Therefore, \( i = \frac{(M \text{ theoretical})}{(M \text{ observed})} \)

Q40. Explain the relationship between vant Hoff factor (i) and degree of dissociation (\( \alpha \)).

Ans. (1) The value of vant Hoff factor may be used to evaluate the degree of dissociation of electrolyte dissolved in the given solution.

(2) Consider an electrolyte \( A_xB_y \) dissolved in the solvent and it undergoes dissociation into \( x \) ions of \( A^{m+} \) and \( y \) ions of \( B^n \) as

\[ A_xB_y \rightleftharpoons x A^{m+} + y B^n \]

When dissolved the molality of electrolyte is \( m \). This means that \( m \) moles of the electrolyte, \( A_xB_y \) is dissolved in 1 kg of solvent. On dilution solute dissociates.

(3) Let \( \alpha \) be the degree of dissociation of the solute. Then at equilibrium, out of original \( m \) moles, \( m\alpha \) moles dissociate and \( m-m\alpha = m(1-\alpha) \) moles of the solute remain undissociated. The dissociated \( m\alpha \) moles of the solute produce \( x\alpha \) moles of \( A^{m+} \) ions and \( y\alpha \) of \( B^n \) ions.

Hence the total number of moles \( m_t \) in the solution at the equilibrium will be, \( m(1-\alpha) \) moles of \( A_xB_y \) and \( x\alpha \) moles of \( A^{m+} \) ions and \( y\alpha \) of \( B^n \) ions.

Hence, \( m_t = m(1-\alpha) + x(m\alpha) + y(m\alpha) \)
(4) It is convenient to represent the total number of ions produced by dissociation of one molecule of solute $A_xB_y$ i.e. $x+y$ by $n^\prime$

Therefore, $m_i = m[1+(n^\prime-1)\alpha]$

Now, Vant Hoff factor,

$$i = \frac{\text{observed number of moles}}{\text{theoretical number of moles}} = \frac{m_t}{m} \cdot \frac{m[1+(n^\prime-1)\alpha]}{m}$$

Hence,

$$i = [1+(n^\prime-1)\alpha]$$

(5) The degree of dissociation,

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

Further

$$i = \frac{M(\text{theoretical})}{M(\text{observed})} = [1+(n^\prime-1)\alpha]$$

Hence, degree of dissociation

$$\alpha = \frac{M(\text{theoretical}) - M(\text{observed})}{M(\text{observed})}$$

Hence, it is possible to determine degree of dissociation of electrolyte by determining experimentally $M(\text{observed})$ and by measuring experimentally any one of the colligative properties.

Q. Derive the equation $\alpha = \left(\frac{n}{n-1}\right)1-i$ in the case of association.

A. Consider a substance $A$ which on association forms $A_n$ and let $\alpha$ be the degree of association,

$\text{nA} \not\Rightarrow \text{A}_n$

at start : $1$ mole $0$ mole

at equilibrium: $1-\alpha$ $\frac{\alpha}{n}$

Total number of particles at equilibrium: $1-\alpha + \frac{\alpha}{n} = 1-\alpha \left(1-\frac{1}{n}\right) = 1-\alpha \left(\frac{n-1}{n}\right)$

Theoretical number of moles=1(considering no association or dissociation)

$$i = \frac{\text{observed number of moles}}{\text{theoretical number of moles}} = 1-\alpha \left(\frac{n-1}{n}\right) / 1-\alpha \left(\frac{n-1}{n}\right)$$

$\therefore \alpha = \left(\frac{n}{n-1}\right)(1-i)$
(1) The vapour pressure of pure benzene is 640 mm of Hg. If \(2.175 \times 10^{-3}\) kg of a non volatile solute is added to 39 g of benzene, the vapour pressure of solution becomes 600 mm of Hg. Calculate the molar mass of the solute.

\[\text{(3 marks)} \text{ (March 2016)}\]

**Solution:**

Molar mass of benzene \(C_6H_6 = 78 \times 10^{-3} \text{ kg mol}^{-1}\)

\[
\left(\frac{p_0^0 - p}{p_0^0}\right) = \frac{W_2M_1}{M_2W_1}
\]

\[
= \left(\frac{640 - 600}{640}\right) = \left(\frac{2.175 \times 10^{-3} \times 78 \times 10^{-3}}{M_2 \times 39 \times 10^{-3}}\right)
\]

\[M_2 = 69.6 \times 10^{-3} \text{ kg mol}^{-1}\]

\[= 69.6 \text{ g mol}^{-1}\]

(2) A solution of glucose in water is labeled as 10% (w/w). Calculate its

(a) molality

(b) molarity. Density of the solution is 1.2 g mol\(^{-1}\). (molar mass of glucose = 180 g mol\(^{-1}\))

\[\text{(3 marks)} \text{ (October 2015)}\]

**Solution:**

Number of moles of glucose = \(10/180 = 0.055\)

Mass of water = 100 – 10 = 90 g

(a) Molality = \(\frac{\text{no. of moles of glucose}}{\text{mass of solvent in kg}}\) = \(\frac{0.0555 \times 1000}{90}\)

\[= 0.616 \text{ mol kg}^{-1}\]

Volume of solution = \(\frac{100}{1.2} = 83.33 \text{ ml}\)

Molarity = \(\frac{\text{no. of moles of glucose}}{\text{vol of solution in L}}\) = \(\frac{0.0555 \times 1000}{83.33} = 0.66 \text{ mol L}^{-1}\)

3. \(1 \times 10^{-3}\) kg of urea when dissolved in 0.0985 kg of a solvent, decreases the freezing point of the solvent by 0.211K. \(1.6 \times 10^{-3}\) kg of another non-electrolyte when dissolved in 0.086 g of the same solvent, depresses the freezing point by 0.34 K. Calculate the molar mass of the other solute. (Molar mass of urea = 60 g mol\(^{-1}\))

\[\text{(3 M)} \text{ (March 2015)}\]

**A. Solution:**

Since solvent is same, \(K_f\) will be same,
K_f = \frac{\Delta T_f}{m}

Molality of urea solution = \frac{mass \ of \ urea \ in \ kg}{molar \ mass \ of \ urea \ in \ kg \times mass \ of \ solvent \ in \ kg}

= \frac{1 \times 10^{-3}}{60 \times 10^{-3} \times 98.5 \times 10^{-3}}

K_f = \frac{0.211}{0.1692} = 1.247 \text{ k kg mol}^{-1}

Molar mass of the other solute = \frac{K_f W_2}{\Delta T_f W_1} = \frac{1.247 \times 1.6 \times 10^{-3}}{0.34 \times 0.086 \times 10^{-3}}

= 68.29 \text{ kg mol}^{-1}

= 0.068 \text{ g mol}^{-1}

(Note: The above answer is unreasonable, because the molar mass cannot be so small)

(4) A solution containing 0.73 g of camphor (molar mass 152 g mol\(^{-1}\)) in 36.8 g of acetone (boiling point 56.3 °C) boils at 56.55 °C. A solution of 0.564 g of unknown compound in the same weight of acetone boils at 56.46 °C. Calculate the molar mass of the unknown compound (3 marks) (October 2014)

A. Solution:

\Delta T_b (\text{camphor}) = 56.55 - 56.3 = 0.25

K_b = \frac{\Delta T_b M_2 W_2}{W_1} \quad (W_1 \text{ in kg})

= \frac{0.25 \times 36.8 \times 10^{-3} \times 152}{0.73}

= 1.916 \text{ K Kg mol}^{-1}

(B) for unknown compound

\Delta T_b = 0.16

M_2 = \frac{K_b W_2}{\Delta T_b W_1}

= \frac{1.916 \times 0.564 \times 10^{-3}}{0.16 \times 36.8 \times 10^{-3}} = 183.5 \times 10^{-3} \text{ Kg mol}^{-1}

= 183.5 \text{ g mol}^{-1}
(5) Calculate the amount of CaCl$_2$ (Van’t Hoff factor, $i = 2.47$) dissolved in 2.5 litres of solution so that its osmotic pressure at 300 K is 0.75 atm. Given molar mass of CaCl$_2$ = 111 g mol$^{-1}$, $R = 0.082$ L atm$^-1$ K$^-1$ (3 marks) (March 2014)

Solution:

$$\pi V = inRT$$
$$n = \frac{\pi V}{iRT} = \frac{0.75 \times 2.5}{2.47 \times 0.082 \times 300}$$
$$= 0.03086$$
$$W = n \times M = 0.03086 \times 111$$
$$= 3.425 \text{ g}$$

(6) Calculate the molality and molarity of 6.3% solution of nitric acid having density 1.04 g cm$^-3$ (3 marks) (October 2013)

Solution:

mass of HNO$_3$ = 6.3 g, and mass of solvent = 100-6.3 = 93.7 g

Molar mass of HNO$_3$ = 1+ 14+ 48 = 63

Molality of HNO$_3$ = \(\frac{\text{no of moles of HNO}_3}{\text{wt of solvent in kg}}\)

\[= \frac{6.3}{93 \times 10 \times 10^{-3}} = 0.167 \text{ mol kg}^{-1}\]

(b) Volume of solution = \(\frac{\text{mass}}{\text{density}}\) \[= \frac{100}{1.04} = 96.15 \text{ cm}^3\]

(c) Molarity of solution = \(\frac{\text{no of moles of HNO}_3}{\text{vol of soln in L}}\)

\[= \frac{6.3}{96.5 \times 10^{-3}} = 1.04 \text{ M}\]

(7) If Na$_2$SO$_4$ dissociates to the extent of 82% in its 0.1 m solution, what will be the freezing point of its aqueous solution. ($K_f = 1.86$ K Kg mol$^{-1}$)

Solution: Freezing point of water = 273 K

Na$_2$SO$_4$ $\rightleftharpoons$ 2Na$^+$ + SO$_4^{2-}$ \quad n=3

For dissociation, \(\alpha = \frac{i-1}{n-1}\) or \(i = 1+2\alpha\)

\[i = 1+2(0.82) = 2.64\]

\[\Delta T_f = i \times K_f \times m\]

\[= 2.64 \times 1.86 \times 0.1 = 0.49\]

Freezing point of solution = 273 - 0.49 = 272.51 K
4.5 g of acetic acid was dissolved in 90 g of benzene. Depression in freezing point = 2.253 K. The value of $K_f = 5.1 \text{ kg mol}^{-1}$. Determine the formula of acetic acid in benzene, van’t Hoff factor and % association.

**Solution**: $M$ (theoretical) of acetic acid = 60 g mol$^{-1}$

$$
\Delta T_f \text{ (observed)} = \frac{K_f \times W_2 \times 1000}{W_1 \times M_2}
$$

$$
2.253 = \frac{5.1 \times 4.5 \times 1000}{90 \times M_2}
$$

$M_2 = 113.2 \text{ g mol}^{-1}$

$$
n = \frac{M_{\text{obs}}}{M_{\text{th}}} = \frac{113.2}{60} = 1.89 \approx 2
$$

$$
i = \frac{M_{\text{th}}}{M_{\text{obs}}} = \frac{60}{113.2} = 0.53
$$

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

$$
= 2(1-0.53) = 0.94 = 94\%
$$

Formula = $(\text{CH}_3\text{COOH})_2$; $i = 0.53$; $\alpha = 94\%$