SOLUTIONS

Topic-1

CLASSIFICATION OF SOLUTIONS, STANDARD SOLUTIONS, CONCENTRATIONS AND THEIR DEFINITIONS

VERY SHORT ANSWER QUESTIONS

1. Define molarity?

Ans: Molarity**:** The number of gram moles of the dissolved solute per litre of solution is known as the molarity of the solution. It is represented by 'M'.

$$= \frac{\text{number of moles of the solute}}{\text{volume of the solution in litres}}$$

$$\mathbf{M} = \frac{w}{M.W} \times \frac{1000}{V_{(ml)}}$$

- Units for molarity are moles/litre.
- The molarity is the most convenient and commonly used method of expressing the concentration of solution.
- The molarity of a solution slightly decreases with increase in temperature of the solution, due to increase in volume

2. State the definition of molality?

Ans: Molality : The number of gram moles of the solute dissolved in one kilogram of the solvent is known as the molality of the solution. It is represented by 'm'.

$$m = \frac{\text{number of gram moles of the solute}}{\text{weight of solvent in kilograms}}$$

- The units for molality are mole / kg.
- Molality is independent of temperature.
- Molality is the most inconvenient method of expressing concentration of a solution because it involves determining the weights of liquids.

3. In a binary solution what is mole fraction?

Ans: The ratio between the number of moles of solute and the total number of moles of solute and solvent in the solution is known as the mole fraction of the solute. It is represented by X_1.

$$X_1 = \frac{n}{n+N}$$ n = No.of moles of solute

N = No.of moles of solvent

The ratio between the number of moles of solvent and the total number of solute and the solvent in the solution is known as the mole fraction of the solvent. It is represented by X_2.

$$X_2 = \frac{N}{n+N}$$

4. What is equivalent weight of a salt?

Ans: Equivalent weight of salt: $= \frac{\text{molecular weight}}{\text{total charge(postive or negative)}}$

Ex: $E_{NaCl} = \frac{\text{molecular weight}}{1}$

$E_{MgCl_2} = \frac{\text{molecular weight}}{2}$

$E_{AlCl_3} = \frac{\text{molecular weight}}{3}$

$E_{Al_2(SO_4)_3} = \frac{\text{molecular weight}}{6}$

5. What is Solubility? Give expression for solubility?

Ans: Solubility: It is the weight of solute dissolved in 100 grams of solvent to form saturated solution.

$$\text{Solubility} = \frac{\text{weight of solute}}{\text{weight of solvent}} \times 100$$

6. Define Normality?

Ans: Normality (N)**:** The number of gram equivalents of the solute dissolved in one litre of solution is known as its normality. Units for normality are gram equivalents/ litre.

.

$$N = \frac{\text{No.of gram equivalent of the solute}}{\text{volume of the solution in litres}}$$

$$N = \frac{\text{number of milli equivalents of solute}}{\text{volume of solution (m}\ell)}$$

Number of equivalent weight of solute = $N \times V_{(lit)}$

Number of milli equivalents of solute = $N \times V_{(ml)}$

*** The normality of a solution decreases with increase in temperature of the Solution.**

7. Define is equivalent weight?

Ans: Equivalent weight (E): The weight of the substance which combines with 1 gram of hydrogen or 8 grams of oxygen is called equivalent weight.

Equivalent weight is the weight of the substance which loses or gains 1 mole of electrons

$$\text{No.of equivalents} = \frac{\text{weight of the substance(g)}}{\text{equivalent weight}}$$

$$\text{No.of milli equivalents} = \frac{\text{weight of the substance(mg)}}{\text{equivalent weight}}$$

$$E_{element} = \frac{\text{Atomic weight}}{\text{valency}}$$

$$E_{acid} = \frac{\text{molecular weight}}{\text{number of replaceble hydrogens}}$$

Ex: $$E_{HCl} = \frac{\text{molecular weight}}{1}$$

8. What is the equivalent weight of a Base?

Ans: Equivalent weight of base $= \frac{\text{molecular weight}}{\text{number of replaceble } OH^- \text{ ions}}$

Ex : $E_{NaOH} = \frac{\text{molecular weight}}{1}$

$E_{Ca(OH)_2} = \frac{\text{molecular weight}}{2}$

$E_{NH_3} = \frac{\text{molecular weight}}{1}$

9. What is equivalent weight of oxidizing or reducing agent?

Equivalent weight of oxidising or reducing agent $= \frac{\text{molecular weight}}{\text{change in oxidation state}}$

Ex: $E_{KMnO_4} = \frac{\text{molecular weight}}{5}$

$(MnO_4^- \rightarrow Mn^{2+}$ in acid medium)

$E_{KMnO_4} = \frac{\text{molecular weight}}{1}$

$(MnO_4^- \rightarrow MnO_4^{2-}$ in basic medium)

$E_{KMnO_4} = \frac{\text{molecular weight}}{3}$

$(MnO_4^- \rightarrow MnO_2$ in neutral medium)

$E_{K_2Cr_2O_7} = \frac{\text{molecular weight}}{6}$

$(Cr_2O_7^{2-} \rightarrow Cr^{3+}$ in acid and basic medium)

10. What is formality?

Ans: Formality (F): Fomality is the number of formula weights of solute per litre of solution.

$$\text{Formality} = \frac{\text{weight of solute}}{\text{formula weight}} \times \frac{1000}{\text{volume of solution}(m\ell)}$$

Ionic compounds and polymers do not contain molecules and molecular weights. Instead of molecular weight, the formula weight to be taken and instead of molarity the formality to be considered.

For any given solution, molarity and formality are same.

SHORT ANSWER TYPE QUESTIONS

1. Define Molarity and Molality?

Ans: Molarity**:** The number of gram moles of the dissolved solute per litre of solution is known as the molarity of the solution. It is represented by 'M'.

$$= \frac{\text{number of moles of the solute}}{\text{volume of the solution in litres}}$$

$$\mathbf{M} = \frac{w}{M.W} \times \frac{1000}{V_{(ml)}}$$

Units for molarity are moles/litre.

The molarity is the most convenient and commonly used method of expressing the concentration of solution. The molarity of a solution slightly decreases with increase in temperature of the solution, due to increase in volume

Molality: The number of gram moles of the solute dissolved in one kilogram of the solvent is known as the molality of the solution. It is represented by 'm'.

$$\mathbf{m} = \frac{\text{number of gram moles of the solute}}{\text{weight of solvent in kilograms}}$$

The units for molality are mole / kg.

Molality is independent of temperature. Molality is the most inconvenient method of expressing concentration of a solution because it involves determining the weights of liquids.

2. What is meant by mole fraction? Explain.

Ans: Mole fraction:

The ratio between the number of moles of solute and the total number of moles of solute and solvent in the solution is known as the mole fraction of the solute. It is represented by X_1.

$$X_1 = \frac{n}{n+N}$$

n = No.of moles of solute

N = No.of moles of solvent

The ratio between the number of moles of solvent and the total number of solute and the solvent in the solution is known as the mole fraction of the solvent. It is represented by X_2.

$$X_2 = \frac{N}{n+N}$$

N = No.of moles of solvent

n = No.of moles of solute

Mole fraction can be expressed with reference to any component of the solution.

If molality of aqueous solutions is known, then

$$X_1 = \frac{m}{m+55.55}$$

Mole fraction of solute has no units. The sum of mole fractions of all components in a solution = 1. Mole fraction is independent of temperature.

3. Define Normality of Solution? What is its relationship with molality?

Ans: The number of gram equivalents of the solute dissolved in one litre of solution is known as its normality.

$$N = \frac{\text{No.of gram equivalent of the solute}}{\text{volume of the solution in litres}}$$

$$N = \frac{\text{number of milli equivalents of solute}}{\text{volume of solution (m}\ell)}$$

Units for normality are gram equivalents/ litre. The normality of a solution decreases with increase in temperature of the solution.

Number of equivalent weight of solute = $N \times V_{(lit)}$

Number of milli equivalents of solute = $N \times V_{(ml)}$

$$N = \frac{\text{weight of solute in grams}}{\text{gram equivalent weight of solute}} \times \frac{1}{V_{(litres)}}$$

$$N = \frac{W}{G.E.W} \times \frac{1000}{V_{(ml)}}$$

$W = N \times G.E.W \times V_{(lit)}$

$$N = \frac{10 \times \%}{G.E.W} \quad \left(\% = \frac{w}{v}\right)$$

$$N = \frac{\text{density of solution} \times 10 \times \%}{G.E.W} \quad \left(\% \frac{W}{W}\right)$$

Normality $\times$ Equivalent weight = molarity $\times$ molecular weight

For any given solute, Mol.weight $\geq$ equivalent weight

For any given solution, $M \leq N$

LONG ANSWER QUESTIONS

1. Explain with suitable examples the terms Molarity, Molality, Normality and Mole fractions. Which method expressing concentration is better than the other? Why?

Ans: Molarity: The number of gram moles of the dissolved solute per litre of solution is known as the molarity of the solution. It is represented by 'M'.

$$M = \frac{\text{number of moles of the solute}}{\text{volume of the solution in litres}}$$

$$M = \frac{n}{v}; \quad M = \frac{\text{no.of milli moles of solute}}{\text{volume of solution in m}\ell}$$

No.of moles of solute = $M \times V$ (lit)

No.of milli moles of solute = $M \times V$ (m ℓ)

$$M = \frac{\text{weight of solute in grams}}{G.M.W \text{ of solute}} \times \frac{1}{V_{(lit)}}$$

$$M = \frac{w}{M.W} \times \frac{1000}{V_{(ml)}}$$

$$w = M \times M.W. \times V_{(lit)}$$

$$M = \frac{\% \times 10}{G.M.W} \quad \left(\% \frac{W}{V}\right)$$

$$M = \frac{\text{density} \times 10 \times \%}{G.M.W} \quad \left(\% \frac{W}{W}\right)$$

Units for molarity are moles/litre. The molarity is the most convenient and commonly used method of expressing the concentration of solution. The molarity of a solution slightly decreases with increase in temperature of the solution, due to increase in volume.

Molality: The number of gram moles of the solute dissolved in one kilogram of the solvent is known as the molality of the solution. It is represented by 'm'.

$$m = \frac{\text{number of gram moles of the solute}}{\text{weight of solvent in kilograms}}$$

$$m = \frac{\text{weight of solute in grams}}{\text{G.M.W of solute}} \times \frac{1000}{\text{weight of solvent in grams}}$$

The molality of a saturated solution is given by

$$m = \frac{10 \times \text{solubility}}{\text{G.M.W.of solute}}$$

The units for molality are mole / kg. Molality is independent of temperature. Molality is the most inconvenient method of expressing concentration of a solution because it involves determining the weights of liquids.

Normality (N):

The number of gram equivalents of the solute dissolved in one litre of solution is known as its normality.

$$N = \frac{\text{No.of gram equivalent of the solute}}{\text{volume of the solution in litres}}$$

$$N = \frac{\text{number of milli equivalents of solute}}{\text{volume of solution (m}\ell)}$$

Number of equivalent weight of solute = $N \times V_{(lit)}$

Number of milli equivalents of solute = $N \times V_{(m/)}$

$$N = \frac{\text{weight of solute in grams}}{\text{gram equivalent weight of solute}} \times \frac{1}{V_{(litres)}}$$

$$N = \frac{W}{G.E.W} \times \frac{1000}{V_{(ml)}}$$

$$W = N \times G.E.W \times V_{(lit)}$$

Normality $\times$ Equivalent weight = molarity $\times$ molecular weight

For any given solute, Mol.weight $\geq$ equivalent weight

For any given solution, $M \leq N$

Units for normality are gram equivalents/ litre. The normality of a solution decreases with increase in temperature of the solution.

Mole fraction:

The ratio between the number of moles of solute and the total number of moles of solute and

solvent in the solution is known as the mole fraction of the solute. It is represented by X_1.

$$X_1 = \frac{n}{n+N}$$ n = No.of moles of solute

N = No.of moles of solvent

The ratio between the number of moles of solvent and the total number of solute and the solvent in the solution is known as the mole fraction of the solvent. It is represented by X_2.

$$X_2 = \frac{N}{n+N}$$ N = No.of moles of solvent

n = No.of moles of solute

Mole fraction can be expressed with reference to any component of the solution.

If molality of aqueous solutions is known, then

$$X_1 = \frac{m}{m+55.55}$$

Mole fraction of solute has no units. The sum of mole fractions of all components in a solution = 1. Mole fraction is independent of temperature.

Both Mole fraction and Molality are the best methods of expressing concentrations as they are temperature independent and depend only on masses. Whereas Molarity and normality are dependent on temperature as the volumes of the solutions are taken for defining concentrations. As the volume of the solution varies with respect to temperature, Molarity and Normality are not the best way of expressing the concentrations.

2. Explain the classification of solutions on their Physical state and amount of solute Dissolved in solvent?

Ans:

Based on the physical state, solutions are of 3 types.

Gaseous solution : Solvent is Gas
The liquid solutions: Solvent is Liquid
Solid solutions : Solvent is solid

In any type of solution the solute may be gas or liquid or solid.

Solutions are of 7 types based on the physical states of solute and solvent.

1) Gas in gas : Mixture of any two gases
2) Gas in liquid : Soda water
3) Liquid in liquid: Alcohol in water
4) Solid in liquid : Sugar in water
5) Gas in solid : H_2 occluded in Pd
6) Liquid in solid : Amalgams
7) Solid in solid : Alloys

Liquid in gas and solid in gas are not considered as true solutions as they are not homogenous. A solution in which water is used as a solvent is known as aqueous solution. A solution in which alcohol is used as a solvent is known as alcoholic solution. A solution in which an organic liquid is used as a solvent is known as non – aqueous solution.

The commonly used solvents in non – aqueous solutions are CCl_4, CS_2, $CHCl_3$, C_6H_6 liquid SO_2,

acetic acid, liquid NH_3 etc.

Based on the amount of dissolved solute, solutions are of 3 types.

Saturated solutions*:* which can not dissolve any more solute. Usually some amount of undissolved solute is present in it. A dynamic equilibrium exists between dissolved solute and undissolved solute.

Unsaturated solutions*:* which can dissolve some more amount of solute. No excess of undissolved solute exists. No dynamic equilibrium exists.

3. Calculate the equivalent weights of H_2SO_4, Na_2SO_4, Na_2CO_3, $KMnO_4$ (in acid medium) and $Ba(OH)_2$.

$$E_{element} = \frac{\text{Atomic weight}}{\text{valency}}$$

$$E_{acid} = \frac{\text{molecular weight}}{\text{number of replaceble hydrogens}}$$

a) Equivalent weight of H_2SO_4

$$E_{H2SO4} = \frac{\text{Molecular Wt.}}{\text{Basicity}}$$

$$E_{H_2SO_4} = \frac{\text{molecular weight}}{2}$$

Molecular weight of H_2SO_4 is = (2 + 32 + 64) = 98

$$E_{H2SO4} = \frac{98}{2} = 49$$

b) Equivalent weight of Na_2CO_3

$$E_{Na2CO3} = \frac{\text{molecular weight}}{\text{total charge(postive or negative)}}$$

Molecular weight of Na_2CO_3 = (23x2 + 12 + 48) = 106

$$E_{Na2CO3} = \frac{106}{2} = 53$$

c) Equivalent weight of $KMnO_4$

$$E_{KMnO4} = \frac{\text{molecular weight}}{\text{change in oxidation state}}$$

$$E_{KMnO_4} = \frac{\text{molecular weight}}{5}$$

$(MnO_4^- \rightarrow Mn^{2+}$ in acid medium)

Molecular weight of $KMnO_4$ = (39 + 55 +64) = 158

$$E_{KMnO4} = \frac{158}{} = 31.6$$

d) Equivalent weight of $Ba(OH)_2$

$$E_{Ba(OH)2} = \frac{\text{molecular weight}}{\text{number of replaceble } OH^- \text{ ions}}$$

Molecular weight of = (137.33 32 + 2) = 171.33

$$E_{Ba(OH)2} = \frac{171.33}{2} = \mathbf{85.67}$$

SOLUTIONS

Topic-2

RAOULT'S LAW, APPLICATIONS AND NUMERICALS

VERY SHORT ANSWER QUESTIONS

1. Define vapour pressure?

Ans: When a liquid is in equilibrium with its own vapour the pressure exerted by the vapour on the surface of the liquid is known as the vapour pressure of the liquid.

2. Stat Raoult's Law?

Ans: For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B}$$

Simplified (or) reduced form of Raoult's law:

3. What prediction can you make for relation between vapour pressure and temperature?

Ans: The vapour pressure of the liquid is directly proportional to the temperature of the liquid. The vapour pressure of a liquid is independent of shape of the vessel. Vapour pressure of liquid increases exponentially with increase in temperature.

4. Solutions A, B, C, D have vapour pressures 30mm, 40mm, 60mm, and 80mm of Hg at 25ºC respectively. Which is the most volatile and why?

Ans: D is the most volatile because of high vapour pressure. This is due the effect of non-volatile on the vapour pressure of the the liquid.

5. What is boiling point of liquid? How it is effected by external pressure?

Ans: The temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure is known as the boiling point of the liquid. Boiling point of a liquid can be changed by changing the external pressure. If external pressure is increased, the boiling point of a liquid is increased and vice-versa.

6. Write any two limitations of Raoult's Law?

Ans: Raoult's Law is applicable to;

1. Dilute solutions only

2. The solute must be non-volatile.
3. Solutes which does not undergo in its molecular weight.
4. to ideal solutions.

7. What is an ideal solution?

Ans: The solutions which obey Raoult's law at all concentrations of temperatures are called ideal solutions. In case of ideal solutions, $\Delta V_{mixing} = 0$ and $\Delta H_{mixing} = 0$.

8. What happens to the magnitude of the boiling point of a solvent if a non-volatile solute is dissolved in it?

Ans: The vapour pressure of solution is less than that of the solvent. Therefore the Temperature required to raise the vapour pressure of the solution to the atmospheric pressure is greater than the temperature required to raise the vapour pressure of the solvent to the value equal to the atmospheric pressure. Hence, the boiling point of solution will be greater than that of the solvent.

SHORT ANSWER QUESTIONS

1. What is vapour pressure? How does it vary with temperature?

Ans: When a liquid is in equilibrium with its own vapour the pressure exerted by the vapour on the surface of the liquid is known as the vapour pressure of the liquid.

The vapour pressure of the liquid must be called as saturated vapour pressure, because actually the atmosphere over the liquid, which is saturated with the vapour of the liquid, exerts the pressure on the liquid. The vapour pressure of the liquid is represented by P.

The vapour pressure of the liquid is directly proportional to the temperature of the liquid. Vapour pressure of liquid increases exponentially with increase in temperature.

Log P Vs $\frac{1}{T}$ gives a straight line with – ve slope.

2. State and explain Raoult's law?

Raoult's law: For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B}$$

Simplified (or) reduced form of Raoult's law:

$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A}$ (for dilute solutions, n_B is very small and it can be neglected)

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W}$$

Where,

P°= Vapour pressure of pure solvent

P_s= Vapour pressure of solution

X_B = mole fraction of solute
m = molecular weight of solute
M = molecular weight of solvent
w = weight of solute W = weight of solvent

3. What is the relation between the vapour pressure and its boiling point?
Ans: The vapour pressure of a liquid increases with increase in temperature. This goes on until the critical temperature of the liquid is reached. Above the critical temperature liquid state does not exist when the vapour pressure of the liquid becomes equal to the external (atmospheric) pressure the liquid is said to be boiling and the temperature at which this happens is known as **boiling point**.

Water boiling point is 100ºC at 1 atm. Pressure. If the external pressure is reduced, the liquid boils at lower temperature. The boiling point of liquid can be increased by increasing the external pressure.

4. What is the role of non-volatile solute in lowering of vapour pressure of solvent?
Ans: 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 ∝ 1/√density

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

5. What is relative lowering of vapour pressure? How is it useful in determining the molecular weight of a solute?

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

If $\mathbf{p_0}$ is the vapour pressure of pure solvent and **ps** is the vapour pressure of the solution,

The difference $\mathbf{(p_0 - p_s)}$ is termed lowering in vapour pressure, and the ratio $\mathbf{[p_0 - p_s / p_0]}$ is termed relative lowering in vapour pressure.

Raoult, established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. Using this relationship one can determine the molecular weight of solute by using this following equation.

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W}$$

Where,

P°= Vapour pressure of pure solvent

P_s= Vapour pressure of solution

X_B = mole fraction of solute

m = molecular weight of solute

M = molecular weight of solvent

w = weight of solute W = weight of solvent

LONG ANSWER QUESTIONS

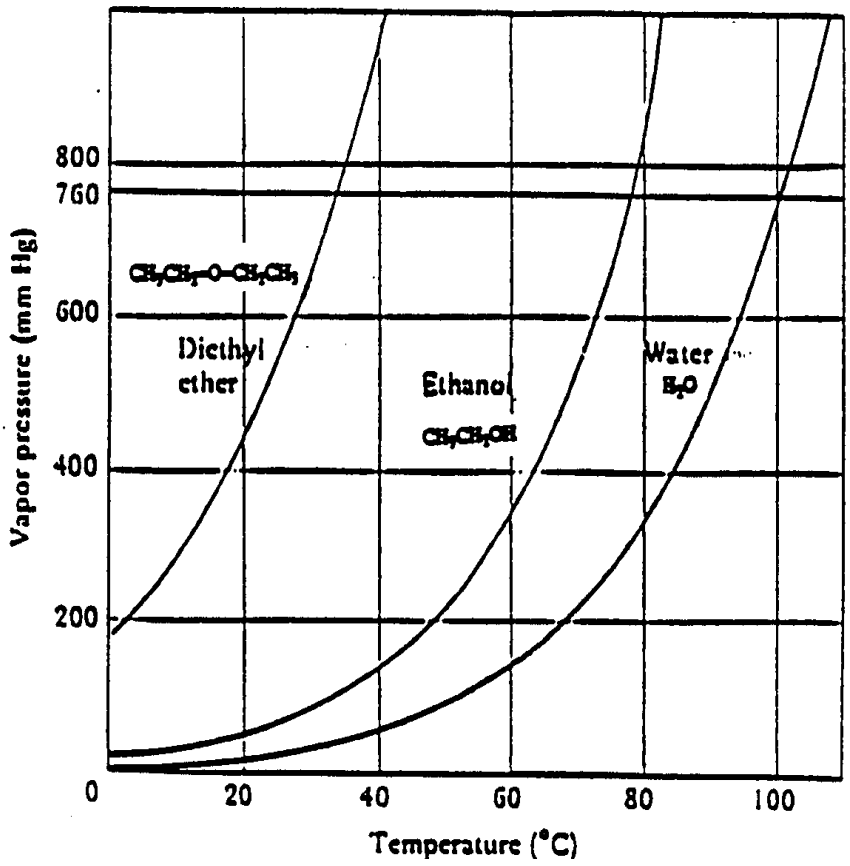
1. **What do you mean by vapour pressure of a liquid? Describe the vapoiurisation and condensation process in a closed vessel. How does vapour pressure change with pressure?**

Ans: The pressure exerted by the vapour of a liquid when it is in equilbrium with liquid is called vapour pressure.

The process of transformation of liquid into vapour is called evaporation and the process of transformation of vapour into liquic is called condensation. In a lquid present in closed vessel rate of evaporation is equal to rate of condensation. This stage is called equilibrium stage and the equilibrium is called dynamic equilibrium.

Effect of temperature: As you know, liquids will evaporate. The rate and extent to which it evaporates depends on the temperature. With rise in temperature of a liquid the average kinetic energy of liquid molecules increases. This increase in kinetic energy overcomes the attractive forces between molecules and hence molecules escape more rapidly into air. Thus the vapour pressure of a liquid increases with increase in temperature. The increase in vpour pressure of a liquid with rise in temperature in non linear but it is exponential.

The amount of evaporation increases when the temperature increases. When the temperature is such that the vapor pressure is just as high as the atmospheric pressure, the liquid boils. That temperature is called the boiling point.



2. Define and explain Raoult's law. How is it useful in determining molecular weight of a non-volatile solute?

Ans: Raoult's law:

For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

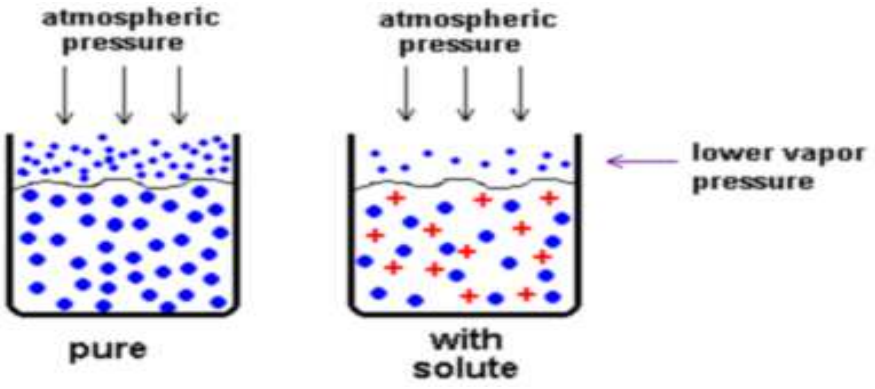
$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B} \quad \text{----------(1)}$$

Simplified (or) reduced form of Raoult's law is given by;

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A}$$ (for dilute solutions, n_B is very small and it can be neglected)

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W} \quad \text{----------(2)}$$



From equation (2) molecular weight of solute (m) can obtained by the following equation.

$$m = \frac{p^{o} \cdot w \cdot M}{(p^{o} - p)\, W}$$

Where,

P°= Vapour pressure of pure solvent
P_s= Vapour pressure of solution
X_B = mole fraction of solute
m = molecular weight of solute
M = molecular weight of solvent
w = weight of solute W = weight of solvent

Raoult's law is applicable to :

- Ideal solutions
- dilute solutions
- solutions containing non volatile solute
- no change in the interactions before and after mixing of liquid components in case of solution containing miscible liquids.
- Solute which neither dissociates nor associates.

3. **Define Raoult's law for lowering of vapour pressure. How is the law useful in determing the molecular weight of solvent when a known non-volatile solute is dissolved?**

Ans: Raoult's law:

For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B} \quad \text{----------(1)}$$

Where, n_B and n_A are number of moles of solute and solvent respectively.

Simplified (or) reduced form of equation (1) is given by;

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A} \text{ ----------(2)}$$

(for dilute solutions, n_B is very small and it can be neglected)

Where,

P°= Vapour pressure of pure solvent

P_s= Vapour pressure of solution

X_B = mole fraction of solute

We know that

n_B = w/m and

n_A = W/M

where,

m = molecular weight of solute

M = molecular weight of solvent

w = weight of solute

W = weight of solvent

By substituting these values in equqtion(2).

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W} \text{ ---------- (3)}$$

Form the above equation the molecular weight of solvent **(M)** is given by;

$$M = \frac{m \cdot (p^o - p) \cdot W}{p^o \cdot w}$$

NUMERICALS

Example: 1

Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

According to Raoult's law,

$p_0 - p_s / p_0 = n/n+N$

or $\Delta p = (n/n+N)p_0$

Given n = 50/342 = 0.416, N = 500/18 = 27.78 and p_0 = 23.8

Substituting the values in the above equation,

$\Delta p = (0.146/0.146+27.78) \times 23.8 = 0.124$ mm Hg

Example: 2

The vapour pressure of pure benzene at a certain temperature is 640mm Hg. A non-volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular mass of the solid substance?

Solution: According to Raoult's law.

$$(p_0 - p_s)/p_0 = n/(n+N)$$

Let m be the molecular mass of the solid substance.

n = 2.175/m ; N = 39/78 = 0.5

[Molecular mass of benzene = 78]

Substituting the values in the equation

$$m = \frac{p^o \cdot w \cdot M}{(p^o - p)\, W}$$

$$m = \frac{640 \cdot 2.175 \cdot 78}{(640 - 600)\, 39}$$

m = 65.25

Thus molecular weight of solute is 65.25

Example: 3

A solution containing 30 g of a non-volatile solute in exactly 90 g of water has a vapour pressure of 21.85 mm of Hg at 25°C. Further 18 g of water is then added to the solution; the new vapour pressure becomes 22.15 mm Hg of at 25°C. Calculate (a) molecular mass o the solute and (b) vapour pressure of water at 25°C.

Solution:

Let the vapour pressure of water at 25°C be p_0 and molecular mass of the solute be m.

Using Raoult's law in the following form.

For solution (I), **$(p_0 – 21.85)/21.85 = 30 \times 18/90 \times m$ …(i)**

For solution (II), **$(p_0 – 22.15)/22.15 = 30 \times 18/108 \times m$ …(ii)**

Dividing Eq. (i) by Eq. (ii),

$$(p_0 – 21.85)/21.85 \times 22.15/(p_0 – 22.15) = 108/90 = 6/5$$

Substituting the value of p_0 in Eq. (i) the value of m is given by;

$$M = 67.9$$

Example:4

What mass of non-volatile solute (urea) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 5%. What will be the molality of solution?

Solution: Using Raoult's law in the following form,

$$p_0 – p_s/p_s = wM/Wm$$

If $p_0 = 100$ mm, then $p_s = 75$ mm

$100 – 75/75 = w \times 18/100 \times 60$

$w = 111.1$

Molality $= w \times 1000/m \times W = 111.1 \times 1000/60 \times 100 = 18.52$ m

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 ($\mathbf{K_b}$)

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

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 $K_b = 2\times(373)^2/1000\times540 = 0.515$

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 deprssion in freezing oint observed in one molal solution of a non-volatile solute is known as molal elevation constant($\mathbf{K_b}$)

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

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

$$\pi = hdg$$

5. Expalin 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 decreases 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, exbhit higher colligative property than expected. Molecular weight of solute is inversely proportional to the colligative property. From this one conclude 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) $BaCl_2$?

Ans: The elevation in boiling point is more in BaCl2 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 perspon involved in accident, when admitted to hospital is administered with saline. Why?

Ans: The patient looses 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 $BaCl_2$ of same concentration the (i) factor is more for which compound and why?**

Ans: For Nacl the (i) factor is more.

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

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

For $BaCl_2$ $i = 1 + (3 - 1)\,\alpha = 1 + 2\,\boldsymbol{\alpha}$

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) = (wt. of glucose / 180)

St. of glucose = 0.1 x 180 = 18 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.

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

(ii) Heat change on mixing should be zero.

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

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

Solvent + solute → solution

$H_2O + NH_3 \rightarrow NH_4OH$

$H_2O + CO_2 \rightarrow H_2CO_3$ Non-ideal

$H_2O + CaO \rightarrow Ca(OH)_2$

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

Aqueous medium

$NaCl \longrightarrow Na^+ + Cl^-$

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

(ΔT) = Freezing point of the solvent – 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

ΔT_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 (Π or α) 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 Π / T = constant or $\Pi = KT$ where, K is constant

5. Derive the equatin $\Pi = CRT$.

Ans

Acoording to Boyle-van't Hoff law**,**

$\Pi \propto C$ (when temperature is constant) --------(1)

Acoording to Gay-Lussac-van't Hoff law

$\Pi \propto T$ ----------(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

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

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.

$$(1-\alpha) \leftrightarrow n\alpha$$

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

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

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

Therfore, **α ionisation** $= \dfrac{\mathbf{i-1}}{\mathbf{n-1}}$

For solute association process: If nA molecules cnmbine to $\mathbf{A_n}$,we have

$$\mathbf{n\,A \leftrightarrow A_n}$$

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

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

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

Form this the value of α 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 g 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/√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 $\mathbf{p_0}$ is the vapour pressure of pure solvent and **ps** is the vapour pressure of the solution, the difference $\mathbf{(p_0 - p_s)}$ 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,

ΔT = Boiling point of the solution – 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

ΔT = Freezing point of the solvent – 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 is 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 stationery. 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 osmaotic pressure?

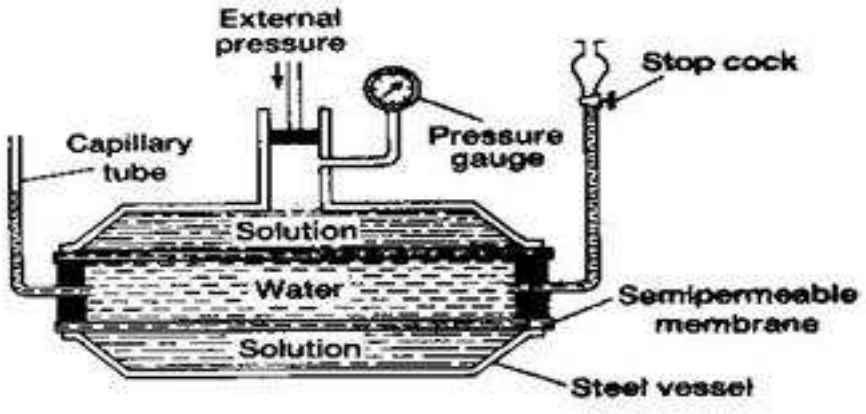
Osmosis: Osmosis is defined as the spontaneous flow of solvent molecules through semi permeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

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 in 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.



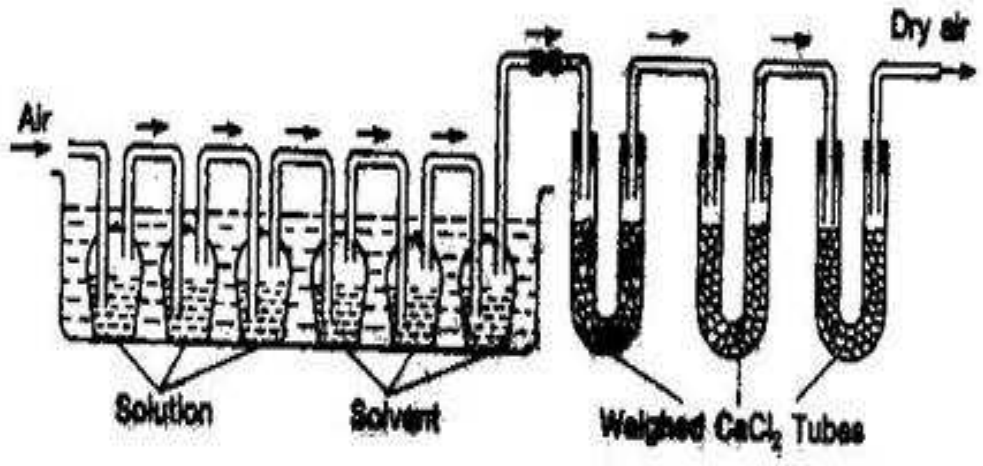
Advantages:

- 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.

Loss in mass(x) in the solution bulbs $\propto p_s$

Loss in mass(y) in the solvent bulbs $\propto (p_0 - p_s)$

Total loss(x+y) in both sets of bulb $\propto [p_s + (p_0 - p_s)]$

$\propto p_0$

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

Thus,

$$\frac{P_0 - ps}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$

$$\frac{\text{Loss in mass in solvents bulbs}}{}$$

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

Further we know from Raoult's law;

$$\frac{P_0 - p_s}{p_0} = \frac{n_s}{n_0} = \frac{y}{x + y} = X_s \text{ ----------(1)}$$

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.

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

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

Where,

a = wt. of solute

b = wt. of solvent

M = molecular wt. of solute

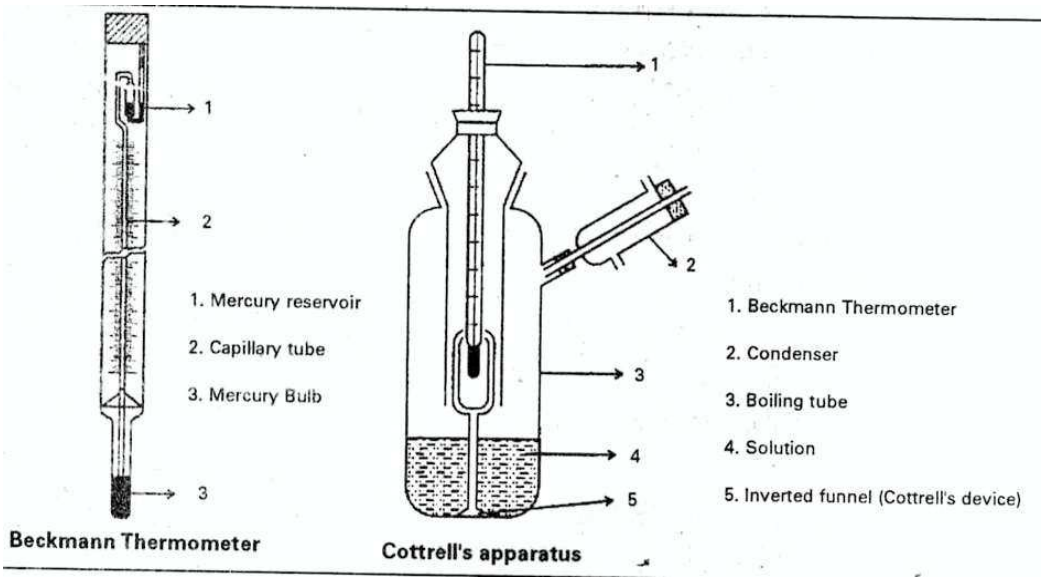
W = molecular wt. of solvent

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 (ΔT) 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 (-6^0 to 300^0 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 fussed 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 = $T - T_0 = \Delta T$

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

$$\frac{M}{b} \qquad \frac{\Delta T_b \times b}{}$$

K_b = molal elevation constant of solvent.

M = molar mass of solute

5. How molecular weight of solid hydrocarbon is 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 motor. 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 ΔT_f.

From the values a, b & ΔT_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

$$\frac{a}{M} \qquad \frac{1000}{b} \qquad \Delta T_f = k_f \times \frac{a}{M} \times \frac{1000}{b} \quad \Rightarrow \quad M = \frac{k_f \times a \times 1000}{\Delta T_f \times b}$$

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 (α)

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

α = 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 subtituted 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 (α)

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

Knowing the values of n and α 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 20×10^{-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^{o}K kg mol^{-1})

Solution:

Observed mol. mass

= 1000×Kf×w/W?T

= $1000\times5.12\times20\times10^{-3}/1\times0.69 = 148.4$

Normal mol. mass of phenol (C_6H_5OH) = 94

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

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

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

or $\alpha = 0.733$ 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 freeing point of of water when (a) 120 g of urea. (b) 117 g of sodium chloride, (c) 488.74 g of $BaCl_2.2H_2O$ 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.

Thus, $\Delta T = 1000\times K_f\times w/W\times m = 1000\times1.86\times120/1000\times60 = 3.72^oC$

No. of moles of urea = 120/60 = 2

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

NaCl is an electrolyte. It ionizes compeletely.

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.

So $\Delta T_{NaCl} = 2 \times \Delta T_{urea} = 2 \times 3.72 = 6.44^oC$

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

No. of moles of $BaCl_2.H_2O$ = 488.74/244.37 = 2

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

$$\text{So } \Delta T_{BaCl2} = 3 \ .\Delta T_{urea} = 3 \times 3.72 = 11.16^oC$$

Example: 3

On dissolving 10.8 glucose (m.w. = 180) in 240 g of water, its boiling point increases by 0.13°C. Calculate the molecular elevation constant of water.

Solution: ΔT = 100K'×w/W×m

or K' = ?T×W×m/100×w

Given, Δ T =0.13°C, W = 240 g, m = 180 and 2 = 10.8 g

K' = 0.13×240×180/100×10.8 = 5.2°

Example: 4

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^{-1}.

Solution: m = 1000K_b×w/W×?T

Given, K_b = 2.67, w = 2.5 g, W = 100 g, ΔT = 0.42

m = 1000×2.67×2.5/100×0.42 = 158.9

The molecular mass of substance is 158.9.

Example: 5

The molal elevation constant for water is 0.56 K kg mol^{-1}. Calculate the boiling point of a solution made by dissolving 6.0 g of urea (NH_2CONH_2) in 200 g of water.

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

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

$\Delta T = 1000 \times 0.56 \times 6.0/200 \times 60 = 0.28^oC$

Thus, The boiling point of solution = boiling point of water + ?T = ($100^oC + 0.28^oC$) = 100.28^oC

Example: 6

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

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

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

w = 13.6 g, W = 20 g, $\Delta T = 3.7^oC$

m = 1000×1.863×13.6/20×3.7 = 243.39

Example: 7

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^oC. Calculate the molecular mass of non-volatile substance (K_f = 5.12 K kg mol^{-1}).

Solution: Mass of benzene, W = volume × density

= 30 × 0.8 = 24 g

Given, Kf = 5.12 K kg mol^{-1}, w = 0.25 g, Δ T = 0.40^{o}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: 8

A solution of 1.25 f 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 K kg mol^{-1}]

Solution: Freezing point of water = 273.0 K

ΔT = (273–271.94) = 1.06K

We know that m = 1000K_f×w/W×?T

Given K_f = 1.86 K kg mol^{-1}, w = 1.25 g, W = 20 g and ΔT = 1.06 K.

$$m = 1000 \times 1.86 \times 1.25/20 \times 1.06 = 109.66$$

T = 100K'×w/W×m

or K' = ΔT×W×m/100×w

Given, ΔT =0.13^{o}C, W = 240 g, m = 180 and 2 = 10.8 g

K' = 0.13×240×180/100×10.8 = 5.2^{o}

Example: 9

A solution of 2.5 g of a non-volatile solid in 100 g benzene boiled at 0.42^{o}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^{-1}.

Solution: m = 1000K_b×w/W×? T

Given, K_b = 2.67, w = 2.5 g, W = 100 g, ΔT = 0.42

m = 1000×2.67×2.5/100×0.42 = 158.9

The molecular mass of substance is 158.9.

Example: 10

The molal elevation constant for water is 0.56 K kg mol^{-1}. Calculate the boiling point of a solution made bt dissolving 6.0 g of urea (NH_2CONH_2) in 200 g of water.

Solution: Δ T = 1000K_b×w/m×W

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

ΔT = 1000×0.56×6.0/200×60 = 0.28^{o}C

Thus, The boiling point of solution = b.pt. of water + ΔT = (100^{o}C + 0.28^{o}C) = 100.28^{o}C

Example: 11

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

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

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

$w = 13.6$ g, $W = 20$ g, $\Delta T = 3.7^oC$

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

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^oC. Calculate the molecular mass of non-volatile substance ($K_f = 5.12$ K kg mol^{-1}).

Solution: Mass of benzene, W = volume × density

$= 30 \times 0.8 = 24$ g

Given, Kf = 5.12 K kg mol^{-1}, w = 0.25 g, $\Delta T = 0.40^oC$.

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 f 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 K kg mol^{-1}]

Solution: Freezing point of water = 273.0 K

ΔT = (273–271.94) = 1.06K

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

Given K_f = 1.86 K kg mol^{-1}, w = 1.25 g, W = 20 g and ΔT = 1.06 K.

m = 1000×1.86×1.25/20×1.06 = 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 vpour 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 equqtion $\Pi = CRT$.
7. What is Van't Hoff's factor (i) and how is it related to α 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 bahaviour of electrolyte in colligative properties?
7. What are isotonic solutions give one example?