3. DEPRESSION IN FREEZING POINT

$\Delta T_f = K_f m$ where, $\Delta T_f = T^0_f - T_f$

K_f = molal depression constant / Cryoscopic constant

m = molality

$M = k_f 1000 W_B / \Delta T_f W_A$

4. OSMOTIC PRESSURE

The excess pressure that must be applied to a solution side to prevent osmosis i.e. to stop the passage of solvent molecules into it through semi-permeable membrane is called osmotic pressure.

$\Pi = CRT$

$\Pi = n/VRT$ (n=no. of moles; V=volume of solution(L)

R=0.0821L atm mol^{-1}; T= temperature in kelvin

ISOTONIC SOLUTION

Two solutions having same osmotic pressure and same concentration are called isotonic solutions.

Hypertonic solution have higher osmotic pressure and hypotonic solution have lower osmotic pressure than the other solution.

0.91% of sodium chloride is isotonic with fluid present inside blood cell.

VAN'T HOFF FACTOR (i)

Ratio of normal molecular mass to the observed molecular mass of the solute.

i = normal molecular mass/ observed molecular mass

= observed colligative properties / calculated value of colligative properties

i<1 (for association) i>1 (for dissociation)

MODIFIED FORMS OF COLLIGATIVE PROPERTIES

1) $P^0_A - P_A / P^0_A = i\, n_B / n_A$
3) $\Delta T_b = iK_b m$
4) $\Delta T_f = iK_f m$
5) $\Pi = iCRT$

FREQUENTLY ASKED QUESTIONS (1 MARK QUESTIONS)

Q 1. Two liquids X and Y boil at 380 K and 400K respectively, which of them is more volatile?

Ans. X is more volatile since it has low boiling point.

Q2. How does the molarity of a solution change with temperature?

Ans. Molarity decreases with increase in temperature as volume of solution increases with increase in temperature.

Q3. Under what condition do non ideal solutions show negative deviation ?

Ans. When the new forces of interaction between the components are stronger than those in the pure components, then non ideal solutions show negative deviation.

Q4. What are minimum boiling azeotropes? Give one example.

Ans. Minimum boiling azeotropes are those which boil at lower temperature than boiling point of each component in pure state, e.g., 95.5% ethyl alcohol and 4.5% water by mass.

Q5. What do you understand by the term that K_f for water is 1.86 Kkg/mol?

Ans. It means that the freezing point of water is lowered by 1.86 K when 1 mol of non volatile solute is dissolved in 1 kg of water.

Q6. Why is osmotic pressure of 1M KCl higher than 1M urea solution ?

Ans. This is because KCl dissociates to give K^+ and Cl^- ions while urea being a molecular solid does not dissociate into ions in the solution.

Q 7. What is the value of van't Hoff factor for a dilute solution of

(i) K_2SO_4 in water

(ii) acetic acid in benzene.

Ans .(i) 3 (ii) 1/2

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.

(b) Both assertion and reason are true but reason is not the correct explanation of assertion.

(c) Assertion is true but reason is false.

(d) Both assertion and reason are false.

1. Assertion : In an ideal solution, $\Delta_{mix}H$ is zero.
   Reason : In an ideal solution, A - B interactions are lower than A-A and B-B interactions. (Ans -c)
2. Assertion : Osmosis does not take place in two isotonic solutions separated by semi-permeable membrane.
   Reason : Isotonic solutions have same osmotic pressure. (Ans - a)
3. Assertion : Lowering of vapour pressure is not dependent on the number of species present in the solution.
   Reason : Lowering of vapour pressure and relative lowering of vapour pressure are colligative properties. (Ans - d)
4. Assertion : 1 M solution of KCl has greater osmotic pressure than 1 M solution of glucose at same temperature.
   Reason : In solution KCl dissociates to produce more number of particles. (Ans - a)
5. Assertion : Two liquids nitric acid and water form a maximum boiling azeotrope when mixed in the ratio of 68% and 32% respectively.
   Reason : Interaction between nitric acid and water are stronger than nitric acid - nitric acid interactions and water - water interactions. (Ans - a)

One - word answers

1. Liquid 'Y' has higher vapour pressure than liquid ' X' . Which of them will have higher boiling point. (Ans - X)
2. Liquids A and B on mixing produce a warm solution. Which type of deviation from Raoult's law is shown? (Ans - Negative deviation)
3. Under what condition Van't Hoff factor is less than 1? (Ans - Association)

2 MARKS QUESTIONS

Q1. State Henry's law. What is the significance of K_H?

Ans. Henry's Law: It states that "the partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction of the gas (x) in the solution", and is expressed as: $p = K_H X$ where, K_H is the Henry's Law constant

Significance of K_H : Higher the value of Henry's law constant K_H, the lower is the solubility of the gas in the liquid.

Q2. How is that measurement of osmotic pressure is more widely used for determining molar masses of macromolecules than the elevation in boiling point or depression in freezing point of their solutions?

Ans. The osmotic pressure method has the advantage over elevation in boiling point or depression in freezing point for determining molar masses of macromolecules because

1. Osmotic pressure is measured at the room temperature and the molarity of solution is used instead of molality.
2. Compared to other colligative properties, its magnitude is large even for very dilute solutions.

Q3. Suggest the most important type of intermolecular interaction in the following pairs:

i) N-hexane and n-octane

ii) methanol and acetone

Ans. i) Dispersion or London forces as both are non-polar.

ii) Dipole-dipole interactions as both are polar molecules.

Q4. Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN.

Ans. Mass of solution = 6.5g + 450g = 456.5g

$$\text{Mass \% of aspirin} = \frac{\text{Mass of aspirin}}{\text{Mass of solution}} \times 100$$

$= 6.5/456.5 \times 100 = 1.424\%$

3 MARK QUESTIONS

Q1. Non-ideal solution exhibit either positive or negative deviations from Raoult's law. What are these deviation and why are they caused? Explain with one example for each type.

Ans. When the vapour pressure of a solution is either higher or lower than that predicted by Raoult's law, then the solution exhibits deviation from Raoult's law. These deviation are caused when solute -solvent molecular interactions A–B are either weak or stronger than solvent – solvent A – B or solute – solute B – B molecular interactions. Positive deviations : When A – B molecular interactions are weaker than A – A and B – B molecular interaction . For example, a mixture of ethanol and acetone.

Negative deviations: When A – B molecular interaction are stronger than A – A and B – B molecular interaction. For example, a mixture of chloroform and acetone.

Q2 .a) Why is an increase in temperature observed on mixing chloroform and acetone?

b) Why does sodium chloride solution freeze at a lower temperature than water?

Ans: a) The bonds between chloroform molecules and molecules of acetone are dipole-dipole interactions but on mixing, the chloroform and acetone molecules, they start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.

b) When a non- volatile solute is dissolved in a solvent, the vapour pressure decreases. As a result, the solvent freezes at a lower temperature.

Q3. A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500g of water. This solution has a boiling point of 100.42C while pure water boils at 100-C. What mass of glycerol was dissolved to make the solution ? (K_b of water=0.512Kkg/mol)

Ans. $\Delta T_b = 100.42°C - 100°C = 0.42°C$ or $0.42K$; $W_A = 500g$; $K_b = 0.512Kkg/mol$; $M_B = 92$ g /mol Substituting these values in the expressions,

$$W_B = \frac{\Delta T_b \times M_B \times W_A}{K_b \times 1000}$$

$$W_B = \frac{0.42 \times 92 \times 500}{0.512 \times 1000} = 37.73 \text{ g}$$

Q4. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27^0C.

Ans. $$\pi = \frac{i \times W_B \times R \times T}{M_B \times V}$$

Molar mass of CaCl ,M =40+2 X 35.5 = 111 g mol^{-1}

Therefore, Molar mass of $CaCl_2$, $$W_B = \frac{0.75 \text{ atm} \times 111 \text{g/mol} \times 2.5 \text{L}}{2.47 \times 0.0821 \times 300 \text{K}}$$

$$= 3.42\text{g}$$

Q5. The molar freezing point depression constant for benzene is 4.90K kgmol^{-1}. Selenium exists as polymer Se_X. When 3.26 gm of Se is dissolved in 226 gm of benzene, the observed freezing point is 0.112^{0}C lower than for pure benzene. Decide the molecular formula of Selenium. (At.wt. of selenium is 78.8 g mol^{-1})

Ans $\Delta T_f = \frac{1000 \times K_f \times W_B}{W_A \times M_B}$

$0.112\ K = \frac{1000 \times 4.9 \times 3.26}{226 \times M_B}$

M_B = 1000X4.90X3.26/226X0.1112 = 63g/mol

No. of Se atoms in a molecule = 631g / mol/78.8 g/mol = 8

Therefore, molecular formula of Selenium = Se_8

5 MARKS QUESTION

Q1. a) State Raoult's Law for a solution containing volatile components.

How does Raoult's law become a special case of Henry's Law?

b) 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of a benzene by 0.40K. Find the molar mass of the solute. (K_f for benzene = 5.12K kg mol^{-1})

Ans. a) For a solution of volatile liquids , Raoult's law states that the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution, i.e., $p_A \propto x_A$

OR

$p_A = p_A^0 x_A$

According to Henry's Law, the partial pressure of a gas in vapour phase (p) is

Directly proportional to mole fraction (x) of the gas in the solution.

i.e., $p = K_H x$ on comparing it with Raoult's Law it can be seen that partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution

i.e; $p \propto x$

only the proportionality constant K differs from p^0. Thus, it becomes a special case of Henry's law in which $K_H = p^0_A$.

b) Substituting the values of various terms involved in equation $M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$

$M_B = \frac{5.12 \times 1.00 \times 1000}{0.40 \times 50} = 256 g\ mol^{-1}$

Q2.a) Calculate the molarity of a sulphuric acid solution in which the mole fraction of water is 0.85.

b) The graphical representation of vapour pressure of two component system as a function of composition is given alongside.

i) Are the A–B interactions weaker, stronger or of the same magnitude as A–A and B–B

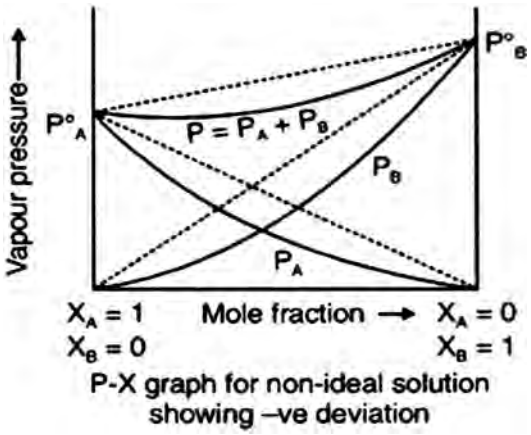
ii) Name the type of deviation shown by this system from Raoult's law.

iii) Predict the sign of $\Delta_{mix}H$ for this system.

iv) Predict the sign of $\Delta_{mix}V$ for this system.

v) Give an example of such a system.

vi) What type of azeotrope will this system form, if possible?



P-X graph for non-ideal solution showing –ve deviation

Ans. a) $\frac{n_A}{n_A + n_B} = 0.85$ ..... i)

$\frac{n_B}{n_B + n_A} = 1-0.85 = 0.15$ ii

Dividing (ii) by (i), we get

$\frac{n_B}{n_A} = \frac{0.15}{0.85}$ or $1000/18 = \frac{0.15}{0.85}$ or $n_B = \frac{0.15 \times 1000}{0.85 \times 18}$

hence molality = 9.8 m $\frac{n_B}{\quad}$

b) i) Stronger
ii) Negative deviation
iii) Negative
iv) Negative
v) 20% acetone and 80% chloroform by mass
vi) maximum boiling azeotrope