DAY TWENTY

Solutions

Learning & Revision for the Day

- Expressions for Concentration of Solutions
- Raoult's Law
- Ideal Solutions and Non-ideal Solutions
- Solubility of Gases in Liquids
- Solid Solutions
- Colligative Properties
- Abnormal Molecular Masses

Solution is a homogeneous mixture of two or more substances on molecular level. A solution of two substances is called a **binary solution**. The substances forming the solution are called **components of the solutions**. As a generalisation, the component present in smaller amount is called **solute** and the other present in larger amount is called **solvent**.

Types of Solution

Different types of solution are tabulated as follows :

Types of Solutions

Solute	Solvent	Type/Name of solution	Examples
Solid	Solid	Solid in solid	Alloys, amalgam
Liquid	Solid	Liquid in solid	Hydrated salts
Gas	Solid	Gas in solid	Dissolved gases in minerals
Solid	Liquid	Solid in liquid	Salt solution in water
Liquid	Liquid	Liquid in liquid	Emulsion, alcohol in water
Gas	Liquid	Gas in liquid	Aerated drinks
Solid	Gas	Solid in gas	Iodine vapour in air, adsorption of hydrogen over palladium
Liquid	Gas	Liquid in gas	Mist, humidity in air
Gas	Gas	Gas in gas	Air

Aerosol is solution of solid in gas or liquid in gas while emulsion is solution of liquid in liquid.

Expressions for Concentration of Solutions

The different ways by which concentration of the solution can be described quantitatively are as follows

- **Mass Percentage** (w/W) The mass percentage of a component in a given solution is the mass of the component per 100 g of the solution.

  $$\text{Mass \% of a component} = \frac{\text{mass of the component in the solution}}{\text{total mass of the solution}} \times 100$$

- **Volume Percentage** (v/V) The volume percentage is the volume of the component per 100 parts by volume of the solution.

Volume % of a component

$$= \frac{\text{volume of the component}}{\text{total volume of solution}} \times 100$$

- **Parts per million** (ppm) When a solute is present in trace quantities, the concentration is expressed in **parts per million** (ppm)

$$\text{ppm} = \frac{\text{number of parts of the component}}{\begin{bmatrix}\text{total number of parts of all} \\ \text{components of the solution}\end{bmatrix}} \times 10^6$$

- **Parts per billion** (ppb) It is the amount of solute, which is dissolved in 10^9 parts of a solution.

$$\text{ppb} = \frac{\text{mass of a solute particles}}{\text{mass of a solution}} \times 10^9$$

- **Concentration or Strength in g/L** Strength in g/L represents the number of grams present in 1L of solution.

$$\text{Strength of solution} = \frac{\text{mass of solute (in g)}}{\text{volume of solution (in L)}}$$

- **Mole Fraction** (χ) It is the ratio of the number of moles (n) of one component (either solute or solvent) to the total number of moles of solute and solvent.

$$\chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}, \ \chi_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

- **Molality** (m) It is the number of moles of the solute dissolved in 1000 g of the solvent.

$$\text{Molality } (m) = \frac{\text{number of moles of solute}}{\text{mass of solvent (in g)}} \times 1000$$

- **Normality** (N) Normality is the number of gram equivalents of substance dissolved per litre of the solution.

$$\text{Normality } (N) = \frac{\text{number of g - equivalent of solute}}{\text{volume of solution (in L)}}$$

- **Molarity** (M) It is the number of moles of solute present in one litre of the solution.

$$\text{Molarity } (M) = \frac{\text{number of moles of solute}}{\text{volume of solution (in L)}}$$

Inter-relation between Different Concentration of Solution

Various expressions for concentration of solutions can be related as given below

- **Relation between molality** (m) **and weight percentage** (W)

$$= \frac{1000 \times \text{weight \% of solute } (x)}{(100 - x) \times \text{molecular weight of solute}}$$

- **Relation between molality** (m) **and mole fraction** (χ)

$$\chi = \frac{m\, M_1}{(1000 + m\, M_1)}$$

- **Relation between molality** (m) **and molarity** (M)

$$\text{Molality } (m) = \frac{M}{d - MM_2}$$

- **Relation between normality** (N) **and strength in gL**$^{-1}$

$$N = \frac{x \times d \times 10}{E}$$

where, x = % of the solute by mass
d = density of solution in g mL^{-1}
E = equivalent mass of solute

- **Relation between molarity and strength in g/L**

$$\text{Molarity } (M) = \frac{\text{weight of solute (in g)}}{\begin{bmatrix}\text{molecular weight of solute} \times \text{volume of} \\ \text{solution (in L)}\end{bmatrix}}$$

$$\text{Molarity } (M) = \frac{\text{strength in g L}^{-1}}{\text{molecular weight of solute}}$$

- **Relation between normality and molarity**

$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{molecular weight}}{\text{equivalent weight}}$$

For an acid, $\dfrac{\text{molecular weight}}{\text{equivalent weight}} = \text{basicity}$

$\therefore$ Normality of an acid = molarity × basicity

For a base, $\dfrac{\text{molecular weight}}{\text{equivalent weight}} = \text{acidity}$

$\therefore$ Normality of a base = molarity × acidity

- **Relation between molarity** (M) **and mole fraction of the solute** (χ)

$$\chi = \frac{MM_1}{M(M_1 - M_2) + 1000d}$$

where, d = density of the solution g mL^{-1}
M_1 = molar mass of solvent
M_2 = molar mass of solute
M = molarity of solution

Raoult's Law

- The partial vapour pressure of a volatile component is directly proportional to its mole fraction in solution.

  For a solution possessing two components, A and B, the partial vapour pressure of A is

$$p_A = \chi_A p_A^\circ$$

Similarly, $$p_B = \chi_B p_B^\circ$$

where, A and B are volatile solute and solvent respectively. p_A° and p_B° are the vapour pressures in pure state.

According to Dalton's law of partial presences, the total presence over the solution phase is given by,

$$p_{\text{total}} = p_A + p_B$$

- The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If χ_A and χ_B are the mole fraction of the components A and B respectively in the vapour phase then,

$$p_A = \chi_A \cdot p_{\text{total}} \Rightarrow p_B = \chi_B \cdot p_{\text{total}}$$

Solutions of Solid in Liquid

The vapour pressure of the solution of a non-volatile solute at a given temperature is lower than the vapour pressure of the pure solvent at the same temperature. The decrease in the vapour pressure of solvent depends on the amount of non-volatile solute present in the solution, irrespective of its nature.

- Raoult's law for solutions of solids in liquids, i.e. for non-volatile solutes,

$$\boxed{p_{\text{solution}} = \chi_{\text{solvent}}\, p^{\circ}_{\text{solvent}}}$$

- Raoult's law have following limitations
  - (i) It is applicable only to very dilute solutions.
  - (ii) It is applicable only to solutions containing non-volatile and non-electrolytic solutes which exist as a single molecule.
  - (iii) It is not applicable to solutes which dissociate or associate in the particular solution.

Raoult's Law as a Special Case of Henry's Law

- According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = \chi_i\, p_i^{\circ}$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we can state that its solubility can be given by Henry's law, which states that

$$\boxed{p = K_{\text{H}}\, \chi}$$

- If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial presssure of the volatile component or gas is directly proportional to its mole fraction in the solution. Only the proportionality constant k_{H} differs from p_i°, Thus, Raoult's law becomes a special case of Henry's law in which k_{H} becomes equal to p_i°.

Ideal Solutions and Non-ideal Solutions

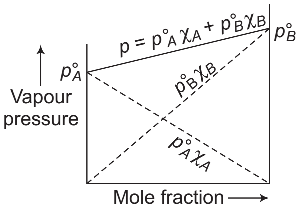
The solutions, which obey Raoult's law are called **ideal solutions**.

For ideal solutions, $\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$

Solute-solute and solvent-solvent interactions

$\approx$ solute-solvent interactions.

- **Ideal Solution** Practically no solution is ideal. The graphical representation of ideal solutions is given below



Graphical representation of the solution showing ideal behaviour

- **Non-ideal solution** The solution which shows deviation from Raoult's law is called **non-ideal solution**.

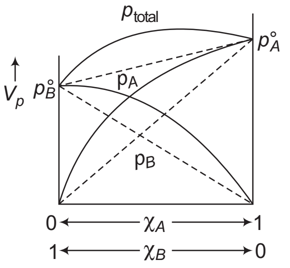
  For such solutions, $\Delta H_{\text{mix}} \neq 0$, $\Delta V_{\text{mix}} \neq 0$

  Depending upon the nature of solute and solvent, non-ideal solutions may exhibit following deviations.

- When the observed vapour pressure is more than that expected by Raoult's law, **positive deviation** is observed.
  - (i) For such a deviation,

$$p_A > p^{\text{o}}_A\, \chi_A \text{ and } p_B > p^{\text{o}}_B\chi_B$$

$$\therefore \quad p_{\text{total}} > p^{\text{o}}_{\text{A}}\chi_A + p^{\text{o}}_B\chi_B$$

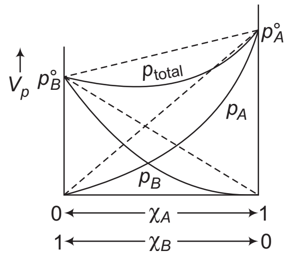


Graphical representation of the solution showing positive deviation

  - (ii) For such solutions, $\Delta H_{\text{mix}} > 0$, i.e. energy is absorbed on mixing and $\Delta V_{\text{mix}} > 0$. These are usually obtained by mixing of polar liquids with non-polar ones.
    e.g. cyclohexane and ethanol, H_2O and C_2H_5OH.
  - (ii) In case of positive deviation we get **minimum boiling azeotropes.**

    e.g. C_2H_5OH (95.57%) + H_2O(4.43%) (by mass).

- When the observed vapour pressure is less than that expected by Raoult's law, **negative deviation** is observed.
  - (i) For such solutions, $\Delta H_{\text{mix}} < 0$, i.e. energy is released on mixing and $\Delta V_{\text{mix}} < 0$, i.e. attractive forces between unlike molecules are greater than the forces of attraction between like molecules. e.g. chloroform and acetone.



Graphical representation of the solution showing negative deviation

  - (ii) For a solution showing negative deviation,

$$p_A < p^{\text{o}}_A \times \chi_A \text{ or } p_B < p^{\text{o}}_B \times \chi_B$$

$$p_{\text{total}} < p^{\text{o}}_A\chi_A + p^{\text{o}}_B\chi_B$$

  - (iii) In case of negative deviation we get maximum boiling azeotropes, e.g. H_2O (20.22% by mass) + HCl.

Solubility of Gases in Liquids

- The maximum amount of a solute that can be dissolved in a given amount of solvent at given temperature is termed as solubility at that temperature.
- All gases are soluble in water as well as in other liquids to a greater or smaller extent.
- The solubility of most of the gases decreases with increase in temperature.
- The quantitative relation between solubility and pressure of a gas in a solvent was first given by Henry and accordingly gave a law which is called **Henry's law.**
- It states that, at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.
- In other words, "The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution."

$$\boxed{p \propto \chi \text{ or } p = K_{\mathrm{H}} \cdot \chi}$$

where, K_{H} is called Henry's law constant.

- Higher the value of K_{H} at a given pressure, the lower is the solubility of the gas in the liquid.

Solid Solutions

Solid solutions are formed by mixing of two solid components. These solutions can be :

(i) **Substitutional Solid Solutions** These are the solutions, in which atoms, molecules or ions of one substance substitute. The similar species of other substance in its crystal lattice. e.g. Brass, bronze, steel etc.

(ii) **Interstitial Solid Solutions** These are the solutions in which atoms of one kind are placed into voids. Tungsten carbide is this type of solution.

Colligative Properties

- The properties which depend only on the number of moles of non-volatile solute are called **colligative properties**.
- For different solutions of same molar concentration, of different non-electrolyte solutes, the colligative properties have the same value for all.
- For different molar concentrations of the same solute, the colligative property has greater value for more concentrated solution.
- For solutions of different solutes having same % strength, the colligative property has greater value for the solute having least molecular weight.

There are four types of colligative properties as given below

1. Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a solvent, the vapour pressure gets lowered. So, vapour pressure of a solution (p) is always less than the vapour pressure of pure solvent ($p°$) at that temperature.

This leads to the lowering of vapour pressure as follows :

$$\frac{p° - p}{p°} = \chi_{\text{solute}} \text{ or } \frac{p° - p}{p°} = \frac{n}{N}$$

where, $\frac{p° - p}{p°}$ = relative lowering of vapour pressure

n = moles of solute N = moles of solvent

$p°$ = vapour pressure of pure solvent

Determination of molecular mass of solute

$$\therefore \qquad M_B = \frac{w_B \cdot M_A}{w_A \cdot \left(\frac{p° - p}{p°}\right)}$$

where, w_B and w_A = mass of solute and solvent respectively.

M_B and M_A = molecular weight of solute and solvent respectively.

2. Elevation of Boiling Point (ΔT_b)

The boiling point of the solvent is elevated by the addition of non-volatiles solute to it. This is known as elevation of boiling point. For dilute solutions,

$$\Delta T_b = K_b \times \text{Molality}$$

$$\Delta T_b = T_b - T°$$

where, T_b = boiling point of solution

$T°$ = boiling point of pure solvent.

K_b is ebullioscopic constant or molal elevation constant (K_b depends only on solvent).

Determination of molecular mass of solute

$$\therefore \quad M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A} \qquad K_b = \frac{RT_0^2}{1000\ \Delta H_V}$$

where, R = gas constant and ΔH_V = latent heat of vaporisation.

3. Depression of Freezing Point (ΔT_f)

The freezing point of pure solvent decreases when non–volatile solute is dissolved in it. The decrease in freezing point is known as depression in freezing point.

For dilute solutions,

$$\Delta T_f = K_f \times \text{Molality}, \ \Delta T_f = T° - T_f$$

where, $T°$ = freezing point of pure solvent

T_f = freezing point of solution

K_f = cryoscopic constant or molal depression constant

Determination of molecular mass of solute

$$\therefore \qquad M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

and $$K_f = \frac{RT_0^2}{1000\ \Delta H_f}$$

where, H_f = latent heat of fusion

4. Osmosis and Osmosis Pressure

It is defined as the spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to concentrated solution).

Osmotic Pressure $(\pi) = \frac{n}{V} RT = CRT$

where, $n =$ moles of solute
$C =$ molar concentration
$V =$ volume of solution (in litre)
$R =$ gas constant
$T =$ temperature in Kelvin (K).

Determination of molecular mass of solute

$$\therefore \qquad M_B = \frac{w_B RT}{\pi V}$$

- The two solutions having same osmotic pressures at same temperature are termed as **isotonic solutions.**
- When two solutions are being compared, the solution with higher osmotic pressure is termed as **hypertonic** and the solution with lower osmotic pressure is termed as **hypotonic.**
- Osmotic pressure can be determined quite accurately, hence it is used in the determination of molecular weights of large proteins and similar substances.

Abnormal Molecular Mass

The molecular mass is inversely related to the colligative properties. In case of dissociation of solute, the observed molecular mass will be less whereas in case of association, it will be more than the calculated value.

van't Hoff Factor (i)

- In order to account for the abnormal colligative properties, van't Hoff introduced a factor 'i' known as van't Hoff factor. This factor i is defined as

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

$$\text{or} \quad i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

- It can be used to calculate the degree of association and the degree of dissociation as follow:

$$i = \frac{\text{Number of particles after dissociation or association}}{\text{Number of particles before association or dissociation}}$$

Degree of dissociation, $\alpha = \frac{i-1}{n-1}$

where, $n =$ number of particles after dissociation.

Degree of association, $\alpha = \frac{i-1}{\frac{1}{n}-1}$

Here, $n =$ number of particles after association

Modified Expressions of Colligative Properties

- **Relative lowering of vapour pressure**

$$\frac{p^\circ - p}{p^\circ} = i\,\frac{n_B}{n_B + n_A}; \left(\begin{array}{c} n_B = n \\ n_B + n_A \approx N \end{array}\right)$$

- **Elevation in boiling point** $\Delta T_b = i \cdot K_b \cdot m$

Here, $m =$ molality

- **Depression in freezing point** $\Delta T_f = i \cdot K_f \cdot m$
- **Osmotic pressure** (π) $\pi = i \cdot CRT$

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 The aqueous solution of glucose is 10% in strength. The volume in which 1 g mole of it is dissolved will be

(a) 8 L (b) 9 L (c) 0.9 L (d) 1.8 L

2 What mass of solution of 0.50 molal glucose solution is required to obtain 0.15 mole of glucose?

(a) 327 g (b) 300 g
(c) 273 g (d) None of these

3 Assuming that sea water is a 3.50 weight per cent aqueous solution of NaCl. What is the molality of sea water?

(a) 0.062 m (b) 0.0062 m (c) 0.62 m (d) 6.2 m

4 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of solution is → **NEET 2013**

(a) 0.01 M (b) 0.001 M (c) 0.1 M (d) 0.02 M

5 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, then the molar concentration of sodium ion, Na^+ and carbonate ion, CO_3^{2-} are respectively
(molar mass of $Na_2CO_3 = 106\text{ g mol}^{-1}$) → **CBSE-AIPMT 2012**

(a) 0.955 M and 1.910 M (b) 1.910 M and 0.955 M
(c) 1.90 M and 1.910 M (d) 0.477 M and 0.477 M

6 Which of the following is dependent on temperature? → **NEET 2017**

(a) Molality (b) Molarity
(c) Mole fraction (d) Weight percentage

7 Mole fraction of the solute in a 1.00 molal aqueous solution is → **CBSE-AIPMT 2011**

(a) 9.0177 (b) 0.0344 (c) 1.7700 (d) 0.0177

8 Glucose solution is 25% by weight of solution. Its per cent age concentration by weight of solvent is

(a) 20% (b) 25% (c) 33.3% (d) 16.66%

9 Persons are medically considered to have lead poisoning if they have a concentration of greater than 10 μg of lead per decilitre of blood. Concentration in parts per billion is

(a) 1000 (b) 100 (c) 10 (d) 1

10 The volume of water to be added to 100 cm^3 of 0.5 $(NH_4)_2SO_4$ to get decinormal concentration is

(a) 400 cm^3 (b) 450 cm^3 (c) 500 cm^3 (d) 100 cm^3

11 Molarity of a given orthophosphoric acid solution is 3 M. Its normality is

(a) 9 N (b) 0.3 N (c) 3 N (d) 1 N

12 At a given temperature, total vapour pressure in torr of a mixture of a volatile components A and B is given by

$$p = 120 - 75\chi_B$$

hence, vapour pressures of pure A and B respectively (in torr) are

(a) 120, 75 (b) 120,195 (c) 120, 45 (d) 75,45

13 Mole fraction of the component A in vapour phase is χ_1 and mole fraction of component A in liquid mixture is χ_2 (p_A° = vapour pressure of pure A; p_B° = vapour pressure of pure B) , then total vapour pressure of the liquid mixture is

(a) $\frac{p_A^\circ \chi_2}{\chi_1}$ (b) $\frac{p_A^\circ \chi_1}{\chi_2}$ (c) $\frac{p_B^\circ \chi_1}{\chi_2}$ (d) $\frac{p_B^\circ \chi_2}{\chi_1}$

14 The vapour pressure of a pure liquid A is 40 mm Hg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mm Hg. Mole fraction of A in the solution, if it obeys Raoult's law, is

(a) 0.8 (b) 0.5
(c) 0.2 (d) 0.4

15 Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%

(a) 20 g (b) 10 g (c) 30 g (d) 45 g

16 The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what should be the partial pressure of gas?

(a) 4.2 bar (b) 7.6 bar (c) 8.9 bar (d) 9.8 bar

17 Which one is not equal to zero for an ideal solution?
→ CBSE-AIPMT 2015

(a) ΔH (b) ΔS_{mix}
(c) ΔV_{mix} (d) $\Delta p = p_{observed} - p_{Raoult}$

18 Which of the following statements about the composition of the vapour over an ideal 1:1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C. **→ NEET 2016, Phase I**

(Given, vapour pressure data at 25°C, benzene = 12.8 kPa, toluene = 3.85 kPa)

(a) The vapour will contain a higher percentage of toluene
(b) The vapour will contain equal amounts of benzene and toluene
(c) Not enough information is given to make a prediction
(d)The vapour will contain a higher percentage of benzene

19 An aqueous solution is 1.00 molal of KI. Which change will cause the vapour pressure of the solution to increase? **→ CBSE-AIPMT 2010**

(a) Addition of NaCl (b) Addition of Na_2SO_4
(c) Addition of 1.00 molal KI (d) Addition of water

20 K_H value for Ar(g), CO_2(g), HCHO(g) and CH_4(g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively.

Arrange these gases in the order of their increasing solubility.

(a) $HCHO < CH_4 < CO_2 < Ar$ (b) $HCHO < CO_2 < CH_4 < Ar$
(c) $Ar < CO_2 < CH_4 < HCHO$ (d) $Ar < CH_4 < CO_2 < HCHO$

21 Moles of K_2SO_4 to be dissolved in 12 moles of water to lower its vapour pressure by 10 mm Hg at a temperature at which vapour pressure of pure water is 50 mm is

(a) 3 mol (b) 2 mol (c) 1 mol (d) 0.5 mol

22 Elevation in boiling point of an aqueous urea solution is 0.52° [$K_b = 0.52° \text{ mol}^{-1}$ kg]. Hence, mole fraction of urea in this solution is

(a) 0.982 (b) 0.567 (c) 0.943 (d) 0.018

23 Aluminium phosphate is 100% ionised in 0.01 molal aqueous solution. Hence, $\frac{\Delta T_b}{K_b}$ is

(a) 0.01 (b) 0.015
(c) 0.0175 (d) 0.02

24 A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be (K_f for water = 1.86 K kg mol^{-1}) **→ CBSE-AIPMT 2010**

(a) –0.372°C (b) –0.520°C
(c) + 0.372°C (d) –0.570°C

25 Pure benzene freezes at 5.3°K. A solution of 0.223 g of phenylacetic acid ($C_6H_5CH_2COOH$) in 4.4 g of benzene (K_f = 5.12 kg mol^{-1}) freezes at 4.47°K. From this observation, one can conclude that

(a) phenylacetic acid exists as such in benzene
(b) phenylacetic acid undergoes partial ionisation in benzene
(c) phenylacetic acid undergoes complete ionisation in benzene
(d) phenylacetic acid dimerises in benzene

26 Of the following 1.10 m aqueous solutions which one will exhibit the largest freezing point depression?
→ CBSE-AIPMT 2014

(a) KCl (b) $C_6H_{12}O_6$
(c) $Al_2(SO_4)_3$ (d) K_2SO_4

27 60 g of urea is dissolved in 1100 g solution. To keep $\frac{\Delta T}{K_f}$ as 1 mol/kg, water separated in the form of ice is

(a) 40 g (b) 60 g (c) 100 g (d) 200 g

28 What is the freezing point of a solution containing 8.1 g HBr in 100 g water assuming the acid to be 90% ionised ? (K_f for HBr = 1.86 K mol^{-1})

(a) 0.85°C (b) – 3.53°C (c) 0°C (d) – 0.35°C

29 A solution of urea (mol. mass 56 g mol^{-1}) boils at 100.18°C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol^{-1} respectively, the above solution will freeze at

(a) – 6.54°C (b) 6.54°C
(c) 0.654°C (d) – 0.654°C

30 Which one of the following statements is false?

(a) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction
(b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where, M is the molarity of the solution
(c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is
$BaCl_2 > KCl > CH_3COOH >$ sucrose
(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

31 Solution *A* contains 7 g/L of $MgCl_2$ and solution *B* contains 7 g/L of NaCl. At room temperature, the osmotic pressure of

(a) solution *A* is greater than *B*
(b) both have same osmotic pressure
(c) solution *B* is greater than *A*
(d) cannot be determine

32 At temperature 327°C and concentration *C*, osmotic pressure of a solution is *p*, the same solutions at concentration *C*/2 at 427°C shows osmotic pressure 2 atm, value of *p* will be

(a) $\frac{12}{7}$ (b) $\frac{24}{7}$ (c) $\frac{6}{5}$ (d) $\frac{5}{6}$

33 A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g/mol is

(a) 136.2 (b) 171.2 (c) 68.4 (d) 34.2

34 A solution containing 10 g per dm^3 of urea (molecular mass = 60 g mol^{-1}) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of non-volatile solute is

(a) 300 g mol^{-1} (b) 350 g mol^{-1}
(c) 200 g mol^{-1} (d) 250 g mol^{-1}

35. The boiling point of 0.2 mol kg^{-1} solution of *X* in water is greater than equimolal solution of *Y* in water. Which one of the following statements is true in this case?

→ **CBSE-AIPMT 2015**

(a) *X* is undergoing dissociation in water
(b) Molecular mass of *X* is greater than the molecular mass of *Y*
(c) Molecular mass of *X* is less than the molecular mass of *Y*
(d) *Y* is undergoing dissociation in water while *X* undergoes no change

36 When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (*i*) is

(a) 0.5 (b) 1
(c) 2 (d) 3

37 Which one of the following electrolytes has the same value of van't Hoff factor (*i*) as that of $Al_2(SO_4)_3$ (if all are 100% ionised)? → **CBSE-AIPMT 2015**

(a) K_2SO_4
(b) $K_3[Fe(CN)_6]$
(c) $Al(NO_3)_3$
(d) $K_4[Fe(CN)_6]$

38 The van't Hoff factor, *i* for a compound which undergoes dissociation in one solvent and association in other solvent is respectively → **CBSE-AIPMT 2011**

(a) less than one and less than one
(b) greater than one and less than one
(c) greater than one and greater than one
(d) less than one and greater than one

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 50 cm^3 of 0.2 N HCl is titrated against 0.1 N NaOH solution. The titration is discontinued after adding 50 cm^3 of NaOH. The remaining titration is completed by adding 0.5 N KOH. The volume of KOH required for completing the titration is

(a) 12 cm^3 (b) 10 cm^3
(c) 25 cm^3 (d) 10.5 cm^3

2 p_A and p_B are the vapour pressure of pure liquid components, *A* and *B*, respectively of an ideal binary solution. If χ_A represents the mole fraction of component A, the total pressure of the solution will be

→ **CBSE-AIPMT 2012**

(a) $p_A + \chi_A(p_B - p_A)$ (b) $p_A + \chi_A(p_A - p_B)$
(c) $p_B + \chi_A(p_B - p_A)$ (d) $p_B + \chi_A(p_A - p_B)$

3 A mixture of ethane and ethene occupies 41 L at 1 atm and 500 K, the mixture reacts completely with $\frac{10}{3}$ mole of O_2 to produce CO_2 and H_2O. The mole fraction of ethane and ethene in the mixture are ($R = 0.0821$ L atm $K^{-1} mol^{-1}$) respectively

(a) 0.40, 0.50 (b) 0.75, 0.25
(c) 0.67, 0.32 (d) 0.25, 0.75

4 Water and chlorobenzene are immiscible liquids. Their mixture boils at 90°C under a reduced pressure of 7.82×10^4 Pa. The vapour pressure of pure water at 90°C is 7.03×10^4 Pa. On weight per cent basis, chlorobenzene in the distillate is equal to (molecular weight of chlorobenzene is 112.5 g mol^{-1})

(a) 50 (b) 60
(c) 70 (d) 80

5 Two liquids X and Y form an ideal solution. The mixture has a vapour pressure of 400 mm at 300 K, when mixed in the molar ratio of 1 : 1 and a vapour pressure of 350 mm, when mixed in the molar ratio of 1 : 2 at the same temperature. The vapour pressures of the two pure liquids X and Y respectively are

(a) 250 mm, 550 mm
(b) 350 mm, 450 mm
(c) 350 mm, 700 mm
(d) 550 mm, 250 mm

6 Relative decrease in vapour pressure of an aqueous solution containing 2 moles of $[Cu(NH_3)_3Cl]$ Cl in 3 moles of H_2O is 0.50. On reaction with $AgNO_3$ this solution will form

(a) 1 mol AgCl (b) 0.25 mol AgCl
(c) 2 mol AgCl (d) 0.40 mol AgCl

7 The boiling point of water is 100°C. The vapour pressure of water at 25°C is 23 mm Hg and enthalpy of vaporisation is 40.650 kJ mol^{-1}. What will be the temperature at which water will be boil, if atmospheric pressure become 23 mm Hg?

(a) 12.5 K (b) 51.6 K (c) 298 K (d) 250 K

8 Ratio of $\Delta T_b / K_b$ of 6% AB_2 and 9% A_2B (AB_2 and A_2B both are non-electrolytes) is 1 mol/kg in both cases. Hence, atomic masses of A and B are respectively.

(a) 60, 90 (b) 40, 40
(c) 40, 10 (d) 10, 40

9 A complex of iron and cyanide ions is 100% ionised at 1 m (molal). If its elevation in boiling point is 2.08K. ($K_b = 0.52$ K mol^{-1} kg) then the complex is

(a) $K_3[Fe(CN)_6]$ (b) $Fe(CN)_2$
(c) $K_4[Fe(CN)_6]$ (d) $Fe(CN)_4$

10 25 mL of an aqueous solution of KCl was found to require 20 mL of 1 M $AgNO_3$ solution when titrated using a K_2CrO_4 as indicator. Depression in freezing point of KCl solution with 100 % ionisation will be ($K_f = 2.0°$ mol^{-1} kg and molarity = molality)

(a) 5.0° (b) 3.2° (c) 1.6° (d) 0.8°

11 Human blood gives rise to an osmotic pressure of approximately 7.65 atm at the body temperature 37°C. Hence, molarity of an intravenous glucose solution to have the same osmotic pressure as blood should be

(a) 0.30 M (b) 0.20 M (c) 0.10 M (d) 0.50 M

12 The freezing point of an aqueous solution of urea is – 0.52° C. If the molarity and molarity are same and K_f, for H_2O is equal to 1.86 K $molality^{-1}$, the osmotic pressure of solution would be

(a) 0.686 atm (b) 6.886 atm (c) 68.86 atm (d) 688.6 atm

13 Consider the following cases,

I. 2M CH_3COOH solution in benzene at 27°C where there is dimer formation to the extent of 100%.

II. 0.5 M KCl *aq.* solution at 27 °C, which ionises 100%, which of the above is/are true statements (s)?

Choose the correct option.

(a) Both are isotonic (b) II is hypertonic
(c) I is hypertonic (d) None of these

14 What will be the ratio of the masses of formalin (HCHO) and glucose ($C_6H_{12}O_6$) contained equal volumes of solutions having same osmotic pressure at the given temperature?

(a) 1 : 1 (b) 1 : 2 (c) 1 : 3 (d) 1 : 6

15 Total vapour pressure of mixture of 1 mole of volatile component A ($p_A^\circ = 100$ mm Hg) and 3 moles of volatile component B ($p_B^\circ = 60$ mm Hg) is 75 mm. For such case

(a) there is positive deviation from Raoult's law
(b) boiling point has been lowered
(c) force of attraction between A and B is smaller than that between A and A or between B and B
(d) All the above statements are correct

ANSWERS

SESSION 1	**1** (d)	**2** (a)	**3** (c)	**4** (a)	**5** (a)	**6** (b)	**7** (d)	**8** (c)	**9** (b)	**10** (a)
	11 (a)	**12** (c)	**13** (a)	**14** (a)	**15** (b)	**16** (b)	**17** (b)	**18** (d)	**19** (d)	**20** (a)
	21 (c)	**22** (d)	**23** (d)	**24** (a)	**25** (d)	**26** (c)	**27** (a)	**28** (b)	**29** (d)	**30** (d)
	31 (c)	**32** (b)	**33** (c)	**34** (a)	**35** (a)	**36** (a)	**37** (d)	**38** (b)		
SESSION 2	**1** (b)	**2** (d)	**3** (c)	**4** (c)	**5** (d)	**6** (a)	**7** (c)	**8** (c)	**9** (a)	**10** (b)
	11 (a)	**12** (b)	**13** (a)	**14** (d)	**15** (d)					

Hints and Explanations

SESSION 1

1 10% glucose solution means it has 10 g glucose in it.

$\therefore$ Moles of glucose $= \frac{10}{180}$

These moles are present in 100 cc or 0.1 L .

$\therefore$ 1 mole of glucose will be present in

$$= \frac{0.1 \times 180}{10} = 1.8\text{ L}$$

2 0.50 molal glucose solution means;

1000 g water = 0.50 mol glucose

$= 180 \times 0.50 = 90$ g glucose

Total mass of solution

$= 1000 + 90 = 1090$ g

90 g glucose is present in

$= 1090$ g solution

0.15 mol (= 27 g) is present in

$$= \frac{1090 \times 27}{90} = 327\text{ g}$$

3 3.50 weight per cent of aqueous solution of NaCl means 100 g of sea water contains 3.50 g NaCl.

Water in sea water

$= 100 - 3.50 = 96.50$ g

$= 0.0965$ kg

$$\text{Molality} = \frac{3.50}{58.5 \times 0.0965} = 0.62\text{ m}$$

4 $M = \frac{6.02 \times 10^{20} \times 1000}{100 \times 6.02 \times 10^{23}} = 0.01\text{ M}$

5 Molarity

$$= \frac{\text{Number of moles of solute}}{\text{Volume of solution (in mL)}} \times 1000$$

$$= \frac{25.3 \times 1000}{106 \times 250} = 0.9547 \approx 0.955\text{ M}$$

Na_2CO_3 in aqueous solution remains dissociated as

$$\underset{x}{Na_2CO_3} \rightleftharpoons \underset{2x}{2Na^+} + \underset{x}{CO_3^{2-}}$$

Since, the molarity of Na_2CO_3 is 0.955 M, the molarity of CO_3^{2-} is also 0.955 M and that of Na^+ is $2 \times 0.955 = 1.910$ M

6 Molarity and normality are temperature dependent because they involve volume of solutions. Volume is dependent on temperature.

Molarity (M)

$$= \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}}$$

Molality, mole fraction and weight percentage does not depend on temperature because they involve masses of solute and solvent.

7 1.00 molal aqueous solution = 1.0 mol in 1000 g water

$n_{\text{solute}} = 1;\ W_{\text{solvent}} = 1000$ g

$\Rightarrow n_{\text{solvent}} = \frac{1000}{18} = 55.56$

$n_{\text{solute}} = \frac{1}{1 + 55.56} = 0.0177$

8 $\frac{w_1}{w_1 + w_2} = 0.25 = \frac{1}{4} \Rightarrow \frac{w_1 + w_2}{w_2} = \frac{4}{1}$

$1 + \frac{w_2}{w_1} = 4 \Rightarrow \frac{w_2}{w_1} = 4 - 1 = 3$

$\frac{w_1}{w_2} = \frac{1}{3} = 0.33$

$\Rightarrow \frac{w_1}{w_2}\% = 0.33 \times 100 = 33.3\%$

9 10 μg per decilitre $= 10 \times 10^{-6}$ g in 100 mL

10^9 parts (1 billion) have

$$= \frac{10 \times 10^{-6}}{100} \times 10^9\text{ g}$$

= 100 g parts per billion

10 $N_1V_1 = N_2V_2$

$0.5 \times 100 = 0.1 \times V_2$

$\therefore \quad V_2 = 500\text{ cm}^3$

Amount of water to be added to 100 cm^3 solution = 500 – 100 = 400 cm^3

11 Orthophosphoric acid (H_3PO_4) is a tribasic acid.

$\because$ Normality = Molarity × Basicity

$\therefore$ Normality $= 3\text{ M} \times 3 = 9$ N

12 $p = p_A^\circ \chi_A + p_B^\circ \chi_B$

$= p_A^\circ (1 - \chi_B) + p_B^\circ \chi_B$

$= p_A^\circ - (p_A^\circ - p_B^\circ)\chi_B = 120 - 75\ \chi_B$

$p_A^\circ = 120$ torr

$p_A^\circ - p_B^\circ = 75$ torr

$\Rightarrow \quad p_B^\circ = 45$ torr

13 χ_1 (mole fraction of A in vapour phase)

$$= \frac{p_A^\circ \chi_2}{p_{(\text{total})}}$$

$$\Rightarrow p_{\text{total}} = \frac{p_A^\circ \chi_2}{\chi_1}$$

14 According to Raoult's law,

$p_A = p_A{}^\circ \chi_A$

Vapour pressure of pure liquid, ($p^\circ{}_A$) = 40 mm Hg

Vapour pressure of liquid in a solution , (p_A) = 32 mm Hg

$\therefore \quad 32 = 10\chi_A$

$\chi_A = 0.8$

15 According to Raoult's law, relative lowering of vapour pressure,

$$\frac{\overset{\circ}{p}_A - p_S}{\overset{\circ}{p}_A} = \chi_B \qquad \ldots\text{(i)}$$

$$\chi_B = \frac{n_B}{n_B + n_A} = \frac{W_B/M_B}{\frac{W_B}{M_B} + \frac{W_A}{M_A}} \qquad \ldots\text{(ii)}$$

Given vapour pressure is reduced to 80% when non-volatile solute is dissolved in octane. It means

If $\overset{\circ}{p}_A = 1$ atm then $p_S = 0.8$ atm;

$p_A^\circ - p_S = 0.2$ atm;

M_A (C_8H_{18}) = 114 g mol^{-1}; $W_A = 114$ g;
$M_B = 40$ g mol^{-1}; $W_B = ?$

Applying Eq. (ii)

$$\frac{0.2}{1} = \frac{W_B/40}{\frac{W_B}{40} + \frac{114}{114}} = \frac{W_B/40}{\frac{W_B}{40} + 1}$$

$$0.2 = \frac{W_B}{W_B + 40}$$

$$0.2W_B + 8 = W_B$$

$$W_B = 10$$

16 According to Henry's law,
Mass of the gas (m) dissolved in solution $\propto$ partial pressure (p)
(at constant temperature)

$\therefore$ $(6.56 \times 10^{-3}\text{g}) \propto 1\,\text{bar}$

$(5.00 \times 10^{-2}\text{ g}) \propto p$

or $p = \dfrac{(5.0 \times 10^{-2}\text{g})}{(6.56 \times 10^{-3}\text{g})} \times (1\,\text{bar}) = 7.62$ bar

17 For an ideal solution :

(i) There will be no change in volume on mixing the two components, i.e. $\Delta V_{\text{mixing}} = 0$

(ii) There will be no change in volume on $\Delta H_{\text{mixing}} = 0$
So, $\Delta S_{\text{mix}} \neq 0$ for an ideal solution.

18 Since, component having higher vapour pressure will have higher percentage in vapour phase. Benzene has vapour pressure 12.8 kPa which is greater than toluene 3.85 kPa. Therefore, the vapour will contain a higher percentage of benzene.

19 Vapour pressure depends upon the surface area of the solution. Larger the surface area, higher is the vapour pressure. Addition of solute decreases the vapour pressure as some sites of the surface are occupied by solute particles, resulting in decreased surface area. However, addition of solvent, i.e. dilution, increases the surface area of the liquid surface, thus results in increased vapour pressure. Hence, addition of water to the aqueous solution of (1 molal) KI, results in increased vapour pressure.

20 $p_A = K_H \chi_A$

i.e. dower the value K_H, higher is the solubility at same partial pressure and at the same temperature.

Thus, the correct order of the increasing solubility of given gases is HCHO< CH_4 < CO_2 < Ar.

21 Lowering of vapour pressure is colligative property.

i for $K_2SO_4 = 3$

$$\frac{\Delta p}{p^\circ} = \frac{n_1 i}{n_1 i + n_2}$$

$$\frac{10}{50} = \frac{3\,n_1}{3n_1 + 12} = \frac{n_1}{n_1 + 4},\quad n = 1$$

22 ΔT_b = molality $\times K_b \Rightarrow 0.52 = m \times 0.52$

Molality = 1 mol kg^{-1}

$\therefore$ Moles of urea = 1 mol

and moles of water $= \dfrac{1000}{18} = 55.55$

Mole fraction of urea $= \dfrac{1}{1 + 55.55} = 0.018$

23 $AlPO_4 \rightleftharpoons Al^{3+} + PO_4^{3-}$

$i = 2$

$\Delta T_b = iK_b m \quad \dfrac{\Delta T_b}{K_b} = 2 \times 0.01 = 0.02$

24 Depression in freezing point,

$$\Delta T_f = K_f \times m$$

where, m = molarity $= \dfrac{w_B \times 12000}{M_B \cdot W_A}$

$$= \frac{68.5 \times 1000}{342 \times 1000} = \frac{68.5}{342}$$

$$\Delta T_f = 1.86 \times \frac{68.5}{342} = 0.372°\text{C}$$

$$\Delta T_f = T^\circ - T_s = 0 - 0.372°\text{C}$$

$$= -0.372°\text{C}$$

25 Depression in freezing point, $\Delta T_f = K_f m$

(where, m = molarity)

$$= 5.12 \times \frac{0.223 \times 1000}{4.4 \times 136}$$

$$= 5.12 \times 0.372 = 1.91\,\text{K}$$

$\therefore$ Theoretical $\Delta T_f = 1.91$

Actual $\Delta T_f = 5.3\text{K} - 4.47\text{K} = 0.83\text{K}$

$\therefore \quad i = \dfrac{0.83}{1.91} = 0.43$

$\because \quad i < 1$

$\therefore$ Association will take place.

Thus, it can be said that phenylacetic acid dimerises in benzene.

26 van't Hoff factor of $Al_2(SO_4)_3$ is maximum, i.e. =5. Thus, $Al_2(SO_4)_3$ will exhibit largest freezing point depression.

27 1100 g solution has 60 g urea

$\therefore$ Mass of water = 1040 g

$$\Delta T_f = \frac{1000\,K_f w_1}{m_1 w_2}$$

$$\frac{\Delta T_f}{K_f} = \frac{1000 \times 60}{60 \times w_2} = 1$$

$$w_2 = 1000\,\text{g}$$

Thus, ice formed = 1040 – 1000 = 40 g

28 $\Delta T_f = i \times K_f \times m$

$$HBr \longrightarrow H^+ + Br^-$$

Ions at equilibrium $1 - \alpha \quad \alpha \quad \alpha$

Total ions $= 1 - \alpha + \alpha + \alpha$

$\therefore \quad = 1 + \alpha \Rightarrow i = 1 + \alpha$

where, (α) = degree of ionisation = 90%

$i = 1 + \alpha = 1 + 90/100 = 1.9$

m(molality)

$$= \frac{\text{Mass of solute / mol. wt. of solute}}{\text{Mass of solvent in kg}}$$

Given, $K_f = 1.86$ K mol^{-1}

Mass of HBr = 8.1 g

Mass of H_2O = 100 g $= \dfrac{8.1/81}{100/1000} = 1$

$$\Delta T_f = i \times K_f \times m$$

$$= 1.9 \times 1.86 \times 1 = 3.534°\text{C}$$

ΔT_f = depression in freezing point
= freezing point of water
– freezing point of solution
= 0 – freezing point of solution

$\therefore$ Freezing point of solution = –3.534°C

29 $\Delta T_f = K_f \times$ Molality of solution

$\Delta T_b = K_b \times$ Molality of solution

$$\frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b}$$

$\Delta T_b = T_2 - T_1 = 100.18 - 100 = 0.18$

K_f for water = 1.86 K kg mol^{-1}

K_b for water = 0.512 K kg mol^{-1}

$\therefore \quad \dfrac{\Delta T_f}{0.18} = \dfrac{1.86}{0.512}$

$$\Delta T_f = \frac{1.86 \times 0.18}{0.512} = 0.6539 \approx 0.654°\text{C}$$

$$\Delta T_f = T_1 - T_2$$

$$0.654 = 0°\text{C} - T_2$$

$$T_2 = -0.654°\text{ C}$$

(freezing point of *aq*. urea solution)

30 (a) $p_A = \chi_A p^\circ_A$ true

(b) $\pi = iMRT = MRT$

true (if van't Hoff factor, $i = 1$)

(c) $i = [1 + (y - 1)x]$,

where, y = number of ions

x = degree of ionisation

$i = 3$ for $BaCl_2, x = 1$

(strong electrolyte)

$i = 2$ for KCl, $x = 1$

(strong electrolyte)

$i = (1 + x)$ for $CH_3COOH x << 1$

(weak)

$i = 1$ for sucrose (non-electrolyte)

i = (for $BaCl_2$) > KCl > CH_3COOH > sucrose.

Thus, (c) is also true.

31 Osmotic pressure is a colligative property. More the number of particles (or ions) in solution, more will be osmotic pressure.

NaCl solution

Given, mass of NaCl = 7 g, V = 1 L

$$\therefore \text{Concentration} = \frac{\text{Mass}}{\text{Molecular mass}} = \frac{7}{58.5} = 0.119\ \text{M}$$

NaCl dissociates as follows,

$$NaCl \longrightarrow Na^+ + Cl^- \text{ (2 ions)}$$

$\therefore$ Concentration of ions in solution

$$= 2 \times 0.119\ \text{M} = 0.238\ \text{M}$$

$MgCl_2$ solution

Given, mass of $MgCl_2$ = 7 g, V = 1 L

$$\text{Concentration} = \frac{7}{45} = 0.0747$$

$MgCl_2$ dissociates as follows,

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^- \text{ (3 ions)}$$

$\therefore$ Concentration of ions in solution

$$= 3 \times 0.074\ \text{M} = 0.222\ \text{M}$$

$\because$ Number of particles in solution B(NaCl) are more than in solution A.

$\therefore$ Osmotic pressure of solution B(NaCl) will be more than solution A.

32 $\pi = CRT$

$$\frac{\pi_1}{\pi_2} = \frac{C_1RT_1}{C_2RT_2}$$

$$\pi_1 = p,\ \pi_2 = 2\ \text{atm},\ C_1 = C,\ C_2 = \frac{C}{2}$$

$$T_1 = 600\ \text{K},\ T_2 = 700\ \text{K}$$

$$\frac{p}{2} = \frac{C \times R \times 600 \times 2}{C \times R \times 700},\quad p = \frac{24}{7}$$

33 Two solutions are isotonic if their osmotic pressure are equal.

i.e. $\pi_1 = \pi_2$

At a given temperature,

$$M_1 = M_2$$

$$\frac{1000\ w_1}{m_1V_1} = \frac{1000\ w_2}{m_2V_2} \quad (V_1 = V_2 = 100\ \text{mL})$$

Cane sugar Unknown

$$\therefore \quad \frac{w_1}{m_1} = \frac{w_2}{m_2}$$

$$\Rightarrow \quad \frac{5}{342} = \frac{1}{m_2}$$

$$m_2 = \frac{342}{5} = 68.4\ \text{g mol}^{-1}$$

34 Concentration of urea $= \frac{10}{60}$ per dm^3

Concentration of non-volatile solute,

$$= \frac{5}{M} \text{ per 100 mL } = \frac{50}{M} \text{ per dm}^3$$

Since, the solutions are isotonic

$$\therefore \quad \frac{10}{60} = \frac{50}{M} \Rightarrow M = 300\ \text{g mol}^{-1}$$

35 Molality of solution X = Molality of solution Y = 0.2 mol/kg

We know that, elevation in the boiling point (ΔT_b) of a solution is proportional to the molal concentration of the solution, i.e.

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = K_b m$$

where, m is the molality of the solution and K_b is molal elevation boiling point constant or ebullioscopic constant.

$\therefore$ By elevation in boiling point relation

$$\Delta T_b = iK_b m \quad \text{or} \quad \Delta T_b \propto i$$

where, i is van't Hoff is factor.

Since, ΔT_b of solution X is greater than ΔT_b of solution Y.

(Observed colligative property is greater than normal colligative property).

$\therefore$ i of solution X > i of solution Y

$\therefore$ Solution X undergoing dissociation.

36 Actual molecular mass of naphthoic acid ($C_{11}H_8O_2$) = 172

Molecular mass (calculated)

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

$$= \frac{1000 \times 1.72 \times 20}{50 \times 2}$$

$$= 344$$

van't Hoff factor (i)

$$= \frac{\text{Actual molecular mass}}{\text{Calculated molecular mass}}$$

$$= \frac{172}{344} = 0.5$$

37 $Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$

Value of van't Hoff's factor (i) = 5

(a) $K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$ ($i = 3$)

(b) $K_3[Fe(CN)_6] \rightleftharpoons 3K^+ + [Fe(CN)_6]^{3-}$

($i = 4$)

(c) $Al(NO_3)_3 \rightleftharpoons Al_3^{3+} + 3NO_3^-$ ($i = 4$)

(d) $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{3-}$

($i = 5$)

Therefore, $K_4[Fe(CN)_6]$ has same value of i that of $Al_2(SO_4)_3$, i.e. $i = 5$

38 For dissociation, van't Hoff factor is greater than unity. While for association, Van't Hoff factor is less than unity.

SESSION 2

1 When 0.1 N NaOH is used,

$$N_1V_1 = N_2V_2$$

(For HCl) (For NaOH)

$$0.2\ \text{N} \times V_1 = 50 \times 0.1\ \text{N}$$

$$V_1 = \frac{50 \times 0.1}{0.2} = 25\ \text{cm}^3$$

When 0.5 N KOH is used,

$$N_1V_1 = N_3V_3$$

(For remaining HCl) (For KOH)

$$0.2\ \text{N} \times 25 = 0.5\ \text{N} \times V_3$$

$$\Rightarrow \quad V_3 = \frac{0.2 \times 25}{0.5} = 10\ \text{cm}^3$$

2 Vapour pressure of $A = p_A$

Mole fraction of $A = \chi_A$

Vapour pressure of $B = p_B$

Mole fraction of $B = \chi_B = 1 - \chi_A$

$\therefore$ Total pressure of the solution

$$= p_A\chi_A + p_B\chi_B$$

$$= p_A\chi_A + p_B(1 - \chi_A)$$

$$= p_A\chi_A + p_B - p_B\chi_A$$

$$= p_B + \chi_A(p_A - p_B)\ .$$

3 $pV = nRT$, $1 \times 41 = n \times 0.821 \times 500$

$n = 0.998$ mol

The number of moles of ethane = x

So, number of moles of ethene

$$= (0.998 - x)$$

Reaction of ethane and ethene with O_2

(i) $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$

(ii) $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

According to (i) reaction,

$\because$ 2 moles ethane react with 7 moles of O_2

$\therefore$ x moles ethane react with $\frac{7x}{2}$ moles of O_2

According to (ii) reaction

$\because$ 1 mole ethene reacts with 3 moles of O_2

$\therefore$ $(0.998 - x)$ mole ethene reacts

$= 3(0.998 - x)$ mole of O_2

$$\frac{7x}{2} + [3\,(0.998 - x)] = \frac{10}{3} \text{ moles of } O_2$$

$$3.5x + 2.994 - 3x = \frac{10}{3} \text{ moles of } O_2$$

$$0.5x = 3.333 - 2.994 = 0.3393$$

$$x = \frac{0.3393}{0.5} = 0.678 \text{ mole of ethane}$$

Moles of ethene = 0.998 − 0.678 = 0.32

4 $\therefore \quad pV = nRT$

$\because \quad p_1 + p_2 = 7.82 \times 10^4$ Pa

and $\quad p_1 = 7.03 \times 10^4$ Pa

$\therefore \quad p_2 = 0.79 \times 10^4$ Pa

Again, $\quad p \propto n$ i.e. $p \propto \frac{w}{m}$

$$\therefore \frac{p_2}{p_1} = \frac{w_2 m_1}{w_1 m_2} \text{ or } w_2 = w_1\,\frac{p_2 m_2}{p_1 m_1}$$

$$= \frac{0.79 \times 10^4 \times 112.5}{7.03 \times 10^4 \times 18} = 0.70 \times 100$$

$\therefore$Weight per cent of chlorobenzene = 70%

5 **In Ist case,**

When two liquids X and Y are mixed in the molar ratio 1 : 1.

Moles of $X = 1$, Moles of $Y = 1$

Mole fraction of $X(\chi_X) = \frac{1}{2}$,

Mole fraction of $Y(\chi_Y) = \frac{1}{2}$

We know that $p = p^\circ{}_X\,\chi_X + p^\circ{}_Y\,\chi_Y$

(p = total pressure of mixture)

$$400 = \frac{1}{2} p^\circ{}_X + \frac{1}{2} p^\circ{}_Y$$

$$400 \times 2 = p^\circ{}_X + p^\circ{}_Y \qquad \ldots\text{(i)}$$

In IInd case,

When liquids are mixed in the molar ratio of 1 : 2.

Mole of $X = 1$, Moles of $Y = 2$

Mole fraction of $X(\chi_X) = \frac{1}{3}$

Mole fraction of $Y(\chi_Y) = \frac{2}{3}$

$$p = p^\circ_X\,\chi_X + p^\circ_Y \chi_Y,\ 350 = \frac{1}{3} p^\circ_X + \frac{2}{3} p^\circ_Y$$

$$350 \times 3 = p^\circ{}_X + 2p^\circ_Y \qquad \ldots\text{(ii)}$$

From Eqs. (i) and (ii), we get

$p^\circ_x = 550$ mm, $\quad p^\circ_Y = 250$ mm

6 $[Cu(NH_3)_3Cl]\,Cl$

$$\rightleftharpoons [Cu(NH_3)_3Cl]^+ + Cl^-$$

Complex ionises in aqueous solution and Ag^+ reacts with free Cl^- ion.

Degree of ionisation $= x \quad i = (1 + x)$

$$\frac{\Delta p}{p^\circ} = \frac{n_2(1+x)}{n_2(1+x)+n_1} = \frac{2(1+x)}{2(1+x)+3} = 0.5$$

$\therefore x = 0.5$ hence, complex is 50% ionised.

$\therefore \quad Cl^- = 2 \times 0.5 = 1$ mol

$$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$$

$$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$$

$\therefore \quad$ AgCl = 1mol

7 Boiling point of a solvent is a characteristic temperature at which vapour pressure of liquid becomes equal to 1 atm. A decrease in pressure results a decrease in temperature at which water boils.

i.e. $273 + 25 = 298$ K

8 $$\Delta T = \frac{1000 K_b\, w_2}{m_2\, w_1}$$

$$\frac{\Delta T}{K_b}(A\,B_2) = \frac{1000 \times 6}{m_2 \times 100} \Rightarrow 1 = \frac{10 \times 6}{m_2}$$

$$\therefore \quad m_2(A\,B_2) = 60 = A + 2B \qquad \ldots\text{(i)}$$

$$\frac{\Delta T}{K_b}(A_2 B) = \frac{1000 \times 9}{m_2 \times 100} = 1$$

$$\therefore m_2(A_2 B) = 90 = 2A + B \qquad \ldots\text{(ii)}$$

By solving equation (i) and (ii), we get the value of A and B.

$\therefore \quad A = 40,\ B = 10$

9 $$\Delta T_b = mK_b i$$

$$2.08 = 1 \times 0.52\, i,\ i = 4$$

$$i = [1 + (y-1)x]$$

$$4 = 1 + (y-1)$$

$\therefore \quad y = 4 \quad$ (total 4 ions)

$$K_3[Fe(CN)_6] \equiv 3K^+ + [Fe(CN)_6]^{4-}$$

10 $$M(KCl) = \frac{20 \times 1}{25} = 0.8M$$

$i = 2$ for KCl

$\therefore \quad \Delta T_f = i\,K_f m = 2 \times 2 \times 0.8 = 3.2°$

11 $C = ? \Rightarrow \pi = CRT$

$$\Rightarrow \quad C = \frac{\pi}{RT}$$

$\pi = 7.65$ atm, $R = 0.0821$ atm $K^{-1} mol^{-1,}$

$T = 37°C$

$= 37 + 273 = 310$K

$$\therefore \quad C = \frac{7.65}{0.0821 \times 310} = 0.30\text{ M}$$

Molarity of an intravenous glucose solution to have the same osmotic pressure as blood should be 0.03M.

12 $$\because \quad \Delta T = \frac{1000 \times K_f' \times W}{m \times W} = K_f' \times \text{molality}$$

$\therefore \quad 0.52 = 1.86 \times$ molality

$$\text{Molality} = \frac{0.52}{1.86} = \text{molarity}\left(\frac{n}{V}\right)$$

(given)

ow, $\quad \pi = CRT$ or $\pi = \frac{n}{V} RT$

$$\therefore \quad \pi = \frac{0.52}{1.86} \times 0.0821 \times 300$$

$$\pi = 6.886 \text{ atm}$$

13 (i) Due to dimer formation of CH_3COOH in benzene, it is therefore, 1M.

(ii) 0.5M KCl ionises in aqueous solution hence, it is 1M.

$$\underset{2M}{2CH_3COOH} \rightleftharpoons \underset{1M}{(CH_3COOH)_2}$$

$$\underset{0.5\,M}{KCl} \rightleftharpoons \underbrace{K^+ + Cl^-}_{1\,M}$$

Thus, both are isotonic (equal osmotic pressure).

14 Solutions are isotonic, hence, number of moles are equal

$$\therefore \quad n_1\,(HCHO) = n_2\,(C_6H_{12}O_6)$$

$$\frac{w_1}{m_1} = \frac{w_2}{m_2}$$

$$\frac{w_1}{w_2} = \frac{m_1}{m_2} = \frac{30}{180} = 1 : 6$$

15 $$p = p^\circ_A \chi_A + p^\circ_B \chi_B = \frac{100}{4} + \frac{60 \times 3}{4}$$

= 70 mm < 75 mm (experimental)

Thus, there is positive deviation (a) as true mixture is more volatile due to decrease in boiling point.

Thus, (b) is true; also force of attraction is decreased thus (c) is true.