

## DAY EIGHT

# Solutions

### Learning & Revision for the Day

- Concentration of Solution
- Solubility
- Vapour Pressure
- Raoult's Law
- Ideal Solutions
- Non-ideal Solutions
- Henry's Law
- Colligative Properties
- Abnormal Molar Masses

Solution is a homogeneous mixture of two or more substances on molecular level. The substances forming the solution are called **components** (solute, solvent) of the solutions.

### Concentration of Solution

Various methods for expressing concentration of solutions are as follows:

#### 1. Molality ( $m$ )

It is the number of moles of solute dissolved in 1000 g of solvent.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent (in kg)}}$$

#### 2. Molarity ( $M$ )

It is the number of solute present in one litre of the solution.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$$

- Relation between molality ( $m$ ) and molarity ( $M$ ),

$$\text{Molarity} = \frac{m \times d}{1 + \frac{m \times M_2}{1000}}$$

where,  $M_2$  = molar mass of solute,  $d$  = density of the solution,  $m$  = molality of solution

- Relation between molarity and density

$$\text{Molarity} = 10 \times \text{density} \times \% \text{ by wt. of solute/mol. wt. of solute}$$

#### 3. Mole Fraction ( $\chi$ )

It is the ratio of the number of moles of one component (i.e. solute or solvent) to the total number of moles of solute and solvent (i.e. moles of solution).

$$\text{Mole fraction of solute in the solution, } \chi_{\text{solute}} = \frac{\text{Moles of solute } (n_{\text{solute}})}{\text{Total moles of solution } (n_{\text{solute}} + n_{\text{solvent}})}$$

Mole fraction of solvent in the solution

$$\chi_{\text{solvent}} = \frac{\text{Moles of solvent } (n_{\text{solvent}})}{\text{Total moles of solution } (n_{\text{solute}} + n_{\text{solvent}})}$$

Sum of mole fractions is always equal to one, i.e.

$$\chi_{\text{solute}} + \chi_{\text{solvent}} = 1$$

- Relation between molarity ( $M$ ) and mole fraction ( $\chi$ )

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

Here,  $M_1$  = molar mass of solvent

$M_2$  = molar mass of solute

$d$  = density of the solution

#### 4. Percentage by Weight or Mass Per cent

It is the amount of solute present in 100 g of the solution.

$$\text{Percentage by weight} = \frac{\text{Weight of solute} \times 100}{\text{Weight of solution}}$$

#### 5. Percentage by Volume

The volume of solute (in mL) present in 100 mL of the solution is called volume per cent

$$\text{Percentage by volume} = \frac{\text{Volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$$

#### 6. Mass by Volume Percentage

It is the mass of solute dissolved in 100 mL of the solution.

$$\begin{aligned} \text{Mass/volume percentage} \\ = \frac{\text{Mass of solute}}{\text{Total volume of solution (mL)}} \times 100 \end{aligned}$$

#### 7. Parts Per Million (ppm)

When the amount of solute (in g) is present in one million mL (1 million =  $10^6$ ) per mL of solution, the concentration of the solution is expressed in ppm.

$$\text{ppm concentration} = \frac{10^6 \times \text{mass of solute (g)}}{\text{Mass of (solute + solvent) (mL)}}$$

#### 8. Normality

It is the number of gram-equivalents of substance dissolved per litre of the solution.

$$\text{Normality} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution (in L)}}$$

$$\text{where, gram-equivalents} = \frac{\text{Weight of solute}(w)}{\text{Equivalent weight of solute}(E)}$$

## Solubility

The maximum amount of a solute that can be dissolved in a given amount of solvent at a given temperature is termed as **solubility** at that temperature. Solubility of a gas in liquid depends upon temperature and pressure.

The quantitative relation between pressure and solubility of a gas in a solvent is given by Henry.

## Vapour Pressure

The pressure exerted by the vapour molecules above liquid surface which are in equilibrium with it at a given temperature is called **vapour pressure**.

## Factor Affecting Vapour Pressure

Vapour pressure gets affected by the following factors:

1. **Purity of the Liquid** Pure liquid always has a vapour pressure higher than its solution.
2. **Nature of the Liquid** Liquids which have weak intermolecular forces are volatile and have greater vapour pressure.
3. **Temperature** The vapour pressure of a liquid increases with increase in temperature. This is because on increasing the temperature, the kinetic energy of molecules increases that results into the fact that more molecules of the liquid can go into vapour phase.
4. **Effect of Adding Solute** When a liquid contains a solute, some of the solvent molecules are replaced by the solute particles on the liquid surface and therefore, the available surface area for the escape of solvent molecule decreases.

Due to the less available area on the surface of liquid for escape, rate of evaporation and the rate of condensation both decreases.

- The vapour pressure of liquid in solution is known as its **partial vapour pressure** and is less than the vapour pressure of the pure liquid at the same temperature.
- If  $p^\circ$  be the vapour pressure of pure liquid and  $p_s$  be that of liquid in solution then lowering of vapour pressure of the liquid =  $p^\circ - p_s$

$$\therefore \text{Relative lowering in vapour pressure} = \frac{p^\circ - p_s}{p^\circ}$$

## Raoult's Law

Raoult's law for the solutions of liquids in liquids states "The partial vapour pressure of each component of the solution is directly proportional to the mole fraction of that component present in solution.

$$p_A = \chi_A p_A^\circ \quad \text{and} \quad p_B = \chi_B p_B^\circ$$

where,  $A$  and  $B$  are volatile solute and solvent respectively and  $p_A^\circ$  and  $p_B^\circ$  are the vapour pressures of  $A$  and  $B$  in pure state.

- If  $\chi_A$  and  $\chi_B$  are the mole fraction of the components  $A$  and  $B$  respectively in the vapour phase then,

$$p_A = \chi_A \cdot p_{\text{total}}$$

$$p_B = \chi_B \cdot p_{\text{total}}$$

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

$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^\circ$$



Limitations of Raoult's Law are as follows :

- (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.

## Ideal Solutions

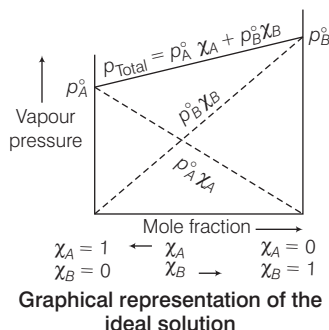
- The solutions, which obey Raoult's law over all ranges of concentration and temperature are called **ideal solutions**.

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

where,  $\Delta H_{\text{mix}}$  = enthalpy of mixing to form the solution  
 $\Delta V_{\text{mix}}$  = volume of mixing to the solution

- For such solutions, solute-solute and solvent-solvent interactions  $\approx$  solute-solvent interactions.
- Solution of *n*-hexane and *n*-heptane, benzene and toluene etc., fall in this category.

Practically, no solution is ideal. The graphical representation of ideal solutions is given below:



## Non-ideal Solutions

The solutions which show deviation from Raoult's law are called **non-ideal solution**.

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

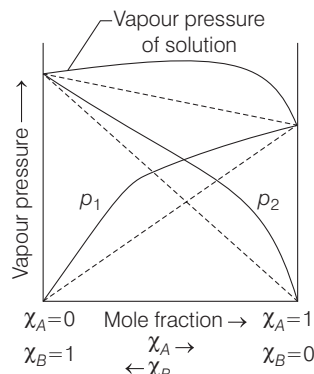
### Non-ideal Solutions Showing Positive Deviation

- When the observed partial vapour pressure is more than that expected by Raoult's law, then positive deviation is observed.
- For such a deviation,

$$p_A > p_A^0 \chi_A$$

$$p_B > p_B^0 \chi_B$$

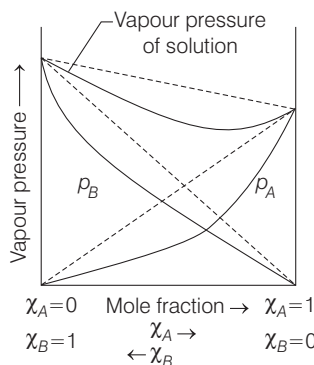
$$p_{\text{Total}} > p_A^0 \chi_A + p_B^0 \chi_B$$



- For such solutions,  $\Delta H_{\text{mix}} > 0$ ,  $\Delta V_{\text{mix}} > 0$ . These are usually obtained by mixing of polar liquids with non-polar ones. e.g. cyclohexane and ethanol,  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_5\text{OH}$ .

### Non-ideal Solutions Showing Negative Deviation

- When the observed partial vapour pressure is less than that expected by Raoult's law, then negative deviation is observed.
- For such solutions,  $\Delta H_{\text{mix}} < 0$ ,  $\Delta V_{\text{mix}} < 0$ , e.g. chloroform and acetone.



For a solution showing negative deviation,

$$p_A < p_A^0 \chi_A \text{ or } p_B < p_B^0 \chi_B$$

$$p_{\text{Total}} < p_A^0 \chi_A + p_B^0 \chi_B$$

## Azeotropes

Mixture of liquids that boils at a constant temperature and distills over without any change in composition are called **azeotropes**.

Azeotropes are of two types :

1. **Minimum Boiling Azeotropes** These are formed by those liquid pairs which show positive deviation from ideal behaviour. Such azeotropes have boiling points lower than either of the components. e.g. ethanol + water, ether-acetone, water-methanol.

2. **Maximum Boiling Azeotropes** These are formed by those liquid pairs which show negative deviation from ideal behaviour. Such azeotropes have boiling points higher than either of the components. e.g. water (20.22% by mass) + hydrochloric acid, acetone + chloroform, water + nitric acid.

## Henry's law

It states that, at 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 liquids or solution. In other words, "The partial pressure of the gas in vapour phase ( $p$ ) is proportional to the mole fraction of the gas ( $\chi$ ) in the solution". Thus,

$$p \propto \chi \Rightarrow p = K_H \chi$$

where,  $K_H$  is 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.

## 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  $p_i = \chi_i p_i^\circ$ . In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and its partial pressure is directly proportional to its mole fraction in the solution and this is stated by Henry's law as  $p = K_H \chi$ .
- If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in the solution. Only the proportionality constant  $K_H$  differs from  $p_i^\circ$ . Thus, Raoult's law becomes a special case of Henry's law in which  $K_H$  becomes equal to  $p_i^\circ$ .

## Colligative Properties

The properties which depend only on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution as **colligative properties**, e.g. relative lowering of vapour pressure, depression in freezing point, elevation in boiling point, osmotic pressure etc.

- 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 percent 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

Addition of non-volatile solute leads to the lowering of vapour pressure.

$$\frac{p^\circ - p}{p^\circ} = \chi_{\text{solute}} \quad \text{or} \quad \frac{p^\circ - p}{p^\circ} = \frac{n_B}{n_A}$$

[For dilute solution  $n_B \ll n_A$ ]

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

$n_B$  = moles of solute,  $n_A$  = moles of solvent

$p^\circ$  = vapour pressure of pure solvent

## Determination of Molecular Mass from Relative Lowering of Vapour Pressure

Relationship between molecular mass and relative lowering of vapour pressure can be given as:

$$M_B = \frac{w_B \cdot M_A}{w_A \cdot \left( \frac{p^\circ - p}{p^\circ} \right)}$$

where,  $w_B$  and  $w_A$  = mass of solute and solvent respectively and  $M_B$  and  $M_A$  = molecular weight of solute and solvent respectively.

## 2. Elevation in Boiling Point ( $\Delta T_b$ )

As the vapour pressure of a solution is decreased due to presence of a non-volatile solute, the solution boils at a higher temperature as compared to the pure solvent. Thus, the boiling point of the solution is higher than the boiling point of the pure solvent.

For dilute solutions,  $\Delta T_b = K_b \times \text{molality}$

$$\Delta T_b = T_b - T_b^\circ$$

where,  $T_b$  = boiling point of solution

$T_b^\circ$  = boiling point of pure solvent.

$$K_b = \frac{M_A R (T_b^\circ)^2}{1000 \Delta H_V}$$

where,  $R$  = gas constant and  $\Delta H_V$  = latent heat of vapourisation.

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

## Determination of Molecular Mass from Elevation in Boiling Point

The relationship between molar mass and elevation in boiling point can be given as :

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

### 3. Depression in Freezing Point ( $\Delta T_f$ )

When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent.

For dilute solutions,

$$\Delta T_f = K_f \times \text{molality}, \quad \Delta T_f = T_f^\circ - T_f$$

where,  $T_f^\circ$  = freezing point of pure solvent

$T_f$  = freezing point of solution

$K_f$  = cryoscopic constant or molal depression constant

$$K_f = \frac{MR(T_f^\circ)^2}{1000 \Delta H_f}$$

where,  $\Delta H_f$  = latent heat of fusion

#### Determination of Molecular Mass from Depression in Freezing Point

The relationship between molar mass and depression in freezing point given as:

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

### 4. Osmosis and Osmotic Pressure

Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to concentrated solution) is termed as **osmosis**. The external pressure which must be applied on the solution in order to stop the flow of solvent into the solution through semi-permeable membrane is termed as **osmotic pressure**.

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

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 from Osmotic Pressure

Relationship between osmotic pressure and molar mass can be given as:

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

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**.

### Abnormal Molar Masses

Molar masses that are either lower or higher than the expected or normal values are called **abnormal molar masses**.

Association of molecules leads to decreases in the number of particles in solution resulting in decrease in the value of colligative properties while in case of dissociation, the number of particles increases in solution (when substance is an electrolyte) and the colligative properties increases accordingly.

#### van't Hoff Factor ( $i$ )

In 1880 van't Hoff introduced a factor  $i$ , known as the van't Hoff factor, to account for the extent of dissociation or association. This factor  $i$  is defined as

$$(i) \quad i = \frac{\text{number of particles after association / dissociation}}{\text{number of particles before association / dissociation}}$$

$$(ii) \quad i = \frac{\text{normal molecular mass}}{\text{abnormal molecular mass}}$$

$$(iii) \quad i = \frac{(\text{abnormal}) \text{ observed value of colligative property}}{(\text{normal}) \text{ calculated value of colligative property}}$$

#### Significance of van't Hoff Factor

Quantitatively the extent to which a solute is being associated or dissociated can be expressed by van't Hoff factor  $i$ .

- For dissociation,  $i > 1$  while for association  $i < 1$ .

- **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

Modified expressions of colligative properties are as follows:

- Relative lowering of vapour pressure

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

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

Here,  $m$  = molality

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

## DAY PRACTICE SESSION 1

# FOUNDATION QUESTIONS EXERCISE

- 1** A one molal solution of sodium chloride has a density of  $1.21 \text{ g mL}^{-1}$ . The molarity of this solution is  
 (a) 4.15 M (b) 1.143 M  
 (c) 2.95 M (d) 3.15 M
- 2** The density (in  $\text{g mL}^{-1}$ ) of a 3.60 M sulphuric acid solution having 29%  $\text{H}_2\text{SO}_4$  (molar mass =  $98 \text{ g mol}^{-1}$ ) by mass, will be  
 (a) 1.64 (b) 1.88 (c) 1.22 (d) 1.45
- 3** The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be → JEE Main 2013  
 (a) 1.00 M (b) 1.75 M  
 (c) 0.975 M (d) 0.875 M
- 4** 10 mL of 2 M NaOH solution is added to 200 mL of 0.5 M of NaOH solution. What is the final concentration?  
 → JEE Main (Online) 2013  
 (a) 0.57 M (b) 5.7 M (c) 11.4 M (d) 1.14 M
- 5** The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is  $1.15 \text{ g/mL}$ . The molarity of this solution is → AIEEE 2012  
 (a) 0.50 M (b) 1.78 M  
 (c) 1.02 M (d) 2.05 M
- 6** The density of 3 M solution of sodium chloride is  $1.252 \text{ g mL}^{-1}$ . The molality of the solution will be (molar mass, NaCl =  $58.5 \text{ g mol}^{-1}$ ) → JEE Main 2013  
 (a) 2.60 m (b) 2.18 m  
 (c) 2.79 m (d) 3.00 m
- 7** A 5.2 molal aqueous solution of methyl alcohol,  $\text{CH}_3\text{OH}$  is supplied. What is the mole fraction of methyl alcohol in the solution? → AIEEE 2011  
 (a) 0.100 M (b) 0.190 M  
 (c) 0.086 M (d) 0.050 M
- 8** 25 mL of a solution of barium hydroxide on titration with 0.1 molar solution of hydrochloric acid gave a titre value of 35 mL. The molarity of barium hydroxide solution was  
 (a) 0.07 M (b) 0.14 M  
 (c) 0.28 M (d) 0.35 M
- 9** At  $100^\circ\text{C}$ , benzene and toluene have vapour pressure of 1375 torr and 558 torr, respectively. Assuming, these two form an ideal binary solution, then calculate the mole fraction of benzene in vapour phase at 1 atm and  $100^\circ\text{C}$ ?  
 (a) 0.247 (b) 0.753  
 (c) 0.447 (d) 0.553
- 10** An aqueous solution of 2% (wt/wt) non-volatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute?  
 (a) 0.3655 (b) 36.55 (c) 41.37 (d) 40.16
- 11** Vapour pressure of pure benzene is 119 torr and that of toluene is 37.0 torr at the same temperature. Mole fraction of toluene in vapour phase, which is in equilibrium with a solution of benzene and toluene having a mole fraction of 0.50 will be → JEE Main (Online) 2013  
 (a) 0.137 (b) 0.237  
 (c) 0.435 (d) 0.205
- 12** On mixing, heptane and octane form an ideal solution at 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25 g of heptane and 35 g of octane will be (molar mass of heptane =  $100 \text{ g mol}^{-1}$  and of octane =  $114 \text{ g mol}^{-1}$ ). → AIEEE 2010  
 (a) 72.0 kPa (b) 36.1 kPa  
 (c) 96.2 kPa (d) 144.5 kPa
- 13** A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? → AIEEE 2009  
 (a) The solution formed is an ideal solution  
 (b) The solution is non-ideal, showing positive deviation from Raoult's law  
 (c) The solution is non-ideal, showing negative deviation from Raoult's law  
 (d) *n*-heptane shows positive deviation while ethanol show negative deviation from Raoult's law
- 14** If two liquids *A* and *B* form minimum boiling azeotrope at some specific composition then .....  
 (a) *A*—*B* interactions are stronger than those between *A*—*A* or *B*—*B*  
 (b) vapour pressure of solution increases because more number of molecules of liquids *A* and *B* can escape from the solution  
 (c) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution  
 (d) *A*—*B* interactions are weaker than those between *A*—*B* or *B*—*B*
- 15** An unknown compound is immiscible with water. It is steam distilled at  $98.0^\circ\text{C}$ . At  $98.0^\circ\text{C}$ , *p* and  $p_{\text{H}_2\text{O}}^\circ$  are respectively 737 and 707 torr. This distillate was 75% by weight of water. The molecular weight of the unknown compound will be  
 (a)  $318.15 \text{ g mol}^{-1}$  (b)  $300 \text{ g mol}^{-1}$   
 (c)  $306.76 \text{ g mol}^{-1}$  (d) None of these

- 16** The relative lowering of vapour pressure of an aqueous solution containing a non-volatile solute is 0.0125. The molality of the solution is  
 (a) 0.69 m (b) 0.50 m  
 (c) 0.80 m (d) 0.40 m
- 17** The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g glucose ( $C_6H_{12}O_6$ ) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be  
 (a) 16.500 mm Hg (b) 17.325 mm Hg  
 (c) 17.675 mm Hg (d) 15.750 mm Hg
- 18** A and B are ideal gases. The molecular weight of A and B are in the ratio of 1 : 4. The pressure of a gas mixture containing equal weight of A and B is  $p$  atm. What is the partial pressure (in atm) of B in the mixture?  
 (a)  $p/5$  (b)  $p/2$  (c)  $p/2.5$  (d)  $3p/4$
- 19** 18 g of glucose ( $C_6H_{12}O_6$ ) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is → JEE Main 2016  
 (a) 76.0 (b) 752.4 (c) 759.0 (d) 7.6
- 20** The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20 °C, its vapour pressure was 183 torr. The molar mass of the substance is → JEE Main 2015  
 (a) 32 (b) 64 (c) 128 (d) 488
- 21** 12 g of a non-volatile solute dissolved in 108g of water produces the relative lowering of vapour pressure of 0.1. The molecular mass of the solute (in g mol<sup>-1</sup>) is → JEE Main (Online) 2013  
 (a) 80 (b) 60 (c) 20 (d) 40
- 22** The Henry's law constant for the solubility of N<sub>2</sub> gas in water at 298 K is  $1.0 \times 10^5$  atm. The mole fraction of N<sub>2</sub> in air is 0.8. The number of moles of N<sub>2</sub> from air dissolved in 10 moles of water at 298 K and 5 atm pressure is  
 (a)  $4.0 \times 10^{-4}$  (b)  $4.0 \times 10^{-5}$   
 (c)  $5.0 \times 10^{-4}$  (d)  $4.0 \times 10^{-6}$
- 23** For a dilute solution containing 2.5 g of non-volatile, non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure of solution is ( $K_b = 0.76$  K kg mol<sup>-1</sup>) → AIEEE 2012  
 (a) 724 (b) 740 (c) 736 (d) 718
- 24** An aqueous solution freezes at  $-0.186^\circ\text{C}$  ( $K_f = 1.86$  K kg mol<sup>-1</sup>,  $K_b = 0.512$  K kg mol<sup>-1</sup>). What is the elevation in boiling point?  
 (a)  $0.186^\circ\text{C}$  (b)  $0.512^\circ\text{C}$   
 (c)  $0.86^\circ\text{C}$  (d)  $0.0512^\circ\text{C}$
- 25** When mercuric iodide is added to the aqueous solution of potassium iodide, the  
 (a) freezing point is raised  
 (b) freezing point is lowered  
 (c) freezing point does not change  
 (d) boiling point does not change
- 26** The molecular weight of benzoic acid in benzene is determined by depression in freezing point method corresponds to  
 (a) ionisation of benzoic acid  
 (b) dimerisation of benzoic acid  
 (c) trimerisation of benzoic acid  
 (d) solvation of benzoic acid
- 27** The depression in freezing point of 0.01 M aqueous solution of urea, sodium chloride and sodium sulphate is in the ratio of  
 (a) 1 : 1 : 1 (b) 1 : 2 : 3 (c) 1 : 2 : 4 (d) 2 : 2 : 3
- 28** During depression in freezing point of a solution, the following are in equilibrium  
 (a) liquid solvent, solid solvent  
 (b) liquid solvent, solid solute  
 (c) liquid solute, solid solute  
 (d) liquid solute, solid solvent
- 29** How many grams of methyl alcohol should be added to 10 L tank of water to prevent its freezing at 268 K? ( $K_f$  for water is 1.86 K kg mol<sup>-1</sup>) → JEE Main (Online) 2013  
 (a) 880.07 g (b) 899.04 g  
 (c) 886.02 g (d) 868.06 g
- 30**  $K_f$  for water is 1.86 K kg mol<sup>-1</sup>. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ( $C_2H_6O_2$ ) you must add to get the freezing point of the solution lowered to  $-2.8^\circ\text{C}$ ? → AIEEE 2012  
 (a) 72 g (b) 93 g (c) 39 g (d) 27 g
- 31** Ethylene glycol is used as an antifreeze in cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at  $-6^\circ\text{C}$  will be ( $K_f$  for water = 1.86 K kg mol<sup>-1</sup> and molar mass of ethylene glycol = 62 g mol<sup>-1</sup>). → AIEEE 2011  
 (a) 800.00 g (b) 204.30 g (c) 400.00 g (d) 304.60 g
- 32** The molar mass of a solute  $\chi$  in g mol<sup>-1</sup>. If its 1% solution is isotonic with 95% solution of cane sugar (molar mass = 342 g mol<sup>-1</sup>) is  
 (a) 68.4 (b) 34.2 (c) 136.2 (d) 171.2
- 33** Match the following and choose the correct option.
- |    | Column I                   | Column II                                    |
|----|----------------------------|--|
| A. | Raoult's law               | 1. $p = K_H \chi$                            |
| B. | Elevation of boiling point | 2. $\pi = CRT$                               |
| C. | Henry's law                | 3. $p = \chi_1 p_1^\circ + \chi_2 p_2^\circ$ |
| D. | Osmotic pressure           | 4. $\Delta T_b = K_b m$                      |
- |     |   |   |   |   |
|-----|---|---|---|---|
|     | A | B | C | D |
| (a) | 3 | 4 | 1 | 2 |
| (b) | 2 | 1 | 4 | 3 |
| (c) | 4 | 1 | 2 | 3 |
| (d) | 1 | 3 | 2 | 4 |
- 34** 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<sup>-1</sup>), 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

**35** We have 3 aqueous solution of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solution will be in the order of

- (a)  $i_A < i_B < i_C$  (b)  $i_A > i_B > i_C$   
 (c)  $i_A = i_B = i_C$  (d)  $i_A < i_B > i_C$

**36** Which one of the following aqueous solutions will exhibit highest boiling point?

- (a) 0.01 M  $\text{Na}_2\text{SO}_4$  (b) 0.01 M  $\text{KNO}_3$   
 (c) 0.015 M urea (d) 0.015 M glucose

**37** A compound X undergoes tetramerisation in a given organic solvent. The van't Hoff factor is

- (a) 4.0 (b) 0.25  
 (c) 0.125 (d) 2.0

**38** The degree of dissociation ( $\alpha$ ) of a weak electrolyte,  $A_xB_y$ , is related to van't Hoff factor ( $i$ ) by the expression

- (a)  $\alpha = \frac{i-1}{(x+y-1)}$  (b)  $\alpha = \frac{i-1}{x+y+1}$   
 (c)  $\alpha = \frac{x+y-1}{i-1}$  (d)  $\alpha = \frac{x+y+1}{i-1}$  → AIEEE 2011

**39** Which of the following aqueous solutions should have the highest boiling point?

- (a) 1.0 M NaOH (b) 1.0 M  $\text{Na}_2\text{SO}_4$   
 (c) 1.0 M  $\text{NH}_4\text{NO}_3$  (d) 1.0 M  $\text{KNO}_3$

**40** In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionisation is 0.3. Taking  $K_f$  for water as  $1.85 \text{ K kg mol}^{-1}$ , the freezing point of the solution will be nearest to

- (a)  $-0.360^\circ\text{C}$  (b)  $-0.260^\circ\text{C}$   
 (c)  $+0.480^\circ\text{C}$  (d)  $-0.481^\circ\text{C}$

**41** In comparison to a 0.01M solution of glucose, the depression in freezing point of a 0.01M  $\text{MgCl}_2$  solution is

- (a) the same (b) about twice  
 (c) about three times (d) about six times

**42** The freezing point (in  $^\circ\text{C}$ ) of a solution containing 0.1 g of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (mol. wt.  $329 \text{ gmol}^{-1}$ ) in 100 g of water ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ) is

- (a)  $-2.3 \times 10^{-2}$  (b)  $-5.7 \times 10^{-2}$   
 (c)  $-5.7 \times 10^{-3}$  (d)  $-1.2 \times 10^{-2}$

**43** For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point?

→ JEE Main 2018

- (a)  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$  (b)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (d)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$

**44** The freezing point of benzene decreases by  $0.45^\circ\text{C}$  when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene,

percentage association of acetic acid in benzene will be ( $K_f$  for benzene =  $5.12 \text{ K kg mol}^{-1}$ ) → JEE Main 2017

- (a) 64.6 % (b) 80.4 %  
 (c) 74.6 % (d) 94.6 %

**45** If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water ( $\Delta T_f$ ), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ) → AIEEE 2010

- (a) 0.0372 K (b) 0.0558 K  
 (c) 0.0744 K (d) 0.0186 K

**46** Consider separate solution of 0.500 M  $\text{C}_2\text{H}_5\text{OH}(aq)$ , 0.100M  $\text{Mg}_3(\text{PO}_4)_2(aq)$ , 0.250M  $\text{KBr}(aq)$  and 0.125M  $\text{Na}_3\text{PO}_4(aq)$  at  $25^\circ\text{C}$ . Which statement is true about these solution, assuming all salts to be strong electrolytes? → JEE Main 2014

- (a) They all have the same osmotic pressure  
 (b) 0.100 M  $\text{Mg}_3(\text{PO}_4)_2(aq)$  has the highest osmotic pressure  
 (c) 0.125 M  $\text{Na}_3\text{PO}_4(aq)$  has the highest osmotic pressure  
 (d) 0.500 M  $\text{C}_2\text{H}_5\text{OH}(aq)$  has the highest osmotic pressure

**Direction** (Q. Nos. 47-50) In the following question, Assertion (A) followed by a Reason (R) is given. Choose the correct option.

- (a) Both A and R are true and R is correct explanation of A  
 (b) Both A and R are true but R is not correct explanation of A  
 (c) A is true but R is false  
 (d) Both A and R are false

**47 Assertion** (A) When methyl alcohol is added to water, boiling point of water increases.

**Reason** (R) When a volatile solute is added to a volatile solvent, elevation in boiling point is observed.

**48 Assertion** (A) Molarity of a solution in liquid state changes with temperature.

**Reason** (R) The volume of a solution changes with change in temperature.

**49 Assertion** (A) Osmotic pressure of 1 M glucose is lesser than 1 M NaCl (aq) but vapour pressure of 1 M glucose is higher than 1 M NaCl.

**Reason** (R) Osmotic pressure is a colligative property but vapour pressure is not a colligative property, however relative lowering in vapour pressure is a colligative property.

**50 Assertion** (A) Ebullioscopy or cryoscopy cannot be used for the determination of molecular weight of polymers.

**Reason** (R) High molecular weight solute leads to very low value of  $\Delta T_b$  or  $\Delta T_f$ .

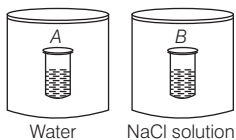


## DAY PRACTICE SESSION 2

# PROGRESSIVE QUESTIONS EXERCISE

- 1** The elevation in boiling point of a solution of 13.44 g of  $\text{CuCl}_2$  in 1 kg of water using the following information will be (molecular weight of  $\text{CuCl}_2 = 134.4$  and  $K_b = 0.52 \text{ K mol}^{-1}$ )  
 (a) 0.16 (b) 0.05 (c) 0.1 (d) 0.2
- 2** How many mL of 0.1 M HCl are required to react completely with 1g mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  containing equimolar amount of these two?  
 (a) 157.8 mL (b) 0.1578 mL (c) 210.4 mL (d) 105.2 mL
- 3** Which of the following liquid pairs shows a positive deviation from Raoult's law?  
 (a) Water — Hydrochloric acid  
 (b) Benzene — Methanol  
 (c) Water — Nitric acid  
 (d) Acetone — Chloroform
- 4** To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorus acid ( $\text{H}_3\text{PO}_3$ ), the volume of 0.1 M aqueous KOH solution required is  
 (a) 10 mL (b) 20 mL  
 (c) 40 mL (d) 60 mL
- 5** At  $10^\circ\text{C}$ , the osmotic pressure of urea solution is 500 mm Hg. The solution is diluted and the temperature is raised to  $25^\circ\text{C}$ . The osmotic pressure of dilute solution is 105.3 mm Hg at  $25^\circ\text{C}$ . The extent of dilution can be shown as  
 (a)  $V_{\text{final}} = 5 V_{\text{initial}}$  (b)  $V_{\text{initial}} > V_{\text{final}}$   
 (c)  $V_{\text{final}} = 4 V_{\text{initial}}$  (d)  $V_{\text{final}} = 6 V_{\text{initial}}$
- 6** Plot of  $\frac{1}{\chi_A}$  vs  $\frac{1}{\chi_A}$  ( $\chi_A =$  mole fraction of A in liquid and  $\chi_A$  in vapour) is linear whose slope and intercept respectively are given  
 (a)  $\frac{p_B^\circ}{p_A^\circ}, \frac{p_B^\circ - p_A^\circ}{p_B^\circ}$  (b)  $p_A^\circ - p_B^\circ, \frac{p_A^\circ - p_B^\circ}{p_B^\circ}$   
 (c)  $\frac{p_A^\circ}{p_B^\circ}, \frac{p_B^\circ - p_A^\circ}{p_B^\circ}$  (d)  $\frac{p_B^\circ}{p_A^\circ}, \frac{p_A^\circ - p_B^\circ}{p_B^\circ}$
- 7** Two liquids X and Y form an ideal solution at 300 K, vapour pressure of the solution containing 1 mole of X and 3 moles of Y is 550 mm Hg. At the same temperature, if 1 mole of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively  
 (a) 200 and 300  
 (b) 300 and 400  
 (c) 400 and 600  
 (d) 500 and 600
- 8** 58.5 g of NaCl and 180 g of glucose were separately dissolved in 1000 mL of water. Identify the correct statement regarding the elevation of boiling point (b.p.) of the resulting solutions.  
 (a) NaCl solution will show higher elevation of boiling point  
 (b) Glucose solution will show higher elevation of boiling point  
 (c) Both the solutions will show equal elevation of boiling point  
 (d) The boiling point elevation will be shown by neither of the solution
- 9** The vapour pressure of benzene at a certain temperature is 640 mm Hg. A non-volatile, non-electrolyte solute 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 weight of the solid substance?  
 (a) 6.96  
 (b) 65.3  
 (c) 63.8  
 (d) None of the above
- 10** The vapour pressure of a solvent decreases by 10 mm of mercury, when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent, if the decrease in vapour pressure is to be 20 mm of mercury?  
 (a) 0.8 (b) 0.6  
 (c) 0.4 (d) 0.7
- 11** At 310 K, the vapour pressure of an ideal solution containing 2 moles of A and 3 moles of B is 550 mm of Hg. At the same pressure if one mole of B is added to this solution, the vapour pressure of solution increased by 10 mm of Hg. What is the vapour pressure of A in its pure state?  
 (a) 460 mm (b) 610 mm  
 (c) 360 mm (d) 750 mm
- 12** 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 ( $\pi$ ) 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  $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{sucrose}$   
 (d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

- 13** Two beakers of capacity 500 mL were taken. One of these beakers, labelled as A, was filled with 400 mL water whereas, the beaker labelled B was filled with 400 mL of 2 M solution of NaCl. At the same temperature, both the beakers were placed in closed containers of same material and same capacity as shown in the figure. At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution?



- (a) Vapour pressure in container A is more than that in container B  
 (b) Vapour pressure in container A is less than that in container B

- (c) Vapour pressure is equal in both the containers  
 (d) Vapour pressure in container B is twice the vapour pressure in container A

- 14** A 0.001 molal solution of  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_4]$  in water had a freezing point depression of  $0.0054^\circ\text{C}$ . If  $K_f$  for water is 1.80, the correct formulation of the above molecule is  
 (a)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_3]\text{Cl}$  (b)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$   
 (c)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}]\text{Cl}_3$  (d)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_4]$

- 15** Sea water is found to contain 5.85% NaCl and 9.5%  $\text{MgCl}_2$  by weight of solution. Calculate its normal boiling point assuming 70% ionisation for NaCl and 50% ionisation of  $\text{MgCl}_2$  [ $K_b(\text{H}_2\text{O}) = 0.51 \text{ K kg mol}^{-1}$ ]  
 (a)  $101.4^\circ\text{C}$  (b)  $102.29^\circ\text{C}$   
 (c)  $103.27^\circ\text{C}$  (d)  $99.46^\circ\text{C}$

## ANSWERS

<b>SESSION 1</b>									
1 (b)	2 (c)	3 (d)	4 (a)	5 (d)	6 (c)	7 (c)	8 (b)	9 (c)	10 (c)
11 (b)	12 (a)	13 (b)	14 (b)	15 (a)	16 (a)	17 (b)	18 (a)	19 (b)	20 (b)
21 (c)	22 (a)	23 (a)	24 (d)	25 (a)	26 (b)	27 (b)	28 (a)	29 (c)	30 (b)
31 (a)	32 (a)	33 (a)	34 (a)	35 (b)	36 (a)	37 (b)	38 (a)	39 (b)	40 (d)
41 (c)	42 (a)	43 (d)	44 (d)	45 (b)	46 (a)	47 (d)	48 (a)	49 (a)	50 (a)
<b>SESSION 2</b>									
1 (a)	2 (a)	3 (b)	4 (c)	5 (a)	6 (c)	7 (c)	8 (a)	9 (b)	10 (b)
11 (a)	12 (d)	13 (a)	14 (b)	15 (b)					

## Hints and Explanations

### SESSION 1

- 1** Molar mass of  $\text{NaCl} = M_2 = 58.5 \text{ g}$

$$M = \frac{m \times d}{1 + \frac{m \times M_2}{1000}}$$

$$M = \frac{1 \times 1.21}{1 + \frac{1 \times 58.5}{1000}} = 1.143 \text{ M}$$

- 2** Molarity

$$= \frac{10 \times \text{density} \times \% \text{ by weight of solute}}{\text{molecular weight of the solute}}$$

$$\text{Density} = \frac{3.60 \times 98}{10 \times 29} = 1.216 \text{ g/mL}$$

$$\approx 1.22 \text{ g/mL}$$

- 3**  $M_1V_1 + M_2V_2 = MV$  (Total moles)

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

$$M = \frac{0.5 \times 750 + 2 \times 250}{1000}$$

$$M = 0.875 \text{ M}$$

- 4** Final concentration,  $M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$

$$= \frac{10 \times 2 + 200 \times 0.5}{200 + 10}$$

$$= \frac{20 + 100}{210} = \frac{120}{210} = 0.57 \text{ M}$$

- 5** Total mass of solution

$$= 1000 \text{ g water} + 120 \text{ g urea}$$

$$= 1120 \text{ g}$$

$$\text{Density of solution} = 1.15 \text{ g/mL}$$

$$\text{Volume of solution}$$

$$= \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{1120 \text{ g}}{1.15 \text{ g/mL}}$$

$$= 973.91 \text{ mL} = 0.974 \text{ L}$$

$$\text{Moles of solute} = \frac{120}{60} = 2$$

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

$$= \frac{2}{0.974} = 2.05 \text{ mol/L}$$

- 6** 3M solution means 3 moles of solute

(NaCl) are present in 1000 L of solution.

$$\text{Mass of solution} = \text{volume of solution} \times \text{density}$$

$$= 1000 \times 1.252 = 1252 \text{ g}$$

$$\text{Mass of solute} = \text{Number of moles} \times \text{molar mass of NaCl}$$

$$= 3 \times 58.5 \text{ g}$$

$$= 175.5 \text{ g}$$

$$\text{Mass of solvent} = (1252 - 175.5) \text{ g}$$

$$= 1076.5 \text{ g}$$

$$= 1.076 \text{ kg}$$

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

$$= \frac{3}{1.076} = 2.79 \text{ m}$$

$$\begin{aligned} \text{7 Molality} &= \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}} \\ &= \frac{5.2 \text{ mol CH}_3\text{OH}}{1 \text{ kg (1000 g) H}_2\text{O}} \end{aligned}$$

$$n_1 (\text{CH}_3\text{OH}) = 5.2$$

$$n_2 (\text{H}_2\text{O}) = \frac{1000}{18} = 55.56$$

$$\therefore n_1 + n_2 = 5.20 + 55.56 = 60.76 \text{ mol}$$

$$\begin{aligned} \therefore \text{Mole fraction of CH}_3\text{OH, } \chi_{\text{CH}_3\text{OH}} &= \frac{n_1}{n_1 + n_2} = \frac{5.2}{60.76} = 0.086 \end{aligned}$$

8 Let, molarity of  $\text{Ba(OH)}_2 = M_1$

Let the molarity of  $\text{HCl} = M_2$

$$\therefore M_1 V_1 = M_2 V_2$$

$$M_1 \times 25 = 0.1 \times 35$$

$$M_1 = \frac{3.5}{25} \text{ M} = 0.14 \text{ M}$$

9 Let  $\chi_1$  be the mole fraction of benzene in solution and  $(1 - x)$  be the mole fraction of toluene.

Applying Raoult's law,

$$p_r = \chi_1 p_1^\circ + (1 - \chi_1) p_2^\circ$$

$$\text{or } 760 = \chi_1 (1375) + (1 - \chi_1) (558)$$

$$\text{or } \chi_1 = \frac{760 - 558}{1375 - 558} = 0.247 \text{ torr}$$

Mole fraction of benzene in vapour phase at 1 atm

$$\chi_1 = \frac{\chi_1 p_1^\circ}{p} = \frac{0.247 \times 1375}{760} = 0.447$$

10  $p^\circ = 1.013 \text{ bar} = 1 \text{ atm}$  (at boiling point)

$$w_{\text{solvent}} = 100 - 2 = 98 \text{ g,}$$

According to Raoult's law,

$$\frac{p^\circ - p_1}{p^\circ} = \frac{w_{\text{solute}}}{M_{\text{solute}}} \times \frac{M_{\text{solvent}}}{w_{\text{solvent}}}$$

$$\frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{M_{\text{solute}} \times 98}$$

$$\therefore M_{\text{solute}} = 41.37 \text{ g mol}^{-1}$$

11 From Raoult's law, for ideal solution,

$$p_{\text{total}} = p_B^\circ \chi_B + p_T^\circ \chi_T$$

$$= 119 \times 0.5 + 37 \times 0.5 \quad (\because \chi_B = 1 - \chi_T)$$

$$= 59.5 + 18.5 = 78 \text{ torr}$$

Mole fraction of toluene in vapour phase

$$(\chi_T)_v = \frac{p_T^\circ \chi_T}{p} = \frac{18.5}{78} = 0.237$$

12  $p_T = \chi_H \cdot p_H^\circ + \chi_O \cdot p_O^\circ$

$$\chi_H = \frac{25/100}{\frac{25}{100} + \frac{35}{114}} = 0.45$$

$$\therefore \chi_O = 1 - 0.45 = 0.55$$

$$p_T = 0.45 \times 105 + 0.55 \times 45 = 72 \text{ kPa}$$

13 *n*-heptane and ethanol forms non-ideal solution. As a result, *n*-heptane-ethanol molecular interaction is very poor in comparison to ethanol-ethanol or *n*-heptane-*n*-heptane interactions. So, the resulting solution gives positive deviation from Raoult's law.

14 Minimum boiling azeotrope shows positive deviations from Raoult's law due to the stronger solute-solute interactions.

15 Since, unknown compound is immiscible with water, hence vapour pressure  $\propto$  moles.

$$\text{Given, } p_{\text{total}}^\circ = 737 \text{ torr}$$

$$p_{\text{H}_2\text{O}}^\circ = 707 \text{ torr,}$$

$$\therefore p_{\text{unknown}}^\circ = 737 - 707 = 30 \text{ torr}$$

$$\begin{aligned} \frac{p_{\text{unknown}}^\circ}{p_{\text{water}}^\circ} &= \frac{n_{\text{unknown}}}{n_{\text{H}_2\text{O}}} \\ &= \frac{W_{\text{unknown}} \times m_{\text{H}_2\text{O}}}{W_{\text{H}_2\text{O}} \times m_{\text{unknown}}} \end{aligned}$$

$$\text{or } \frac{30}{707} = \frac{75.0 \times 18}{100 \times m_{\text{unknown}}}$$

$$\text{or } m_{\text{unknown}} = 318.15 \text{ g mol}^{-1}$$

$$16 \frac{p^\circ - p_1}{p^\circ} = x_2 = \frac{mM_1}{1000 + mM_1}$$

(For dilute solutions,  $1000 \gg mM_1$ )

$$\frac{p^\circ - p_1}{p^\circ} = \frac{m \times M}{1000}$$

$$0.0125 = \frac{m \times 18}{1000}$$

$$m = \frac{0.0125 \times 1000}{18} = 0.69 \text{ mol}$$

$$17 \frac{p^\circ - p_1}{p^\circ} = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$$

$$\text{or } \frac{17.5 - p_1}{p^\circ} = \frac{18/180}{178.2/18 + 18/180}$$

$$\text{or } \frac{17.5 - p_1}{17.5} = \frac{1/10}{9.9 + 0.1}$$

$$\text{or } p_1 = 17.325 \text{ mm Hg.}$$

18 Molecular weight ratio of A and B = 1:4

$\therefore$  Mole ratio of A and B, if equal weight of A and B are taken = 4:1

$$\text{Partial pressure of B} = \frac{1}{5} \times p = \frac{p}{5}$$

19 (b) Vapour pressure of water ( $p^\circ$ ) = 760 torr

Number of moles of glucose

$$= \frac{\text{Mass (in g)}}{\text{Molecular mass (g mol}^{-1}\text{)}}$$

$$= \frac{18 \text{ g}}{180 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

Molar mass of water = 18 g/mol

Mass of water (given) = 178.2g

Number of moles of water

$$= \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{178.2 \text{ g}}{18 \text{ g/mol}} = 9.9 \text{ mol}$$

Total number of moles = (0.1 + 9.9) moles = 10 mol

Now, mole fraction of glucose in solution = Change in pressure with respect to initial pressure,

$$\text{i.e. } \frac{\Delta p}{p^\circ} = \frac{0.1}{10}$$

$$\text{or } \Delta p = 0.01 p^\circ = 0.01 \times 760 = 7.6 \text{ torr}$$

$$\therefore \text{Vapour pressure of solution} = (760 - 7.6) \text{ torr} = 752.4 \text{ torr}$$

20 Given,  $p^\circ = 185 \text{ torr}$  at  $20^\circ\text{C}$ ,

$$p_1 = 183 \text{ torr at } 20^\circ\text{C}$$

Mass of non-volatile substance,

$$m = 1.2 \text{ g}$$

Mass of acetone taken = 100 g

$$\text{As, we have } \frac{p^\circ - p_1}{p_1} = \frac{n_B}{n_A}$$

$$\therefore \frac{185 - 183}{183} = \frac{\frac{1.2}{M}}{\frac{100}{100 \times M}} \Rightarrow \frac{2}{183} = \frac{12 \times 58}{100 \times M}$$

$$\therefore M = \frac{183 \times 12 \times 58}{2 \times 100}$$

$$M = 63.684 \approx 64 \text{ g/mol}$$

21 The relationship between molar mass of solute and relative lowering in vapour pressure is given as:

$$\Delta p = \frac{p^\circ - p}{p^\circ} = \frac{n_B}{n_A} = \frac{w}{m} \times \frac{M}{W}$$

$$w = 12 \text{ g; } W = 108 \text{ g, } m = ?$$

$$M = 18 \text{ g, } \Delta p = 0.1$$

$$\Delta p = \frac{w}{m} \times \frac{M}{W}, 0.1 = \frac{12}{m} \times \frac{18}{108}$$

$$m = \frac{12 \times 18}{10.8} = 20$$

22 According to Henry's law,  $p = K_H \chi$

where,  $\chi$  = mole fraction

$$n_{\text{N}_2} = n_{\text{H}_2\text{O}} \times \frac{p_{\text{N}_2}}{K_H} \Rightarrow p_{\text{N}_2} = \chi_{\text{N}_2} \times p$$

$$p_{\text{N}_2} = 0.8 \times 5 = 4 \text{ atm}$$

$$\therefore n_{\text{N}_2} = 10 \times \frac{4}{1 \times 10^5} = 4 \times 10^{-4} \text{ moles}$$

23 The elevation in boiling point is

$$\Delta T_b = K_b \cdot m \left( \text{where, } m = \frac{n_2 \times 1000}{w_1} \right)$$

$$\Delta T_b = 2 = \frac{0.76 \times n_2 \times 1000}{100} \quad \text{or } n_2 = \frac{5}{19}$$

From Raoult's law of lowering of vapour pressure

$$\frac{\Delta p}{p^\circ} = \chi_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} (\because n_1 \gg n_2)$$

$$\Delta p = 760 \times \frac{5 \times 18}{19 \times 100} = 36 \text{ mm of Hg}$$

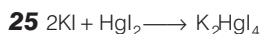
$$p = 760 - 36 = 724 \text{ mm of Hg}$$

$$24 \quad \Delta T_f = T_f^\circ - T_f = 0 - (-0.186) = 0.186^\circ\text{C}$$

$$\Delta T_f = K_f \times m \Rightarrow 0.186 = 1.86 \times m$$

$$\text{or } m = 0.1,$$

$$\Delta T_b = K_b \times m = 0.512 \times 0.1 = 0.0512^\circ\text{C}$$



As a result of this reaction, number of ions decreases. So, the lowering in freezing point is less or the actual freezing point is raised.

26 Benzoic acid undergoes dimerisation in benzene.

27 Concentrations of particles of 0.01 M urea, NaCl and  $\text{Na}_2\text{SO}_4$  are 0.01 M, 0.02 M, 0.03 M respectively, i.e. they are in the ratio of 1:2:3. Hence, depression in freezing point will be in the same ratio.

28 When freezing starts, liquid solvent is in equilibrium with the solid solvent (both have the same vapour pressure).

29 Normal freezing point of water = 273.15K. In order to prevent freezing at 268 K, let the amount of methanol added be  $x$  g.

$$\therefore \text{Molality, } m = \frac{x}{32 \times 10} = \frac{x}{320}$$

[ $\because$  Molar mass of  $\text{CH}_3\text{OH} = 32 \text{ g mol}^{-1}$  and mass of  $\text{H}_2\text{O} = V$  of  $\text{H}_2\text{O}$  because density of water  $\approx 1 \text{ g L}^{-1}$ ]

Lowering, in freezing point =  $K_f \cdot m$

$$273.15 - 268 = 1.86 \times \frac{x}{320}$$

$$5.15 = \frac{1.86x}{320}$$

$$\text{or } x = \frac{5.15 \times 320}{1.86} = 886.02 \text{ g}$$

30 Coolant is glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ), which is non-electrolyte.

$$\Delta T_f = 2.8^\circ\text{C}$$

$$\Delta T_f = \frac{1000 K_f w_2}{M_1 \times w_1}$$

$$2.8 = \frac{1000 \times 1.86 \times w_1}{62 \times 1000}$$

$$\therefore w_1 = 93.33 \text{ g} \approx 93 \text{ g}$$

31  $\Delta T_f =$  Freezing point of  $\text{H}_2\text{O}$  - freezing point of ethylene glycol solution =  $0 - (-6) = 6^\circ\text{C}$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$w_2 =$  Mass of ethylene glycol in grams

$w_1 =$  Mass of solvent ( $\text{H}_2\text{O}$ ) in grams = 4000 g

$m_2 =$  Molar mass of ethylene glycol =  $62 \text{ g mol}^{-1}$

$i =$  van't Hoff factor = 1

( $\because$  ethylene glycol is non-electrolyte)

$$\text{From, } \Delta T_f = \frac{i \times 1000 K_f w_2}{m_2 w_1}$$

$$\therefore 6 = \frac{1000 \times 1.86 \times w_2 \times 1}{62 \times 4000}$$

$$w_2 = 800 \text{ g}$$

32 For isotonic solutions,  $\pi_1 = \pi_2$

$$\frac{n_1 RT}{V_1} = \frac{n_2 RT}{V_2} \Rightarrow \frac{n_1}{V_1} = \frac{n_2}{V_2}$$

$$\text{Thus, } \frac{w_1}{V_1 m_1} = \frac{w_2}{V_2 m_2}, \frac{w_1}{V_1} = 1, \frac{w_2}{V_2} = 5$$

$$m_1 = ?, m_2 = 342, \frac{1}{m_1} = \frac{5}{342}$$

$$\therefore m_1 = \frac{342}{5} = 68.4 = x$$

i.e. molar mass of solute  $x$  is  $68.4 \text{ g mol}^{-1}$ .

33  $A \rightarrow 3, B \rightarrow 4, C \rightarrow 1, D \rightarrow 2$

34 Actual molecular weight of naphthoic acid, ( $\text{C}_{11}\text{H}_8\text{O}_2$ ) = 172

Molecular mass (calculated)

$$= \frac{1000 \times K_f \times w_{\text{solute}}}{w_{\text{solvent}} \times \Delta T_f}$$

$$= \frac{1000 \times 1.72 \times 20}{50 \times 2} = 344$$

van't Hoff factor ( $i$ )

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

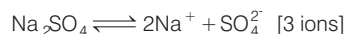
$$= \frac{172}{344} = 0.5$$

35 Greater the dilution, greater is the dissociation into ions and hence, greater is the van't Hoff factor.

The value of van't Hoff factor for these solution will be in the order of,  $i_A > i_B > i_C$

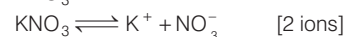
36 Boiling point of the solution is directly proportional to van't Hoff factor. Thus, for

(a)  $\text{Na}_2\text{SO}_4$



$$\therefore i = 3$$

(b)  $\text{KNO}_3$



$$\therefore i = 2$$

Urea [ $(\text{NH}_2\text{CONH}_2)$ ] and glucose are poor electrolytes, therefore  $i$  for these two solutes are equal to zero.

Hence, 0.01 M  $\text{Na}_2\text{SO}_4$  possess highest boiling point.

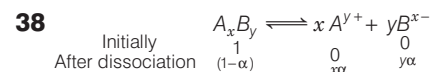


Initially 1 0  
After association  $1 - \alpha$   $\alpha/4$

$$i = \frac{1 - \alpha + \frac{\alpha}{4}}{1} = 1 - \frac{3}{4}\alpha$$

$\alpha =$  degree of dissociation = 1 or 100%

$$\therefore i = 1 - \frac{3}{4} = 0.25$$



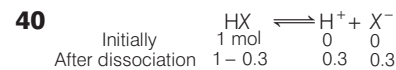
$$i = n(A_x B_y) + n(A^{y+}) + n(B^{x-})$$

$$= 1 - \alpha + x\alpha + y\alpha$$

$$= 1 + \alpha(x + y - 1)$$

$$\therefore \alpha = \frac{i - 1}{(x + y - 1)}$$

39 Boiling point of the solution is directly proportional to van't Hoff factor.  $\text{Na}_2\text{SO}_4$  possess larger value of  $i$  than other given solutions. Hence, 1.0 M  $\text{Na}_2\text{SO}_4$  solution would have highest boiling point.



Total moles =  $1 - 0.3 + 0.3 + 0.3 = 1.3$ ,

$$i = \frac{1.3}{1} = 1.3$$

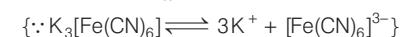
$$\Delta T_f = i K_f m = 1.3 \times 1.85 \times 0.2 = 0.418 \text{ K}$$

$$\therefore T_f = 273 - 0.418 \text{ K} = 272.519 \text{ K}$$

or  $-0.418^\circ\text{C}$

41 Being a non-electrolyte glucose does not undergo ionisation when dissolved in water whereas,  $\text{MgCl}_2$  releases 3 ions [ $\text{Mg}^{2+} + 2\text{Cl}^-$ ] when dissolved in water. Thus,  $i$  for  $\text{MgCl}_2$  is 3, while that of glucose is 0. Therefore, depression of freezing point of 0.01 M  $\text{MgCl}_2$  solution is about three times than 0.01 M glucose solution.

42 van't Hoff factor ( $i$ ) = 4



$$\text{Molality} = \frac{0.1 \times 1000}{329 \times 100} = \frac{1}{329}$$

$$-T_f = i K_f m$$

$$\Rightarrow -4 \times 1.86 \times \frac{1}{329} = -2.3 \times 10^{-2}$$

(As freezing point of water is  $0^\circ\text{C}$ .)

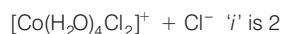
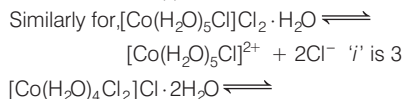
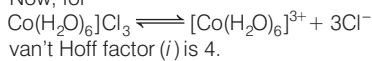
43 "Addition of solute particles to a pure solvent results into depression in its freezing point."

All the compounds given in question are ionic in nature. So, consider their van't Hoff factor ( $i$ ) to reach at final conclusion.

The solution with maximum freezing point must have minimum number of solute particles. This generalisation can be done with the help of van't Hoff factor ( $i$ ), i.e. number of solute particles  $\propto$  van't Hoff factor ( $i$ ).

Thus, we can say directly solution with maximum freezing point will be the one in which solute with minimum van't Hoff factor is present

Now, for



and for  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ , ' $i$ ' is 1 as it does not show ionisation. Hence,  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$  have minimum number of particles in the solution.

So, freezing point of its solution will be maximum.

- 44** Let the degree of association of acetic acid ( $\text{CH}_3\text{COOH}$ ) in benzene is  $\alpha$ , then



Initial moles	1	0
Moles at equilib.	$1 - \alpha$	$\frac{\alpha}{2}$

$$\therefore \text{Total moles} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$\text{or } i = 1 - \frac{\alpha}{2}$$

Now, depression in freezing point ( $\Delta T_f$ ) is given as

$$\Delta T_f = i K_f m \quad \dots (i)$$

where,  $K_f$  = molal depression constant or cryoscopic constant.

$m$  = molality

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent (in kg)}}$$

$$= \frac{0.2}{60} \times \frac{1000}{20}$$

Putting the values in Eq. (i),

$$\therefore 0.45 = \left[1 - \frac{\alpha}{2}\right] (5.12) \left[\frac{0.2}{60} \times \frac{1000}{20}\right]$$

$$1 - \frac{\alpha}{2} = \frac{0.45 \times 60 \times 20}{5.12 \times 0.2 \times 1000}$$

$$\Rightarrow 1 - \frac{\alpha}{2} = 0.527 \Rightarrow \frac{\alpha}{2} = 1 - 0.527$$

$$\therefore \alpha = 0.946$$

Thus, percentage of association = 94.6%

- 45**  $\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$

$\therefore$  van't Hoff factor ( $i$ ) for  $\text{Na}_2\text{SO}_4$  = 3

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

$$= 3 \times 1.86 \times 0.01 = 0.0558 \text{ K}$$

$$\left[ \therefore m = \frac{0.01}{1} = 0.01 \right]$$

- 46** Effective molarity

= van't Hoff factor  $\times$  molarity

$$0.5 \text{ M C}_2\text{H}_5\text{OH}(aq) \quad i = 1$$

Effective molarity = 0.5

$$0.25 \text{ M KBr}(aq), \quad i = 2$$

Effective molarity = 0.5 M

$$0.1 \text{ M Mg}_3(\text{PO}_4)_2(aq), \quad i = 5$$

Effective molarity = 0.5 M

$$0.125 \text{ M Na}_3\text{PO}_4(aq), \quad i = 4$$

Effective molarity = 0.5 M

Hence, all solutions have same osmotic pressure.

- 47 Assertion** When methyl alcohol is added to water, boiling point of water decreases.

**Reason** When a more volatile solute is added to volatile solvent, vapour pressure of solvent increases and hence boiling point decreases but for non-volatile solute it is *vice-versa*.

- 48 Assertion and Reason both are correct statements and Reason is the correct explanation of Assertion.**

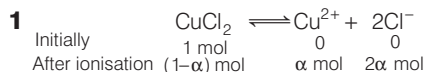
Volume of solutions is a function of temperature which varies with temperature. Hence, molarity of solution in liquid state changes with temperature.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

- 49 Both Assertion and Reason are correct and Reason is the correct explanation of the Assertion.** Osmotic pressure is a colligative property while vapour pressure is not a colligative property.

- 50** The changes observed in these properties are very small, (e.g. 0.00001 K for substances having molar masses of the order of  $10^6 \text{ g mol}^{-1}$ ). A little error in measurement of  $\Delta T_b$  or  $\Delta T_f$  will cause abnormal values of molecular weight.

## SESSION 2



After ionisation (1- $\alpha$ ) mol       $\alpha$  mol      2 $\alpha$  mol

Thus, number of particles after ionisation

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

van't Hoff factor ( $i$ )

$$= \frac{\text{Number of particles after ionisation}}{\text{Number of particles before ionisation}}$$

$$i = \frac{1 + 2\alpha}{1} \quad (\text{on } 100\% \text{ ionisation, } \alpha = 1)$$

$$= \frac{1 + 2 \times 1}{1} = 3$$

$$\therefore \Delta T_b = i K_b m$$

$$\therefore \Delta T_b = \frac{3 \times 0.52 \times 13.44}{134.4 \times 1}$$

$$= 0.156 \approx 0.16^\circ \text{C}$$

- 2** Let, amount of  $\text{Na}_2\text{CO}_3$  be ' $x$ ' g and  $\text{NaHCO}_3$  will be (1 -  $x$ ) g.

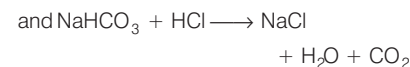
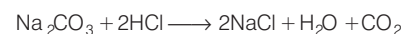
$$\therefore n_{\text{Na}_2\text{CO}_3} = n_{\text{NaHCO}_3}$$

$$\therefore \frac{x}{106} = \frac{1-x}{84} \Rightarrow x = \frac{106}{190} = 0.5578 \text{ g,}$$

$$1 - x = 0.4422 \text{ g}$$

$$n_{\text{Na}_2\text{CO}_3} = n_{\text{NaHCO}_3}$$

$$= \frac{0.5578}{106} = 0.00526 \text{ mol}$$



$$M_1 V_1 = M_2 V_2 + M_3 V_3$$

$$(\text{HCl}) \quad (\text{Na}_2\text{CO}_3) \quad (\text{NaHCO}_3)$$

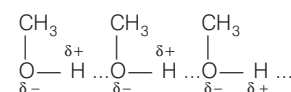
$$0.1 \times V_1 = 2 \times 0.00526 + 0.00526$$

$$V_1 = 157.8 \text{ mL}$$

- 3** Water and hydrochloric acid and water and nitric acid form miscible solutions. They show negative deviation.

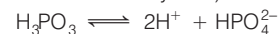
In case of  $\text{CH}_3\text{COCH}_3$  and  $\text{CHCl}_3$ , there is interaction between them, thus force of attraction between  $\text{CH}_3\text{COCH}_3 \dots \text{CHCl}_3$  is larger than between  $\text{CHCl}_3 \dots \text{CHCl}_3$  or  $\text{CH}_3\text{COCH}_3 \dots \text{CH}_3\text{COCH}_3$  and thus, vapour pressure is less than expected—a negative deviation.

In case of  $\text{CH}_3\text{OH}$ , there is association by intermolecular H-bonding. When benzene is added to  $\text{CH}_3\text{OH}$ , H-bonding breaks and thus, force of attraction between  $\text{CH}_3\text{OH}$  and benzene molecule is smaller than between  $\text{CH}_3\text{OH}$  or benzene molecules (in pure state). Vapour pressure of mixture is greater than expected—a positive deviation.



- 4**  $\text{H}_3\text{PO}_3$  is a dibasic acid

(i.e. contains two ionisable protons attached directly to O).



$$\therefore 0.1 \text{ M H}_3\text{PO}_3 = 0.2 \text{ N H}_3\text{PO}_3$$

and 0.1 M KOH = 0.1 N KOH

$$N_1 V_1 = N_2 V_2$$

$$(\text{KOH}) \quad (\text{H}_3\text{PO}_3)$$

$$0.1 V_1 = 0.2 \times 20$$

$$V_1 = 40 \text{ mL}$$

- 5** For initial solution,

$$\therefore \pi = \frac{500}{760} \text{ atm, } T = 283 \text{ K}$$

$$\therefore \frac{500}{760} \times V_{\text{initial}} = n \times R \times 283 \quad \dots (i)$$

$$\text{After dilution, } \pi = \frac{105.3}{760} \text{ atm, } T = 298 \text{ K}$$

$$\therefore \frac{105}{760} \times V_{\text{final}} = n \times R \times 298 \quad \dots(\text{ii})$$

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

$$\frac{V_{\text{initial}}}{V_{\text{final}}} = \frac{1}{5}$$

i.e. solution was diluted to 5 times.

$$6 \quad \chi_A = \frac{\chi_A p_A^\circ}{p} \quad \text{and} \quad \chi_B = \frac{\chi_B p_B^\circ}{p}$$

$$\therefore \frac{\chi_B p_B^\circ}{\chi_A p_A^\circ} = \frac{\chi_B}{\chi_A}$$

$$\text{or} \quad \frac{p_B^\circ (1 - \chi_A)}{p_A^\circ \chi_A} = \frac{1 - \chi_A}{\chi_A}$$

$$\text{or} \quad \frac{p_B^\circ}{p_A^\circ} \left( \frac{1}{\chi_A} - 1 \right) = \left( \frac{1}{\chi_A} - 1 \right)$$

$$\text{or} \quad \frac{1}{\chi_A} = \frac{p_A^\circ}{p_B^\circ} \times \frac{1}{\chi_A} + \left[ 1 - \frac{p_A^\circ}{p_B^\circ} \right]$$

$$\text{or} \quad \frac{1}{\chi_A} = \frac{p_A^\circ}{p_B^\circ} \times \frac{1}{\chi_A} + \frac{p_B^\circ - p_A^\circ}{p_B^\circ}$$

This is the equation of straight line, where,  $\frac{p_A^\circ}{p_B^\circ}$  is slope and  $\frac{p_B^\circ - p_A^\circ}{p_B^\circ}$  is intercept.

7 According to Dalton's law,

$$p_T = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$550 = p_A^\circ \times \frac{1}{4} + p_B^\circ \times \frac{3}{4}$$

$$\text{Thus, } p_A^\circ + 3p_B^\circ = 2200 \quad \dots(\text{i})$$

When, 1 mole of  $y$  is further added to the solution

$$560 = p_A^\circ + \frac{1}{5} + p_B^\circ \times \frac{4}{5}$$

$$\text{Thus, } p_A^\circ + 4p_B^\circ = 2800 \quad \dots(\text{ii})$$

On subtracting, Eq. (ii) and Eq (i)

$$p_B^\circ = 2800 - 2200 = 600 \text{ mm Hg}$$

Putting the value of  $p_B^\circ$  in Eq. (i)

$$p_A^\circ + 3 \times 600 = 2200$$

$$p_A^\circ = 2200 - 1800 = 400 \text{ mm Hg}$$

8 Elevation in boiling point,

$$\Delta T_b = i \times K_b \times m$$

Molality of NaCl solution

$$= \frac{n}{w} \times 1000 = \frac{58.5}{w_{\text{H}_2\text{O}}} \times 1000 = \frac{1000}{w_{\text{H}_2\text{O}}}$$

Molality of  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose) solution

$$= \frac{180}{w_{\text{H}_2\text{O}}} \times 1000 = \frac{1000}{w_{\text{H}_2\text{O}}}$$

Both the solutions have same molality, but the value of  $i$  for NaCl and glucose are 2 and 1 respectively.

$$\therefore \Delta T_{b(\text{NaCl})} = 2 \times \Delta T_{b(\text{C}_6\text{H}_{12}\text{O}_6)}$$

Hence, NaCl will show higher elevation boiling point.

$$9 \quad \frac{p^\circ - p_1}{p^\circ} = \frac{w_2/M_2}{w_2/M_2 + w_1/M_1}$$

$$\frac{640 - 600}{640} = \frac{2.175/M_2}{2.175/M_2 + 39/78}$$

$$\text{or } 0.0625 \left[ \frac{2.175}{M_2} + 0.5 \right] = \frac{2.175}{M_2}$$

$$\text{or } 0.9375 \times \frac{2.175}{M_2} = 0.0625 \times 0.5$$

$$\text{or } M_2 = 65.3$$

$$10 \quad \frac{\Delta p}{p^\circ} = \chi_2$$

$$\therefore \frac{10}{p^\circ} = 0.2 \quad \text{or } p^\circ = 50 \text{ mm}$$

$$\text{Similarly, } \frac{20}{50} = \chi_2, \text{ i.e. } \chi_2 = 0.4$$

$$\therefore \chi_1 = 1 - 0.4 = 0.6$$

11 According to Dalton's law,

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

$$\text{or } 550 = p_A^\circ \left( \frac{2}{5} \right) + p_B^\circ \left( \frac{3}{5} \right)$$

$$\text{or } 2p_A^\circ + 3p_B^\circ = 2750 \quad \dots(\text{i})$$

$\Rightarrow$  When 1 mole of  $B$  is added to it,

$$560 = p_A^\circ \left( \frac{2}{6} \right) + p_B^\circ \left( \frac{4}{6} \right)$$

$$\text{or } 2p_A^\circ + 4p_B^\circ = 3360 \quad \dots(\text{ii})$$

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

$$p_A^\circ = 460 \text{ mm}$$

12 (a)  $p_A = \chi_A p_A^\circ$  true

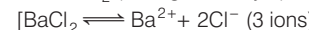
$$(b) \quad \pi = iMRT = MRT$$

true [If van't Hoff factor,  $i = 1$ ]

$$(c) \quad \pi \propto i$$

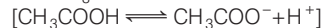
Greater the value of  $i$ , larger is the value of  $\pi$ .

$i$ , for  $\text{BaCl}_2$  (strong electrolyte) is 3.



$i$  for  $\text{KCl}$  is 2.  $[\text{KCl} \rightleftharpoons \text{K}^+ + \text{Cl}^-]$

$i$  for  $\text{CH}_3\text{COOH}$  is less than 2



But,  $\text{CH}_3\text{COOH}$  is weak electrolyte than  $\text{KCl}$ .

$i$  for sucrose is 1, as it is a non-electrolyte.

Thus,  $i$  (for  $\text{BaCl}_2$ ) >  $\text{KCl}$  >  $\text{CH}_3\text{COOH}$  < sucrose

Thus, (c) is also true.

$$(d) \quad \Delta T_f = K_f m$$

$K_f$  is dependent on solvent.

Thus, freezing point

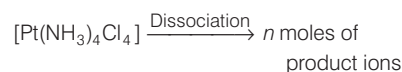
=  $[T(\text{solvent}) - \Delta T_f]$  are different.

Thus, (d) is false.

13 Due to the presence of non-volatile solute, NaCl in the beaker  $B$ , the vapour pressure

of beaker  $B$  decreases and becomes less than that of  $A$ .

14 Suppose,



$$\therefore i = n.$$

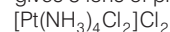
But from the given data

$$\Delta T_f = iK_f m$$

$$\Rightarrow 0.0054 = n \times 1.80 \times 0.001$$

$$\therefore n = 3$$

Hence, the formula must be the one which gives 3 ions of products, i.e.



15 100 g solution contains

$$= 5.85 \text{ g NaCl}$$

$$= 0.1 \text{ mole of NaCl}$$

100 g solution contains

$$= 9.50 \text{ g MgCl}_2$$

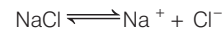
$$= 0.1 \text{ mole of MgCl}_2$$

Hence, weight of solvent ( $\text{H}_2\text{O}$ )

$$= 100 - (5.85 + 9.50)$$

$$= 84.65 \text{ g}$$

NaCl ionises 80%,



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

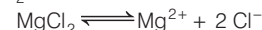
$$= 1 + 0.8 = 1.8$$

Here,  $y$  is the number of ions per mole of solute and  $x$  is the degree of ionisation.

Hence, number of moles of NaCl from 0.1 mole due to ionisation

$$= 1.8 \times 0.1 = 0.18 \text{ mol}$$

$\text{MgCl}_2$  ionises 50%,



$$\therefore i = 1 + (y - 1)x = 1 + 2x$$

$$= 1 + 2 \times 0.5 = 2$$

Hence, number of moles of  $\text{MgCl}_2$  from 0.1 mole

$$= 2 \times 0.1 = 0.20$$

Total moles of NaCl and  $\text{MgCl}_2$  in solution =  $0.18 + 0.20 = 0.38$

$$(n_1 + n_2) i = 0.38$$

Elevation in boiling point

$$(\Delta T_b) = \frac{1000 K_b (n_1 + n_2) i}{w_2}$$

$$= \frac{1000 \times 0.51 \times 0.38}{84.65} = 2.29^\circ \text{C}$$

Hence, boiling point of solution

$$= 100 + 2.29 = 102.29^\circ \text{C}$$