## 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.

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

#### 2. Molarity (M)

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

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

• Relation between molality (*m*) and molarity (*M*),

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

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

· Relation between molarity and density

Molarity =  $10 \times \text{density} \times \%$  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).

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

Mole fraction of solvent in the solution

$$\chi_{ ext{solvent}} = rac{ ext{Moles of solvent} \left( n_{ ext{solvent}} 
ight)}{ ext{Total moles of solution} \left( n_{ ext{solvent}} + n_{ ext{solvent}} 
ight)}$$

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,  $M_1 = \text{molar mass of solvent}$   $M_2 = \text{molar mass of solute}$ 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.

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

#### 5. Percentage by Volume

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

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.

Mass/volume percentage

$$= \frac{\text{Mass of solute}}{\text{Total volume of solution (mL)}} \times 100$$

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

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

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

#### 8. Normality

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

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

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  $p_{\rm s}$  be that of liquid in solution then lowering of vapour pressure of the liquid =  $p^{\circ} p_{\rm s}$ 
  - $\therefore$  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.

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

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**

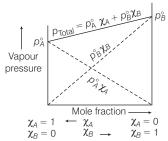
 The solutions, which obey Raoult's law over all ranges of concentration and temperature are called ideal solutions.

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

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

- For such solutions, solute-solute and solvent-solvent interactions ≈ 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:



Graphical representation of the ideal solution

#### **Non-ideal Solutions**

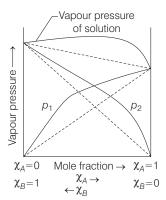
The solutions which shows deviation from Raoult's law are called **non-ideal solution**.

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

## 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,

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

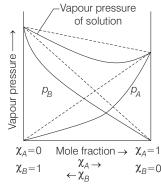


Graphical representation of the solution showing positive deviation

• 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,  $H_2O$  and  $C_2H_5OH$ .

#### 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,  $\Delta H_{\rm mix} < 0, \, \Delta V_{\rm mix} < 0, \, {\rm e.g.}$  chloroform and acetone.



Graphical representation of the solution showing negative deviation

For a solution showing negative deviation,

$$\begin{aligned} p_{\scriptscriptstyle A} &< p_{\scriptscriptstyle A}^{\circ} \times \chi_{\scriptscriptstyle A} \ \, \text{or} \ \, p_{\scriptscriptstyle B} &< p_{\scriptscriptstyle B}^{\circ} \times \chi_{\scriptscriptstyle B} \\ p_{\scriptscriptstyle \text{total}} &< p_{\scriptscriptstyle A}^{\circ} \chi_{\scriptscriptstyle A} + p_{\scriptscriptstyle B}^{\circ} \chi_{\scriptscriptstyle B} \end{aligned}$$

#### 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,

$$p \propto \chi \implies p = K_{\rm H} \chi$$

where,  $K_{\rm H}$  is Henry's law constant.

Higher the value of  $K_{\rm H}$  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  $K_{\rm H}$  differs from  $p_i^{\circ}$ , Thus, Raoult's law becomes a special case of Henry's law in which  $K_{\rm H}$  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.

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

[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,  $\Delta T_b = K_b \times \text{molality}$ 

$$\Delta T_b = T_b - T_b$$
°

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  $\Delta H_V = \text{latent}$  heat of vaporisation.

 $K_b$  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,

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

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**.

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 vant Hoff factor, to account for the extent of dissociation or association. This factor i is defined as

- (i)  $i = \frac{\text{number of particles after association / dissociation}}{\text{number of particles before association / dissociation}}$
- (ii)  $i = \frac{\text{normal molecular mass}}{\text{abnormal molecular mass}}$
- (iii)  $i = \frac{\text{(abnormal) observed value of colligative property}}{\text{(normal) calculated value of colligative property}}$

#### 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

$$\frac{p^{\circ}-p}{p^{\circ}}=i\frac{n_{B}}{n_{B}+n_{A}};\begin{pmatrix}n_{B}=n\\n_{B}+n_{A}\approx N\end{pmatrix}$$

- 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**

11 Vapour pressure of pure benzene is 119 torr and that of

1 A one molal solution of sodium chloride has a density of

<ul> <li>1.21 g mL<sup>-1</sup>. The molarity</li> <li>(a) 4.15 M</li> <li>(c) 2.95 M</li> <li>2 The density (in g mL<sup>-1</sup>) of acid solution having 29%</li> </ul>	(b) 1.143 M (d) 3.15 M a 3.60 M sulphuric H <sub>2</sub> SO <sub>4</sub>		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  a) JEE Main (Online) 2013  (a) 0.137 (b) 0.237 (c) 0.435 (d) 0.205					
(molar mass = $98 \text{ g mol}^-$ (a) 1.64 (b) 1.88	(c) 1.22 (d) 1.	.43	2 On mixing, heptane and octane form an ideal solution at 373 K, the vapour pressures of the two liquid components					
<ul> <li>The molarity of a solution</li> <li>0.5 M HCl with 250 mL of</li> <li>(a) 1.00 M</li> <li>(c) 0.975 M</li> </ul>			(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 g mol <sup>-1</sup> and of octane					
4 10 mL of 2 M NaOH soluti of NaOH solution. What is	the final concentration  → JEE Main (Or	n? nline) 2013	= 114 g mol <sup>-1</sup> ). → AIEEE 2010 (a) 72.0 kPa (b) 36.1 kPa (c) 96.2 kPa (d) 144.5 kPa					
<ul><li>(a) 0.57 M</li><li>(b) 5.7 M</li><li>5 The density of a solution purea (mol. mass = 60 u) in</li></ul>	prepared by dissolving 1000 g of water is 1.1	g 120 g of	A binary liquid solution is prepared by mixing <i>n</i> -heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution?					
The molarity of this solution (a) 0.50 M (c) 1.02 M	on is → A (b) 1.78 M (d) 2.05 M	AIEEE 2012	<ul> <li>→ AIEEE 2009</li> <li>(a) The solution formed is an ideal solution</li> <li>(b) The solution is non-ideal, showing positive deviation</li> </ul>					
6 The density of 3 M solutio 1.252 g mL <sup>-1</sup> . The molality (molar mass, NaCl = 58.5 (a) 2.60 m (c) 2.79 m	of the solution will be	S Main 2013	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					
<ul><li>7 A 5.2 molal aqueous soluti supplied. What is the mole solution?</li><li>(a) 0.100 M</li><li>(c) 0.086 M</li></ul>	fraction of methyl alco	0	<ul> <li>If two liquids A and B form minimum boiling azeotrope at some specific composition then</li></ul>					
8 25 mL of a solution of bar 0.1 molar solution of hydrof 35 mL. The molarity of I (a) 0.07 M (c) 0.28 M	ochloric acid gave a tit	tre value	number of molecules of liquids <i>A</i> and <i>B</i> 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) <i>A</i> — <i>B</i> interactions are weaker than those between <i>A</i> — <i>B</i> or <i>B</i> — <i>B</i> 15 An unknown compound is immiscible with water. It is steam distilled at 98.0°C. At 98.0°C, <i>p</i> and $p_{H_2O}^{\circ}$ are respectively 737 and 707 torr. This distillate was 75% by					
<b>9</b> At 100°C, benzene and to 1375 torr and 558 torr, resform an ideal binary solutifraction of benzene in vap (a) 0.247	spectively. Assuming, ton, then calculate the pour phase at 1 atm and (b) 0.753	these two mole <b>15</b>						
(c) 0.447  On An aqueous solution of 29 exerts a pressure of 1.004 solvent. What is the molec (a) 0.3655 (b) 36.55	bar at the boiling poin	nt of the e?	weight of water. The molecular weight of the unknown compound will be  (a) 318.15 g mol <sup>-1</sup> (b) 300 g mol <sup>-1</sup> (c) 306.76 g mol <sup>-1</sup> (d) None of these					

16	The relative lowering of vap solution containing a non-v molality of the solution is	olatile solute		26 The molecular weight of benzoic acid in b determined by depression in freezing poir corresponds to								
	(a) 0.69 m (c) 0.80 m	(b) 0.50 m (d) 0.40 m		(b)	(a) ionisation of benzoic acid (b) dimerisation of benzoic acid							
17	The vapour pressure of water at $20^{\circ}$ C is 17.5 mm Hg. If 18 g glucose ( $C_6$ H <sub>12</sub> O <sub>6</sub> ) is added to 178.2 g of water at $20^{\circ}$ C, the vapour pressure of the resulting solution will be			(d)	solvation	rimerisation of benzoic acid solvation of benzoic acid depression in freezing point of 0.01 M aqueous						
	(a) 16.500 mm Hg (c) 17.675 mm Hg	(b) 17.325 n (d) 15.750 n	nm Hg nm Hg	solu in th	ition of une ratio c	rea, soc of	lium chlo	ride and	sodi	um sulphate is		
	A and B are ideal gases. T B are in the ratio of 1:4. T containing equal weight of partial pressure (in atm) of (a) p/5 (b) p/2	<ul> <li>(a) 1:1:1 (b) 1:2:3 (c) 1:2:4 (d) 2:2:3</li> <li>28 During depression in freezing point of a solution, the following are in equilibrium</li> <li>(a) liquid solvent, solid solvent</li> <li>(b) liquid solvent, solid solute</li> <li>(c) liquid solute, solid solute</li> </ul>										
19	18 g of glucose (C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> ) is vapour pressure of water (i solution is	(d)	<ul><li>(c) liquid solute, solid solute</li><li>(d) liquid solute, solid solvent</li><li>29 How many grams of methyl alcohol should be added to</li></ul>									
	(a) 76.0 (b) 752.4	(c) 759.0	→ JEE Main 2016 (d) 7.6	10 L	10 L tank of water to prevent its freezing at 268 K'							
20	The vapour pressure of acc When 1.2 g of a non-volatil 100 g of acetone at 20 °C, it	e substance v	was dissolved in	(a)	or water 880.07 ( 886.02 (	g	_	-') → JE (b) 899.0 (d) 868.0	)4 g	iin (Online) 2013		
	The molar mass of the substantial (a) 32 (b) 64	stance is (c) 128	→ JEE Main 2015 (d) 488	holo	<b>30</b> $K_f$ for water is 1.86 K kg mol <sup>-1</sup> . If your automobile radiate holds 1.0 kg of water, how many grams of ethylene							
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				glycol ( $C_2H_6O_2$ ) you must add to get the freezing point of the solution lowered to $-2.8^{\circ}$ C? $\rightarrow$ AIEEE 2012 (a) 72 g (b) 93 g (c) 39 g (d) 27 g							
→ JEE Main (Online) 2013 31 Ethylene glyd (a) 80 (b) 60 (c) 20 (d) 40 Mass of ethy							ycol whic	h should	be a	dded to 4 kg		
22	? The Henry's law constant for the solubility of $N_2$ gas in water at 298 K is $1.0 \times 10^5$ atm. The mole fraction of $N_2$ in air is 0.8. The number of moles of $N_2$ from air dissolved in 10 moles of water at 298 K and 5 atm pressure is				of water to prevent it from freezing at $-6^{\circ}$ C will be $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1} \text{ and molar mass of ethylene glycol} = 62 \text{ g mol}^{-1}). \rightarrow \text{AIEEE 2011} (a) 800.00 g (b) 204.30 g (c) 400.00 g (d) 304.60 g$							
	(a) $4.0 \times 10^{-4}$ (c) $5.0 \times 10^{-4}$	<b>32</b> 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										
23	For a dilute solution contain non-electrolyte solute in 10				lar mass 68.4	s = 342 g (b) 34	j mol <sup>-1</sup> ) is I.2	s (c) 136.2		(d) 171.2		
	boiling point at 1 atm press	sure is 2°C. A	ssuming				and choo					
	concentration of solute is n concentration of solvent, th					Colun	nn I			umn II		
	is $(K_b = 0.76 \text{ K kg mol}^{-1})$	( ) 700	→ AIEEE 2012	A.	Raoult		ina naint	1.		$\frac{K_{H}\chi}{CRT}$		
21	(a) 724 (b) 740 An aqueous solution freeze	(c) 736	(d) 718	B. C.	Henry's	on of boil	ing point	2. 3.		$\frac{CRT}{\chi_1 p_1^{\circ} + \chi_2 p_2^{\circ}}$		
24	$(K_f = 1.86 \text{ K kg mol}^{-1}, K_b = 0)$ elevation in boiling point?			D.		ic pressu	re	4.		$= K_b m$		
	(a) 0.186°C (c) 0.86°C	(b) 0.512°C (d) 0.0512°C	0	(a) (b)	A 3 2	B 4 1	1	D 2 3				
25	When mercuric iodide is as of potassium iodide, the	dded to the a	queous solution	(c) (d)	4 1	1 3	2	3 4				
	<ul><li>(a) freezing point is raised</li><li>(b) freezing point is lowered</li><li>(c) freezing point does not change</li></ul>			of b	enzene (	$K_f = 1.73$	2K kg ma	ol <sup>-1</sup> ), a fre	ezing	ssolved in 50 g g point ff factor (i) is		
	(d) boiling point does not ch	nange			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)  $i_A < i_B < i_C$ (c)  $i_A = i_B = i_C$  (b)  $i_A > i_B > i_C$ (d)  $i_A < i_B > i_C$ 

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

(a) 0.01 M Na<sub>2</sub>SO<sub>4</sub>

(b) 0.01 M KNO<sub>2</sub>

(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,  $A_x B_y$  is related to van't Hoff factor (i) by the expression → AIEEE 2011

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

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

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

(a) 1.0 M NaOH

(b) 1.0 M Na<sub>2</sub>SO<sub>4</sub>

(c) 1.0 M NH<sub>4</sub> NO<sub>3</sub>

(d) 1.0 M KNO.

40 In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionisation is 0.3. Taking  $K_t$  for water as 1.85 K kg mol<sup>-1</sup>, the freezing point of the solution will be nearest to

(a) -0.360°C

(b) -0.260°C

(c) +0.480°C

(d) -0.481°C

41 In comparison to a 0.01M solution of glucose, the depression in freezing point of a 0.01M MgCl<sub>2</sub> solution is

(a) the same

(b) about twice

(c) about three times

- (d) about six times
- 42 The freezing point (in °C) of a solution containing 0.1 g of  $K_a$ [Fe(CN)<sub>a</sub>] (mol. wt. 329 gmol<sup>-1</sup>) in 100 g of water  $(K_f = 1.86 \text{ K kg mol}^{-1}) \text{ is}$

(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)  $[Co(H_2O)_6]CI_3$ 

(b) [Co(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>·H<sub>2</sub>O

(c)  $[Co(H_2O)_4CI_2]CI \cdot 2H_2O$ 

- (d) [Co(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub>]·3H<sub>2</sub>O
- 44 The freezing point of benzene decreases by 0.45°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  $(K_{\epsilon} \text{ for benzene} = 5.12 \text{ K kg mol}^{-1})$ → 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 1kg 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 C<sub>2</sub>H<sub>5</sub>OH (aq),  $0.100 \text{M Mg}_3(PO_4)_2(aq), 0.250 \text{M KBr}(aq)$  and 0.125MNa<sub>3</sub>PO<sub>4</sub>(aq) at 25° C. Which statement is true about these solution, assuming all salts to be strong → JEE Main 2014 electrolytes?
  - (a) They all have the same osmotic pressure
  - (b)  $0.100 \,\mathrm{M}\,\mathrm{Mg}_3$  (PO<sub>4</sub>)<sub>2</sub> (aq) has the highest osmotic pressure
  - (c) 0.125 M Na<sub>3</sub>PO<sub>4</sub> (aq) has the highest osmotic pressure
  - (d) 0.500 M C<sub>2</sub>H<sub>2</sub>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
	CuCl <sub>2</sub> in 1 kg of water using the following information will
	be (molecular weight of CuCl <sub>2</sub> = 134.4 and
	$K_b = 0.52 \mathrm{K  mol^{-1}})$

(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 Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> 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 (H<sub>3</sub>PO<sub>3</sub>), 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°C, the osmotic pressure of urea solution is 500 mm Hg. The solution is diluted and the temperature is raised to 25°C. The osmotic pressure of dilute solution is 105.3 mm Hg at 25°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  $\frac{1}{\chi_A}(\chi_A = \text{mole fraction of } A \text{ in liquid})$ 

and  $\chi_{\rm A}$  in vapour) is linear whose slope and intercept respectively are given

(b)  $p_{A}^{\circ} - p_{B}^{\circ}$ ,  $\frac{p_{A}^{\circ} - p_{B}^{\circ}}{p_{B}^{\circ}}$ (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

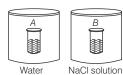
(b) 610 mm

(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
  - (c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is BaCl<sub>2</sub> > KCl > CH<sub>3</sub>COOH > 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 [Pt(NH<sub>3</sub>)<sub>4</sub> Cl<sub>4</sub>] in water had a freezing point depression of 0.0054° C. If K, for water is 1.80, the correct formulation of the above molecule is
  - (a) [Pt(NH<sub>2</sub>), Cl<sub>2</sub>]Cl
- (b) [Pt(NH<sub>2</sub>), Cl<sub>2</sub>]Cl<sub>2</sub>
- (c)  $[Pt(NH_3)_4Cl]Cl_3$
- (d)  $[Pt(NH_3)_4CI_4]$
- 15 Sea water is found to contain 5.85% NaCl and 9.5% MgCl<sub>2</sub> by weight of solution. Calculate its normal boiling point assuming 70% ionisation for NaCl and 50% ionisation of MgCl<sub>2</sub> [ $K_b$  (H<sub>2</sub>O) = 0.51 K kg mol<sup>-1</sup>]
  - (a) 101.4°C
- (b) 102.29°C
- (c) 103.27°C
- (d) 99.46°C

### **ANSWERS**

## **Hints and Explanations**

#### **SESSION 1**

**1** Molar mass of NaCl = 
$$M_2$$
 = 58.5 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

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

Density = 
$$\frac{3.60 \times 98}{10 \times 29}$$
 = 1.216 g/mL  
  $\approx 1.22$  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, 
$$M = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

$$= \frac{10 \times 2 + 200 \times 0.5}{200 + 10}$$
$$= \frac{20 + 100}{210} = \frac{120}{210} = 0.57 \text{ M}$$

5 Total mass of solution

Density of solution = 1.15 g/mL Volume of solution

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

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

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

Molarity = 
$$\frac{\text{Moles of solute}}{\text{Volume (L) of solution}}$$
  
=  $\frac{2}{0.974}$  = 2.05 mol/L

6 3M solution means 3 moles of solute (NaCl) are present in 1000 L of solution. Mass of solution = volume of solution  $\times$ 

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

Mass of solute = Number of moles × molar mass of NaCl

$$= 3 \times 58.5 g$$
  
= 175.5 g

Mass of solvent = (1252 - 175.5) g

$$= 1076.5 g$$
  
= 1.076 kg

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

$$=\frac{3}{1.076}=2.79\,\mathrm{m}$$

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

$$n_1 \text{ (CH}_3\text{OH)} = 5.2$$
  
 $n_2 \text{ (H}_2\text{O)} = \frac{1000}{18} = 55.56$ 

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

:. Mole fraction of CH<sub>3</sub>OH, 
$$\chi_{\text{CH}_3\text{OH}}$$
  
=  $\frac{n_1}{n_1 + n_2} = \frac{5.2}{60.76} = 0.086$ 

**8** Let, molarity of Ba(OH)<sub>2</sub> =  $M_1$ 

Let the molarity of  $HCI = M_2$ 

$$M_1V_1 = M_2V_2$$

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

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

**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,

$$pr = \chi_1 p^{\circ}_1 + (1 - \chi_1) p^{\circ}_2$$
or 
$$760 = \chi_1 (1375) + (1 - \chi_1) (558)$$
or 
$$\chi_1 = \frac{760 - 558}{1375 - 558} = 0.247 \text{ torr}$$

Mole fraction of benzene in vapour phase at

$$\chi_1 = \frac{\chi_1 p^{\circ}_1}{p} = \frac{0.247 \times 1375}{760} = 0.447$$

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

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

According to Raoult's law,

$$\frac{\rho^{\circ} - \rho_{1}}{\rho^{\circ}} = \frac{w_{\text{solute}}}{M_{\text{solute}}} \times \frac{M_{\text{solvent}}}{w_{\text{solvent}}}$$

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

$$M_{\text{solute}} = 41.37 \text{ gmol}^{-1}$$

11 From Raoult's law, for ideal solution,

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

= 
$$119 \times 0.5 + 37 \times 0.5$$
 (:  $\chi_B = 1 - \chi_T$ )  
=  $59.5 + 18.5 = 78 \text{ torr}$ 

Mole fraction of toluene in vapour phase

$$(\chi_T)_v = \frac{p_T^0 \chi_T}{p} = \frac{18.5}{78} = 0.237$$

**12** 
$$\rho_T = \chi_H \cdot \rho_H^\circ + \chi_O \cdot \rho_O^\circ$$

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

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

$$\rho_T = 0.45 \times 105 + 0.55 \times 45$$

$$= 72 \text{ kPa}$$

- **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 ∞ moles.

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

$$p_{H_2O}^{\circ} = 707 \text{ torr,}$$

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

$$\frac{\rho_{\text{unknown}}^{\circ}}{\rho_{\text{water}}^{\circ}} = \frac{n_{\text{unknown}}}{n_{\text{H}_2\text{O}}}$$
$$= \frac{W_{\text{unknown}} \times m_{\text{H}_2\text{O}}}{W_{\text{H}_2\text{O}} \times m_{\text{unknown}}}$$

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

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,  $1000 >> mM_1$ )

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

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

$$m = \frac{0.0125 \times 1000}{18} = 0.69 \,\mathrm{m}$$

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

or 
$$\frac{17.5 - \rho_1}{\rho^{\circ}} = \frac{18 / 180}{178.2 / 18 + 18 / 180}$$

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

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

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

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

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

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

Number of moles of glucose

$$= \frac{\text{Mass (in g)}}{\text{Molecular mass (g mol}^{-1})}$$
$$= \frac{18 \text{ g}}{180 \text{ g mol}^{-1}} = 0.1 \text{mol}$$

Molar mass of water = 18 g/mol

Mass of water (given) = 178.2g

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

Total number of moles = (0.1 + 9.9) moles  $= 10 \, \text{mol}$ 

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

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

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

.. Vapour pressure of solution

$$= (760 - 7.6) \text{ torr} = 752.4 \text{ torr}$$

**20** Given,  $p^{\circ} = 185$  torr at 20 °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

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

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

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

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

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

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

$$w = 12 g$$
;  $W = 108 g$ ,  $m = ?$ 

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

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

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

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

where,  $\chi$  = mole fraction

$$n_{\text{N}_2} = n_{\text{H}_2\text{O}} \times \frac{\rho_{\text{N}_2}}{K_{\text{H}}} \Rightarrow \rho_{\text{N}_2} = \chi_{\text{N}_2} \times \rho$$

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

$$p_{N_2} = 0.8 \times 5 = 4 \text{ atm}$$
  

$$\therefore n_{N_2} = 10 \times \frac{4}{1 \times 10^5} = 4 \times 10^{-4} \text{ moles}$$

23 The elevation in boiling point is

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

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

From Raoult's law of lowering of vapour pressure

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

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

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

**24** 
$$\Delta T_f = T_f^{\circ} - T_f = 0 - (-0.186) = 0.186^{\circ}\text{C}$$
  
 $\Delta T_f = K_f \times m \Rightarrow 0.186 = 1.86 \times m$   
or  $m = 0.1$ ,  
 $\Delta T_h = K_h \times m = 0.512 \times 0.1 = 0.0512^{\circ}\text{C}$ 

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 Na <sub>2</sub>SO<sub>4</sub> 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* σ.

the amount of methanol added be 
$$x$$
 g.  

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

[: Molar mass of CH<sub>3</sub>OH = 32 g mol<sup>-1</sup> and mass of H<sub>2</sub>O = V of H<sub>2</sub>O because density of water  $\approx 1 \text{ gL}^{-1}$ ]

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

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

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

**30** Coolant is glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), which is non-electrolyte.

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

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

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

$$w_1 = 93.33 \, g \approx 93 \, g$$

**31**  $\Delta T_f$  = Freezing point of H<sub>2</sub>O – freezing point of ethylene glycol solution = 0 – (– 6) = 6°C

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

 $w_2$  = Mass of ethylene glycol in grams

 $w_1$  = Mass of solvent (H<sub>2</sub>O) in grams = 4000 g

 $m_2$  = Molar mass of ethylene glycol = 62 g mol<sup>-1</sup>

i = van't Hoff factor = 1

(: ethylene glycol is non-electrolyte)

From, 
$$\Delta T_f = \frac{i \times 1000 \ K_f \ W_2}{m_2 \ W_1}$$
  

$$\therefore \qquad 6 = \frac{1000 \times 1.86 \times W_2 \times 1000}{62 \times 1000}$$

$$w_2 = 800 \,\mathrm{g}$$

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

$$\frac{n_1RT}{V_1} = \frac{n_2RT}{V_2} \implies \frac{n_1}{V_1} = \frac{n_2}{V_2}$$
Thus,
$$\frac{w_1}{V_1m_1} = \frac{w_2}{V_2m_2}, \frac{w_1}{V_1} = 1, \frac{w_2}{V_2} = 5$$

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

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

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,  $(C_{11}H_8O_2) = 172$

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) Na <sub>2</sub>SO<sub>4</sub>

$$Na_2SO_4 \Longrightarrow 2Na^+ + SO_4^{2^-}$$
 [3 ions]

$$i = 3$$

(b) 
$$KNO_3$$
  
 $KNO_3 \longrightarrow K^+ + NO_3^-$  [2 ions]  
 $\therefore i = 2$ 

Urea [(NH<sub>2</sub>CONH<sub>2</sub>) and glucose are poor electrolytes, therefore *i* for these two solutes are equal to zero.

Hence, 0.01 M Na<sub>2</sub>SO<sub>4</sub> possess highest boiling point.

37  $4A \Longrightarrow (A)_4,$ Initially  $1 \qquad 0$ After association  $1-\alpha \qquad \alpha/4$   $i = \frac{1-\alpha + \frac{\alpha}{4}}{1} = 1 - \frac{3}{4}\alpha$ 

 $\alpha$  = degree of dissociation = 1 or 100%  $\therefore i = 1 - \frac{3}{4} = 0.25$ 

38  $A_x B_y \longrightarrow x A^{y+} + y B^{x-}$ After dissociation  $A_x B_y \longrightarrow x A^{y+} + y B^{x-}$   $A_x B_$ 

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

oles = 
$$1 - 0.3 + 0.3 + 0.3 = 1.3$$
  
 $i = \frac{1.3}{1} = 1.3$ 

$$\Delta T_f = iK_f m = 1.3 \times 1.85 \times 0.2 = 0.418 \text{ K}$$
  
 $\therefore T_f = 273 - 0.418 \text{ K} = 272.519 \text{ K}$   
or  $-0.418^{\circ}\text{C}$ 

- 41 Being a non-electrolyte glucose does not undergo ionisation when dissolved in water whereas, MgCl<sub>2</sub> releases 3 ions [Mg<sup>+</sup> + 2Cl<sup>-</sup>] when dissolved in water. Thus, i for MgCl<sub>2</sub> is 3, while that of glucose is 0. Therefore, depression of freezing point of 0.01 M. MgCl<sub>2</sub> solution is about three times than 0.01 M glucose solution.
- **42** van't Hoff factor (i) = 4

$$\{ \because K_3 [Fe(CN)_6] \Longrightarrow 3K^+ + [Fe(CN)_6]^{3-} \}$$
Molality =  $\frac{0.1 \times 1000}{329 \times 100} = \frac{1}{329}$ 

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

(As freezing point of water is 0°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  $\infty$  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

 $Co(H_2O)_6]CI_3 \longrightarrow [Co(H_2O)_6]^{3+} + 3CI^{-}$ van't Hoff factor (i) is 4.

Similarly for,[Co(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub> ⋅ H<sub>2</sub>O <del>C</del>

$$[Co(H2O)5CI]2+ + 2CI- 'i' is 3$$

[Co(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl · 2H<sub>2</sub>O <del>←</del>

$$[Co(H_2O)_4CI_2]^+ + CI^-$$
 'i' is 2

and for  $[Co(H_2O)_3Cl_3] \cdot 3H_2O$ , 'i' is 1 as it does not show ionisation. Hence,  $[Co(H<sub>2</sub>O)<sub>3</sub>CI<sub>3</sub>] \cdot 3H<sub>2</sub>O$  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 (CH<sub>3</sub>COOH) in benzene is  $\alpha$ , then

$$2CH_3COOH \longrightarrow (CH_3COOH)_2$$

Initial moles Moles at equili.  $1 - \alpha$ 

$$\frac{\alpha}{2}$$

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

or 
$$i = 1$$

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

$$\Delta T_f = i K_f m$$
 ... (i)

where,  $K_f = \text{molal depression}$ constant or cryoscopic constant.

m = molality

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

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

Putting the values in Eq. (i),

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

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

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

$$\alpha = 0.946$$

Thus, percentage of association = 94.6%

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

 $\therefore$  van't Hoff factor (i) for Na  $_2$ SO<sub>4</sub> = 3  $\Delta T_f = i \times K_f \times m$ 

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

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

46 Effective molarity

= van't Hoff factor 
$$\times$$
 molarity  
5 M C<sub>2</sub>H<sub>5</sub>OH(aq)  $i = 1$ 

$$0.5 \,\mathrm{MC}_2\mathrm{H}_5\mathrm{OH}(aq)$$
 i

Effective molarity = 0.5

0.25 M KBr (aq),

$$i = 2$$

Effective molarity = 0.5 M

$$0.1 \,\mathrm{MMg_3}(\,\mathrm{PO_4})_2(aq), \ i = 5$$

$$0.125M \text{ Na}_{3} \text{PO}_{4}(aq), \quad i = 4$$
  
Effective molarity = 0.5 M

Hence, all solutions have some 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 Reson 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.

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

- **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<sup>6</sup> g mol<sup>-1</sup>). A little error in measurement of  $\Delta T_b$  or  $\Delta T_f$  will cause abnormal values of molecular weight.

#### **SESSION 2**

Thus, number of particles after ionisation

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

van't Hoff factor (i)

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

$$i = \frac{1+2\alpha}{1} \text{ (on 100\% ionisation, } \alpha = 1)$$
$$= \frac{1+2\times 1}{1} = 3$$

$$\Delta T_b = iK_b m$$

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

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

**2** Let, amount of Na  $_2$ CO $_3$  be 'x' g and NaHCO<sub>3</sub> will be (1 - x) g.

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

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

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

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

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

$$Na_2CO_3 + 2HCI \longrightarrow 2NaCI + H_2O + CO_2$$

and 
$$NaHCO_3 + HCI \longrightarrow NaCI$$

$$+ H_2O + CO_2$$

$$M_1V_1 = M_2V_2 + M_3V_3$$
  
(HCl) (Na<sub>2</sub>CO<sub>3</sub>) (NaHCO<sub>3</sub>)

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

$$V_1 = 157.8 \,\mathrm{mL}$$

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

In case of CH<sub>3</sub>COCH<sub>3</sub> and CHCl<sub>3</sub>, there is interaction between them, thus force of attraction between CH<sub>3</sub>COCH<sub>3</sub>... CHCl<sub>3</sub> is larger than between CHCl<sub>3</sub>... CHCl<sub>3</sub> or CH3COCH3 ... CH3COCH3 and thus, vapour pressure is less than expected—a negative deviation.

In case of CH<sub>3</sub>OH, there is association by intermolecular H-bonding. When benzene is added to CH<sub>2</sub>OH, H-bonding breaks and thus, force of attraction between CH<sub>3</sub>OH and benzene molecule is smaller than between CH<sub>3</sub>OH or benzene molecules (in pure state). Vapour pressure of mixture is greater than expected—a positive deviation.

4 H<sub>3</sub>PO<sub>3</sub> is a dibasic acid

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

$$H_3PO_3 \implies 2H^+ + HPO_4^{2-}$$
  
∴ 0.1 M  $H_3PO_3 = 0.2$  N  $H_3PO_3$   
and 0.1 M KOH = 0.1 N KOH  
 $N_1V_1 = N_2V_2$   
(KOH)  $(H_3PO_3)$ 

 $0.1 V_1 = 0.2 \times 20$ 

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

**5** For initial solution,

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

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

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

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

From Eqs. (i) and (ii), we get  $\frac{V_{\rm initial}}{V_{\rm final}} = \frac{1}{5},$ 

i.e. solution was diluted to 5 times.

6 
$$\chi_A = \frac{\chi_A \rho_A^{\circ}}{\rho}$$
 and  $\chi_B = \frac{\chi_B \rho_B^{\circ}}{\rho}$   

$$\therefore \frac{\chi_B \rho_A^{\circ}}{\chi_A \rho_A^{\circ}} = \frac{\chi_B}{\chi_A}$$
or  $\frac{\rho_B^{\circ} (1 - \chi_A)}{\rho_A^{\circ} \chi_A} = \frac{1 - \chi_A}{\chi_A}$ 
or  $\frac{\rho_B^{\circ}}{\rho_A^{\circ}} \left(\frac{1}{\chi_A} - 1\right) = \left(\frac{1}{\chi_A} - 1\right)$ 
or  $\frac{1}{\chi_A} = \frac{\rho_A^{\circ}}{\rho_B^{\circ}} \times \frac{1}{\chi_A} + \left[1 - \frac{\rho_A^{\circ}}{\rho_B^{\circ}}\right]$ 
or  $\frac{1}{\chi_A} = \frac{\rho_A^{\circ}}{\rho_B^{\circ}} \times \frac{1}{\chi_A} + \frac{\rho_B^{\circ}}{\rho_B^{\circ}} = \frac{\rho_A^{\circ}}{\rho_B^{\circ}}$ 

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

7 According to Dalton's law,

$$\begin{split} \rho_T &= \rho_A^{\circ} \ \chi_A + \rho_B^{\circ} \ \chi_B \\ 550 &= \rho_A^{\circ} \ \times \frac{1}{4} + \rho_B^{\circ} \ \times \frac{3}{4} \end{split}$$
 Thus,  $\rho_A^{\circ} + 3\rho_B^{\circ} = 2200$  ...(i)

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

$$560 = \rho_A^o + \frac{1}{5} + \rho_B^o \times \frac{4}{5}$$
 Thus,  $\rho_A^o + 4\rho_B^o = 2800$  ...(ii) On subtracting, Eq. (ii) and Eq (i) 
$$\rho_B^o = 2800 - 2200 = 600 \text{ mm Hg}$$
 Putting the value of  $\rho_B^o$  in Eq. (i) 
$$\rho_A^o + 3 \times 600 = 2200$$
 
$$\rho_A^o = 2200 - 1800 = 400 \text{ mm Hg}$$

8 Elevation in boiling point,

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

Molality of NaCl solution

$$= \frac{n}{W} \times 1000 = \frac{\frac{58.5}{58.5}}{\frac{58.5}{W_{\text{H}_2\text{O}}}} \times 1000 = \frac{1000}{W_{\text{H}_2\text{O}}}$$

Molality of C  $_6\!H_{12}\!O_6$  (glucose) solution

$$=\frac{\frac{180}{180}\times1000}{\frac{W_{HoO}}{W_{HoO}}}=\frac{1000}{\frac{W_{HoO}}{W_{HoO}}}$$

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.

 $9 \frac{p^{\circ} - p_1}{p^{\circ}} = \frac{w_2/M_2}{w_2/M_2 + w_1/M_1}$   $\frac{640 - 600}{640} = \frac{2.175/M_2}{2.175/M_2 + 39/78}$ or  $0.0625 \left[ \frac{2.175}{M_2} + 0.5 \right] = \frac{2.175}{M_2}$ 

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

or 
$$M_2 = 65.3$$

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

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

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

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

**11** According to Dalton's law.

$$\rho = \chi_A \rho^{\circ}_A + \chi_B \rho^{\circ}_B$$
or
$$550 = \rho^{\circ}_A \left(\frac{2}{5}\right) + \rho^{\circ}_B \left(\frac{3}{5}\right)$$

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

or  $2p_A^{\circ} + 4p_B^{\circ} = 3360$  ...( From Eqs. (i) and (ii), we get

$$p_{\Delta}^{\circ} = 460 \, \text{mm}$$

**12** (a)  $p_A = X_A p_A^{\circ}$  true

(b) 
$$\pi = iMRT = MRT$$
  
true [If van't Hoff factor,  $i = 1$ ]

(c) π α i

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

i, for BaCl<sub>2</sub> (strong electrolyte) is 3. [BaCl<sub>2</sub>  $\Longrightarrow$  Ba<sup>2+</sup>+ 2Cl<sup>-</sup> (3 ions)] i for KCl is 2. [KCl  $\Longrightarrow$  K<sup>+</sup>+Cl<sup>-</sup>] i for CH<sub>3</sub>COOH is less than 2 [CH<sub>3</sub>COOH  $\Longrightarrow$  CH<sub>3</sub>COO<sup>-</sup>+H<sup>+</sup>]

But, CH<sub>3</sub>COOH is weak electrolyte than

*i* for sucrose is 1, as it is a non-electrocyte.

Thus, *i* (for BaCl<sub>2</sub>)> KCl > CH<sub>3</sub>COOH

< SUCROSE

Thus, (c) is also true.

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

 $K_f$  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,

$$[\operatorname{Pt}(\operatorname{NH}_3)_4\operatorname{Cl}_4] \xrightarrow{\operatorname{Dissociation}} n \text{ moles of}$$
 product ions

i = n.

But from the given data

$$\Delta T_f = iK_f m$$

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

$$n = 3$$

Hence, the formula must be the one which gives 3 ions of products, i.e.  $[Pt(NH_3)_4CI_2]CI_2$ 

15 100 g solution contains

= 0.1 mole of NaCl

100 g solution contains

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

= 0.1 mole of MgCl<sub>2</sub>

Hence, weight of solvent (H2O)

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

$$= 84.65g$$

NaCl ionises 80%,

NaCl 
$$\longrightarrow$$
 Na + Cl<sup>-</sup>  
 $i = 1 + (y - 1) x = (1 + x)$   
 $= 1 + 0.8 = 1.8$ 

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

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

MgCl<sub>2</sub> ionises 50%,

MgCl<sub>2</sub> 
$$\longrightarrow$$
 Mg<sup>2+</sup> + 2 Cl<sup>-</sup>  
∴  $i = 1 + (y - 1) x = 1 + 2x$   
= 1 + 2 × 0.5 = 2

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

$$= 2 \times 0.1 = 0.20$$

Total moles of NaCl and MgCl<sub>2</sub> 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 °C