# 02

## **Solutions**

- **Types of Solutions** 2.1
- 2.2 **Expressing Concentration of Solutions**
- 2.3 Solubility
- 2.4 **Vapour Pressure of Liquid Solutions**
- 2.5 **Ideal and Non-ideal Solutions**
- 2.6 **Colligative Properties and Determination** of Molar Mass
- **Abnormal Molar Masses** 2.7

### **Topicwise Analysis of Last 10 Years' CBSE Board Questions**





Solution : A perfectly homogeneous mixture of  $\bigcirc$ two or more components is called *solution*.

Solute : The component which is present

in lesser amount or whose physical state is changed during the formation of solution is called solute.



Solvent : The component which is present in larger amount and determines the physical state of the solution is called *solvent*.

• Types of solution : Depending upon the nature of solute and solvent, solutions are classified as follows :

Gaseous solutions : Solutions in which gas acts as solvent are known as gaseous solutions.

Solute	Solvent	Examples
Solid	Gas	Iodine vapours in air, dust or smoke particles in air.
Liquid	Gas	Water vapours in air (humidity)
Gas	Gas	Air

► Liquid solutions : Solutions in which liquids are present in larger amount.

Solute	Solvent	Examples	
Solid	Liquid	Salt/sugar in water	
Liquid	Liquid	Alcohol in water	
Gas	Liquid	Aerated drinks, O <sub>2</sub> in water	

 Solid solutions : Solutions in which solids are present in larger amount.

Solute	Solvent	Examples
Solid	Solid	Alloys, copper
		dissolved in gold
Liquid	Solid	Hg in Ag, Hg in Zn
		(Amalgam)
Gas	Solid	Solution of hydrogen
		in palladium.

Different methods for expressing concentration of solution :

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Method of expressing	Formula
Mass percentage	$\left(\frac{w}{W}\right)\% = \frac{w_2}{(w_1 + w_2)} \times 100$

Volume percentage	$\left(\frac{\nu}{V}\right)\% = \frac{V_2}{(V_1 + V_2)} \times 100$
Mass by volume percentage	$\left(\frac{w}{V}\right)\% = \frac{w_2}{V_{\text{solution(in mL)}}} \times 100$
Mass fraction	$x_1 = \frac{w_1}{w_1 + w_2}$ or $x_2 = \frac{w_2}{w_1 + w_2}$
Strength (g L <sup>-1</sup> )	$\frac{w_{2(\text{in g})}}{V_{\text{solution (in mL)}}} \times 1000$
Parts per million (ppm)	$\frac{w_2}{(w_1+w_2)} \times 10^6$
Molarity, $(M)$ $(mol L^{-1})$	$\frac{w_2 \times 1000}{M_2 \times V_{\text{solution(in mL)}}}$
Molality, ( <i>m</i> ) (mol kg <sup>-1</sup> )	$\frac{w_2 \times 1000}{M_2 \times w_{1(\text{in g})}}$
Mole fraction, ( <i>x</i> )	$x_1 = \frac{n_1}{n_1 + n_2}$ or $x_2 = \frac{n_2}{n_1 + n_2}$ ,
	$(x_1 + x_2 = 1)$ In case of gases only, $y_1 = \frac{p_1}{p_1 + p_2}$ or $y_2 = \frac{p_2}{p_1 + p_2}$ , $(y_1 + y_2 = 1)$

- Solubility : Maximum amount of substance that can be dissolved in a specified amount of solvent at a specified temperature is called its *solubility*.
- Factors affecting solubility of a solid in a liquid :
  - ▶ Nature of solute and solvent : Polar solutes dissolve in polar solvents and non-polar solutes in non-polar solvents. (*i.e.*, like dissolves like).
  - ► Effect of temperature :
    - If the dissolution process is endothermic  $(\Delta_{sol}H > 0)$ , the solubility **increases** with **rise** in temperature.
    - If dissolution process is exothermic  $(\Delta_{sol}H < 0)$ , the solubility decreases with **rise** in temperature.

- Effect of pressure : Pressure does not have any significant effect on solubility of solids in liquids as these are highly incompressible.
- Factors affecting solubility of a gas in a liquid :
  - ► Effect of pressure : Henry's law states that "the partial pressure of the gas in vapour phase (*p*) is proportional to the mole fraction of the gas (*x*) in the solution"

 $p = K_{\rm H} x$  where,  $K_{\rm H}$  is the Henry's law constant and is different for different gases at a particular temperature.

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

► Effect of temperature : As dissolution is an exothermic process, then according to Le Chatelier's principle, the solubility should decrease with increase of temperature.

Raoult's law : It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.  $p_1 = p_1^{\circ} x_1$  and  $p_2 = p_2^{\circ} x_2$  where  $p_1^{\circ}$  and  $p_2^{\circ}$  are vapour pressures of pure components 1 and 2 respectively, at the same temperature.

 $P_{\text{total}} = p_1 + p_2 = x_1 p_1^{\circ} + x_2 p_2^{\circ}$  $= (1 - x_2) p_1^{\circ} + x_2 p_2^{\circ}$  $= p_1^{\circ} + (p_2^{\circ} - p_1^{\circ}) x_2$ 

- If  $y_1$  and  $y_2$  are the mole fractions of the components 1 and 2 respectively in the vapour phase then,  $p_1 = y_1 P_{\text{total}}$  and  $p_2 = y_2 P_{\text{total}}$
- Raoult's law for solid-liquid solutions : It states that relative lowering in vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute.

$$\frac{p^{\circ} - p_s}{p^{\circ}} = x_2 \text{ where,}$$

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

- $p_s$  = vapour pressure of solution
- $x_2$  = mole fraction of solute.

Ideal solutions	Non-idea	solutions
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
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$A - B$ interactions $\approx A - A$ and $B - B$ interactions	A - B interactions $<< A - A$ and $B - B$ interactions	A - B interactions >> $A - A$ and $B - B$ interactions
$\Delta H_{\rm mix} = 0,  \Delta V_{\rm mix} = 0$	$\Delta H_{\rm mix} > 0,  \Delta V_{\rm mix} > 0$	$\Delta H_{\rm mix} < 0,  \Delta V_{\rm mix} < 0$
<i>e.g.</i> , dilute solution, benzene + toluene, <i>n</i> -hexane + <i>n</i> -heptane	<i>e.g.</i> , acetone + ethanol, acetone + CS <sub>2</sub> , water + methanol	<i>e.g.</i> , acetone + aniline, acetone + chloroform, CH <sub>3</sub> OH + CH <sub>3</sub> COOH

### Ideal and non-ideal solutions :

- Azeotropes : The mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as vapour phase are called *constant boiling mixtures* or *azeotropic mixtures*.
  - ► Minimum boiling azeotropes : They formed by those liquid pairs which show positive deviations from ideal behaviour *e.g.*, ethanol-water mixture.
- Maximum boiling azeotropes : They are formed by those liquid pairs which show negative deviations from ideal behaviour *e.g.*, nitric acid-water mixture.
- **Colligative properties :** Properties which depend only on the number of solute particles dissolved in a definite amount of the solvent and not on the nature of the solute are called *colligative properties*.



- Two solutions having same osmotic pressure at a given temperature are called *isotonic solutions*.
- If one solution is of lower osmotic pressure, it is called *hypotonic* with respect to the more concentrated solution. The more concentrated solution is said to be *hypertonic* with respect to the dilute solution.
- ► If a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semipermeable membrane and the process is called *reverse osmosis*. It is used in *desalination of sea water*.
- Abnormal molecular mass : When the molecular mass of a substance determined by any of the colligative properties comes out to be different than the expected value, the substance is said to show *abnormal molecular mass*.
  - ► Abnormal molecular masses are observed when the solution is non-ideal (not dilute) or the solute undergoes *association* or *dissociation*.
- **van't Hoff Factor :** It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

- $i = \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$  $i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$ (Total number of moles of particles  $i = \frac{\text{after association} / \text{dissociation})}{(\text{Total number of moles of particles} + 1)}$
- (Total number of moles of particles before association / dissociation)
- ▶ If *i* > 1, solute undergoes dissociation in the solution and if *i* < 1, solute undergoes association in the solution.

$$\alpha_{\text{dissociation}} = \frac{i-1}{n-1}$$
$$\alpha_{\text{association}} = \frac{1-i}{1-\frac{1}{n}}$$

 For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows :

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = ix_2; \ \Delta T_b = iK_bm; \ \Delta T_f = iK_fm;$$
  
$$\pi = iCRT$$

### **Previous Years' CBSE Board Questions**

### **2.2** Expressing Concentration of Solutions

### VSA (1 mark)

- 1. Define the following term : Molarity (1/5 AI 2014)
- 2. Define the following term : Mole fraction (1/2 Delhi 2012, AI 2012, 2009)
- 3. What is meant by molality of a solution? (1/5 AI 2009)
- State the main advantage of molality over molarity as the unit of concentration. (Delhi 2009C)

### SAI (2 marks)

5. Calculate the molarity of 9.8% (w/W) solution of H<sub>2</sub>SO<sub>4</sub> if the density of the solution is 1.02 g mL<sup>-1</sup>.

(Molar mass of  $H_2SO_4 = 98 \text{ g mol}^{-1}$ ) (2/5 Foreign 2014)

- **6.** Differentiate between molarity and molality of a solution. How can we change molality value of a solution into molarity value?
- 7. Define :

   (i) Mole fraction
   (ii) Molality
   (2/5 AI 2014 C)
- 8. A solution of glucose  $(C_6H_{12}O_6)$  in water is labelled as 10% by weight. What would be the molality of the solution? (Molar mass of glucose = 180 g mol<sup>-1</sup>)

(2/5 AI 2013)

(Delhi 2014C)

- **9.** Differentiate between molarity and molality in a solution. What is the effect of temperature change on molarity and molality in a solution? *(2/5 Delhi 2011, 2009, 2/5 AI 2011)*
- Differentiate between molarity and molality of a solution. Explain how molarity value of a solution can be converted into its molality? (Foreign 2011)

- Define the term, 'molarity of a solution'. State one disadvantage in using the molarity as the unit of concentration. (2/3 AI 2010C)
- 12. An antifreeze solution is prepared from 222.6 g of ethylene glycol  $(C_2H_4(OH)_2)$  and 200 g of water. Calculate the molality of the solution. If the density of this solution be 1.072 g mL<sup>-1</sup> what will be the molality of the solution?

(Delhi 2007)

### SAII (3 marks)

13. A solution of glucose (molar mass = 180 g mol<sup>-1</sup>) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution?

(Density of solution =  $1.2 \text{ g mL}^{-1}$ )

(3/5 AI 2014)

### 2.3 Solubility

### VSA (1 mark)

- 14. Gas (*A*) is more soluble in water than gas (*B*) at the same temperature. Which one of the two gases will have the higher value of  $K_{\rm H}$  (Henry's constant) and why? (1/2 AI 2016)
- 15. Explain the following : Henry's law about dissolution of a gas in a liquid. (1/5 AI 2012)
- 16. State the following : Henry's law about partial pressure of a gas in a mixture. (1/5 Delhi, AI 2011)

### SAI (2 marks)

- 17. State Henry's law and mention two of its important applications. (2/5, AI 2013C, 2012C)
- Explain why aquatic species are more comfortable in cold water rather than in warm water. (Delhi 2012C)
- State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law. (*Delhi 2008*)

### SAII (3 marks)

- **20.** The partial pressure of ethane over a saturated solution containing  $6.56 \times 10^{-2}$  g of ethane is 1 bar. If the solution contains  $5.0 \times 10^{-2}$  g of ethane, then what will be the partial pressure of the gas? (*Delhi 2013C, AI 2012C*)
- 21. If  $N_2$  gas is bubbled through water at 293 K, how many millimoles of  $N_2$  gas would dissolve in 1 litre of water? Assume that  $N_2$  exerts a partial pressure of 0.987 bar. Given that Henry's law constant for  $N_2$  at 293 K is 76.48 k bar. (AI 2012C)
- **22.** What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air of 0.78.

 $[K_{\rm H} \text{ for nitrogen} = 8.42 \times 10^{-7} \text{ M/mm Hg}]$ (3/5 AI 2009)

### **2.4** Vapour Pressure of Liquid Solutions

### VSA (1 mark)

- **23.** Define Raoult's law. (1/5 AI 2014C)
- 24. State the following : Raoult's law in its general form in reference to solutions. (1/5 Delhi, 1/2 AI 2011)
- **25.** State 'Raoult's law' for a solution of volatile liquids. (*AI 2009C*)

### SAI (2 marks)

**26.** State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law?

(Delhi 2014, AI 2013)

- State Raoult's law for a solution containing volatile components. Name the solution which follows Raoult's law at all concentrations and temperatures. (2/5 Foreign 2014)
- **28.** State Raoult's law. How is it formulated for solutions of non-volatile solutes? (*Delhi 2012C*)

### SAII (3 marks)

**29.** The vapour pressure of pure liquids *A* and *B* are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid

mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase. (3/5 AI 2013C)

### **2.5** Ideal and Non-ideal Solutions

### VSA (1 mark)

- **30.** In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? (1/2 AI 2016)
- **31.** Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? (*Delhi 2014*)
- **32.** Define the following term : Azeotrope (1/5 Foreign 2014)
- 33. Define the following term : Ideal solution (1/5 AI 2013, 2012, 1/2 Delhi 2012)
- **34.** How is it that alcohol and water are miscible in all proportions ? (*AI 2007*)

### SAI (2 marks)

- **35.** What is meant by positive deviations from Raoult's law? Give an example. What is the sign of  $\Delta_{mix}H$  for positive deviation? (*Delhi 2015*)
- **36.** Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. (*Delhi 2015*)
- 37. What is meant by negative deviation from Raoult's law? Give an exmaple. What is the sign of  $\Delta_{mix}H$  for negative deviation?

(Foreign 2015)

- **38.** Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. (*Foreign 2015*)
- **39.** What type of deviation is shown by a mixture of ethanol and acetone? Give reason.

(2/5 AI 2014)

- **40.** What is meant by positive and negative deviations from Raoult's law and how is the sign of  $\Delta_{mix}H$  related to positive and negative deviations from Raoult's law? (AI 2013 C)
- **41.** Explain why a solution of chloroform and acetone shows negative deviation from Raoult's law. (2/5 Delhi 2011C)
- **42.** Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type.

(Delhi 2010)

- 43. What type of intermolecular attraction exists in each of the following pairs of compounds:(i) *n*-hexane and *n*-octane
  - (ii) methanol and acetone (Delhi 2010C)
- **44.** State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law. (*Delhi, AI 2008*)
- **45.** What is meant by negative deviation from Raoult's law? Draw a diagram to illustrate the relationship between vapour pressure and mole fractions of components in a solution to represent negative deviation. (*AI 2008C*)

### **2.6** Colligative Properties and Determination of Molar Mass

### VSA (1 mark)

<b>46</b> .	What are isotonic solution	ons?	(Dell	hi 2014)
47.	Define the following terr	m :		
	Molal elevation constant	$t(K_b)$	(1/5 F	AI 2014)
48.	How is the vapour pressu when a non-volatile solu	ire of a so ite is disso	lvent olved	affected in it?
		(1/2	Delhi	2014C)
<b>49</b> .	Define the following terr	m :		
	Osmotic pressure		(1/5 A	AI 2013)
50.	Define the following terr	m :		
	Isotonic solutions	(1/	2 Dell	hi 2012)
51.	Explain the following :			
	Boiling point elevation c	onstant f	or a s	olvent.
			(2	AI 2012)
52.	What is meant by colligation	tive prop	erties	?
			(1/5 A	AI 2009)
53.	State the condition	resulting	in	reverse
	osmosis.		(A	AI 2007)
SA	A   (2 marks)			

- 54. (i) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?
  - (ii) What happens when the external pressure applied becomes more than the osmotic pressure of solution? (2/5 Delhi 2016)
- **55.** Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing

- (i) 1.2% sodium chloride solution?
- (ii) 0.4% sodium chloride solution?

(2/5 Delhi 2016)

- 56. Why does a solution containing non-volatile solute have higher boiling point than the pure solvent? Why is elevation of boiling point a colligative property? (AI 2015)
- 57. Calculate the mass of compound (molar mass = 256 g mol<sup>-1</sup>) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K.  $(K_f = 5.12 \text{ K kg mol}^{-1})$ . (Delhi 2014)
- **58.** 18 g of glucose,  $C_6H_{12}O_6$  (Molar mass = 180 g mol<sup>-1</sup>) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil?

 $(K_b \text{ for water} = 0.52 \text{ K kg mol}^{-1}, \text{ boiling point}$ of pure water = 373. 15 K) (Delhi 2013)

- **59.** An aqueous solution of sodium chloride freezes below 273 K. Explain the lowering in freezing point of water with the help of a suitable diagram. (*Delhi 2013C*)
- **60.** Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain. (2/5 Delhi 2011)
- **61.** List any four factors on which the colligative properties of a solution depend.

(2/5 AI 2011C)

- **62.** Define the terms, 'osmosis' and 'osmotic pressure'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions? (*AI 2010*)
- **63.** Outer hard shells of two eggs are removed. One of the egg is placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why? (*AI 2010C*)
- 64. Find the boiling point of a solution containing 0.520 g of glucose  $(C_6H_{12}O_6)$  dissolved in 80.2 g of water.

[Given :  $K_b$  for water = 0.52 K/m] (AI 2010C)

**65.** Define the term 'osmotic pressure'. Describe how the molecular mass of a substance can be determined on the basis of osmotic pressure measurement. (*Delhi, AI 2008*)

### SA II (3 marks)

**66.** Calculate the freezing point of the solution when 31 g of ethylene glycol  $(C_2H_6O_2)$  is dissolved in 500 g of water.

 $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1})$  (AI 2015)

- **67.** A solution containing 15 g urea (molar mass =  $60 \text{ g mol}^{-1}$ ) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass =  $180 \text{ g mol}^{-1}$ ) in water. Calculate the mass of glucose present in one litre of its solution. (3/5 AI 2014)
- **68.** Calculate the boiling point elevation for a solution prepared by adding 10 g of CaCl<sub>2</sub> to 200 g of water. ( $K_b$  for water = 0.52 K kg mol<sup>-1</sup>, molar mass of CaCl<sub>2</sub> = 111 g mol<sup>-1</sup>)

(2/3 Foreign 2014)

- 69. Define the following terms :
  - (i) Osmotic pressure
  - (ii) Colligative properties (Foreign 2014)
- **70.** Some ethylene glycol, HOCH<sub>2</sub>CH<sub>2</sub>OH, is added to your car's cooling system along with 5 kg of water. If the freezing point of water-glycol solution is -15.0°C, what is the boiling point of the solution?

 $(K_b = 0.52 \text{ K kg mol}^{-1} \text{ and } K_f = 1.86 \text{ K kg mol}^{-1}$ for water) (Delhi 2014C)

- **71.** 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol<sup>-1</sup>. Find the molar mass of the solute. (*AI 2013, 2008*)
- **72.** A 5% solution (by mass) of cane-sugar in water has freezing point of 271 K. Calculate the freezing point of 5% solution (by mass) of glucose in water if the freezing point of pure water is 273.15 K.

[Molecular masses : Glucose  $C_6H_{12}O_6$  : 180 amu; Cane-sugar  $C_{12}H_{22}O_{11}$  : 342 amu]

- 73. A solution of glycerol  $(C_3H_8O_3)$  in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution?
  - $(K_b \text{ for water} = 0.512 \text{ K kg mol}^{-1})$ (Delhi 2012, 2010, AI 2012)

74. 15.0 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at  $-0.34^{\circ}$ C. What is the molar mass of this material? ( $K_f$  for water = 1.86 K kg mol<sup>-1</sup>)

(Delhi 2012, 3/5, AI 2012, 2010)

- **75.** A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is added to this solution. The new vapour pressure becomes 2.9 kPa at 298 K. Calculate
  - (i) the molecular mass of solute and
  - (ii) vapour pressure of water at 298 K.

(Delhi 2012C)

**76.** Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.00 g of water. ( $K_b$  for water = 0.512 K kg mol<sup>-1</sup>), (Molar mass of NaCl = 58.44 g)

(3/5 Delhi 2011)

- 77. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is a non-electrolyte, determine its molar mass. (3/5 Delhi, AI 2011)
- **78.** What would be the molar mass of a compound if 6.21 g of it dissolved in 24.0 g of chloroform to form a solution that has a boiling point of 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant,  $K_b$  for chloroform is 3.63°C/m.

(3/5 Delhi 2011)

**79.** What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant ( $K_f$ ) for water is 1.86°C/m. Assume van't Hoff factor for NaCl is 1.87.

(Molar mass of NaCl =  $58.5 \text{ g mol}^{-1}$ ). (AI 2011)

- 80. The molecular masses of polymers are determined by osmotic pressure method and not by measuring other colligative properties. Give two reasons. (3/5 AI 2011C)
- **81.** Calculate the boiling point of one molar aqueous solution (density 1.06 g mL<sup>-1</sup>) of KBr. [Given :  $K_b$  for H<sub>2</sub>O = 0.52 K kg mol<sup>-1</sup>, atomic mass : K = 39, Br = 80] (3/5 AI 2011C)

- 82. A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound. (B.pt. of pure benzene =  $80.10^{\circ}$ C and  $K_b$  for benzene =  $2.53^{\circ}$ C kg mol<sup>-1</sup>) (Delhi 2010)
- 83. What mass of ethylene glycol (molar mass = 62.0 g mol<sup>-1</sup>) must be added to 5.50 kg of water to lower the freezing point of water from 0°C to - 10.0°C?

 $(K_f \text{ for water } 1.86 \text{ K kg mol}^{-1})$ (AI 2010)

- 84. 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein?  $(R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \text{ and } 760 \text{ mm Hg}$ = 1 atm.) (Delhi, 3/5, AI 2009)
- 85. Calculate the amount of sodium chloride which must be added to one kilogram of water so that the freezing point of water is depressed by 3 K. [Given :  $K_f = 1.86$  K kg mol<sup>-1</sup>, atomic mass : Na = 23.0, Cl = 35.5] (3/5, Delhi, AI 2009C)
- 86. x g of a non-electrolytic compound (molar mass = 200) is dissolved in 1.0 L of 0.05 M NaCl aqueous solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of x. Assume complete dissociation of NaCl and ideal behaviour of the solution. ( $R = 0.082 \text{ L} \text{ atm mol}^{-1} \text{ K}^{-1}$ )

(AI 2009C)

- 87. Calculate the freezing point of a solution containing 18 g glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> and 68.4 g sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> in 200 g of water. The freezing point of pure water is 273 K and  $K_f$  for water is  $1.86 \text{ K m}^{-1}$ . (AI 2009C)
- 88. Calculate the temperature at which a solution containing 54 g of glucose, (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), in 250 g of water will freeze.

 $(K_f \text{ for water} = 1.86 \text{ K mol}^{-1} \text{ kg})$  (*Delhi 2008*)

89. A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86°C, whereas pure ether boils at 35.60°C. Determine the molecular mass of the solute. (For ether  $K_h = 2.02 \text{ K kg mol}^{-1}$ (AI 2008) 90. A 0.1539 molal aqueous solution of cane sugar (mol. mass =  $342 \text{ g mol}^{-1}$ ) has a freezing point of 271 K while the freezing point of pure water is 273.15 K. What will be the freezing point of an aqueous solution containing 5 g of glucose (mol. mass =  $180 \text{ g mol}^{-1}$ ) per 100 g of solution. (AI 2007)

### 2.7 Abnormal Molar Masses

### VSA (1 mark)

**91.** Define the following term : Van't Hoff factor (1/5 Delhi 2012, AI 2009)

### SAI (2 marks)

- What is van't Hoff factor? What types of values 92. can it have if in forming the solution the solute molecules undergo (i) Dissociation
  - (ii) Association?

(2/5 AI 2014C)

93. Assuming complete dissociation, calculate the expected freezing point of a solution prepared by dissolving 6.00 g of Glauber's salt,  $Na_2SO_4 \cdot 10H_2O$  in 0.100 kg of water.

> $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1}, \text{ atomic masses} :$ Na = 23, S = 32, O = 16, H = 1) (2/5, AI 2014C)

94. A 1.00 molal aqueous solution of trichloroacetic acid (CCl<sub>3</sub>COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid.

 $(K_b \text{ for water} = 0.512 \text{ K kg mol}^{-1})$  (*Delhi 2012*)

95. What is van't Hoff factor? What possible value can it have if the solute molecules undergo dissociation? (2/5 Delhi 2011C)

### SAII (3 marks)

- 96. Calculate the freezing point of solution when 1.9 g of MgCl<sub>2</sub>(M = 95 g mol<sup>-1</sup>) was dissolved in 50 g of water, assuming MgCl<sub>2</sub> undergoes complete ionization.  $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1})$  (*Delhi 2016*)
- 97. When 2.56 g of sulphur was dissolved in 100 g of CS<sub>2</sub>, the freezing point lowered by 0.383 K. Calculate the formula of sulphur  $(S_x)$ .  $(K_f \text{ the } \text{CS}_2 = 3.83 \text{ K kg mol}^{-1}, \text{ atomic mass of }$ sulphur =  $32 \text{ g mol}^{-1}$ ) (3/5 Delhi 2016)

**98.** Calculate the boiling point of solution when 4 g of MgSO<sub>4</sub> ( $M = 120 \text{ g mol}^{-1}$ ) was dissolved in 100 g of water, assuming MgSO<sub>4</sub> undergoes complete ionization.

 $(K_b \text{ for water} = 0.52 \text{ K kg mol}^{-1})$  (AI 2016)

- **99.** 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated). (Given : Molar mass of benzoic acid =  $122 \text{ g mol}^{-1}$ ,  $K_f$  for benzene = 4.9 K kg mol<sup>-1</sup>) (Delhi 2015)
- **100.** Calculate the mass of NaCl (molar =  $58.5 \text{ g mol}^{-1}$ ) to be dissolved in 37.2 g of water to lower the freezing point by 2°C, assuming that NaCl undergoes complete dissociation.

 $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1})$  (Foreign 2015)

101. Determine the osmotic pressure of a solution prepared by dissolving  $2.5 \times 10^{-2}$  g of K<sub>2</sub>SO<sub>4</sub> in 2 L of water at 25°C, assuming that it is completely dissociated.

 $(R = 0.0821 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1}, \text{ molar mass of } \text{K}_2\text{SO}_4 = 174 \text{ g mol}^{-1})$  (Delhi 2013)

- **102.** Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2 K (the  $K_f$  for water = 1.86 K kg mol<sup>-1</sup>). (Delhi 2012)
- **103.** Calculate the freezing point of an aqueous solution containing 10.50 g of MgBr<sub>2</sub> in 200 g of water. (Molar mass of MgBr<sub>2</sub> =  $184 \text{ g mol}^{-1}$ ) ( $K_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ )

(3/5 Delhi 2011)

- **104.** A 0.561 m solution of an unknown electrolyte depresses the freezing point of water by 2.93°C. What is van't Hoff factor for this electrolyte? The freezing point depression constant ( $K_f$ ) for water is 1.86°C kg mol<sup>-1</sup>. (Foreign 2011)
- **105.** Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20 g of phenol in 1.0 kg of benzene has its freezing point lowered by 0.69 K. Calculate the fraction of phenol that has dimerised

[Given  $K_f$  for benzene = 5.1 K m<sup>-1</sup>]

(3/5 Delhi 2011C)

**106.** An aqueous solution containing 12.48 g of barium chloride in 1.0 kg of water boils at 373.0832 K. Calculate the degree of dissociation of barium chloride.

[Given  $K_b$  for  $H_2O = 0.52 \text{ K m}^{-1}$ ;

- Molar mass of  $BaCl_2 = 208.34 \text{ g mol}^{-1}$ ] (3/5, Delhi 2011C)
- **107.** A decimolar solution of potassium ferrocyanide  $K_4[Fe(CN)_6]$  is 50% dissociated at 300 K. Calculate the value of van't Hoff factor for potassium ferrocyanide. (*Delhi 2010C*)
- **108.** The boiling point elevation of 0.30 g acetic acid in 100 g benzene is 0.0633 K. Calculate the molar mass of acetic acid from this data. What conclusion can you draw about the molecular state of the solute in the solution? [Given  $K_b$  for benzene = 2.53 K kg mol<sup>-1</sup>]

(AI 2008C)

- **109.** The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C. Calculate.
  - (i) the molar mass of acetic acid from this data
  - (ii) van't Hoff factor [For benzene,  $K_f = 5.12 \text{ K kg mol}^{-1}$ ] What conclusion can you draw from the value of van't Hoff factor obtained?

(AI 2008C)

### LA (5 marks)

water.

- **110.** (i) The depression in freezing point of water observed for the same molar concentration of acetic acid, trichloroacetic acid and trifluroacetic acid increases in the order as stated above. Explain.
  - (ii) Calculate the depression in freezing point of water when 20.0 g of CH<sub>3</sub>CH<sub>2</sub>CHClCOOH is added to 500 g of

[Given :  $K_a = 1.4 \times 10^{-3}$ ,  $K_f = 1.86$  K kg mol<sup>-1</sup>] (Delhi 2008C)

### **Detailed Solutions**

**1.** Number of moles of solute dissolved in one litre solution is called molarity. It is denoted by *M*.

#### 

Volume of solution in litre

2. Mole fraction is the ratio of number of moles of solute or solvent and total number of moles of solution. It is denoted by *x*.

$$x_{\text{solute}} = \frac{n_2}{n_1 + n_2}, x_{\text{solvent}} = \frac{n_1}{n_1 + n_2}$$

**3.** Molality of a solution can be defined as the number of moles of solute dissolved in one kg solvent. It is denoted by *m*.

$$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{n_2}{W_1}$$

**4.** Molality is independent of temperature, whereas molarity is a function of temperature.

5. Mass of solute = 9.8 g Mass of solution = 100 gDensity of solution =  $1.02 \text{ g mL}^{-1}$ 

 $\therefore \quad \text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$  $= \frac{100 \text{ g}}{1.02 \text{ g mL}^{-1}} = 98.039 \text{ mL}$ = 0.098 LNumber of moles of solute,  $n = \frac{9.8 \text{ g}}{98 \text{ g}} = 0.1 \text{ mol}$ Molarity =  $\frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$  $= \frac{0.1 \text{ mol}}{0.098 \text{ L}} = 1.02 \text{ M}$ 

6.

Molarity	Molality		
Number of moles of solute dissolved in one litre solution is called molarity.	Number of moles o solute dissolved in one ka solvent is called molality		
$M = \frac{\text{No. of moles of}}{\text{Volume of solution}}$ in litre	$m = \frac{\text{No. of moles}}{\text{Mass of solute}}$ in kg		

Molarity depends on	Molality is independent	
temperature as volume	of temperature as mass	
depends on temperature.	does not change with	
Molarity decreases with	temperature.	
rise in temperature.		

- 7. (i) Refer to answer 2.
- (ii) Refer to answer 3.

8. Mass of solution = 100 g

Mass of solute = 10 g

Mass of solvent = 
$$100 - 10 = 90 \text{ g} = \frac{90}{1000} \text{ kg} = 0.09 \text{ kg}$$

Number of moles of solute, 
$$n = \frac{10}{180} = 0.055 \text{ mol}$$
  
0.055 mol

$$m = \frac{0.000 \text{ mor}}{0.09 \text{ kg}} = 0.61 \text{ m}$$

**9.** *Refer to answer 6.* 

**10.** *Refer to answer 6.* 

If  $M_B$  is the molar mass of solute, d is the density of solution then molarity (M) value of a solution can be converted into its molality (m) by using the following formula,

m –	$1000 \times M$
<i>m</i> –	$\overline{(1000 \times d) - (M \times M_B)}$

**11.** Refer to answer 1.

Disadvantage in using molarity as the unit of concentration is that it depends upon temperature.

12. Mass of the solute, 
$$C_2H_4(OH)_2 = 222.6 \text{ g}$$
  
Molar mass of solute,  $C_2H_4(OH)_2 = 62 \text{ g mol}^{-1}$   
 $\therefore$  Moles of the solute  $= \frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59$   
Mass of the solvent  $= 200 \text{ g} = 0.200 \text{ kg}$   
Volume of solution  $= \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}} = 394.2 \text{ mL}$   
 $= 0.3942 \text{ L}$   
Molality  $= \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{3.59}{0.2}$   
 $= 17.95 \text{ m}$ 

Molarity = 
$$\frac{3.59 \text{ moles}}{0.3942 \text{ L}} = 9.11 \text{ mol L}^{-1}$$

13. Given : Mass of solute,  $W_2 = 10 \text{ g}$ Mass of solvent,  $W_1 = 90 \text{ g}$ Molar mass of solute,  $M_2 = 180 \text{ g mol}^{-1}$ Density of solution = 1.2 g mL<sup>-1</sup> (i) Molality  $= \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{10 \times 1000}{180 \times 90}$   $= 0.62 \text{ mol kg}^{-1}$ (ii) Volume of solution  $= \frac{\text{mass}}{\text{density}} = \frac{100 \text{ g}}{1.2 \text{ g mL}^{-1}}$ Molarity  $= \frac{W_2 \times 1000}{M_2 \times V}$  $M = \frac{10 \times 1000}{180 \times \frac{100}{1.2}} = \frac{10 \times 1000 \times 1.2}{180 \times 100} = 0.66 \text{ mol L}^{-1}$ 

14. According to Henry's law, the solubility of a gas is inversely proportional to the Henry's law constant  $(K_{\rm H})$  for that gas. Hence, gas (B) being less soluble, would have a higher  $K_{\rm H}$  value.

**15.** Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

 $p = K_{\text{H}} \cdot x$  where,  $K_{\text{H}}$  = Henry's law constant. Different gases have different  $K_{\text{H}}$  values at the same temperature.

16. Refer to answer 15.

17. Refer to answer 15.

Applications of Henry's law :

(i) To increase the solubility of  $CO_2$  in soft drinks and soda water, the bottle is sealed under high pressure. (ii) To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

**18.** Increase in temperature decreases the solubility of oxygen in water. As a result, amount of dissolved oxygen decreases. It becomes more difficult to breathe as oxygen is less. Hence, the aquatic species are not comfortable in warm water.

**19.** Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

Refer to answers 17.

**20.** Applying the relationship,  $m = K_{\rm H} \times p$ In the first case,  $6.56 \times 10^{-2}$  g =  $K_{\rm H} \times 1$  bar or,  $K_{\rm H} = 6.56 \times 10^{-2}$  g bar<sup>-1</sup>

In the second case,  

$$5.0 \times 10^{-2} \text{ g} = (6.56 \times 10^{-2} \text{ g bar}^{-1}) \times p$$
  
 $p = \frac{5.0 \times 10^{-2} \text{ g}}{6.56 \times 10^{-2} \text{ g bar}^{-1}} = 0.762 \text{ bar}$ 

**21.** According to Henry's law,  $p_{N_2} = K_H \times x_{N_2}$ 

$$x_{\rm N_2} = \frac{p_{\rm N_2}}{K_{\rm H}} = \frac{0.987 \,\rm bar}{76480 \,\rm bar} = 1.29 \times 10^{-5}$$

If *n* moles of N<sub>2</sub> are present in 1 L (*i.e.*, 55.55 moles),

$$x_{N_2} = \frac{n}{n+55.55} \approx \frac{n}{55.55} \text{ of water}$$
  

$$\therefore \quad \frac{n}{55.55} = 1.29 \times 10^{-5}$$
  
or  $n = 1.29 \times 10^{-5} \times 55.55 \text{ moles}$   
 $= 71.659 \times 10^{-5} \text{ moles} = 0.716 \text{ millimoles}$ 

**22.**  $T = 25^{\circ}\text{C} + 273 = 298 \text{ K}$ 

Total pressure  $(P_{total}) = 1$  atm

 $p_{N_2}$  = mol fraction of N<sub>2</sub> in air ×  $P_{total}$  = 0.78 × 1 atm = 0.78 atm = 0.78 × 760 mm = 592.8 mm

As  $K_{\rm H}$  is in the units of M(mm)<sup>-1</sup>, Henry's law is applied in the form :

Conc. in solution =  $K_{\rm H} p_{\rm N_2} = 8.42 \times 10^{-7} \,\mathrm{M} \,(\mathrm{mm})^{-1} \times 592.8 \,\mathrm{mm}$ =  $4.99 \times 10^{-4} \,\mathrm{M}$ 

**23.** Raoult's law : For a solution of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction. Thus, for any component, partial vapour pressure,  $p \propto x \Rightarrow p = p^\circ$ . *x* 

where  $p^{\circ}$  = vapour pressure of pure component x = mole fraction of that component

- 24. Refer to answer 23.
- **25.** *Refer to answer 23.*
- **26.** *Refer to answer 23.*

Henry's law : If gas is the solute and liquid is the solvent, then according to Henry's law,

$$p = K_{\rm H}$$

*i.e.*, partial pressure of the volatile component (gas) is directly proportional to the mole fraction of that component (gas) in the solution.

Hence, Raoult's law and Henry's law has been identical except that their proportionality constant are different. It is equal to  $p^{\circ}$  for Raoult's law and K<sub>H</sub> for Henry's law.

Therefore, Raoult's law becomes a special case of Henry's law in which  $K_{\rm H}$  becomes equal to vapour pressure of pure component  $p^{\circ}$ .

#### 27. Refer to answer 23.

Let a solution consists of two volatile liquids *A* and *B* with their mole fraction  $x_A$  and  $x_B$  respectively. If  $p_A$  and  $p_B$  are their partial vapour pressures, then,

 $p_A \propto x_A \Longrightarrow p_A = p_A^{\circ} x_A$  and  $p_B \propto x_B \Longrightarrow p_B = p_B^{\circ} x_B$ where  $p_A^{\circ}$  and  $P_B^{\circ}$  represent the vapour pressures of pure liquid components *A* and *B*.

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

A plot of  $p_A$  or  $p_B$  against  $x_A$  or  $x_B$  for a solution will be a straight line.



Ideal solutions obey Raoult law at all concentrations and temperature.

### **28.** *Refer to answer 23.*

**Raoult's law for solution containing non-volatile solute :** It states that partial vapour pressure of a solution of non-volatile solute,  $p_{solution}$  is directly proportional to the mole fraction of the solvent in the solution.

Mathematically,

 $p_{\text{solution}} = p_{\text{solvent}}^{\circ} \times x_{\text{solvent}}$ 

where  $p_{\text{solvent}}^{\circ}$  = vapour pressure of the pure solvent at the given temperature.

or, 
$$\frac{p^\circ - p_{\text{sol}}}{p^\circ} = x_2$$

250

**29.** Given :  $p_A^\circ = 450$  mm Hg,  $p_B^\circ = 700$  mm Hg,  $P_{\text{Total}} = 600$  mm Hg,  $x_A = ?$ 

Applying Raoult's law, 
$$p_A = x_A \times p_A^\circ$$
  
 $p_B = x_B \times p_B^\circ = (1 - x_A)p_B^\circ$   
 $P_{\text{Total}} = p_A + p_B = x_A \times p_A^\circ + (1 - x_A)p_B^\circ$   
 $= p_B^\circ + (p_A^\circ - p_B^\circ)x_A$   
Substituting the given values, we get  
 $600 = 700 + (450 - 700)x_A$  or,  $250x_A = 100$   
or  $x_A = \frac{100}{2} = 0.40$ 

Thus, composition of the liquid mixture will be  $x_A = 0.40$  $x_B = 1 - 0.40 = 0.60$  Calculation of composition in the vapour phase,  $p_A = x_A \times p_A^\circ = 0.40 \times 450 \text{ mm Hg} = 180 \text{ mm Hg}$   $p_B = x_B \times p_B^\circ = 0.60 \times 700 \text{ mm Hg} = 420 \text{ mm Hg}$ Mole fraction of *A* in the vapour phase

$$=\frac{p_A}{p_A+p_B}=\frac{180}{180+420}=0.30$$

Mole fraction of *B* in the vapour phase = 1 - 0.30= 0.70

**30.** Non-ideal solutions that show negative deviation from Raoult's law form maximum boiling azeotropes.

**31.** Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phases and that have constant boiling points.

It is not possible to separate the components of azeotropes by fractional distillation.

**32.** *Refer to answer 31.* 

**33.** A solution which obeys Raoult's law at all concentrations and temperatures is called an ideal solution.

**34.** Both alcohol and water are polar in nature hence, they are miscible in all proportions. Water and ethanol molecules attract  $\cdots H - O \cdots H - O$  each other because of the formation  $\begin{vmatrix} I \\ I \end{vmatrix}$  of H-bonds. This property also H R makes them miscible.

**35. Positive deviation** : For non-ideal solutions, if the vapour pressure is higher, then it is said to exhibit positive deviation. A-B interactions are weaker than A-A or B-B interactions. Due to this, vapour pressure increases which results in positive deviation. In positive deviation, intermolecular force decreases, volume increases, vapour pressures increases. enthalpy increases. Therefore,  $\Delta H_{mix} = +ve$ ,  $\Delta V_{mix} = +ve$ . *e.g.*, ethanol + acetone and carbon disulphide + acetone show positive deviation.



Plot for non-ideal solution showing positive deviation

#### **36.** *Refer to answer 31.*

A minimum boiling azeotrope is formed by solutions showing a large positive deviation from Raoult's law at a specific composition. For example an ethanolwater mixture containing approximately 95% ethanol by volume.

**37.** Negative deviation : For non-ideal solution, if the vapour pressure is lower, then it is said to exhibit negative deviation. A-B interactions are stronger than A-A and B-B interactions. Due to this, vapour pressure decreases which results in negative deviation. In negative deviation, intermolecular force increases, volume decreases, vapour pressure decreases and heat is released. Therefore,  $\Delta H_{mix} = -\text{ve}, \Delta V_{mix} = -\text{ve Example, phenol + aniline}$ and chloroform + acetone show negative deviation.



**38.** Refer to answer 31.

A maximum boiling azeotrope is formed by solutions showing a large negative deviation from Raoult's law at a specific compostion.

For example Chloroform – acetone mixture.

**39.** A mixture of ethanol and acetone shows positive deviation from Raoult's law. Pure ethanol possesses hydrogen bonding. Introduction of acetone between the molecules of ethanol results in breaking of some of these hydrogen bonds. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

#### 40. Refer to answers 35 and 37.

**41.** A mixture of chloroform and acetone shows negative deviation from Raoult's law because chloroform molecule forms H-bonding with acetone molecule. As a result of this A-B interaction becomes stronger than A-A and B-B interactions.

This leads to the decrease in vapour pressure and resulting in negative deviation.

$$H_{3C}$$
 C=O-H-C  $Cl$ 

**42.** *Refer to answers 35 and 37.* 

43. (i) *n*-Hexane and *n*-octane : London dispersion forces as both the molecules are non-polar.(ii) Methanolandacetone: Dipole-dipole interactions

as both the molecules are polar.

**44.** *Refer to answers 23, 35 and 37.* 

45. Refer to answer 37.

**46.** Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

47. Molal elevation constant may be defined as the elevation in boiling point when the molality of the solution is unity (*i.e.*, 1 mole of the solute is dissolved in 1 kg (1000 g) of the solvent). The units of  $K_b$  are therefore, degree/molality *i.e.*, K/m or °C/m or K kg mol<sup>-1</sup>.

**48.** When a non-volatile solute is added to a solvent, the vapour pressure of the solvent (above the resulting solution) is lower than the vapour pressure above the pure solvent.

**49.** Osmotic pressure is the extra pressure which is applied on the solution to just prevent the flow of solvent into the solution through a semi-permeable membrane.

**50.** *Refer to answer* 46.

**51.** Ebullioscopic constant is the boiling point elevation constant when one mole of solute is dissolved in 1000 g of solvent. It is denoted by  $K_b$ .

**52.** Colligative properties are the properties of solution which depend upon the number of solute particles and not upon the nature of the solute.

**53.** Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution side.

**54.** (i) The elevation in boiling point of a solution is a colligative property which depends on the number of moles of solute added. Higher the concentration of solute added, higher will be the elevation in boiling point. Thus, 2 M glucose has higher boiling point than 1 M glucose solution.

(ii) When the external pressure applied becomes more than the osmotic pressure of solution then the

solvent molecules from the solution pass through the semipermeable membrane to the solvent side and the process is called reverse osmosis.

**55.** (i) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution exosmosis takes place that results in shrinking of cells.

(b) 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution endosmosis takes place that results in swelling of cells.

**56.** The boiling point of the solution is always higher than that of the pure solvent. As the vapour pressure of the solution is lower than that of the pure solvent and vapour pressure increases with increase in temperature. Hence, the solution has to be heated more to make the vapour pressure equal to the atmospheric pressure.

Elevation of boiling point is a colligative property because it depends on number of solute particles present in a solution.

57. Given:  $W_2 = ?$ ,  $M_2 = 256 \text{ g mol}^{-1}$ ,  $\Delta T_f = 0.48 \text{ K}$   $W_1 = 75 \text{ g}$ ,  $K_f = 5.12 \text{ K kg mol}^{-1}$   $\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$  $W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times 1000} = \frac{0.48 \times 256 \times 75}{5.12 \times 1000} = 1.8 \text{ g}$ 

58. Given  $W_1 = 1 \text{ kg} = 1000 \text{ g}$ ,  $W_2 = 18 \text{ g}$ ,  $M_2 = 180 \text{ g mol}^{-1}$   $T_b^o = 373.15 \text{ K}$ ,  $K_b = 0.52 \text{ K Kg mol}^{-1}$ ,  $T_b = ?$ Using formula,

$$\Delta T_b = K_b \times \frac{W_2 \times 1000}{M_2 \times W_1}$$
  
or 
$$\Delta T_b = \frac{0.52 \text{ K} \times 18 \times 1000}{180 \times 1000} = 0.052 \text{ K}$$
$$\Delta T_b = T_b - T_b^\circ$$
$$0.052 = T_b - 373.15$$
$$T_b = 373.15 + 0.052 = 373.202 \text{ K}$$

**59.** When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute.

Plot for the lowering in freezing point of water when NaCl is added to it is shown as :



**60. Osmosis** : The spontaneous movement of the solvent molecules from the pure solvent or from a dilute solution to a concentrated solution through a semi-permeable membrane is called osmosis.

**Osmotic Pressure :** The minimum excess pressure that has to be applied on the solution to prevent the passage of solvent molecules into it through semipermeable membrane is called osmotic pressure.

Osmotic pressure is a colligative property because it depends on the number of solute particles and not on their nature.

- **61.** (i) Number of particles of solute
- (ii) Association or dissociation of solute
- (iii) Concentration of solute
- (iv) Temperature
- 62. Refer to answer 60.

The osmotic pressure method has the advantage over other methods because

(i) osmotic pressure can be measured at room temperature and the molarity of the solution is used instead of molality.

(ii) its magnitude is large as compared to other colligative properties even for very dilute solutions.

**63.** The egg placed in pure water will swell because the concentration of proteins is high inside the egg as compared to water. Therefore, endosmosis occurs and water diffuses through the semipermeable membrane. The egg which is placed in sodium chloride solution will shrink due to osmosis of water out of the egg.

64. Given,  $W_2 = 0.520$  g,  $W_1 = 80.2$  g,  $K_b = 0.52$  K m<sup>-1</sup>  $M_2$  of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> = 6 × 12 + 12 × 1 + 6 × 16 = 180 g mol<sup>-1</sup>

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$
  
=  $\frac{0.52 \times 0.520 \times 1000}{180 \times 80.2}$  = 0.019 K  
Boiling point of solution,  $T_b = T_b^\circ + \Delta T_b$   
= 373 K + 0.019 K = 373.019 K

65. Refer to answer 49.

Relation between osmotic pressure and molar mass,  $\pi V = \mu PT$ 

$$\pi V = n_2 R T$$

$$\pi V = \frac{W_2 R T}{M_2}$$

$$\left[ \because n_2 = \frac{W_2}{M_2} \right]$$

$$M_2 = \frac{W_2 R T}{\pi V}$$

where  $\pi$  is osmotic pressure and  $M_2$  is molar mass of solute.

66. Mass of ethylene glycol ( $C_2H_6O_2$ ),  $W_2 = 31$  g Mass of water,  $W_1 = 500$  g  $M_2$  (Mol. mass of C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) = 62 g mol<sup>-1</sup>,  $K_f = 1.86 \text{ K kg mol}^{-1}, T_f = ?$ Using formula,  $\Delta T_f = K_f \times \frac{W_2 \times 1000}{M_2 \times W_1}$  $=1.86 \times \frac{31 \times 1000}{62 \times 500} = 1.86 \text{ K}$  $\Delta T_f = T_f^{\circ} - T_f$ or  $T_f = T_f^{\circ} - \Delta T_f = 273 - 1.86 = 271.14 \text{ K}$ **67.** Mass of urea = 15 gMolar mass of urea =  $60 \text{ g mol}^{-1}$ Molar mass of glucose =  $180 \text{ g mol}^{-1}$ Mass of glucose = ? For isotonic solution, osmotic pressure,  $\pi_1 = \pi_2$  $n_1 = n_2$  (when volume is same)  $\frac{W_1}{M_1} = \frac{W_2}{M_2} \Longrightarrow \frac{15}{60} = \frac{W_2}{180}$ or  $\implies W_2 = \frac{15 \times 180}{60} = 45 \text{ g}$ **68.** Mass of  $CaCl_2(W_2) = 10 \text{ g}$ Mass of water  $(W_1) = 200 \text{ g}$ Molar mass of  $\operatorname{CaCl}_2(M_2) = 111 \text{ g mol}^{-1}$ Molal Elevation constant =  $0.512 \text{ K kg mol}^{-1}$  $m = \frac{W_2 \times 1000}{M_2 \times W_1}$ m

$$m = \frac{11}{111} \times \frac{1000}{200} = 0.450$$

 $\Delta T_h = K_h m = 0.512 \times 0.450 = 0.2306 \text{ K}$ **69.** (i) *Refer to answer* 61. (ii) Refer to answer 52. **70.**  $T_f = -15^{\circ}$ C,  $K_f = 1.86$  K kg mol<sup>-1</sup>  $\Delta T_f = T_f^{\circ} - T_f = 0 - (-15^{\circ}\text{C}) = 15^{\circ}\text{C} = 288 \text{ K}$  $\Delta T_f = K_f \times m$  $288 = 1.86 \times \frac{W_2}{0.062 \times 5}$  $W_2 = 48 \text{ kg}$  $\Delta T_b = K_b \times m$  $\Delta T_b = 0.52 \times \frac{48}{0.062 \times 5}$  $\Delta T_h = 80.51 \text{ K}$  $\Delta T_b = T_b - T_b^{\circ}$  $80.51 = T_b - 373$  $T_b = 80.51 + 373 = 453.51 \text{ K}$ 71.  $W_2 = 1.00$  g,  $W_1 = 50$  g,  $K_f = 5.12$  K kg mol<sup>-1</sup>,  $\Delta T_f = 0.40 \text{ K}$  $\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$  $M_{2} = \frac{K_{f} \times W_{2} \times 1000}{W_{1} \times \Delta T_{f}} = \frac{5.12 \times 1 \times 1000}{50 \times 0.40}$  $= 256 \text{ g mol}^{-1}$ 72. Molality of sugar solution  $= = \frac{W_2 \times 100}{M_2 \times W_1} = \frac{5}{342} \times \frac{1000}{95} = 0.154 \text{ m}$  $\Delta T_f = T_f^{\circ} - T_f = 273.15 - 271 = 2.15 \text{ K}$  $\Delta T_f = K_f \times m \quad \therefore \quad K_f = \frac{\Delta T_f}{m} = \frac{2.15}{0.154}$ Molality of glucose solution  $= = \frac{W_2 \times 100}{M_2 \times W_1} = \frac{5}{180} \times \frac{1000}{95} = 0.292 \text{ m}$ :.  $\Delta T_f$  (Glucose) =  $K_f \times m = \frac{2.15}{0.154} \times 0.292 = 4.08$ *:*. Freezing point of glucose solution = = 273.15 - 4.08 = 269.07 K 73.  $W_1 = 500 \text{ g}$ Boiling point of solution  $(T_b) = 100.42$  °C  $K_b$  for water = 0.512 K kg mol<sup>-1</sup>  $M_2(C_3H_8O_3) = (3 \times 12) + (8 \times 1) + (3 \times 16)$  $= 92 \text{ g mol}^{-1}$  $\Delta T_{L} = T_{C} - T^{\circ}$ 

$$\Delta I_b = I_b - I_b$$
  
= 373.42 K - 373 K = 0.42 K

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_b \times M_2 \times W_1}{K_b \times 1000} = \frac{0.42 \times 92 \times 500}{0.512 \times 1000} = 37.73 \text{ g}$$
74.  $W_1 = 450 \text{ g}, W_2 = 15.0 \text{ g}$ 

$$\Delta T_f = T_f^\circ - T_f = 273 \text{ K} - 272.66 \text{ K} = 0.34 \text{ K}$$

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

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

$$M_2 = \frac{1.86 \times 15 \times 1000}{0.34 \times 450} = 182.35 \text{ g mol}^{-1}$$

75. The relative lowering of vapour pressure is given by the following expression,  $(p^{\circ}_{1}, p_{1}, p_{2}, p_{2}, p_{3})/p^{\circ}_{2}, p_{3} = n_{2}/(n_{1} + n_{2})$ 

$$\begin{aligned} (p^{\circ}_{solvent} - p_{solution})/p^{\circ}_{solvent} &= n_2/(n_1 + n_2) \\ \text{for dilute solutions, } n_2 << n_1, \text{ therefore} \\ (p^{\circ}_{solvent} - p_{solution})/p^{\circ}_{solvent} &= n_2/n_1 \\ &= (W_2 \times M_1)/(M_2 \times W_1) \\ (p^{\circ}_{solvent} - 2.8)/p^{\circ}_{solvent} &= (30 \times 18)/(M_2 \times 90) \\ (p^{\circ}_{solvent} - 2.8)/p^{\circ}_{solvent} &= 6/M_2 \\ \dots (1) \\ \text{Similarly for second case we get,} \\ (p^{\circ}_{solvent} - 2.9)/p^{\circ}_{solvent} &= (30 \times 18)/(M_2 \times 108) \\ (p^{\circ}_{solvent} - 2.9)/p^{\circ}_{solvent} &= 5/M_2 \\ \dots (2) \\ \text{On solving eq. (1) and (2), we get} \\ (p^{\circ}_{solvent} - 2.8)/(p^{\circ}_{solvent} - 2.9) &= 6/5 \\ \dots p^{\circ}_{solvent} &= 3.4 \text{ kP}_a \\ i.e., \text{ vapour pressure of water at 298 K is 3.4 kp_a \\ \text{Substituting the value of } p^{\circ}_{solvent} \text{ in (1) we get,} \\ (3.4 - 2.8)/3.4 &= 6/M_2 \\ \dots M_2 &= 34 \text{ g} \\ \textbf{76.} \quad i = 2, K_b &= 0.512 \text{ K kg mol}^{-1}, W_B &= 15 \text{ g} \\ M_B &= 58.44 \text{ g mol}^{-1}, W_A &= 250 \text{ g} \\ \Delta T_b &= \frac{i \times K_b \times W_B \times 1000}{M_B \times W_A} \\ \Delta T_b &= \frac{2 \times 0.512 \times 15 \times 1000}{58.44 \times 250} \\ \text{Therefore, boiling point of aqueous solution,} \\ T_b &= T_b^{\circ} + \Delta T_b &= 373.15 \text{ K} + 1.05 \text{ K} &= 374.20 \text{ K} \\ \textbf{77.} \quad W_B &= 8.95 \text{ mg} &= 8.95 \times 10^{-3} \text{ g}, \\ R &= 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}, V &= 35 \times 10^{-3} \text{ L} \\ \end{array}$$

$$T = (25 + 273) \text{ K} = 298 \text{ K}, \ \pi = \frac{0.335}{760} \text{ atm}$$
Substituting these values in the equation,  

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

$$M_B = \frac{8.95 \times 10^{-3} \text{ g} \times 0.0821 \text{ Latm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.335} \frac{0.335}{760} \text{ atm} \times 35 \times 10^{-3} \text{ L}}$$

$$M_B = 14193 .29 \text{ g mol}^{-1}$$
78.  $W_2 = 6.21 \text{ g}, W_1 = 24.0 \text{ g}$ 
 $T_b = 68.04 \text{ °C}, T_b^\circ = 61.7 \text{ °C}$ 
and  $K_b = 3.63 \text{ °C/m}$ 

$$\Delta T_b = T_b - T_b^\circ = 68.04 \text{ °C} - 61.7 \text{ °C} = 6.34 \text{ °C}$$

$$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$
or
$$M_2 = \frac{K_b \times W_2 \times 1000}{6.34 \text{ °C} \times 24.0 \text{ g}} = 148.15 \text{ g mol}^{-1}$$
79.  $W_1 = 65.0 \text{ g}, \Delta T_f = 7.50 \text{ °C},$ 
 $K_f = 1.86 \text{ °C/m}, i = 1.87 \text{ and } M_2 = 58.5 \text{ g mol}^{-1}$ 

$$\Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{i \times K_f \times 1000} = \frac{7.50 \text{ °C} \times 58.5 \text{ g mol}^{-1} \times 65 \text{ g}}{1.87 \times 1.86 \text{ °C/m} \times 1000} = 8.199 \text{ g}$$
80. Refer to answer 63.  
81. Concentration of the solution = 1 molar Density of the solution = 1.06 \text{ g mL}^{-1}

$$K_{b} \text{ for } H_{2}O = 0.52 \text{ K kg mol}^{-1}$$
  
Molality,  $m = \frac{M \times 1000}{1000 \times d - M \times M_{2}}$   
 $m = \frac{1 \times 1000}{1000 \times 1.06 - 1 \times 119} = 1.0626 \text{ mol kg}^{-1}$   
 $\Delta T_{b} = K_{b}m = 0.52 \text{ K kg mol}^{-1} \times 1.0626 \text{ mol kg}^{-1}$   
 $\Delta T_{b} = 0.5525 \text{ K} \approx 0.553 \text{ K}$   
 $T_{b} = T_{b}^{\circ} + \Delta T_{b} = 373 \text{ K} + 0.553 \text{ K} = 373.553 \text{ K}$   
**82.**  $W_{2} = 1.25 \text{ g}, W_{1} = 99.0 \text{ g}$   
 $\Delta T_{b} = T_{b} - T_{b}^{\circ} = (80.31 - 80.10)^{\circ}\text{C} = 0.21^{\circ}\text{C} = 0.21 \text{ K}$   
 $\Delta T_{b} = K_{b} \cdot m$ 

$$\Delta T_{b} = K_{b} \times \frac{W_{2} \times 1000}{M_{2} \times W_{1}}, \quad M_{2} = \frac{K_{b} \times W_{2} \times 1000}{\Delta T_{b} \times W_{1}}$$

$$= \frac{2.53 \times 1.25 \times 1000}{0.21 \times 99} = \frac{3162.5}{20.79} = 152.11 = 152 \text{ g mol}^{-1}$$
83.  $M_{2}$  (ethylene glycol) = 62 g mol<sup>-1</sup>,  
 $W_{1} = 5.50 \text{ kg} = 5500 \text{ g}, \Delta T_{f} = T_{f}^{o} - T_{f} = 0^{\circ}\text{C} - (-10^{\circ}\text{C})$   
 $= 10^{\circ}\text{C} = 10 \text{ K}$ 
and  $K_{f} = 1.86 \text{ K kg mol}^{-1}$ 

$$\Delta T_{f} = \frac{K_{f} \times W_{2} \times 1000}{M_{2} \times W_{1}}$$
 $W_{2} = \frac{\Delta T_{f} \times M_{2} \times W_{1}}{K_{f} \times 1000} = \frac{10 \times 62 \times 5500}{1.86 \times 1000} = 1833.33 \text{ g}$ 
84.  $W_{2} = 100 \text{ mg} = 0.1 \text{ g},$ 
 $V = 10.0 \text{ mL} = 0.01 \text{ L},$ 
 $\pi = 13.3 \text{ mm Hg} = \frac{13.3}{760} \text{ atm}$ 
 $T = 25^{\circ}\text{C} = 273 + 25 = 298 \text{ K}$ 
 $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ 
 $\pi V = \frac{W_{2}RT}{M_{2}}$ 
 $M_{2}(\text{Protein}) = \frac{W_{2}RT}{\pi V}$ 
 $= \frac{0.1 \text{ g} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{\frac{13.3}{760} \text{ atm} \times 0.01 \text{ L}}$ 
 $M_{2} = 13980.45 \text{ g mol}^{-1}$ 
85.  $W_{1} = 1 \text{ kg} = 1000 \text{ g}, \Delta T_{f} = 3 \text{ K}$ 
 $K_{f} = 1.86 \text{ K kg mol}^{-1}$ 
 $M_{2}(\text{NaCl}) = 23 + 35.5 = 58.5 \text{ g mol}^{-1}$ 
 $\Delta T_{f} = \frac{i \times K_{f} \times W_{2} \times 1000}{M_{2} \times W_{1}}$ 
 $W_{2} = \frac{\Delta T_{f} \times M_{2} \times W_{1}}{i \times K_{f} \times 1000}$ 
[For NaCl,  $i = 2$  because 1 mole of NaCl on dissociation gives 2 moles of ions]
 $W_{2} = \frac{3 \times 58.5 \times 1000}{2 \times 186 \times 1000} = 47.18 \text{ g}$ 

 $W_2 = \frac{1}{2 \times 1.86 \times 1000} = 47.18$ 86. Total moles in solution

$$= \frac{x}{200} + 0.05 \times 2 = \frac{x}{200} + 0.1 \qquad (\because i = 2 \text{ for NaCl})$$
$$pV = nRT$$

$$n = \frac{\pi V}{RT}$$

$$\frac{x}{200} + 0.1 = \frac{4.92 \text{ atm} \times 1 \text{ L}}{0.082 \text{ L} \text{ atm} \text{ K}^{-1} \text{mol}^{-1} \times 300 \text{ K}} = 0.20$$

$$\frac{x}{200} = 0.20 - 0.1 = 0.1$$

$$x = 0.1 \times 200 = 20 \text{ g}$$
87. Molar mass of glucose,  $C_6H_{12}O_6$ 

$$= 6 \times 12 + 12 \times 1 + 6 \times 16 = 180 \text{ g mol}^{-1}$$
Molar mass of sucrose,  $C_{12}H_{22}O_{11}$ 

$$= 12 \times 12 + 22 \times 1 + 11 \times 16 = 342 \text{ g mol}^{-1}$$
mglucose  $= \frac{18}{180} = 0.1$ ,  $n_{\text{sucrose}} = \frac{68.4}{342} = 0.2$ 
Total moles of solute,  $n_2 = 0.1 + 0.2 = 0.3$ 

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$\Delta T_f = \frac{K_f \times n_2 \times 1000}{200 \text{ g}} = 2.79 \text{ K}$$
Freezing point of aqueous solution,  $T_f = T_f^{\circ} - \Delta T_f$ 

$$= 273 - 2.79 = 270.21 \text{ K}$$
88.  $M_2$  (glucose,  $C_6H_{12}O_6$ ) = 180 g mol<sup>-1</sup>  
 $M_2 = 54 \text{ g}$ ,  $W_1 = 250 \text{ g}$ ,  $K_f = 1.86 \text{ K kg mol}^{-1}$ 

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{1.86 \times 54 \times 1000}{180 \times 250} = 2.23 \text{ K}$$
Freezing point of solution,  $T_f = T_f^{\circ} - \Delta T_f$ 

$$= 273 \text{ K} - 2.23 \text{ K} = 270.77 \text{ K}$$
89.  $T_b = 36.86^\circ \text{C}$ ,  $T_b^{\circ} = 35.60^\circ \text{C}$ 

$$\Delta T_b = T_b - T_b^{\circ} = 36.86 - 35.60 = 1.26^\circ \text{C}$$

$$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} = \frac{8}{M_2} \times \frac{1000}{100} = \frac{80}{M_2}$$

$$\Delta T_b = K_b \cdot m$$
1.26 = 2.02  $\times \frac{80}{M_2}$ 

$$M_2 = \frac{80 \times 2.02}{1.26} = 128.25 \text{ g mol}^{-1}$$
90. Molality = 0.1539 m,  
 $\Delta T_f = T_f^{\circ} - T_f = 273.15 - 271 = 2.15 \text{ K}$ 
 $\therefore \Delta T_f = K_f \cdot m$  or  $K_f = \frac{\Delta T_f}{m} = \frac{2.15}{0.1539}$ 

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Again mass of solute,  $W_2 = 5 \text{ g}$ Molar mass of solute,  $M_2 = 180 \text{ g mol}^{-1}$ Mass of solution = 100 g  $\therefore$  Mass of solvent,  $W_1 = 95 \text{ g}$ Using,  $\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$  $= \frac{2.15 \times 5 \times 1000}{0.1539 \times 180 \times 95} = 4.08 \text{ K}$ 

 $\therefore \quad \text{Freezing point of solution, } T_f = T_f^\circ - \Delta T_f$ = 273.15 - 4.08 = 269.07 K

**91. van't Hoff factor :** It is defined as the ratio of the experimental value of colligative property to the calculated value of the colligative property and is used to find out the extent of dissociation or association. Mathematically, it is represented as

	Experimental (or observed value) of collig	gative
i —	proj	perty
<i>ι</i> –	Calculated (or normal value) of colligative	e
	pro	operty
92.	Refer to answer 91.	

(i) van't Hoff factor (i) > 1 for solutes undergoing dissociation

(ii) van't Hoff factor (i) < 1 For soutes undergoing association

93. Molecular mass of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O =  $[2 \times 23 + 32 + 16 \times 4 + 10 \times (2 \times 1 + 16)]$ = (46 + 32 + 64 + 180) g mol<sup>-1</sup> = 322 g mol<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O ionises as : Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O  $\implies 2Na^+ + SO_4^{2-} + 10H_2O$  $\implies i = 3$  $m = \frac{n_B}{W_A} = \frac{W_B}{M_B \times W_A} = \frac{6.00 \text{ g}}{322 \text{ g mol}^{-1} \times 0.1 \text{ kg}}$ = 0.186 mol kg<sup>-1</sup> = 0.186 m

Also,  $\Delta T_f = i K_f \cdot m$ = 3 × 1.86 K m<sup>-1</sup> × 0.186 m = 1.04 K  $\Rightarrow T_f = T_f^\circ - \Delta T_f = (273 - 1.04)$  K = 271.96 K

**94.** Molality of solution, m = 1.00 mBoiling point of solution,  $T_b = 100.18^{\circ}\text{C} = 373.18 \text{ K}$ Boiling point of water (solvent),  $T_b^{\circ} = 100.00^{\circ}\text{C} = 373 \text{ K}$  $\Delta T_b = T_b - T_b^{\circ} = 373 \cdot 18 \text{ K} - 373 \text{ K} = 0.18 \text{ K}$  $\Delta T_b = i K_b \cdot m$  $0.18 \text{ K} = i \times K_b \cdot m$  $0.18 \text{ K} = i \times 0.512 \text{ K kg mol}^{-1} \times 1 \text{ mol kg}^{-1}$ 

 $i = \frac{0.18 \text{ K}}{0.512 \text{ K kg mol}^{-1} \times 1 \text{ mol kg}^{-1}} = 0.35$ **95.** *Refer to answer 91 and 92 (i).* **96.**  $\Delta T_f = iK_f \cdot m$ *i* for MgCl<sub>2</sub> = 3 Molality,  $m = \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{1.9 \times 1000}{95 \times 50} = 0.4 \text{ m}$  $\Delta T_f = 3 \times 1.86 \times 0.4 = 2.232 \text{ K}$ Freezing point of solution, ,  $T_f = T_f^\circ - \Delta T_f$ = 273 - 2.232 K = 270.77 K **97.**  $W_2 = 2.56$  g,  $W_1 = 100$  g,  $\Delta T_f = 0.383$  K  $K_f = 3.83 \text{ K kg mol}^{-1}, \Delta T_f = K_f \times m$  $\Rightarrow \quad \Delta T_f = K_f \times \frac{W_2}{M_2} \times \frac{1000}{W_1}$  $M_{2} = \frac{W_{2} \times 1000}{\Delta T_{f} \times W_{1}} \times K_{f} = \frac{2.56 \times 1000}{0.383 \times 100} \times 3.83$  $= 256 \text{ g mol}^{-1}$  $i = \frac{\text{Normal atomic mass}}{\text{Observed atomic mass}} = \frac{32}{256} = \frac{1}{8}$ Sulphur exists as S<sub>8</sub>. **98.**  $W_2 = 4$  g,  $M_2 = 120$  g mol<sup>-1</sup>  $W_1 = 100$  g,  $K_b = 0.52$  K kg mol<sup>-1</sup> For complete dissociation, i = 2Using formula,  $\Delta T_b = iK_bm$ or  $\Delta T_b = \frac{i \times K_b \times W_2 \times 1000}{M_2 \times W_1} = 2 \times 0.52 \times \frac{4 \times 1000}{120 \times 100}$ = 0.34 K $\therefore$   $T_{h} = T_{h}^{\circ} + \Delta T_{h} = 100 + 0.34 = 100.34^{\circ}C$ 

**99.**  $W_2 = 3.9 \text{ g}, W_1 = 49 \text{ g}, \Delta T_f = 1.62 \text{ K}, M_2 = 122 \text{ g mol}^{-1}, K_f = 4.9 \text{ K kg mol}^{-1}$  $W_2 \times 1000$ 

$$\Delta T_f = i K_f m = i \times K_f \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$\Rightarrow \quad 1.62 = \frac{i \times 4.9 \times 3.9 \times 1000}{122 \times 49}$$

$$\Rightarrow \quad i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.506$$

As i < 1, solute is associated.

**100.** 
$$\Delta T_f = iK_f m = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$
  
 $2 = \frac{2 \times 1.86 \times W_2 \times 1000}{58.5 \times 37.2}$   
 $\Rightarrow W_2 = 1.17 \text{ g}$ 

101. Mass of K<sub>2</sub>SO<sub>4</sub>, 
$$W_2 = 2.5 \times 10^{-2}$$
 g  
Molar mass of K<sub>2</sub>SO<sub>4</sub>,  $M_2 = 174$  g mol<sup>-1</sup>  
 $V = 2$  L,  $T = 25^{\circ}\text{C} = 298$  K  
 $R = 0.0821$  L atm K<sup>-1</sup> mol<sup>-1</sup>  
We know, osmotic pressure,  $\pi = \frac{W_2 RT}{M_2 V}$   
 $\pi = \frac{2.5 \times 10^{-2} \times 0.0821 \times 298}{174 \times 2}$   
 $= \frac{61.1645 \times 10^{-2}}{348} = 0.1758 \times 10^{-2}$  atm  
102.  $\Delta T_f = 2$  K,  $K_f = 1.86$  K kg mol<sup>-1</sup>,  
 $W_1 = 1$  kg,  $\Delta T_f = i K_f m$ ,  $M_2$ (KCl) = 74.5 g mol<sup>-1</sup>  
 $i = 2$  for KCl  
 $\Delta T_f = \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$   
 $2 = \frac{2 \times 1.86 \times W_2 \times 1000}{74.5 \times 1000}$   
 $\Rightarrow W_2 = 40.05$  g  
103.  $W_2 = 10.50$  g,  $W_1 = 200$  g  
 $M_2$ (MgBr<sub>2</sub>) = 184 g mol<sup>-1</sup>  
 $K_f = 1.86$  K kg mol<sup>-1</sup>  
MgBr<sub>2(aq)</sub>  $\rightarrow$  Mg<sup>2+</sup><sub>(aq)</sub> + 2Br<sup>-</sup><sub>(aq)</sub>,  $i = 3$   
 $\Delta T_f = \frac{3 \times 1.86 \times 10.50 \times 1000}{184 \times 200} = 1.592$  K  
Freezing point of solution,  $T_f = T_f^\circ - \Delta T_f = 273 - 1.592$   
 $= 271.408$  K  
104.  $m = 0.561$  m,  $\Delta T_f = 2.93^{\circ}$ C and  
 $K_f = 1.86^{\circ}$ C kg mol<sup>-1</sup>

$$i = \frac{\Delta T_f}{K_f m} = \frac{2.93^{\circ}\text{C}}{1.86^{\circ}\text{C kg mol}^{-1} \times 0.561 \text{ m}} = 2.807$$

**105.** Here, n = 2 because phenol forms dimer on association.

$$\begin{split} W_2 &= 20 \text{ g, } W_1 = 1 \text{ kg} = 1000 \text{ g, } \Delta T_f = 0.69 \text{ K,} \\ K_f &= 5.1 \text{ K m}^{-1} \\ \Delta T_f &= \frac{K_f \times W_2 \times 1000}{M_2 \times W_1} \\ M_2 &= \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1} = \frac{5.1 \times 20 \times 1000}{0.69 \times 1000} = 147.82 \\ M_{2(\text{observed})} &= 147.82 \end{split}$$

 $M_{2(\text{calculated})}$   $C_{6}H_{5}OH = 6 \times 12 + 6 \times 1 + 16 = 94 \text{ g mol}^{-1}$   $i = \frac{M_{2}(\text{calculated})}{M_{2}(\text{observed})} = \frac{94}{147.82} = 0.635$   $2C_{6}H_{5}OH \rightleftharpoons (C_{6}H_{5}OH)_{2}$   $\alpha = \frac{i-1}{\left(\frac{1}{n}-1\right)} = \frac{0.635-1}{\left(\frac{1}{2}-1\right)} = \frac{0.365}{0.5} = 0.73 = 73\%$  **106.** Here, n = 3 because 1 molecule of BaCl<sub>2</sub> on

dissociation gives three ions.  $W_2 = 12.48$  g,  $W_1 = 1.0$  kg = 1000 g  $T_b = 373.0832$  K,  $K_b$  for H<sub>2</sub>O = 0.52 K m<sup>-1</sup> and  $M_2(\text{BaCl}_2) = 208.34 \text{ g mol}^{-1}$  $\Delta T_b = T_b - T_b^{\circ} = 373.0832 \text{ K} - 373 \text{ K} = 0.0832 \text{ K}$  $M_{2(\text{observed})} = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$  $M_{2(\text{observed})} = \frac{0.52 \times 12.48 \times 1000}{0.0832 \times 1000} = 78$  $M_{2(\text{observed})} = 78 \text{ g mol}^{-1}$  $i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{208.34 \text{ g mol}^{-1}}{78 \text{ g mol}^{-1}} = 2.67$  $\alpha = \frac{i-1}{n-1} = \frac{2.67-1}{3-1} = \frac{1.67}{2} = 0.835 = 83.5\%$ **107.**  $C = \frac{1}{10}$  M  $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$  $\therefore$  n = 5Degree of dissociation,  $\alpha = \frac{50}{100} = 0.5$  $\alpha = \frac{i-1}{n-1}, 0.5 = \frac{i-1}{5-1}, 0.5 = \frac{i-1}{4}$  $\Rightarrow$  i-1=2  $\therefore$  i=3So, osmotic pressure,  $\pi = iCRT$  $= 3 \times \frac{1}{10} \times 0.0821 \times 300 = 90 \times 0.0821 = 7.389$  atm **108.**  $M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1} = \frac{2.53 \times 0.30 \times 1000}{0.0633 \times 100}$  $= 120 \text{ g mol}^{-1}$  $\therefore$  Molar mass of CH<sub>3</sub>COOH = 60 g/mol  $i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{60}{120} = \frac{1}{2} = 0.5$ 

Here, i < 1, therefore the solute acetic acid is associated in benzene.

**109.** (i) 
$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1} = \frac{5.12 \times 0.2 \times 1000}{0.45 \times 20}$$
  
= 113.77 g/mol<sup>-1</sup>

(ii) Molar mass of acetic acid = 60 g/mol

$$i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{60}{113.77} = 0.52$$

i < 1, the solute acetic acid is associated in benzene.

**110.** (i) The depression in freezing point is in the order :

Acetic acid < trichloroacetic < trifluoroacetic acid

$$H$$
  
 $H$   
 $H$   
 $C$ -COOH  $< Cl$   
 $Cl$   
 $C$ -COOH  $< F$   
 $F$   
 $C$ -COOH  $< F$   
 $F$   
 $F$   
 $C$ -COOH  $< F$   
 $F$ 

Fluorine has the highest electron withdrawing inductive effect (-I effect) so trifluoroacetic acid is the strongest acid and acetic acid is the weakest acid. Therefore, trifluoroacetic acid ionises to the greater extent and acetic acid ionises to the minimum extent. Greater the number of ions produced, greater is the depression in freezing point.

(ii) Molar mass of CH<sub>3</sub>CH<sub>2</sub>CHClCOOH

$$= 4 \times 12 + 7 \times 1 + 35.5 + 2 \times 16 = 122.5 \text{ g mol}^{-1}$$

Number of moles of CH<sub>3</sub>CH<sub>2</sub>CHCICOOH  

$$= \frac{20}{122.5} = 0.1632 \text{ mol}$$
Molality of solution =  $\frac{\text{Moles of solute} \times 1000}{\text{Mass of solvent (g)}}$ 

$$m = \frac{0.1632 \times 1000}{500} = 0.3264 \text{ m}$$
CH<sub>3</sub>CH<sub>2</sub>CHCICOOH<sub>(aq)</sub>  $\Longrightarrow$   
CH<sub>3</sub>CH<sub>2</sub>CHCICOOH<sub>(aq)</sub>  $\xleftarrow$   
CH<sub>3</sub>CH<sub>2</sub>CHCICOO<sup>-</sup><sub>(aq)</sub> + H<sup>+</sup><sub>(aq)</sub>  
Initial conc. C = 0 = 0  
Equili. conc. C - C\alpha = C\alpha<sup>2</sup>  
( $\therefore$  1>>> \alpha)

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$
  
$$\alpha = \frac{i-1}{n-1} \implies 0.065 = \frac{i-1}{2-1} [\because \text{ For the given acid } n = 2 \text{ because 1 molecule gives } 2 \text{ particles on dissociation.}]$$

$$i = 1 + 0.065 = 1.065$$

$$\begin{split} \Delta T_f &= i K_f m \\ &= 1.065 \times 1.86 \times 0.3264 \\ \Delta T_f &= 0.6465 \approx 0.65 \; \mathrm{K} \end{split}$$