CHAPTER



## Solutions

- For 1 molal aqueous solution of the following compounds, 1. which one will show the highest freezing point?
  - (a)  $[Co(H_2O)_6]Cl_3$ (b)  $[Co(H_2O)_5Cl]Cl_2.H_2O$ (c)  $[Co(H_2O)_4Cl_2]Cl_2H_2O$ (d)  $[Co(H_2O)_3Cl_3].3H_2O$ 
    - (2018)
- Two 5 molal solutions are prepared by dissolving a non-2. electrolyte, non-volatile solute separately in the solvents X and Y. The molecular weights of the solvents are  $M_X$  and  $M_{Y}$ , respectively where,  $M_X = \frac{3}{4}M_Y$ . The relative lowering of vapour pressure of the solution in X is "m" times that

of the solution in Y. Given that the number of moles of solute is very small in comparison to that of solvent, the value of "m" is

- (b)  $\frac{4}{3}$  (c)  $\frac{1}{2}$  (d)  $\frac{1}{4}$ (a)  $\frac{3}{4}$ (Online 2018)
- 3. The mass of a non-volatile, non-electrolyte solute (molar mass = 50 g mol<sup>-1</sup>) needed to be dissolved in 114 g octane to reduce its vapour pressure to 75%, is (a) 50 g (b) 37.5 g (c) 75 g (d) 150 g

(Online 2018)

The freezing point of benzene decreases by 0.45°C when 4. 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, for benzene = 5.12 K kg mol<sup>-1</sup>)

(a) 
$$74.6\%$$
 (b)  $94.6\%$   
(c)  $64.6\%$  (d)  $80.4\%$  (2017)

5 g of  $Na_2SO_4$  was dissolved in x g of  $H_2O$ . The change in 5. freezing point was found to be 3.82 °C. If Na<sub>2</sub>SO<sub>4</sub> is 81.5% ionised, the value of x

( $K_{\ell}$  for water = 1.86 °C kg mol<sup>-1</sup>) is approximately (molar mass of S = 32 g mol<sup>-1</sup> and that of Na = 23 g mol<sup>-1</sup>) (a) 15 g (b) 45 g (c) 25 g (d) 65 g (Online 2017)

A solution is prepared by mixing 8.5 g of CH<sub>2</sub>Cl<sub>2</sub> and 6. 11.95 g of CHCl<sub>2</sub>. If vapour pressure of CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>2</sub> at 298 K are 415 and 200 mm Hg respectively, the mole fraction of CHCl<sub>3</sub> in vapour form is (Molar mass of  $Cl = 35.5 \text{ g mol}^{-1}$ ) (b) 0.162 (c) 0.486 (d) 0.325 (a) 0.675 (Online 2017)

- 7. 18 g glucose ( $C_6H_{12}O_6$ ) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is (a) 7.6 (b) 76.0
- (c) 752.4 (d) 759.0 (2016)The solubility of N<sub>2</sub> in water at 300 K and 500 torr partial 8. pressure is 0.01 g L<sup>-1</sup>. The solubility (in g L<sup>-1</sup>) at 750 torr partial pressure is
  - (b) 0.005 (a) 0.0075 (c) 0.02 (d) 0.015 (Online 2016)
- 9. An aqueous solution of salt  $MX_2$  at certain temperature has a van't Hoff factor of 2. The degree of dissociation for this solution of the salt is (d) 0.80 (a) 0.50 (b) 0.33 (c) 0.67

10. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol<sup>-1</sup>) of the substance is (a) 128 (b) 488 (c) 32 (d) 64

- 11. A solution at 20°C is composed of 1.5 mol of benzene and 3.5 mol of toluene. If the vapour pressure of pure benzene and pure toluene at this temperature are 74.7 torr and 22.3 torr, respectively, then the total vapour pressure of the solution and the benzene mole fraction in equilibrium with it will be, respectively
  - (a) 35.0 torr and 0.480 (b) 38.0 torr and 0.589 (c) 30.5 torr and 0.389 (d) 35.8 and 0.280
    - (Online 2015)
- 12. Determination of the molar mass of acetic acid in benzene using freezing point depression is affected by (a) dissociation (b) association
  - (c) partial ionization (d) complex formation.

(Online 2015)

- 13. Consider separate solutions of 0.500 M  $C_2H_5OH_{(aq)}$ , 0.100 M  $Mg_3(PO_4)_{2(aq)}$ , 0.250 M  $KBr_{(aq)}$  and 0.125 M  $Na_3PO_{4(aq)}$  at 25 °C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?
  - (a) 0.500 M  $C_2H_5OH_{(aq)}$  has the highest osmotic pressure.
  - (b) They all have the same osmotic pressure.

  - (c) 0.100 M Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2(aq)</sub> has the highest osmotic pressure.
    (d) 0.125 M Na<sub>3</sub>PO<sub>4(aq)</sub> has the highest osmotic pressure. (2014)

14. K<sub>f</sub> for water is 1.86 K kg mol<sup>-1</sup>. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) must you add to get the freezing point of the solution lowered to -2.8°C?
(a) 93 g
(b) 39 g
(c) 27 g
(d) 72 g

(c) 
$$27$$
 g (d)  $72$  g (2012)

**15.** The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is

(a) 1.78 M (b) 1.02 M (c) 2.05 M (d) 0.50 M (2012)

16. The degree of dissociation ( $\alpha$ ) of a weak electrolyte,  $A^{x}B^{y}$  is related to van't Hoff factor (*i*) by the expression

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

- 17. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at  $-6^{\circ}$ C will be : ( $K_f$  for water = 1.86 K kg mol<sup>-1</sup>, and molar mass of ethylene glycol = 62 g mol<sup>-1</sup>)
  - (a) 804.32 g (b) 204.30 g
  - (c) 400.00 g (d) 304.60 g (2011)
- **18.** A 5.2 molal aqueous solution of methyl alcohol,  $CH_3OH$ , is supplied. What is the mole fraction of methyl alcohol in the solution?

(a)	0.100	(b) 0.190	(c) 0.086	(d)	0.050
					(2011)

**19.** On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressure of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol<sup>-1</sup> and of octane = 114 g mol<sup>-1</sup>)

(a) 144.5 kPa (b) 72.0 kPa

- (c) 36.1 kPa (d) 96.2 kPa (2010)
- **20.** 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 mol of sodium sulphate is dissolved in 1 kg of water, is

$(K_f = 1.86)$	K kg mol <sup>-1</sup> )			
(a) 0.018	6 K (1	b)	0.0372 K	
(c) 0.055	8 K (e	d)	0.0744 K	(2010)

- **21.** A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution?
  - (a) The solution formed is an ideal solution.
  - (b) The solution is non-ideal, showing +ve deviation from Raoult's law.
  - (c) The solution is non-ideal, showing -ve deviation from Raoult's law.
  - (d) *n*-heptane shows +ve deviation while ethanol shows -ve deviation from Raoult's law. (2009)

- 22. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol 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 (2009)
- **23.** The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose  $(C_6H_{12}O_6)$  is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be
  - (a) 17.325 mm Hg (b) 17.675 mm Hg

(c) 15.750 mm Hg (d) 16.500 mm Hg

(2008)

24. At 80°C, the vapour pressure of pure liquid A is 520 mm of Hg and that of pure liquid B is 1000 mm of Hg. If a mixture solution of A and B boils at 80°C and 1 atm pressure, the amount of A in the mixture is

(1 atm = 760 mm of Hg)

- (a) 50 mol percent (b) 52 mol percent
- (c) 34 mol percent (d) 48 mol percent (2008)
- **25.** A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol<sup>-1</sup>) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm<sup>-3</sup>, molar mass of the substance will be  $(a_1 210.0 \text{ g ms}^{-1})$  (b)  $(a_2 210.0 \text{ g ms}^{-1})$

(a) 
$$210.0 \text{ g mol}^{-1}$$
 (b)  $90.0 \text{ g mol}^{-1}$ 

 (c)  $115.0 \text{ g mol}^{-1}$ 
 (d)  $105.0 \text{ g mol}^{-1}$ 
 (2007)

- 26. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 nm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be (a) 360 (b) 350 (c) 300 (d) 700 (2007)
- 27. The density (in g mL<sup>-1</sup>) of a 3.60 M sulphuric acid solution that is 29%  $H_2SO_4$  (molar mass = 98 g mol<sup>-1</sup>) by mass will be (a) 1.45 (b) 1.64 (c) 1.88 (d) 1.22 (2007)
- **28.** 18 g of glucose  $(C_6H_{12}O_6)$  is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is
  - (a) 759.00 torr (b) 7.60 torr (c) 76.00 torr (d) 752.40 torr (2006)
- **29.** Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is
  - (a)  $1.14 \text{ mol } \text{kg}^{-1}$  (b)  $3.28 \text{ mol } \text{kg}^{-1}$
  - (c)  $2.28 \text{ mol kg}^{-1}$  (d)  $0.44 \text{ mol kg}^{-1}$  (2006)
- 30. Equimolal solutions in the same solvent have
  - (a) same boiling point but different freezing point
  - (b) same freezing point but different boiling point
  - (c) same boiling and same freezing points
  - (d) different boiling and different freezing points. (2005)

- **31.** Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 mL of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture?
  - (a) 1.20 M (b) 1.50 M
  - (c) 1.344 M (d) 2.70 M (2005)
- **32.** Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is

(a) 50 (b) 25 (c) 37.5 (d) 53.5 (2005)

- **33.** If  $\alpha$  is the degree of dissociation of Na<sub>2</sub>SO<sub>4</sub>, the vant Hoff's factor (*i*) used for calculating the molecular mass is (a)  $1 + \alpha$  (b)  $1 - \alpha$  (c)  $1 + 2\alpha$  (d)  $1 - 2\alpha$ (2005)
- 34. Which one of the following statements is false?
  - (a) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction.
  - (b) The osmotic pressure  $(\pi)$  of a solution is given by the equation  $(\pi = MRT)$ , where M is the molarity of the solution.
  - (c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is 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. (2004)
- **35.** 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 (2004)
- **36.** To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous 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 (2004)

- **37.**  $6.02 \times 10^{20}$  molecules of urea are present in 100 ml of its solution. The concentration of urea solution is (a) 0.001 M (b) 0.01 M (c) 0.02 M (d) 0.1 M (2004)
- **38.** Which one of the following aqueous solutions will exhibit highest boiling point?
  - (a)  $0.01 \text{ M Na}_2 \text{SO}_4$  (b)  $0.01 \text{ M KNO}_3$
  - (c) 0.015 M urea (d) 0.015 M glucose

(2004)

- 39. If liquids A and B form an ideal solution, the(a) enthalpy of mixing is zero
  - (b) entropy of mixing is zero
  - (c) free energy of mixing is zero
  - (d) free energy as well as the entropy of mixing are each zero.

(2003)

- 40. 25 mL of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a litre value of 35 mL. The molarity of barium hydroxide solution was (a) 0.07 (b) 0.14 (c) 0.28 (d) 0.35 (2003)
- **41.** In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionization is 0.3. Taking  $K_f$  for water as 1.85, the freezing point of the solution will be nearest to

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

- 42. In mixture A and B components show -ve deviation as
  - (a)  $\Delta V_{\text{mix}} > 0$
  - (b)  $\Delta H_{\text{mix}} < 0$
  - (c) A B interaction is weaker than A A and B B interaction
  - (d) A B interaction is stronger than A A and B B interaction.

(2002)

- 43. Freezing point of an aqueous solution is (-0.186)°C. Elevation of boiling point of the same solution is K<sub>b</sub> = 0.512°C, K<sub>f</sub> = 1.86°C, find the increase in boiling point.
  (a) 0.186°C
  (b) 0.0512°C
  - (c) 0.092°C (d) 0.2372°C (2002)

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

1. (d):  $\Delta T_f = iK_f m$ *m* is same for all the solutions thus,  $\Delta T_f \propto i$  (number of ions or molecules) where,  $\Delta T_f = T_f - T_i$  $[Co(H_2O)_6]Cl_3 \Rightarrow 4 \text{ ions } (i = 4)$  $[Co(H_2O)_5Cl] Cl_2 \cdot H_2O \Rightarrow 3 \text{ ions } (i = 3)$  $[Co(H_2O)_4Cl_2]$  Cl·2H<sub>2</sub>O  $\Rightarrow$  2 ions (*i* = 2)  $[Co(H_2O)_3Cl_3]$ ·3H<sub>2</sub>O  $\Rightarrow$  No ion (*i* = 1) Freezing point of solution increases, the value of *i* decreases. So, highest freezing point will be of [Co(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub>]·3H<sub>2</sub>O solution. (a): Molality =  $\frac{\text{No.of moles of solute}}{\text{Mass of solvent (in kg)}}$ 2. No. of moles of solute =  $5 \times 1 = 5$  (in both the solvents) 1000 No. of moles of solvent  $X = \frac{1000}{M_X}$ No. of moles of solvent  $Y = \frac{1000}{M_Y}$ Relative lowering in vapour pressure is given as,  $\frac{p^{\circ} - p_s}{p_s} = \frac{n_2}{n_1}$  $\left(\frac{p^{\circ} - p_s}{p_s}\right)_{\text{solution in } X} = \frac{5}{\frac{1000}{M_X}} = \frac{5M_X}{1000}$  $\left(\frac{p^{\circ} - p_s}{p_s}\right)_{\text{solution in }Y} = \frac{5}{\frac{1000}{M}} = \frac{5M_Y}{1000}$ According to question,  $\frac{1}{m} \times \frac{5M_X}{1000} = \frac{5M_Y}{1000}$  $\frac{1}{m} \times 5 \times \frac{3}{4} M_Y = 5M_Y \quad \left(\text{Given}, M_X = \frac{3}{4} M_Y\right)$  $\therefore m = \frac{3}{4}$ 3. (\*): Molar mass of solute =  $50 \text{ g mol}^{-1}$ Molar mass of octane =  $114 \text{ g mol}^{-1}$ Relative lowering in vapour pressure is given as :  $\frac{p^{\circ} - p_s}{p_s} = \frac{n_2}{n_1}$  $n_2 = \frac{w}{50}$  (where *w* is the mass of solute.);  $n_1 = \frac{114}{114} = 1$  $\frac{p^{\circ} - 0.75 \, p^{\circ}}{0.75 \, p^{\circ}} = \frac{w}{\frac{50}{1}} \implies \frac{0.25 \, p^{\circ}}{0.75 \, p^{\circ}} = \frac{w}{50}$ 

 $w = \frac{50 \times 25}{75} = 16.66 \text{ g}$ 

\* None of the given options is correct.

4. **(b)**:  $\Delta T_f = 0.45 \,^{\circ}\text{C}$ ,  $w_2$  (acetic acid) = 0.2 g  $w_1$  (benzene) = 20 g,  $K_f = 5.12$  K kg mol<sup>-1</sup>  $\Delta T_f = i \times K_f \times m \implies i = \frac{\Delta T_f}{K_f \times m} = \frac{0.45 \times 20 \times 60}{5.12 \times 0.2 \times 1000} = 0.527$  According to question,

2CH<sub>3</sub>COOH  $\rightarrow$ (CH<sub>3</sub>COOH)<sub>2</sub> 1 mol 0 Initially : α After time t:  $(1 - \alpha)$  mol 2  $\Rightarrow i = 1 - \alpha + \frac{\alpha}{2}$  $i=1-\frac{\alpha}{2}$ ...(i) On putting the value of i in equation (i), we get  $0.527 = 1 - \frac{\alpha}{2} \implies -0.946 = -\alpha \implies \alpha = 0.946$ Percentage association of acetic acid in benzene = 94.6%  $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$ 5. (b) : Initial : 1 mol 0 0 After ionisation :  $1 - \alpha$  $2\alpha$ Total no. of moles =  $1 + 2\alpha$  $i = 1 + 2\alpha \Longrightarrow 1 + 2 \times 0.815 = 2.63$  $\therefore \quad \Delta T_f = \frac{1000 \times K_f \times w_2 \times i}{M_2 \times w_1} \quad \Rightarrow \quad 3.82 = \frac{1.86 \times 2.63 \times 5 \times 1000}{142 \times x}$  $\therefore x = \frac{1.86 \times 2.63 \times 5000}{142 \times 3.82} = 45 \text{ g}$ 6. (d): No. of moles of  $CHCl_3 = \frac{11.95}{110.5} = 0.1$  mole No. of moles of  $CH_2Cl_2 = \frac{8.5}{85} = 0.1$  mole Mole fraction of CHCl<sub>3</sub>,  $x_A = \frac{0.1}{0.1 + 0.1} = 0.5$ Mole fraction of  $CH_2Cl_2$ ,  $x_B = 1 - 0.5 = 0.5$  $P_{\text{total}} = p_{\text{CHCl}_3} + p_{\text{CH}_2\text{Cl}_2} = x_A \times p^{\circ}_{\text{CHCl}_3} + x_B \times p^{\circ}_{\text{CH}_2\text{Cl}_2}$  $= 0.5 \times 200 + 0.5 \times 415 = 307.5 \text{ mm Hg}$ As,  $p_{\text{CHCl}_3} = 100 \text{ mm}$ ,  $P_{\text{total}} = 307.5 \text{ mm Hg}$  $\therefore \text{ Mole fraction of CHCl}_3 \text{ in vapour phase will be}$   $\frac{P_{\text{CHCl}_3}}{P_{\text{total}}} = \frac{100}{307.5} = 0.325$ P<sub>total</sub> 7. (c) : Number of moles of glucose  $J_{,O_{67}W}$ .  $=\frac{6=}{6=5}=536$  y { x Number of moles of water -  $O_7W^2 = \frac{6 <= 37}{6} = >39 \text{ y} \{x\}$ Mole fraction of water in solution - O7W  $= \frac{O_7W}{O_7W + J_{;O_{67}W;}} = \frac{>3}{65} = 53>$ Vapour pressure of water in aqueous solution,  $p_{\rm H_2O} = p^{\circ}_{\rm H_2O} x_{\rm H_2O} = 760 \text{ torr} \times 0.99 = 752.4 \text{ torr}$ 8. (d) : Partial pressure = Mole fraction × Solubility  $\frac{p_1}{p_2} = \frac{s_1}{s_2} \implies \frac{500}{750} = \frac{0.01}{s_2} \implies s_2 = 0.015 \text{ g L}^{-1}$ 

9. (a): 
$$\alpha = \frac{i-1}{n-1} = \frac{2-1}{3-1} = \frac{1}{2} = 0.50$$

**10.** (d) : Given :  $P^{\circ} = 185$  torr,  $w_1 = 100$  g,  $w_2 = 1.2$  g,  $P_s = 183$  torr  $M_1 = j_{1} O_{0} W_1 O_{0} = 58 \text{ g mol}^{-1}$ 

$$\frac{m^2 - m}{m^2} = \frac{-jj}{_{6}j} \frac{6}{_{7}}$$

$$\frac{6 = -6 = 8}{_{6} = -6 = 8} = \frac{6\Im \times :}{_{6}55 \times j} \implies j_{7} = \frac{6\Im \times :}{_{6}55 \times 7}$$

$$= 64.38 \approx 64 \text{ g mol}^{-1}$$

11. (b) : Total vapour pressure of solution =  $p_A^{\circ} x_A + p_B^{\circ} x_B$ Total vapour pressure of solution

$$= \left(\frac{63}{:} \times <93 \times +\frac{83}{:} \times 7738\right) = (22.41 + 15.61) = 38.02 \text{ torr}$$

Mole fraction of benzene in vapour form  $=\frac{7736}{9-77}=53 \Rightarrow$ 

12. (b): Molar mass of acetic acid in benzene using freezing point depression is affected by association.

Association results in the decrease in the number of particles and hence decrease in the value of colligative property and increase in the molecular mass.

13. (b) : Applying the equation,  $\pi = iCRT$ 

Solution	i	С	i × C
C <sub>2</sub> H <sub>5</sub> OH <sub>(aq)</sub>	1	0.5	0.5
$Mg_3(PO_4)_{2(aq)}$	5	0.1	0.5
KBr <sub>(aq)</sub>	2	0.25	0.5
Na <sub>3</sub> PO <sub>4(aq)</sub>	4	0.125	0.5

The value of  $i \times C$  indicates that all the solutions have same osmotic pressure.

14. (a):  $K_f = 1.86$  K kg mol<sup>-1</sup>,  $\Delta T_f = 0 - (-2.8) = 2.8$ °C Mass of solvent = 1.0 kg, Mass of solute = ? Molecular mass of solute = 62

 $\Delta T_f = K_f \times m$ 

 $\frac{\frac{\text{Weight of solute}}{\text{Molecular mass of solute}}}{\text{Mass of solvent (g)}} \times 1000 = \frac{w/62}{1000} \times 1000 = \frac{w}{62}$  $\Delta T_f = K_f \times m \implies 2.8 = 1.86 \times \frac{w}{62} \implies w = \frac{62 \times 2.8}{1.86} = 93 \text{ g}$ 15. (c) : Mass of solute taken = 120 gMolecular mass of solute = 60 uMass of solvent = 1000 gDensity of solution = 1.15 g/mL Total mass of solution = 1000 + 120 = 1120 g

Volume of solution =  $\frac{\text{Mass}}{\text{Density}} = \frac{1120}{1.15} \text{ mL}$ 

Mass of solute Molarity =  $\frac{\text{Molecular mass of solute}}{\times 1000}$ Volume of solution  $=\frac{120/60}{1120/1.15}\times1000=\frac{2\times1000\times1.15}{1120}=2.05 \text{ M}$ **16.** (a) :  $A^{x}B^{y} \longrightarrow xA^{y^{+}} + yB^{x^{-}}$  $1 - \alpha$ yα xα  $i = 1 - \alpha + x\alpha + y\alpha = 1 + \alpha(x + y - 1)$  $\therefore \qquad \alpha = \frac{i-1}{(x+y-1)}$ 17. (a) :  $\Delta T_f = K_f \times m = K_f \times \frac{w_2 \times 1000}{w_1 \times m_2}$  $w_1$  and  $w_2$  = wt. of solvent and solute  $m_2$  = molecular wt. of solute,  $\Delta T_f = 0 - (-6) = 6$  $\therefore 6 = \frac{1.86 \times w_2 \times 1000}{4000 \times 62} \implies w_2 = \frac{6 \times 62 \times 4000}{1000 \times 1.86} = 800 \text{ g}$ **18.** (c) : Mole fraction of solute =  $\frac{n}{N+n}$ n = number of moles of solute N = number of moles of solvent Here solute is methyl alcohol, solvent is water. Given n = 5.2,  $N = \frac{1000}{18}$ 

:. Mole fraction = 
$$\frac{5.2}{5.2 + \frac{1000}{18}} = \frac{5.2 \times 18}{93.6 + 1000}$$
  
=  $\frac{93.6}{1093.6} = 0.0855 \approx 0.086$ 

**19.** (b) : Given,  $p^{\circ}_{heptane} = 105 \text{ kPa}$ 

$$p^{\circ}_{\text{octane}} = 45 \text{ kPa}, w_{\text{heptane}} = 25 \text{ g}, w_{\text{octane}} = 35 \text{ g}$$

$$n_{\text{heptane}} = \frac{25}{100} = 0.25, n_{\text{octane}} = \frac{35}{114} = 0.30$$

$$x_{\text{heptane}} = \frac{0.25}{0.25 + 0.30} = 0.45, x_{\text{octane}} = \frac{0.30}{0.25 + 0.30} = 0.54$$

$$p_{\text{Total}} = x_{\text{heptane}} p^{\circ}_{\text{heptane}} + x_{\text{octane}} p^{\circ}_{\text{octane}} = 0.45 \times 105 + 0.54 \times 45$$

$$= 47.25 + 24.3 = 71.55 \approx 72 \text{ kPa}$$
**20.** (c) :Depression in freezing point,  $\Delta T_f = i \times K_f \times m$ 
For sodium sulphate,  $i = 3$ 

$$m = \frac{0.01}{1 \text{ kg}} = 0.01 \text{ m}$$
Given,  $K_f = 1.86 \text{ K kg mol}^{-1}$ 

:. 
$$\Delta T_f = 3 \times 1.86 \times 0.01 = 0.0558 \text{ K}$$

21. (b): The solution containing *n*-heptane and ethanol shows non-ideal behaviour with positive deviation from Raoult's law. This is because the ethanol molecules are held together by strong H-bonds, however the forces between n-heptane and ethanol are not very strong, as a result they easily vapourise showing higher vapour presure than expected.

**22.** (c) : 
$$P_T = p_X^{\circ} x_X + p_Y^{\circ} x_Y$$

where,  $P_T$  = Total presure,  $p_X^{\circ}$  = Vapour pressure of X in pure state,  $p_Y^{\circ} =$  Vapour pressure of Y in pure state,  $x_X =$  Mole fraction of X = 1/4,  $x_Y =$  Mole fraction of Y = 3/4

When T = 300 K,  $P_T = 550$  mm Hg (i) :.  $550 = p_X^* \left(\frac{1}{4}\right) + p_Y^* \left(\frac{3}{4}\right)$  $\Rightarrow p_X^\circ + 3p_Y^\circ = 2200$ ...(1) (ii) When at T = 300 K, 1 mole of Y is added,  $P_T = (550 + 10) \text{ mm Hg}$ :.  $x_X = 1/5$  and  $x_Y = 4/5 \implies 560 = p_X^{\circ}\left(\frac{1}{5}\right) + p_Y^{\circ}\left(\frac{4}{5}\right)$ or  $p_X^{\odot} + 4 p_Y^{\circ} = 2800$ ...(2) On solving equations (1) and (2), we get  $p_{Y}^{\circ} = 600 \text{ mm Hg and } p_{X}^{\circ} = 400 \text{ mm Hg}$ 23. (a) : In solution containing non-volatile solute, pressure is directly proportional to its mole fraction.  $P_{\text{solution}} = \text{Vapour pressure of its pure component}$  $\times$  mole fraction in solution  $\therefore P_{sol} = P^{\circ}X_{solvent}$ Let A be the solute and B the solvent  $\therefore \quad X_B = \frac{n_B}{n_A + n_B} = \frac{\frac{178.2}{18}}{\frac{18}{180} + \frac{178.2}{18}} = \frac{9.9}{10} = 0.99$ Now  $P_{\text{solution}} = P^{\circ}X_{\text{solvent}} = 17.5 \times 0.99 = 17.325$ 24. (a) : We have,  $P_A^{\circ} = 520 \text{ mm Hg and } P_B^{\circ} = 1000 \text{ mm Hg}$ Let mole fraction of A in solution =  $X_A$ and mole fraction of B in solution =  $X_B$ Then, at 1 atm pressure i.e. at 760 mm Hg  $P_{A}^{\circ} X_{A} + P_{B}^{\circ} X_{B} = 760 \text{ mm Hg}$  $P_A^{\circ} X_A + P_B^{\circ} (1 - X_A) = 760 \text{ mm Hg}$  $\Rightarrow$  520  $X_A$  + 1000 - 1000  $X_A$  = 760 mm Hg  $\Rightarrow X_A = \frac{1}{2}$  or 50 mol percent 25. (a) : Isotonic solutions have same osmotic pressure.  $\pi_1 = C_1 RT, \quad \pi_2 = C_2 RT$ For isotonic solution,  $\pi_1 = \pi_2$ 1.5/605.25/M

$$\therefore \quad C_1 = C_2 \quad \text{or,} \quad \frac{1}{V} = \frac{1}{V}$$

[Where M = molecular weight of the substance]

or, 
$$\frac{1.5}{60} = \frac{5.25}{M} \implies M = \frac{60 \times 5.25}{1.5} = 210$$

26. (b) : According to Raoult's law,

$$P = P_A + P_B = P_A^* x_A + P_B^* x_B$$

or 
$$290 = P_A^{\circ} \times (0.6) + 200 \times (1 - 0.6)$$

or 
$$290 = 0.6 \times P_A^\circ + 0.4 \times 200 \implies P_A^o = 350 \text{ mm}$$

**27.** (d) : 3.6 M solution means 3.6 mole of  $H_2SO_4$  is present in 1000 mL of solution.

:. Mass of 3.6 moles of  $H_2SO_4 = 3.6 \times 98$  g = 352.8 g :. Mass of  $H_2SO_4$  in 1000 mL of solution = 352.8 g Given, 29 g of  $H_2SO_4$  is present in 100 g of solution

:. 352.8 g of H<sub>2</sub>SO<sub>4</sub> is present in 
$$\frac{100}{29} \times 352.8 = 1216$$
 g of solution

Now, density =  $\frac{\text{Mass}}{\text{Volume}} = \frac{1216}{1000} = 1.216 \text{ g/mL}$ 

**28.** (d): 
$$\frac{p - p_s}{p_s} = \frac{n}{N} \Rightarrow \frac{760 - p_s}{p_s} = \frac{187180}{178.2/18} = \frac{1710}{9.9}$$
  
 $\Rightarrow 760 - p_s = \frac{1}{99}p_s \Rightarrow 760 \times 99 - 99p_s = p_s$   
 $\Rightarrow 100p_s = 760 \times 99 \Rightarrow p_s = \frac{760 \times 99}{100} = 752.4 \text{ torr}$ 

**29.** (c) : Molality, 
$$m = \frac{M}{1000d - MM_2} \times 1000$$

where M = molarity, d = density,  $M_2 =$  molecular mass

$$m = \frac{2.05}{1000 \times 1.02 - 2.05 \times 60} = \frac{2.05}{897}$$
$$= 2.28 \times 10^{-3} \text{ mol g}^{-1} = 2.28 \text{ mol kg}^{-1}$$

**30.** (c) : According to Raoult's law equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points as well as equal depression in freezing point.

**31.** (c) : Total millimoles of solute =  $480 \times 1.5 + 520 \times 1.2$ 

$$= 720 + 624 = 1344$$

Total volume = 480 + 520 = 1000

Molarity of the final mixture =  $\frac{1344}{1000} = 1.344$  M

52. (a) : According to Rabult's law, 
$$P_B = P_B^2 X_B$$
  
 $P_B^\circ = 75 \text{ torr}$   
 $X_B = \frac{78/78}{(78/78) + (46/92)} = \frac{1}{1 + 0.5} = \frac{1}{1.5}$   
 $P_B = 75 \times \frac{1}{1.5} = 50 \text{ torr}$   
33. (c) : Na<sub>2</sub>SO<sub>4</sub>  $\implies 2 \text{ Na}^+ + \text{ SO}_4^{2-}$   
 $1 \qquad 0 \qquad 0$   
 $1 - \alpha \qquad 2\alpha \qquad \alpha$ 

Vant Hoff factor (i) =  $\frac{1-\alpha+2\alpha+\alpha}{1} = 1 + 2\alpha$ 

34. (d) : The extent of depression in freezing point varies with the number of solute particles for a fixed solvent only and it's a characteristic feature of the nature of solvent also.  $\Delta T_f = k_f \times m$ 

For different solvents, value of  $k_f$  is also different. So, for two different solvents the extent of depression may vary even if number of solute particles be dissolved in them.

**35.** (b) : In solutions showing positive deviation, the observed vapour pressure of each component and total vapour pressure are greater than predicted by Raoult's law, *i.e.* 

$$p_A > p_A^o x_A; p_B > p_B^o x_B; p > p_A + p_B$$

In solution of methanol and benzene, methanol molecules are held together due to hydrogen bonding as shown below:

$$\begin{array}{ccc} CH_3 & CH_3 & CH_3 \\ I & I & I \\ \cdots & O & H \\ \end{array} \begin{array}{c} H \\ \cdots \\ H \\ \end{array} \begin{array}{c} H \\ \end{array} \begin{array}{c} H \\ \end{array} \begin{array}{c} H \\ \end{array}$$

On adding benzene, the benzene molecules get in between the molecules of methanol, thus breaking the hydrogen bonds. As the resulting solution has weaker intermolecular attractions, the escaping tendency of alcohol and benzene molecules from the solution increases. Consequently the vapour pressure of the solution is greater than the vapour pressure as expected from Raoult's law.

**36.** (c) : H<sub>3</sub>PO<sub>3</sub> is a dibasic acid.  $N_1V_1$  (acid) =  $N_2V_2$  (base)  $0.1 \times 2 \times 20 = 0.1 \times 1 \times V_2$  $\therefore V_2 = \frac{0.1 \times 2 \times 20}{0.1 \times 1} = 40$  mL

**37.** (b) : Moles of urea =  $\frac{6.02 \times 10^{20}}{6.02 \times 10^{23}} = 10^{-3}$  moles

Concentration (molarity) of solution =  $\frac{\text{no. of moles of solute}}{\text{no. of litres of solution}}$ 

$$= \frac{10^{-3}}{100} \times 1000 = 0.01 \text{ M}$$

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**38.** (a): Elevation in boiling point is a colligative property which depends upon the number of solute particles.

Greater the number of solute particles in a solution, higher the extent of elevation in boiling point.

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$$

**39.** (a) : For ideal solutions,  $\Delta H_{\text{mix}} = 0$ , neither heat is evolved nor absorbed during dissolution.

40. (b) : Ba(OH)<sub>2</sub> HCl  

$$M_1V_1 = M_2V_2$$
  
 $M_1 \times 25 = 0.1 \times 35$   
 $M_1 = \frac{0.1 \times 35}{25} = 0.14$   
41. (a) : HX  $\longrightarrow$  H<sup>+</sup> + X<sup>-</sup>  
1 0 0 0  
1 - 0.3 0.3 0.3  
Total number of moles after dissociation = 1 - 0.3 + 0.3 + 0.3 = 1.3  
 $\frac{K_f \text{ (observed)}}{K_f \text{ (experimental)}} = \frac{\text{no. of moles after dissociation}}{\text{no. of moles before dissociation}}$   
or,  $\frac{K_f \text{ (observed)}}{1.85} = \frac{1.3}{1}$   
or,  $K_f \text{ (observed)} = 1.85 \times 1.3 = 2.405$   
 $\Delta T_f = K_f \times \text{ molality} = 2.405 \times 0.2 = 0.4810$   
Freezing point of solution = 0 - 0.481 = -0.481°C

**42.** (b, d): For negative deviation, from Raoult's law,  $\Delta V_{\text{mix}} < 0$  and  $\Delta H_{\text{mix}} < 0$ . Here A - B attractive force is greater than A - A and B - B attractive forces.

**43.** (b) : 
$$\Delta T_b = K_b \frac{W_B}{M_B \times W_A} \times 1000$$
  
 $\Delta T_f = K_f \frac{W_B}{M_B \times W_A} \times 1000$   
 $\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} \Rightarrow \frac{\Delta T_b}{0.186} = \frac{0.512}{1.86} \Rightarrow \Delta T_b = 0.0512^{\circ}\text{C}$