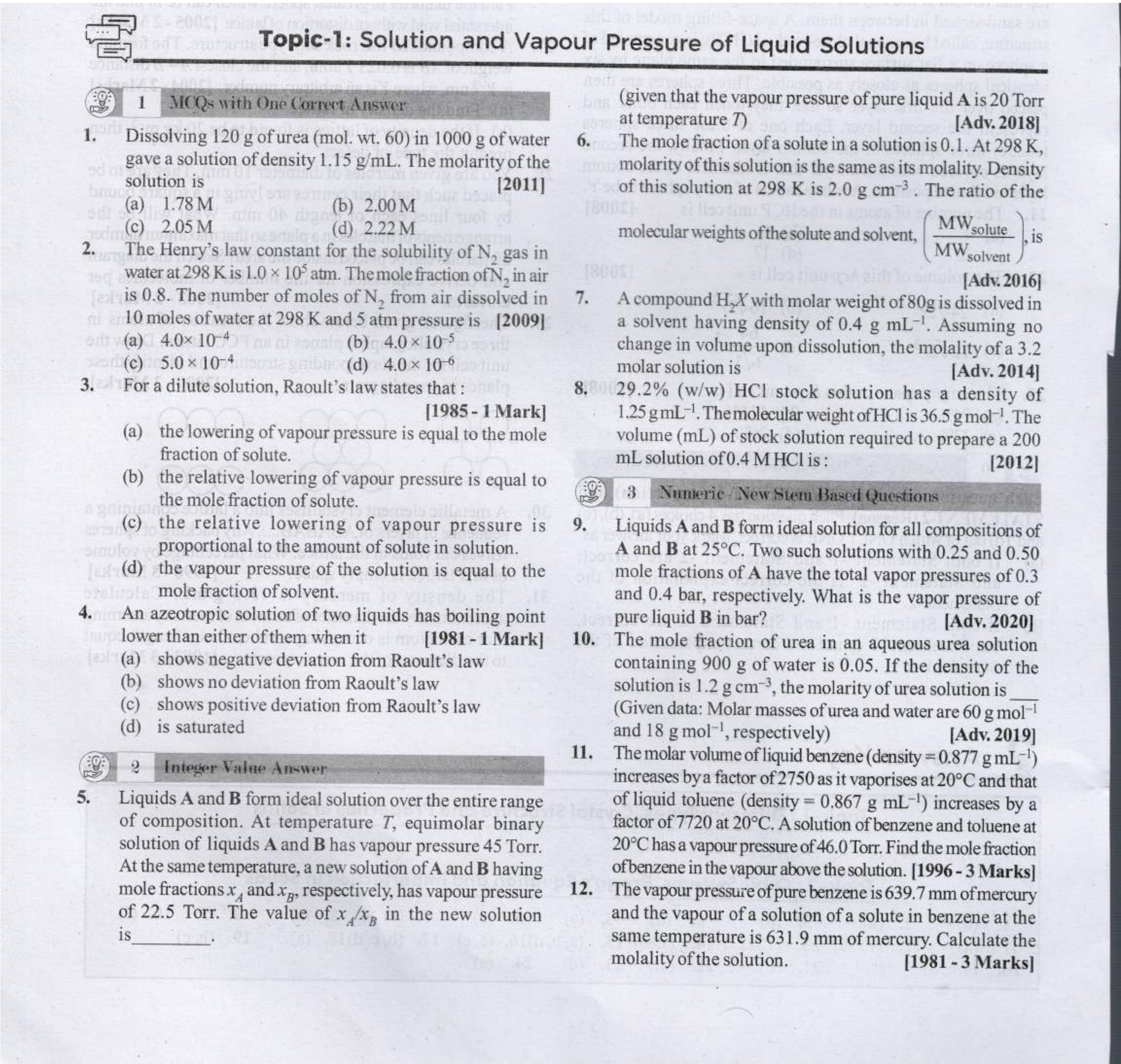
Chapter - Solutions



Topic-1: Solution and Vapour Pressure of Liquid Solutions

1 MCQs with One Correct Answer

1. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is **[2011]**
   (a) 1.78 M (b) 2.00 M
   (c) 2.05 M (d) 2.22 M

2. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is **[2009]**
   (a) 4.0×10^{-4} (b) 4.0×10^{-5}
   (c) 5.0×10^{-4} (d) 4.0×10^{-6}

3. For a dilute solution, Raoult's law states that : **[1985 - 1 Mark]**
   (a) the lowering of vapour pressure is equal to the mole fraction of solute.
   (b) the relative lowering of vapour pressure is equal to the mole fraction of solute.
   (c) the relative lowering of vapour pressure is proportional to the amount of solute in solution.
   (d) the vapour pressure of the solution is equal to the mole fraction of solvent.

4. An azeotropic solution of two liquids has boiling point lower than either of them when it **[1981 - 1 Mark]**
   (a) shows negative deviation from Raoult's law
   (b) shows no deviation from Raoult's law
   (c) shows positive deviation from Raoult's law
   (d) is saturated

2 Integer Value Answer

5. Liquids **A** and **B** form ideal solution over the entire range of composition. At temperature *T*, equimolar binary solution of liquids **A** and **B** has vapour pressure 45 Torr. At the same temperature, a new solution of **A** and **B** having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. The value of x_A/x_B in the new solution is________. (given that the vapour pressure of pure liquid **A** is 20 Torr at temperature *T*) **[Adv. 2018]**

6. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3}. The ratio of the molecular weights of the solute and solvent, $\left(\frac{MW_{solute}}{MW_{solvent}}\right)$, is **[Adv. 2016]**

7. A compound H_2X with molar weight of 80g is dissolved in a solvent having density of 0.4 g mL^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is **[Adv. 2014]**

8. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is : **[2012]**

3 Numeric / New Stem Based Questions

9. Liquids **A** and **B** form ideal solution for all compositions of **A** and **B** at 25°C. Two such solutions with 0.25 and 0.50 mole fractions of **A** have the total vapor pressures of 0.3 and 0.4 bar, respectively. What is the vapor pressure of pure liquid **B** in bar? **[Adv. 2020]**

10. The mole fraction of urea in an aqueous urea solution containing 900 g of water is 0.05. If the density of the solution is 1.2 g cm^{-3}, the molarity of urea solution is____ (Given data: Molar masses of urea and water are 60 g mol^{-1} and 18 g mol^{-1}, respectively) **[Adv. 2019]**

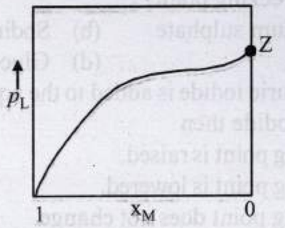
11. The molar volume of liquid benzene (density = 0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density = 0.867 g mL^{-1}) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 Torr. Find the mole fraction of benzene in the vapour above the solution. **[1996 - 3 Marks]**

12. The vapour pressure of pure benzene is 639.7 mm of mercury and the vapour of a solution of a solute in benzene at the same temperature is 631.9 mm of mercury. Calculate the molality of the solution. **[1981 - 3 Marks]**

13. 0.5 g of fuming H_2SO_4 (Oleum) is diluted with water. This solution is completely neutralized by 26.7 mL of 0.4 N NaOH. Find the percentage of free SO_3 in the sample of oleum. **[1980]**

6 MCQs with One or More than One Correct Answer

14. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M, respectively, in the solution. The correct statement(s) applicable to this system is (are) **[Adv. 2017]**



(a) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

(b) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \to 1$

(c) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \to 0$

(d) Attractive intermolecular interactions between L-L in pure liquid L and M-M in pure liquid M are stronger than those between L-M when mixed in solution.

15. Mixture(s) showing positive deviation from Raoult's law at 35 °C is (are) **[Adv. 2016]**

(a) carbon tetrachloride + methanol
(b) carbon disulphide + acetone
(c) benzene + toluene
(d) phenol + aniline

16. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are) **[Adv. 2013]**

(a) ΔG is positive (b) ΔS_{system} is positive
(c) $\Delta S_{\text{surroundings}} = 0$ (d) $\Delta H = 0$

10 Subjective Problems

17. The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solution. **[1989 - 3 Marks]**

18. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. **[1986 - 4 Marks]**

19. 'Two volatile and miscible liquids can be separated by fractional distillation into pure component', is true under what conditions? **[1984 - 1 Mark]**

20. An organic compound $C_xH_{2y}O_y$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0°C and 1 atm. pressure, measured 2.24 liters. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound is dissolved in 1000 g of water. Give the molecular formula of the organic compound. **[1983 - 5 Marks]**

21. A bottle of commercial sulphuric acid (density 1.787 g/mL) is labelled as 86 percent by weight. What is the molarity of the acid? What volume of the acid has to be used to make 1 litre of 0.2 M H_2SO_4? **[1979]**

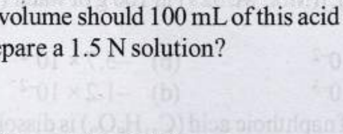
22. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/mL? To what volume should 100 mL of this acid be diluted in order to prepare a 1.5 N solution? **[1978]**

Topic-2: Colligative Properties of Solutions

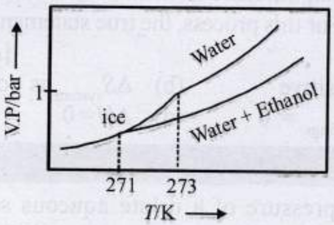
1 MCQs with One Correct Answer

1. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1}. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (*T*). [molecular weight of ethanol is 46 g mol^{-1}] Among the following, the option representing change in the freezing point is **[Adv. 2017]**

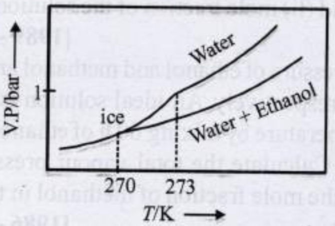
(a)



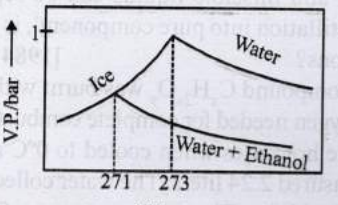
(b)



(c)



(d)



2. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76$ K kg mol^{-1}) **[2012]**

(a) 724 (b) 740
(c) 736 (d) 718

3. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. wt. 329) in 100 g of water ($K_f = 1.86$ K kg mol^{-1}) is **[2011]**

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

4. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72$ K kg mol^{-1}), a freezing point depression of 2K is observed. The van't Hoff factor (i) is **[2007]**

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

5. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (Molecular weight of $CuCl_2$ = 134.4 and K_b = 0.52 K molal^{-1}) **[2005S]**

(a) 0.16 (b) 0.05 (c) 0.1 (d) 0.2

6. During depression of freezing point in a solution, the following are in equilibrium **[2003S]**

(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

7. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to:

(a) ionization of benzoic acid. **[1996 - 1 Mark]**
(b) dimerization of benzoic acid.
(c) trimerization of benzoic acid.
(d) solvation of benzoic acid.

8. 0.2 molal acid HX is 20% ionised in solution. K_f = 1.86 K molality^{-1}. The freezing point of the solution is : **[1995S]**

(a) -0.45 (b) -0.90 (c) -0.31 (d) -0.53

9. The freezing point of equimolal aqueous solutions will be highest for : **[1990 - 1 Mark]**

(a) $C_6H_5NH_3Cl$ (b) $Ca(NO_3)_2$
(c) $La(NO_3)_3$ (d) $C_6H_{12}O_6$ (glucose)

10. Which of the following 0.1 M aqueous solutions will have the lowest freezing point? **[1989 - 1 Mark]**

(a) Potassium sulphate (b) Sodium chloride
(c) Urea (d) Glucose

11. When mercuric iodide is added to the aqueous solution of potassium iodide then **[1987 - 1 Mark]**

(a) freezing point is raised.
(b) freezing point is lowered.
(c) freezing point does not change.
(d) boiling point does not change.

2 Integer Value Answer

12. Vessel-1 contains w_2 g of a non-volatile solute X dissolved in w_1 g of water. Vessel-2 contains w_2 g of another non-volatile solute Y dissolved in w_1 g of water. Both the vessels are at the same temperature and pressure. The molar mass of X is 80% of that of Y. The van't Hoff factor for X is 1.2 times of that of Y for their respective concentrations. The elevation of boiling point for solution in Vessel-1 is ____ % of the solution in Vessel-2. **[Adv. 2024]**

13. 50 mL of 0.2 molal urea solution (density = 1.012 g mL^{-1} at 300 K) is mixed with 250 mL of a solution containing 0.06 g of urea. Both the solutions were prepared in the same solvent. The osmotic pressure (in Torr) of the resulting solution at 300 K is ______. **[Adv. 2023]**

[**Use:** Molar mass of urea = 60 g mol^{-1}; gas constant, R = 62 L Torr K^{-1} mol^{-1} ; Assume, $\Delta_{mix}H = 0$, $\Delta_{mix}V = 0$]

14. An aqueous solution is prepared by dissolving 0.1 mol of an ionic salt in 1.8 kg of water at 35 °C. The salt remains 90% dissociated in the solution. The vapour pressure of the solution is 59.724 mm of Hg. Vapor pressure of water at 35 °C is 60.000 mm of Hg. The number of ions present per formula unit of the ionic salt is ____. **[Adv. 2022]**

15. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is –0.0558°C, the number of chloride(s) in the coordination sphere of the complex is [K_f of water = 1.86 K kg mol^{-1}] **[Adv. 2015]**

16. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is **[Adv. 2014]**

3 Numeric / New Stem Based Questions

Question Stem for Question No. 17 and 18

The boiling point of water in a 0.1 molal silver nitrate solution (solution A) is x °C. To this solution A, an equal volume of 0.1 molal aqueous barium chloride solution is added to make a new solution B. The difference in the boiling points of water in the two solutions A and B is y × 10^{-2} °C.

(Assume : Densities of the solutions A and B are the same as that of water and the soluble salts dissociate completely.)

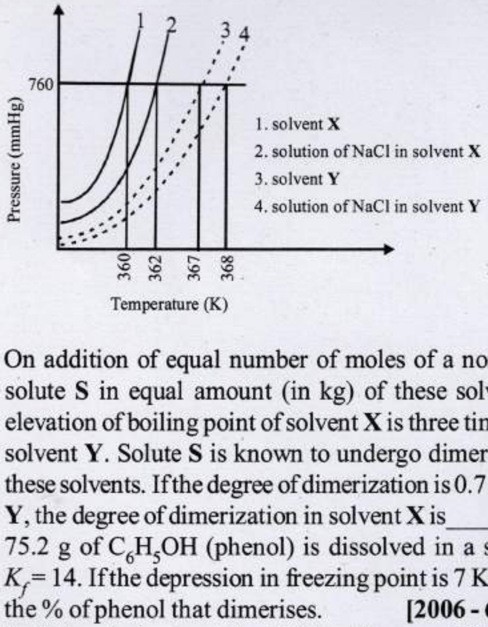
Use: Molal elevation constant (Ebullioscopic Constant), $K_b = 0.5$ K kg mol^{-1}; Boiling point of pure water as 100°C.)

17. The value of x is ______. **[Adv. 2021]**

18. The value of |y| is ______. **[Adv. 2021]**

19. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapour pressure decreases from 650 mm Hg to 640 mm Hg. The depression of freezing point of Benzene (in K) upon addition of the solute is ______ (Given data : Molar mass and the molal freezing point depression constant of benzene are 78 g mol^{-1} and 5.12 K kg mol^{-1}, respectively) **[Adv. 2019]**

20. The plot given below shows P — T curves (where P is the pressure and T is the temperature) for two solvents **X** and **Y** and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents. **[Adv. 2018]**



On addition of equal number of moles of a non-volatile solute **S** in equal amount (in kg) of these solvents, the elevation of boiling point of solvent **X** is three times that of solvent **Y**. Solute **S** is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent **Y**, the degree of dimerization in solvent **X** is______.

21. 75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of $K_f = 14$. If the depression in freezing point is 7 K then find the % of phenol that dimerises. **[2006 - 6 Marks]**

22. To 500 cm^3 of water, 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3}, respectively. **[2000 - 3 Marks]**

23. A solution of a non-volatile solute in water freezes at – 0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 K kg mol^{-1}. Calculate the vapour pressure of this solution at 298 K. **[1998 - 4 Marks]**

24. Addition of 0.643 g of a compound to 50 mL. of benzene (density : 0.879 g/mL.) lowers the freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K kg mol^{-1}, calculate the molecular weight of the compound. **[1992 - 2 Marks]**

25. The degree of dissociation of calcium nitrate in a dilute aqueous solution, containing 7.0 g. of the salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution. **[1991 - 4 Marks]**

26. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance? **[1990 - 3 Marks]**

4 Fill in the Blanks

27. Given that ΔT_f is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m, the quantity $\lim\limits_{m \to 0} (\Delta T_f / m)$ is equal to .... **[1994 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

28. In the depression of freezing point experiment, it is found that the **[1999 - 3 Marks]**

(a) vapour pressure of the solution is less than that of pure solvent

(b) vapour pressure of the solution is more than that of pure solvent

(c) only solute molecules solidify at the freezing point

(d) only solvent molecules solidify at the freezing

8 Comprehension/Passage Based Questions

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Application of colligative properties are very useful in day-to-day life. One of its example is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given : Freezing point depression constant of water (K_f^{water}) = 1.86 K kg mol^{-1}

Freezing point depression constant of ethanol (K_f^{ethanol}) = 2.0 K kg mol^{-1}

Boiling point elevation constant of water (K_b^{water}) = 0.52 K kg mol^{-1}

Boiling point elevation constant of ethanol (K_b^{ethanol}) = 1.2 K kg mol^{-1}

Standard freezing point of water = 273 K
Standard freezing point of ethanol = 155.7 K
Standard boiling point of water = 373 K
Standard boiling point of ethanol = 351.5 K
Vapour pressure of pure water = 32.8 mm Hg
Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol^{-1}
Molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solution to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

29. The freezing point of the solution M is **[2008 - 3 Marks]**
(a) 268.7 K (b) 268.5 K (c) 234.2 K (d) 150.9 K

30. The vapour pressure of the solution M is **[2008 - 3 Marks]**
(a) 39.3 mm Hg (b) 36.0 mm Hg
(c) 29.5 mm Hg (d) 28.8 mm Hg

31. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is **[2008 - 3 Marks]**
(a) 380.4 K (b) 376.2 K
(c) 375.5 K (d) 354.7 K

10 Subjective Problems

32. 1.22g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17° C, while that in the benzene increases by 0.13° C; K_b for acetone and benzene is 1.7 K kg mol^{-1} and 2.6 K kg mol^{-1} respectively. Find molecular weight of benzoic acid in two cases and justify your answer. **[2004 - 2 Marks]**

33. Match the following if the molecular weights of X, Y and Z are same. **[2003 - 2 Marks]**

	Boiling Point	K_b
X	100	0.63
Y	27	0.53
Z	253	0.98

34. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67%, and oxygen: 38.07% (i) Calculate the empirical formula of the minor product. (ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84 °C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol^{-1}.) **[1999 - 10 Marks]**

35. What weight of the non-volatile solute, urea ($NH_2 - CO - NH_2$) needs to be dissolved in 100g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? **[1993 - 3 Marks]**

Answer Key

Topic-1 : Solution and Vapour Pressure of Liquid Solutions

1. (c) **2.** (a) **3.** (b) **4.** (c) **5.** (19) **6.** (9) **7.** (8) **8.** (8) **9.** (0.02)
10. (2.98) **11.** (0.735) **12.** (0.156) **13.** (3.84) **14.** (b, d) **15.** (a, b) **16.** (b, d)

Topic-2 : Colligative Properties of Solutions

1. (c) **2.** (a) **3.** (a) **4.** (a) **5.** (a) **6.** (a) **7.** (b) **8.** (a) **9.** (d) **10.** (a)
11. (a) **12.** (150) **13.** (682) **14.** (5) **15.** (1) **16.** (2) **17.** (100.1) **18.** (2.5) **19.** (1.03) **20.** (0.05)
21. (75) **22.** (0.228) **23.** (23.44) **24.** (156.056) **25.** (746.3) **26.** (65.25) **27.** (K_f) **28.** (a, d) **29.** (d)
30. (b) **31.** (b)

Hints & Solutions

Topic-1: Solution and Vapour Pressure of Liquid Solutions

1. **(c)** Number of moles of urea $= \frac{120}{60} = 2$

Total mass of solution = 1000 + 120 = 1120 g

Total volume of solution (in L)

$$= \frac{\text{Mass}}{\text{Density}} = \frac{1120}{1.15 \times 10^3} = \frac{112}{115} \text{ L}$$

Molarity of the solution

$$= \frac{\text{Number of moles}}{\text{Volume in L}} = \frac{2 \times 115}{112} = 2.05 \text{ mol L}^{-1}$$

2. **(a)** $p_{N_2} = \kappa_H \chi_{N_2}$; $0.8 \times 5 = 1 \times 10^5 \times \chi_{N_2}$

$\therefore \chi_{N_2} = 4 \times 10^{-5}$; Solubility in 10 moles $= 4 \times 10^{-4}$.

3. **(b)** $\frac{p^\circ - p}{p^\circ} = \frac{w/m}{w/m + w/m}$ = mole fraction of solute $= x_B$

[Mathematical statement of Raoult's law]

4. **(c)** Lower the B. pt., higher will be the V.P. The V.P. of the mixture is greater than either of the two liquids.

In case of positive deviation from Raoult's law, the partial vapour pressure of each liquid and total vapour pressure of solution will be greater as compared to initial solution.

5. **(19)** $P_T = p^\circ_A X_A + p^\circ_B X_B$

$$\Rightarrow \quad 45 = 20(0.5) + p_B^o(0.5) \;\Rightarrow\; p_B^o = 70$$

$$22.5 = 20X_A + 70(1 - X_A)$$

$$\Rightarrow \quad X_A = \frac{4.75}{5} = 0.95 \;\Rightarrow\; X_B = 0.05 \Rightarrow \frac{X_A}{X_B} = 19$$

6. **(9)** 1 mole solution has 0.1 mole solute and 0.9 mole solvent.

Let M_1 = Molar mass solute

M_2 = Molar mass solvent

$$\text{Molality, } m = \frac{0.1}{0.9M_2} \times 1000 \quad \text{.......(1)}$$

$$\text{Molarity, } M = \frac{0.1}{0.1M_1 + 0.9M_2} \times 2 \times 1000 \quad \text{.......(2)}$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{(\text{Mass of solution/density})} \quad \because m = M$$

$$\Rightarrow \frac{0.1 \times 1000}{0.9M_2} = \frac{200}{0.1M_1 + 0.9M_2} \Rightarrow \frac{M_1}{M_2} = 9$$

7. **(8)** $\text{Molality} = \frac{\text{wt. of solute in 1 L of solution} \times 1000}{\text{wt. of solvent in 1 L of solution} \times \text{mol. wt. of solute}}$

Calculation of wt. of solvent

1 mL of solvent = 0.4 g

1000 mL of solvent = 400 g

Calculation of wt. of solute

1000 mL of solution contain = 3.2 × 80 g solute = 256 g

$$\therefore \quad \text{Molality} = \frac{256 \times 1000}{400 \times 80} = 8$$

8. **(8)** Molarity of stock solution of HCl

$$= \frac{29.2 \times 1000 \times 1.25}{100 \times 36.5}$$

Let the volume of stock solution required = V mL

$$\text{Thus, } V \times \frac{29.2 \times 1000 \times 1.25}{100 \times 36.5} = 200 \times 0.4$$

$$\Rightarrow \quad V = 8 \text{ mL}$$

9. **(0.02)** Using Raoult's law

$$P_T = P_A^o X_A + P_B^o X_B$$

$$0.3 = P_A^o \times 0.25 + P_B^o \times 0.75 \quad \text{...(i)}$$

$$0.4 = P_A^o \times 0.5 + P_B^o \times 0.5$$

on solving eq^n (i) and (ii)

$$P_A^o = 0.6, \; P_B^o = 0.2$$

10. **(2.98)** $X_{\text{urea}} = 0.05$

Mass of water = 900 g

$$\text{Number of moles of water} = n_{H_2O} = \frac{900}{18} = 50$$

Let moles of urea $= n_U$

$$\frac{n_U}{n_U + 50} = 0.05$$

$$n_U = \frac{50}{19} = 2.63$$

Mass of urea = $2.63 \times 60 = 157.8$ g

Given density (d) of solution = 1.2 g/mL.

$$V_{\text{solution}} = \frac{\text{mass of solution}}{\text{density (g/cc)}} = \frac{900 + 157.8}{1.2} = 881.5 \text{ mL}$$

$$M = \frac{n_V}{V_{\text{mL}}} \times 1000 = \frac{2.63}{881.5} \times 1000 = 2.98$$

11. (0.735)

(i) Volume$=\frac{\text{No. of moles} \times \text{molar mass}}{\text{density}}$

(ii) $PV=nRT$ or $P=\frac{nRT}{V}$

Volume of 1 mole of liq. benzene $=\frac{78}{0.877}$

Volume of 1 mole of toluene $=\frac{92}{0.867}$

In vapour phase,
At 20°C, for 1 mole of benzene,

Volume$=\frac{1\times78\times2750}{0.877}=244583.80\text{ mL}=244.58\text{ L}$

Similarly for 1 mole of toluene,

Volume $=\frac{1\times92}{0.867}\times7720=819192.61\text{ mL}=819.19\text{ L}$

As we know that, $PV=nRT$

For benzene, $P_B^o=\frac{nRT}{V}$

$=\frac{1\times0.0821\times293}{244.58}\text{ atm}=0.098\text{ atm}$

For toluene, $P_T^o=\frac{nRT}{V}$

$=\frac{1\times0.0825\times293}{819.19}\text{ atm}=0.029\text{ atm}$

$P=P_B^o\cdot X_B+P_T^o\cdot X_T$

$P=P_B^o\cdot X_B+P_T^o(1-X_B)$

Total vapour-pressure = 46 torr $=\frac{46}{760}=0.060$ atm

Thus, $0.060=0.098X_B+0.029(1-X_B)$

$\therefore\quad X_B=\frac{0.031}{0.069}=0.45$ (in liquid phase)

$X_B+X_T=1\ \Rightarrow X_T=1-0.45=0.55$ (in liquid phase)

Also, $\quad P_B'=P_B^oX_B=PX_B'$

So, $0.098\times0.045=0.060\times X_B'$

$X_B'=\frac{0.098\times0.45}{0.060}=$ **0.735 (in gas phase)**

12. (0.156) $\frac{P^o-P}{P^o}=\frac{n}{N}$ [Raoult's Equation]

Let the molality of the solution $=m$
Now, the solution contains 'm' moles of solute per 1000 g of benzene.
Vapour pressure of benzene, $P^o=639.7$ mm
Vapour pressure of solution, $P=631.9$ mm

Moles of benzene (Mol. wt. 78), $N=\frac{1000}{78}$
Moles of solute, $n=$?
Substitute these values in the Raoult's equation

$\frac{P^o-P}{P^o}=\frac{n}{N}$ or $\frac{639.7-631.9}{639.7}=\frac{n\times78}{1000}$

or $\frac{7.8}{639.7}=\frac{78n}{1000}\quad\therefore n=\frac{1000\times7.8}{78\times639.7}=\mathbf{0.156}$

Hence, molality of solution = **0.156 m**

13. (3.84) $N_1=1, V_1=?, N_2=26.7, V_2=0.4$

$N_1V_1=N_2V_2;\ 1\times V_1=26.7\times0.4$

$\Rightarrow\quad V_1=\frac{26.7\times0.4}{1}=10.68$

49g ($\because$ eq wt of $H_2SO_4=49$) of H_2SO_4 will be neutralised by = 1N 1000 mL NaOH
$\therefore$ 0.5g of H_2SO_4 will be neutralised by

$=\frac{1000}{49}\times0.5=10.20$ mL 1N NaOH

Volume of 1 N NaOH used by dissolved $SO_3=10.68-10.20=0.48$ mL

$SO_3+2NaOH\longrightarrow Na_2SO_4+H_2O$

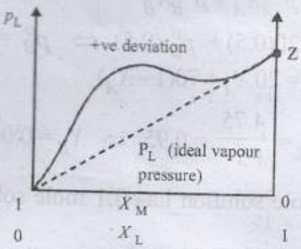
$\therefore$ Eq wt of $SO_3=\frac{\text{Mol wt}}{2}=\frac{80}{2}=40$

Wt of SO_3 in 0.48 mL of 1 M solution

$=\frac{40}{1000}\times0.48=0.0192$ g

% of $SO_3=\frac{0.0192}{0.5}\times100=$ **3.84%**

14. (b, d)



(b) From the given figure it is clear that at point Z, the mole fraction of M is zero, in that case 'Z' represents the vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L\rightarrow1$.

(d) The solution formed by mixing two liquids L and M shows positive deviation from Raoult's law. Thus, intermolecular forces of attraction between L – L in pure liquid L and M – M in pure liquid M are stronger than that between L – M in the solution.

15. (a, b)

(a) H-bonding of methanol breaks when CCl_4 is added so bonds become weaker, resulting positive deviation.

(b) Mixing of polar and non-polar liquids will produce a solution of weaker interaction, resulting positive deviation.

(c) Ideal solution

(d) –ve deviation, because stronger H-bond is formed.

16. **(b, d)** For ideal solution, $\Delta S_{\text{system}} > 0;\ \Delta H_{\text{mixing}} = 0$
Since, there is no heat exchange between system and surrounding;

$$\Delta S_{\text{surroundings}} = 0 \times \Delta G = \Delta H - T\Delta S_{\text{system}} < 0$$

17. **Molality,** $M = \dfrac{\text{moles of solute}}{\text{kg of solvent}}$

Mole fraction, $x_1 = \dfrac{n_1}{n_1 + n_2},\ x_2 = \dfrac{n_2}{n_1 + n_2}$

$p_1 = x_1 p^\circ{}_1$

$\therefore x_1 = \dfrac{p_1}{p_1^\circ} = \dfrac{750}{760} = \mathbf{0.9868}$

x_2 (solute) $= 1 - 0.9868 = 0.0132$

$$\text{Molality, } m = \frac{x_2}{x_1 M_1} \times 1000 = \frac{0.0132 \times 1000}{0.9868 \times 18}$$
$$= \mathbf{0.7503\ mol\ kg^{-1}}$$

$$\text{Molality} = \frac{\text{Mole fraction of solute} \times 1000}{\text{Mole fraction of solvent} \times \text{Mol. mass of solvent}}$$

18. Molecular weight of $CH_3OH = 12 + 3 + 16 + 1 = 32$
Molecular weight of $C_2H_5OH = 24 + 5 + 16 + 1 = 46$
According to Raoult's law, $P_{\text{total}} = p_1 + p_2$
where P_{total} = Total vapour pressure of the solution
p_1 = Partial vapour pressure of one component
p_2 = Partial vapour pressure of other component
Again, p_1 = Vapour pressure $(p^\circ{}_1) \times$ mole fraction
Similarly, p_2 = Vapour pressure $(p^\circ{}_2) \times$ mole fraction

$$\text{Mole fraction of } CH_3OH = \frac{40/32}{40/32 + 60/46} = 0.49$$

Mole fraction of ethanol $= 1 - 0.49 = 0.51$
Thus now let us first calculate the partial vapour pressures, *i.e.,* p_1 and p_2 of the two components.
Partial vapour pressure of $CH_3OH(p_1)$
$= 88.7 \times 0.49 = 43.48$ mm
Partial vapour pressure of $C_2H_5OH(p_2)$
$= 44.5 \times 0.51 = 22.69$ mm
$\therefore$ Total vapour pressure of the solution
$= 43.48 + 22.69$ mm $=$ **66.17 mm**

$$\text{Mole fraction of } CH_3OH \text{ in vapour} = \frac{43.48}{66.17} = \mathbf{0.65}$$

19. If they form an ideal solution which obeys Raoult's Law and for which
$\Delta H_{\text{mixing}} = 0$ and $\Delta V_{\text{mixing}} = 0$
Thus, we can separate two volatile and miscible liquids by fractional distillation if they should not form azeotropic solutions.

20. The chemical equation for the combustion of organic compound $C_xH_{2y}O_y$ can be represented as :
$C_xH_{2y}O_y + 2xO_2 = x\,CO_2 + y\,H_2O + x\,O_2$
The gases obtained after cooling $= x + x = 2x$
$\therefore 2x = 2.24$ litres $\qquad [\because H_2O$ is in liquid state$]$

$$\text{or } x = \frac{2.24}{2} = 1.12 \text{ litres}$$

$$\text{Number of moles of } CO_2 = \frac{1.12 \text{ litres}}{22.4 \text{ litres / mole}}$$

$[\because 22.4\,L$ at NTP $= 1$ mole$]$

$$\Rightarrow \quad x = \frac{1}{20} \text{ mole} = 0.05 \text{ mole}$$

$$\text{Moles of } H_2O \text{ formed } (y) = \frac{0.9}{18} = 0.05;$$

$x : y = 0.05 : 0.05 = 1 : 1$
The empirical formula of the organic compound is
CH_2O ...(1)
The mole fraction of the solute (A)
= relative decrease in vapour pressure of the solvent (B)

$$\frac{p^\circ - p}{p^\circ} = \frac{W_A / M_A}{W_B / M_B + W_B / M_B}$$

$$\text{or } \frac{0.104}{17.5} = \frac{50 / M_A}{50 / M_A + 1000/18} \qquad [M_A = \text{mol.wt. of } A]$$

$$\text{or } \frac{0.104}{17.5} = \frac{50}{M_A\left(\dfrac{50 \times 18 + 1000 M_A}{18 M_A}\right)}$$

$$\text{or } \frac{104}{17500} = \frac{50 \times 18}{900 + 1000 M_A} \text{ or } M_A = 150.6$$

Molecular wt. of the organic compound, $(CH_2O)_n = 150$
Molecular wt. of $CH_2O = 12 + 2 + 16 = 30$

$$\therefore 30 \times n = 150 \text{ or } n = \frac{150}{30} = 5$$

$\therefore$ Molecular formula of the given organic compound is $\mathbf{(CH_2O)_5}$ or $\mathbf{C_5H_{10}O_5}$.

21. $M = \dfrac{86/98}{100/1.787} \times 1000 = \dfrac{0.8775}{55.5} \times 1000 = \mathbf{15.81\ M}$

$M_1V_1 = M_2V_2$
$M_1 = 15.81,\ V_1 = ?$
$M_2 = 0.2,\ V_2 = 1\,L = 1000\,mL$

$$\therefore 15.81 \times V_1 = 0.2 \times 1000 \text{ or } V_1 = \frac{0.2 \times 1000}{15.81} = 12.65\,mL$$

$\therefore$ Amount of acid to be used to make 1 L of 0.2 M H_2SO_4 $=$ **12.65 mL.**

22. (i) $\text{Molarity} = \dfrac{\text{Moles of solute}}{\text{Volume of solution in L}}$

(ii) $N_1V_1 = N_2V_2$

A 13% solution (by weight) contains 13g of solute (*i.e.* H_2SO_4) per 100 g of solution.

$$\text{Moles of solute} = \frac{\text{Mass of } H_2SO_4}{\text{M. wt. of } H_2SO_4} = \frac{13}{98} = 0.1326$$

Volume of solution in L

$$= \frac{\text{Mass of solution}}{\text{density of solution} \times 1000} = \frac{100}{1.02 \times 1000} = 0.0980 \text{ Litre}$$

$$\therefore \quad \text{Molarity of solution} = \frac{0.1326}{0.0980} = \mathbf{1.35\ M}$$

$$\text{Again, Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

Mass of solute in 100 mL of solution = 13 g [13 % solution]
Mass of solvent = Mass of solution – Mass of solvent
$= 100 - 13 = 87$ g

$$\therefore \text{Molality} = \frac{13/98}{87/1000} = \mathbf{1.57\ m}$$

$$\text{Normality} = \text{Molarity} \times \frac{\text{Mol. wt.}}{\text{Eq. wt.}} \text{ or } 1.35 \times \frac{98}{49} = 2.70 \text{ N}$$

$N_1 = 2.70,\ V_1 = 100 \text{ mL},\ N_2 = 1.5,\ V_2 = ?$

$$\left[\because \text{Eq. wt} = \frac{98}{2} = 49\right]$$

$N_1V_1 = N_2V_2;\ 2.70 \times 100 = 1.5 \times V_2$

$$\text{or } V_2 = \frac{2.70 \times 100}{1.5} = 180 \text{ mL.}$$

$\therefore$ 100 mL of this acid should be diluted to 180 mL to prepare 1.5 N solution.

Topic-2: Colligative Properties of Solutions

1. **(c)** As T increase, V.P. increases
$\Delta T_f = K_f \times m$ (m = Molality of solute)

$$273 - T_f' = 2 \times \frac{34.5 \times 1000}{46 \times 500}$$

$\therefore \quad T_f = 270$ K

Thus, freezing point of solution = 270K. Further, as T increases, vapour pressure increases. Hence, these facts coincide with the curve given in (c).

2. **(a)** From elevation in boiling point, $\Delta T_b = K_b \times m$
$2 = 0.76 \times m$

$$m = \frac{2}{0.76} \qquad \text{...(ii)}$$

From Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent + No. of moles of solute}}$$

When the concentration of solute is much lower than the concentration of solvent,

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

$$\frac{760 - p}{760} = \frac{2.5/m}{100/18} \qquad \text{...(i)}$$

From (i) and (ii), $p = 724$ mm

3. **(a)** $\Delta T_f = i \times K_f \times m$
Where m = Molality of the solution
(*i.e.* number of moles of solute per 1000 g of the solvent)

$$\text{Here, } m = \frac{0.1}{329} \times \frac{1000}{100} = \frac{1}{329}$$

Assuming 100% K3[Fe(CN)$_6$] dissociates in 4 ions;
$\therefore$ i = 4 ionization.

$$\text{Thus, } \Delta T_f = 4 \times 1.86 \times \frac{1}{329} = 2.3 \times 10^{-2}$$

$\therefore T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2}$ °C

4. **(a)** Molecular weight of naphthoic acid
$C_{11}H_8O_2 = 172 \text{ gmol}^{-1}$.
The theoretical value of depression in freezing point

$$= K_f \times \text{molality} = 1.72 \times \frac{20 \times 1000}{172 \times 50} = 4\text{K}$$

van't Hoff factor,

$$i = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}} = \frac{2}{4} = 0.5.$$

5. **(a)** (i) $i = \dfrac{\text{No. of particles after ionisation}}{\text{No. of particles before ionisation}}$

(ii) $\Delta T_b = i \times K_b \times m$

$$\begin{array}{lcc} CuCl_2 \longrightarrow & Cu^{2+} + & 2Cl^- \\ 1 & 0 & 0 \\ (1-\alpha) & \alpha & 2\alpha \end{array}$$

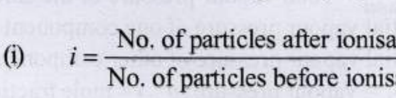
$$i = \frac{1 + 2\alpha}{1} \quad i = 1 + 2\alpha$$

Assuming 100% ionization
So, $i = 1 + 2 = 3$

$$\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16 \quad \left[m = \frac{13.44}{134.4} = 0.1\right]$$

6. **(a)** At the freezing point liquid and solid remain in equilibrium. If a solution of a non-volatile solute is cooled to a temperature below the freezing point of solution, some of liquid solvent will separate as a solid solvent and thus the concentration of solution will increase.

7. **(b)** Benzoic acid exists as dimer in benzene.



[Normal molecular mass = 122 amu and

observed molecular mass = 244 amu, in case of complete association]

8. **(a)** Depression in freezing point, $\Delta T_f = i \times K_f \times m$

van't Hoff factor, $i = \frac{1-\alpha+n\alpha}{1}$, where n = no. of ions produced by complete dissociation of 1 mole of HX.

$$HX \rightleftharpoons H^+ + X^- \quad \Rightarrow n = 2$$

$$\therefore\ i = \frac{1-0.2+2\times 0.2}{1} = 1.2$$

[For 20 % ionisation, $\alpha = \frac{20}{100} = 0.2$]

$\therefore\ \Delta T_f = 1.2 \times 1.86 \times 0.2 = 0.45$ [$\because m = 0.2$]

Hence, freezing point of solution is $0 - 0.45 = \mathbf{-0.45°C}$

9. **(d)** The salt that ionises to least extent will have highest freezing point. [*i.e.,* minimum ΔT_f]

Glucose, being non electrolyte, gives minimum no. of particles and hence, minimum ΔT_f or maximum F. pt.

10. **(a)** The salt producing highest number of ions will have lowest freezing point.

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$; K_2SO_4 gives highest number of particles (2 + 1 = 3).

Glucose, being non-electrolyte gives minimum no. of particles and hence minimum ΔT_f or maximum F. pt.

11. **(a)** Added HgI_2 forms a complex with KI in the solution as follows

$$2KI + HgI_2 \rightarrow K_2[HgI_4]$$

As a result, number of particles decreases and so ΔT_f increases.

Depression in freezing point is a colligative property which is not observed here.

12. **(150) Vessel-1**

$$(\Delta T_b)_1 = i_X \frac{w_2}{M_X} \cdot \frac{1}{w_1} \times 1000 \times k_b$$

M_X = Molar mass of 'X'

Vessel-2

$$(\Delta T_b)_2 = i_Y \frac{w_2}{M_Y} \cdot \frac{1}{w_1} \times 1000 \times k_b$$

M_Y = Molar mass of 'Y'

$$\frac{(\Delta T_b)_1}{(\Delta T_b)_2} \times 100 = \frac{i_X}{i_Y} \cdot \frac{M_X}{M_Y} \times 100$$

$$= 1.2 \times \frac{100}{80} \times 100$$

$$= 150\%$$

13. **(682)**

Weight of 50 mL 0.2 molal urea = V × d = 50 × 1.012 = 50.6 gm

Given 0.2 molal implies

1000 gm solvent has 0.2 moles urea

So weight of solution = 1000 + (0.2 × 60) = 1012 gm.

So wt. of urea in 50.6 gm solution $= \frac{12 \times 50.6}{1012} = 0.6$gm

Total urea = 0.6 + 0.06 = 0.66 gm

Total volume = 300 mL = 0.3 L

Now, osmotic pressure $\pi = C \times R \times T$

$$= \frac{0.66 \times 62 \times 300}{60 \times 0.3} = 682 \text{ Torr.}$$

14. **(5)** Vapour pressure of water, $P° = 60$ mm Hg.

Vapour pressure of solution, $P_s = 59.724$ mm Hg

Let the number of ions present per formula unit of the ionic salt S be n.

$$\begin{array}{ccc} S_n & \longrightarrow & nS \\ 0.1 & & 0 \\ 0.1(1-0.9) & & 0.1\times 0.9 \times n \end{array}$$

$$i = \frac{0.1 \times 0.9 \times n + 0.1\,(1-0.9)}{0.1} \Rightarrow i = 0.1 + 0.9\,n$$

$$\frac{P^o - P_s}{P^o} = i \times \text{mole fraction of solute}$$

$$\Rightarrow \quad \frac{60 - 59.724}{60} = i \times \frac{0.1}{\frac{1800}{18} + 0.1}$$

$$\Rightarrow \quad i = 4.6 \Rightarrow 0.1 + 0.9\,n = 4.6 \Rightarrow n = 5.$$

15. **(1)** Given $\Delta T_f = 0.0558°C$

as we know, $\Delta T_f = i \times K_f \times m \Rightarrow 0.0558 = i \times 1.86 \times 0.01$

$$\boxed{i = 3}$$

Therefore, the complex will be $[Co(NH_3)_5Cl]Cl_2$.

$[Co(NH_3)_5Cl]Cl_2 \rightarrow [Co(NH_3)_5Cl]^+ + 2Cl^-$

Hence, number of chloride in co-ordination sphere is 1.

16. **(2)**

$$\begin{array}{ccccc} MX_2 & \rightleftharpoons & M^{2+} & + & 2X^- \\ 1-\alpha & & \alpha & & 2\alpha \end{array}$$

$$i = \frac{\text{obser. depression in f.pt of aq. solution}}{\text{depression of f.p.t. in absence of ionic dissociation}}$$

$$= \frac{1-\alpha+\alpha+2\alpha}{1} = 1 + 2\alpha = 1 + 2 \times 0.5 = 2$$

17. **(100.1)** In solution-A

$$AgNO_3\,(aq) \longrightarrow Ag^+\,(aq) + NO_3^-\,(aq)$$

$\because\ \Delta T_b = iK_b m$

$\Delta T_b = 2 \times 0.5 \times 0.1 \qquad [i = 2]$

$(T_s - T^0) = 0.1$ K

$T_s = 373 + 0.1 = 373.1$ K = 100.1°C.

18. **(2.5)** In solution – B

$$\underset{0.05\,m}{AgNO_3\,(aq)} \longrightarrow \underset{0.05\,m}{Ag^+\,(aq)} + \underset{0.05\,m}{NO_3^-\,(aq)}$$

$$\underset{0.05\,m}{BaCl_2\,(aq)} \longrightarrow \underset{0.05\,m}{Ba^{2+}\,(aq)} + \underset{0.1\,m}{2Cl^-\,(aq)}$$

Ag^+ and Cl^- combine to form AgCl precipitate.

$$\begin{array}{llll} & Ag^+(aq) + & Cl^-(aq) \longrightarrow & AgCl(s) \\ t=0 & 0.05\,m & 0.1\,m & \\ t=\infty & 0 & 0.05\,m & \end{array}$$

In final solution (B) total concentration of all ions is

$[Cl^-]+[NO_3^-]+[Ba^{2+}] = 0.05+0.05+0.05 = 0.15\,m$

$\Delta T_b = 0.5 \times 0.15 = 0.075\,°C$

B.P. of solution 'B' = 100.075 °C

B.P. of solution 'A' = 100.1 °C

$|y| = 100.1 - 100.075 = 0.025 = 2.5 \times 10^{-2}$

19. (1.03)

We know that,

$$\frac{P^0 - P}{P^0} = \frac{w_2 \times m_1}{m_2 \times w_1};\ \frac{10}{640} = \frac{0.5 \times 78}{m_2 \times 39}$$

$m_2 = 64$ g

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{m_2 \times w_1}$$

$$\Delta T_f = \frac{5.12 \times 0.5 \times 1000}{64 \times 39} = 1.0256 \approx 1.03$$

20. (0.05) From graph

For solvent 'X' $\Delta T_{b(x)} = 362 - 360 = 2$ K

$$\Delta T_{b(x)} = m_{NaCl} \times K_{b(x)} \quad ...(1)$$

For solvent 'Y' $\Delta T_{b(y)} = 368 - 367 = 1$ K

$$\Delta T_{b(y)} = m_{NaCl} \times K_{b(y)} \quad ...(2)$$

Dividing equation (1) by (2)

$$\Rightarrow \frac{K_{b(x)}}{K_{b(y)}} = 2$$

For solute 'S'

Given solute S dimerizes in solvent. Hence,

$$\begin{array}{lll} 2(S) \rightarrow & S_2 & \\ 1 & & \text{........ initial} \\ (1-\alpha) & \alpha/2 & \text{........... after dimerisation} \end{array}$$

$$i = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

For solvent 'Y', $\alpha_Y = 0.7$

$$i_Y = 1 - \frac{0.7}{2} = 0.65$$

For solute 'S', it is given that

$\Delta T_{b(x)} = 3\Delta T_{b(y)}$

$i_x \times K_{b(x)} \times m_5 = i_Y \times K_{b(y)} \times m_5 \times 3$

$$i_x \times \frac{K_{b(x)}}{K_{b(y)}} = i_Y \times 3;\ i_x \times 2 = 3 \times 0.65;\ i_x = 0.975$$

$$1 - \frac{\alpha_x}{2} = 0.975;\ \alpha_x = 0.05$$

21. (75)

$$\begin{array}{lcc} & 2C_6H_5OH \rightleftharpoons & (C_6H_5OH)_2 \\ \text{Initial no. of moles} & 1 & 0 \\ \text{No. of moles at equilibrium} & 1-\alpha & \alpha/2 \end{array}$$

Total number of moles at equilibrium $= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$

$\Delta T_f = iK_f \times (\text{molality})$

$$\Rightarrow 7 = 14 \times \frac{75.2}{94} \times \left(1 - \frac{\alpha}{2}\right) \left[\begin{array}{l} \text{weight of phenol} = 75.2\text{g} \\ \text{mol.wt of phenol} = 94 \end{array}\right]$$

$\therefore \alpha = 0.75$

So, the percentage of phenol that dimerises = **75%.**

22. (0.228) $\Delta T_f = i \times K_f \times m$

Weight of water = 500 × 0.997 = 498.5 g

(weight = volume × density)

No. of moles of acetic acid

$$= \frac{\text{Wt. of } CH_3COOH \text{ in g}}{\text{Mol. wt. of } CH_3COOH} = \frac{3 \times 10^{-3} \times 10^3}{60} = 0.05$$

Since 498.5 g of water has 0.05 moles of CH_3COOH

$$1000 \text{ g of water has} = \frac{0.05 \times 1000}{498.5} = 0.1$$

Therefore, molality of the solution = 0.1

Determination of van't Hoff factor, i

$$\begin{array}{lccc} & CH_3COOH \longrightarrow & CH_3COO^- + & H^+ \\ \text{No. of moles at start} & 1 & 0 & 0 \\ \text{No. of moles at equb.} & 1-0.23 & 0.23 & 0.23 \end{array}$$

Therefore, van't Hoff factor

$$= \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

$$= \frac{1 - 0.23 + 0.23 + 0.23}{1} = 1.23$$

Now, we know that,

$\Delta T_f = i \times K_f \times m = 1.23 \times 1.86 \times 0.1 =$ **0.228 K**

23. (23.44) Depression in freezing point,

$\Delta T_f = 0 - (-0.30) = 0.30$

Now we know that $\Delta T_f = K_f m$

$$\therefore \quad m = \frac{\Delta T_f}{K_f} = \frac{0.30}{1.86} = 0.161$$

According to Raoult's law

$$\frac{p° - p}{p°} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

$$\frac{23.51 - p}{23.51} = \frac{0.161}{1000/18} = \frac{0.161 \times 18}{1000}$$

$$\left(\because \text{No. of moles of } H_2O = \frac{1000}{18}\right)$$

using the relation $\Delta T_b = K_b \times m$
Substituting the given values, we get

$$\Delta T_b = 0.52 \times \frac{0.1 \times 1000}{0.9 \times 18} = \frac{520}{9 \times 18} = 3.20\text{ K}$$

$\therefore$ Boiling point of solution = (373 + 3.20) K = 376.2 K
i.e. option (b) is correct answer.

32. (i) $\Delta T_b = K_b \times m$
In first case,

$$\Delta T_b = K_b \times m = K_b \times \frac{\left(\dfrac{\text{Wt. of solute}}{\text{Mol. wt. of solute}}\right)}{\text{wt. of solvent (in kg)}}$$

or $0.17 = 1.7 \times \dfrac{1.22}{M \times 100 \times 10^{-3}}$ or $\boldsymbol{M = 122}$

Thus, benzoic acid exists as a monomer in acetone
(ii) In second case,

$$\Delta T_b = K_b \times \frac{\dfrac{\text{Wt. of solute}}{\text{M.W. of solute}}}{\text{wt. of solvent} \times 10^{-3}}$$

$$\text{or } 0.13 = 2.6 \times \frac{1.22}{M' \times 100 \times 10^{-3}} \Rightarrow \boldsymbol{M' = 224}$$

Double the expected molecular weight of benzoic acid (244) in benzene solution indicates that benzoic acid exists as a dimer in benzene.

33. Higher the value of dipole-dipole interaction higher is b.p. Higher value of K_b of a solvent suggests larger polarity of solvent molecules which in turn leads to higher dipole – dipole interaction implies higher boiling point due to dipole – dipole interaction. Therefore, the correct order of K_b values of the three given solvents is

Mathematically, $K_b = \dfrac{M_A R T_b^2}{\Delta H_{\text{vap}} \times 1000}$

or $K_b \propto T_b$(b.pt.)

34.

Element	%	Relative no. of atoms	Simplest ratio
C	42.86	$\frac{42.86}{12} = 3.57$	$\frac{3.57}{1.19} = 3$
H	2.40	$\frac{2.40}{1} = 2.40$	$\frac{2.40}{1.19} = 2$
N	16.67	$\frac{16.67}{14} = 1.19$	$\frac{1.19}{1.19} = 1$
O	38.07	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{1.19} = 2$

$\therefore$ Empirical formula of the minor product is $C_3H_2NO_2$
Molar empirical formula mass of the minor product
$= 3 \times 12 + 2 \times 1 + 1 \times 14 + 2 \times 16 = 84\text{ g mol}^{-1}$
Let M be the molar mass of the minor product. For 5.5 g of the minor product dissolved in 45 g benzene, the molality

(m) of the solution $= \dfrac{5.5\text{ g}/M}{0.045\text{ kg}}$

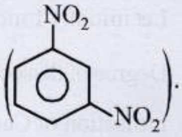
Substituting this in the expression of elevation of boiling point, $\Delta T_b = K_b m$

$$\Rightarrow \quad 1.84\text{ K} = (2.53\text{ K kg mol}^{-1})\left(\frac{5.5\text{ g}/M}{0.045\text{ kg}}\right)$$

or $\boldsymbol{M = 168\text{ g mol}^{-1}}$
No. of unit of empirical formula in molecular formula

$$= \frac{168\text{ g mol}^{-1}}{84\text{ g mol}^{-1}} = 2$$

Hence, the molecular formula of the minor product is $\mathbf{2\,(C_3H_2NO_2)}$, ***i.e.***, $\mathbf{C_6H_4(NO_2)_2}$.

The product is ***m*-dinitrobenzene** .

35. $$\frac{p^\circ - p}{p^\circ} = \frac{\dfrac{w}{m}}{\dfrac{w}{m} + \dfrac{W}{M}}$$

Here, w and m are wt. and molecular wt. of solute, W and M are wt. and molecular weight of solvent.
p = Vap. Pressure of solution; p° = Normal vapour pressure
Let the initial (normal) pressure $(p^\circ) = p$

$\therefore$ Pressure of solution $= \dfrac{75}{100} \times p = \dfrac{3}{4}p$

$m = 60,\ M = 18,\ W = 100\text{ g}$

$$\therefore \frac{p - \frac{3}{4}p}{p} = \frac{w/60}{\dfrac{w}{60} + \dfrac{100}{18}} \Rightarrow \frac{1}{4} = \frac{w/60}{(w/60) + 5.55}$$

$$\frac{4w}{60} = \frac{w}{60} + 5.55 \Rightarrow \frac{3w}{60} = \frac{w}{20} = 5.55 \text{ or } w = \mathbf{111\text{ g}}$$

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Wt. of solvent}} \times 1000$$

$$= \frac{111 \times 1000}{60 \times 100} = \mathbf{18.52\text{ m}}$$

$\Rightarrow 4T_b = 0.0512\,°\text{C}.$