

PHYSICAL CHEMISTRY

LIQUID SOLUTION

1. 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 _____.

[JEE(Advanced) 2023]

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

2. 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 _____.

[JEE(Advanced) 2022]

Question Stem for Question Nos. 3 and 4

The boiling point of water in a 0.1 molal silver nitrate solution (solution **A**) is $x^\circ\text{C}$. 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 $y \times 10^{-2}^\circ\text{C}$.

(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), $K_b = 0.5 \text{ K kg mol}^{-1}$; Boiling point of pure water as 100°C .)

3. The value of x is _____.
- [JEE(Advanced) 2021]
4. The value of $|y|$ is _____.
- [JEE(Advanced) 2021]
5. 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?
- [JEE(Advanced) 2020]
6. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapor 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 $5.12 \text{ K kg mol}^{-1}$, respectively)

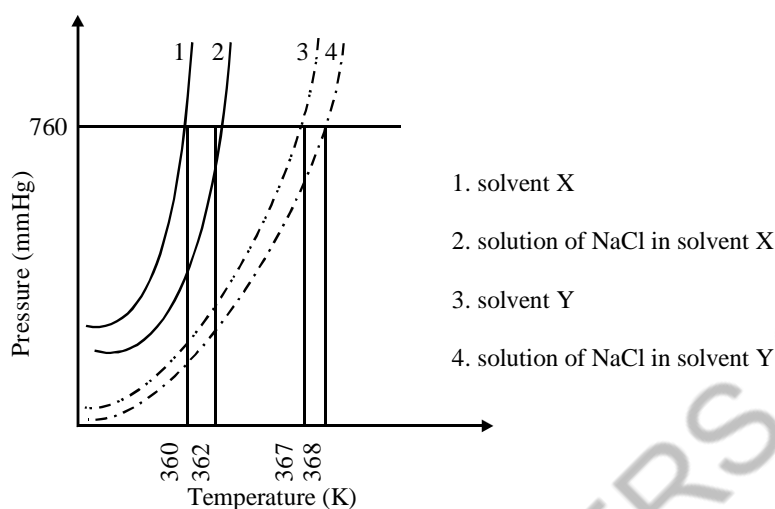
[JEE(Advanced) 2019]

7. 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)

[JEE(Advanced) 2018]

8. 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.

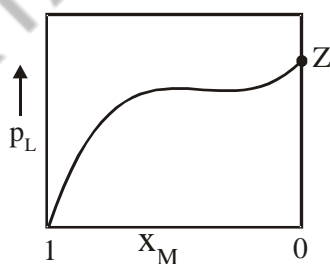


On addition of equal number of moles a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree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

[JEE(Advanced) 2018]

9. 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) –

[JEE(Advanced) 2017]



- (A) Attractive intramolecular 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
- (B) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \rightarrow 0$
- (C) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$
- (D) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$

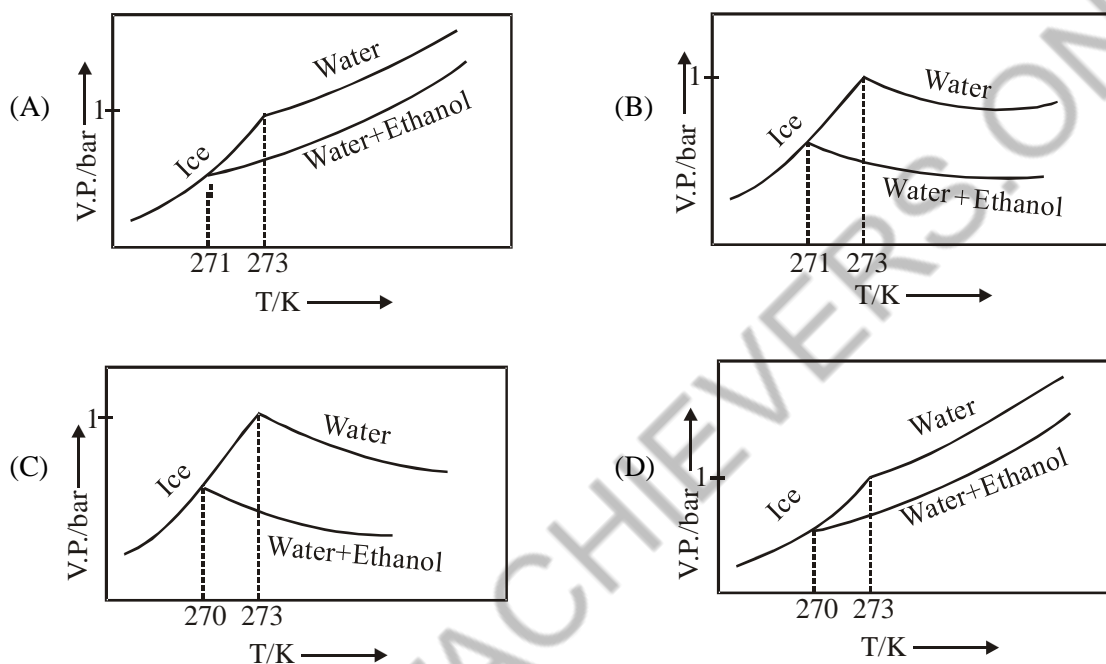
10. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1} .

The figures shown below represents 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 -

[JEE(Advanced) 2017]



11. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are) [JEE(Advanced) 2016]

- (A) carbon tetrachloride + methanol (B) carbon disulphide + acetone
(C) benzene + toluene (D) phenol + aniline

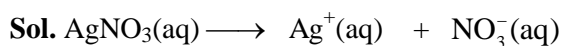
12. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is -0.0558°C , the number of chloride(s) in the coordination sphere of the complex is

[K_f of water = $1.86 \text{ K kg mol}^{-1}$]

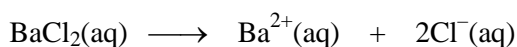
[JEE(Advanced) 2015]

13. 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 [JEE(Advanced) 2014]

4. Ans. (2.50)

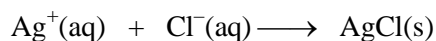


$$0.05 \text{ m} \qquad 0.05 \text{ m} \qquad 0.05 \text{ m}$$



$$0.05 \text{ m} \qquad 0.05 \text{ m} \qquad 0.1 \text{ m}$$

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



$$t = 0 \quad 0.05 \text{ m} \quad 0.1 \text{ m}$$

$$t = \infty \quad 0 \quad 0.05 \text{ m}$$

In final solution total concentration of all ions :

$$[\text{Cl}^-] + [\text{NO}_3^-] + [\text{Ba}^{2+}] = 0.05 + 0.05 + 0.05 \\ = 0.15 \text{ m}$$

$$\Delta T_b = 0.5 \times 0.15 \\ = 0.075 \text{ }^\circ\text{C}$$

B.P. of solution 'B' = 100.075°C

B.P. of solution 'A' = 100.1°C

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

5. Ans. (0.20)

Sol. $P_T = P_A^\circ X_A + P_B^\circ X_B$

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

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

$$0.8 = P_A^\circ + P_B^\circ \quad \dots(\text{ii})$$

on solving eqⁿ (i) & (ii)

$$P_A^\circ = 0.6, \quad P_B^\circ = 0.2$$

6. Ans. (0.97 to 1.06)

Sol. $\frac{P^\circ - P_s}{P^\circ} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$

$$\frac{650 - 640}{650} = \frac{n_{\text{solute}}}{n_{\text{solute}} + 0.5}$$

$$n_{\text{solute}} = \left(\frac{5}{640} \right)$$

$$\text{Molality} = \frac{5 \times 1000}{640 \times 39}$$

$$\Delta T_f = m \times K_b$$

$$= \frac{5.12 \times 5 \times 1000}{640 \times 39} = 1.0256$$

$$\boxed{\Delta T_f \approx 1.03}$$

7. Ans. (19)

Sol. $45 = P_A^{\circ} \times \frac{1}{2} + P_B^{\circ} \times \frac{1}{2}$

$$P_A^{\circ} + P_B^{\circ} = 90 \quad \dots(1)$$

Given $P_A^{\circ} = 20$ torr

$$P_B^{\circ} = 70 \text{ torr}$$

$$\Rightarrow 22.5 \text{ torr} = 20 x_A + 70 (1 - x_A) = 70 - 50 x_A$$

$$x_A = \left(\frac{70 - 22.5}{50} \right) = 0.95$$

$$x_B = 0.05$$

$$\text{So } \frac{x_A}{x_B} = \frac{0.95}{0.05} = 19$$

8. Ans. (0.05)

Sol. From graph

For solvent X' $\Delta T_{bx} = 2$

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

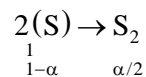
For solvent 'Y' $\Delta T_{by} = 1$

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

Equation (1)/(2)

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

For solute S



$$i = (1 - \alpha/2)$$

$$\Delta T_{b(x)(s)} = \left(1 - \frac{\alpha_1}{2} \right) K_{b(x)}$$

$$\Delta T_{b(y)(s)} = \left(1 - \frac{\alpha_2}{2} \right) K_{b(y)}$$

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

$$\left(1 - \frac{\alpha_1}{2} \right) K_{b(x)} = 3 \times \left(1 - \frac{\alpha_2}{2} \right) \times k_{b(y)}$$

$$2 \left(1 - \frac{\alpha_1}{2} \right) = 3 \left(1 - \frac{\alpha_2}{2} \right)$$

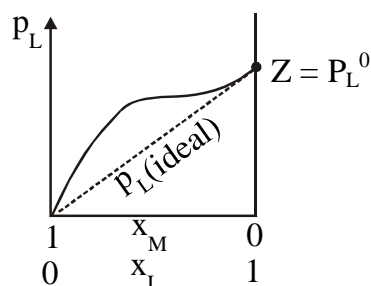
$$\alpha_2 = 0.7$$

so $\alpha_1 = 0.05$

9. Ans. (A, C)

Sol. (A) This is case of positive deviation hence

$$F_{L-L}, F_{M-M} > F_{L-M}$$



(C) $P_L \geq P_L^0 X_L$

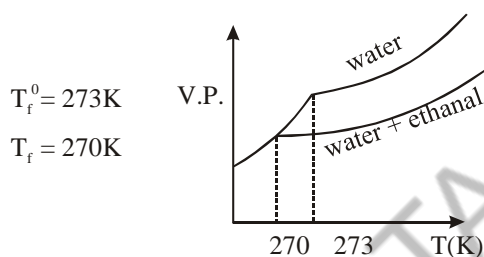
but when $X_L \rightarrow 1$, mixture has almost pure liquid L so, $P_L \rightarrow P_L^0$

10. Ans. (D)

Sol. Ethanol should be considered non volatile as per given option

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

$$\Delta T_f = 2 \times \frac{34.5}{46 \times 0.5} = 3K$$



11. Ans. (A, B)

Sol. (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

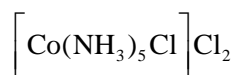
12. Ans. (1)

Sol. $\Delta T_f = i K_f m$

$$0.0558 = i \times 1.86 \times 0.01$$

$$\Rightarrow i = 3$$

Structure should be :



13. Ans. (2)



$$\frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{Theoretical}}} = i = 1 + \alpha (n-1)$$

$$\therefore i = 1 + 0.5 (3-1)$$

$$i = 2$$

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