

## PHYSICAL CHEMISTRY

## LIQUID SOLUTION

1. 50 mL of 0.2 molal urea solution (density =  $1.012 \text{ g mL}^{-1}$  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 =  $60 \text{ g mol}^{-1}$ ; 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  $35^\circ\text{C}$ . 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  $35^\circ\text{C}$  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

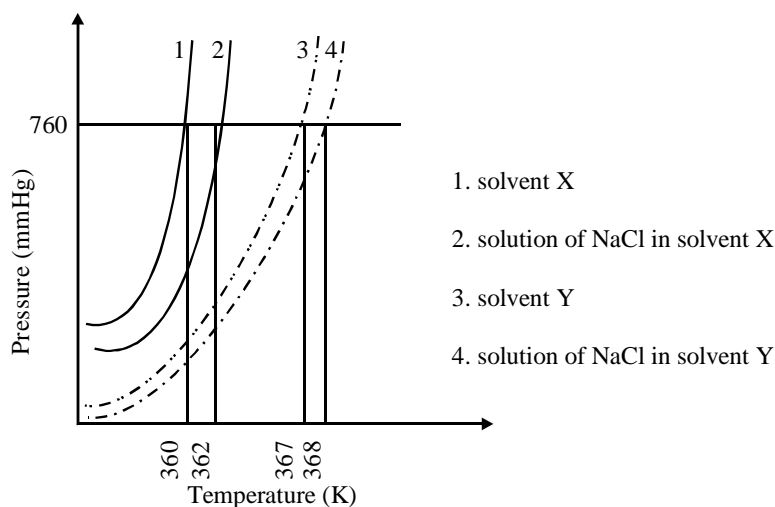
The boiling point of water in a 0.1 molal silver nitrate solution (solution A) is  $x^\circ\text{C}$ . To this solution A, an equal volume of 0.1 molal aqueous barium chloride solution is added to make a new solution B. The difference in the boiling points of water in the two solutions A and B is  $y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

(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  $100^\circ\text{C}$ .)

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  $25^\circ\text{C}$ . 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  $78 \text{ g mol}^{-1}$  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.

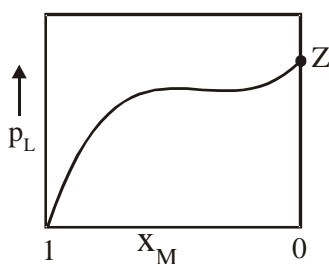


On addition of equal number of moles a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree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

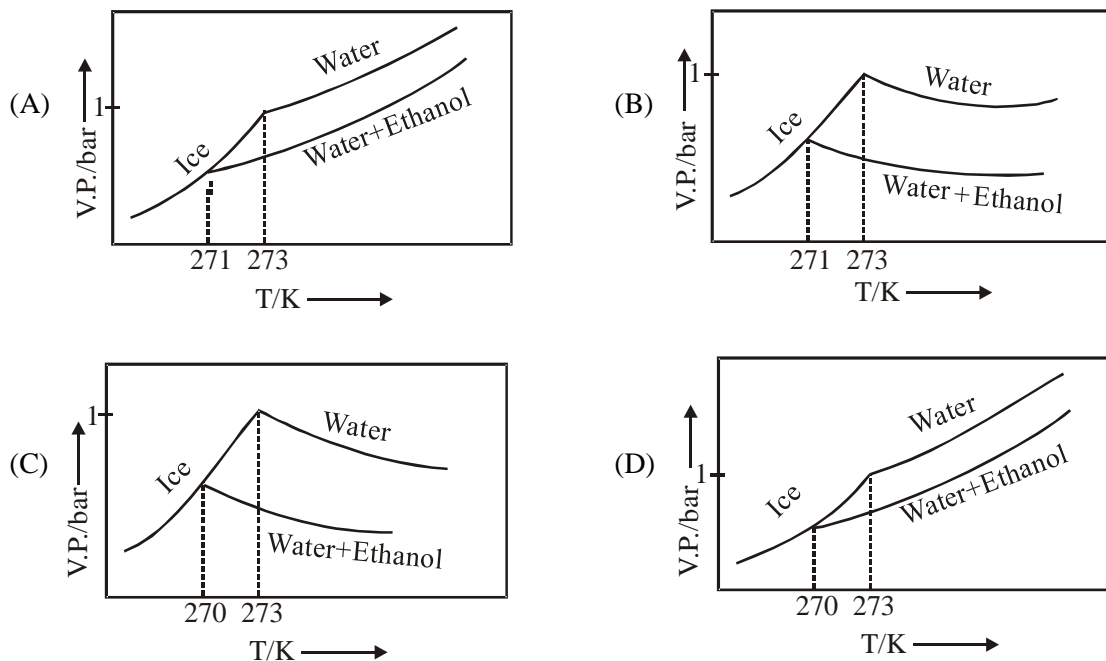


- (A) Attractive intramolecular interactions between L–L in pure liquid L and M–M in pure liquid M are stronger than those between L–M when mixed in solution
- (B) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when  $x_L \rightarrow 0$
- (C) The point Z represents 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  $2 \text{ K kg mol}^{-1}$ . The figures shown below represents plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is  $46 \text{ g mol}^{-1}$ ]

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  $35^\circ\text{C}$  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  $-0.0558^\circ\text{C}$ , the number of chloride(s) in the coordination sphere of the complex is [K<sub>f</sub> of water =  $1.86 \text{ K kg mol}^{-1}$ ] [JEE(Advanced) 2015]
13.  $\text{MX}_2$  dissociates into  $\text{M}^{2+}$  and  $\text{X}^-$  ions in an aqueous solution, with a degree of dissociation ( $\alpha$ ) 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]

## SOLUTIONS

## 1. Ans. (682)

Sol. Weight of 50 ml 0.2 molal urea =  $V \times d = 50 \times 1.012 = 50.6$  gm

Given 0.2 molal implies

1000 gm solvent has 0.2 moles urea

So weight of solution =  $1000 + 0.2 \times 60 = 1012$  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

Now, osmotic pressure  $\pi = C \times R \times T = \frac{0.66 \times 62 \times 300}{60 \times 0.3} = 682$  Torr.

## 2. Ans. (5)

Sol. 0.1 mole ionic salt in 1.8 kg water at 35° C

Vapour pressure of solution = 59.724 mm of Hg

Vapour pressure of pure H<sub>2</sub>O = 60.000 mm of Hg

Let the number of ions present per formula unit of the ionic salt be 'x'

$A_x$	→	$xA$
(Salt)		(Ions)

0.1	-	
$0.1(1 - 0.9)$		$(0.1 \times 0.9)x$

Total moles of non-volatile particles =  $0.01 + 0.09x$   
in 1.8 kg water

Moles of water =  $\frac{1.8 \times 10^3}{18} = 100$  moles

Relative lowering of vapour pressure  $\frac{P^\circ - P_s}{P^\circ} = \text{Mole fraction of non-volatile particles}$

$$\frac{P^\circ - P_s}{P_s} = \frac{\text{moles of non-volatile particles}}{\text{moles of water}}$$

$$\frac{60.000 - 59.724}{59.724} = \frac{0.01 + 0.09x}{100}$$

$$(0.276) \times 100 = 0.59274 + (0.59274 \times 9)x$$

$$27.6 - 0.59274 = (0.59274 \times 9)x$$

$$\Rightarrow x \approx \frac{27}{0.6 \times 9} = 5$$

## 3. Ans. (100.10)

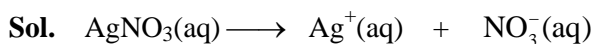
Sol.  $\text{AgNO}_3(\text{aq}) \longrightarrow \text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$   
0.1 m      0.1 m

$$\Delta T_b = 0.2 \times 0.5$$

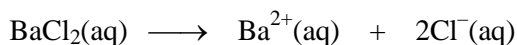
$$= 0.1^\circ\text{C} = 0.1 \text{ K}$$

Boiling point of solution =  $100.1^\circ\text{C} = X$

## 4. Ans. (2.50)

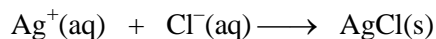


$$0.05 \text{ m} \qquad 0.05 \text{ m} \qquad 0.05 \text{ m}$$



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

$\text{Ag}^+$  and  $\text{Cl}^-$  combine to form  $\text{AgCl}$  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 :

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

$$\Delta T_b = 0.5 \times 0.15$$

$$= 0.075 \text{ }^\circ\text{C}$$

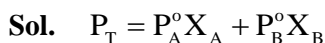
$$\text{B.P. of solution 'B'} = 100.075^\circ\text{C}$$

$$\text{B.P. of solution 'A'} = 100.1^\circ\text{C}$$

$$|y| = 100.1 - 100.075$$

$$= 0.025 = 2.5 \times 10^{-2}$$

## 5. Ans. (0.20)



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

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

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

on solving eq<sup>n</sup> (i) & (ii)

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

## 6. Ans. (0.97 to 1.06)

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

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

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

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

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

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

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

7. Ans. (19)

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

$$P_A^o + P_B^o = 90 \quad \dots(1)$$

Given  $P_A^o = 20$  torr

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

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

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

$$x_B = 0.05$$

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

8. Ans. (0.05)

Sol. From graph

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

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

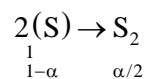
For solvent 'Y'  $\Delta T_{by} = 1$

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

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

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

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

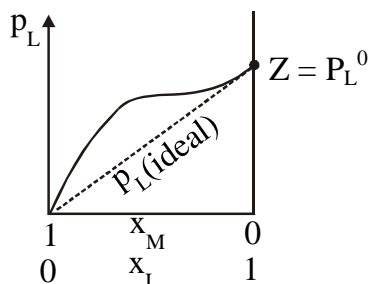
$$\alpha_2 = 0.7$$

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)  $P_L \geq P_L^0 X_L$

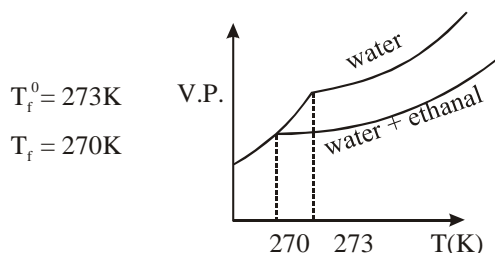
but when  $X_L \rightarrow 1$ , mixture has almost pure liquid L so,  $P_L \rightarrow P_L^0$

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

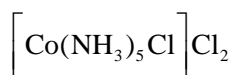
12. Ans. (1)

Sol.  $\Delta T_f = i K_f m$

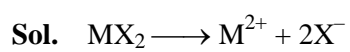
$$0.0558 = i \times 1.86 \times 0.01$$

$$\Rightarrow i = 3$$

Structure should be :



13. Ans. (2)



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

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

$$i = 2$$