Chapter 2

Solutions

Solutions

SECTION - A

Objective Type Questions (One option is correct)

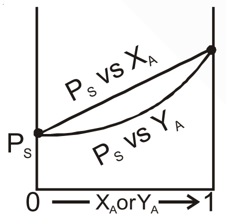
1. In which of the following case ΔH_{mixing} is negative?

(1) n-Hexane and n-Heptane
(2) Benzene and toluene
(3) Bromoethane and chloroethane
(4) Phenol and aniline

Sol. Answer (4)

Phenol and aniline show negative deviations.

2. A and B are volatile liquids and form an ideal solution. Variation of vapour pressure of solution with mole fraction of A is given below at temperature T. The incorrect statement is



$X_A \rightarrow$ Mole fraction of A in solution

$Y_A \rightarrow$ Mole fraction of A in vapour phase

(1) Vapour pressure of pure A is more than pure B at temperature T
(2) Vapour pressure of pure A is less than pure B at temperature T
(3) Vapour pressure of pure A and pure B is not equal at temperature T
(4) Boiling point of pure A is less than boiling point of pure B

Sol. Answer (2)

3. Which of the following aqueous solution has highest boiling point (If solute is non-volatile and non-electrolytic)?

(1) 0.1 m urea solution
(2) 0.2 m urea solution
(3) 0.1 m glucose solution
(4) 0.5 m glucose solution

Sol. Answer (4)

$(T_b)_{solution} - (T_b)_{solvent} = K_b m$

m ↑ Boiling point of solution increases.

4. Mole fraction of urea in a solvent is 0.1. If molality of this solution is 10/9 m then molar mass of solvent (in g/mol) is

(1) 18 (2) 100 (3) 1000 (4) $\frac{1}{100}$

Sol. Answer (2)

$$m = \frac{x_{\text{solute}} \times 1000}{x_{\text{solvent}} \times \text{molar mass of solvent (g/mol)}}$$

$$\frac{10}{9} = \frac{1 \times 1000}{9\,M}$$

M = 100 (g/mol)

5. Solution I = 0.1 mol of NaCl in 1 kg of H_2O.

Solution II = 0.05 mol of urea in 1 kg of H_2O.

Assume solution is dilute and [m = M].

If degree of dissociation of NaCl is 1, then

(1) Boiling point of solution I is 4 times of boiling point of solution II.

(2) Freezing point of solution I is 2 times of freezing point of solution II.

(3) Boiling point of solution I is 2 times of boiling point of solution II.

(4) Osmotic pressure of solution I is 4 times of osmotic pressure of solution II if both are at same temperature.

Sol. Answer (4)

π = iCRT

6. Which of the following solution is isotonic with 3 M aqueous urea solution at 300 K?

(1) 1 M aqueous $AlCl_3$ solution at 300 K $(\alpha_{AlCl_3} = 1)$

(2) 2 M aqueous NaCl solution at 300 K $(\alpha_{NaCl} = 1)$

(3) 1 M aqueous $MgCl_2$ solution at 300 K $(\alpha_{MgCl_2} = 1)$

(4) 1 M aqueous KCl solution at 300 K $(\alpha_{KCl} = 1)$

Sol. Answer (3)

$i_{MgCl_2} = 3$

π_{MgCl_2} = i × 1 × R × T

= 3 × R T

7. 300 mL of 4.6% (by volume) of ethyl alcohol solution is present in a container. If 100 mL of this solution is taken and diluted with water such that final volume become 2 litre. The molarity of diluted solution is (Density of pure ethyl alcohol is 2 g/mL)

(1) 0.1 M (2) 0.2 M (3) 0.3 M (4) 0.4 M

Sol. Answer (1)

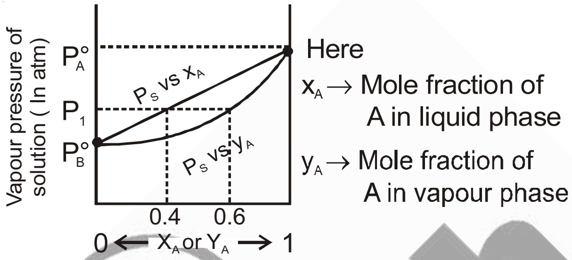
$$M = \frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}}$$

Volume of solution = 2 L

Moles of $C_2H_5OH = 0.2$

M = 0.1 M

8. A and B are volatile liquid and form an ideal solution. Graph is given below in which upper dark line represent vapour pressure of solution and mole fraction of A in liquid while lower dark line represent vapour pressure of solution and mole fraction of A in vapour phase at temperature T. Select the correct statement



(1) When $x_A = 0.4$ then $y_A = 0.4$ and vapour pressure of solution is P_1

(2) When $x_A = 0.4$ then $y_A = 0.6$

(3) Liquid B is more volatile than liquid A

(4) Both are equally volatile

Sol. Answer (2)

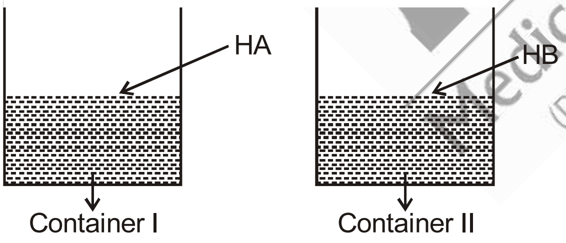
9. Which of following is example of solid in gas type of solution?

(1) Camphor in nitrogen gas (2) Chloroform mixed with nitrogen gas

(3) Solution of hydrogen in palladium (4) Brass

Sol. Answer (1)

10.



If both containers have 540 g of water each at 90°C. If 2 mole of HA is added in container I and 3 mole of HB is added in container II, then lowering in vapour pressure of both solutions is same. The correct statement (HA and HB are electrolytic and non-volatile solute. Assume no change in volume due to addition of HA and HB in water) is

(1) Boiling point of solution of container I is more than boiling point of solution of container II.

(2) Boiling point of solution of container II is more than boiling point of solution of container I.

(3) Both solutions have same boiling point.

(4) Both solutions have different freezing point.

Sol. Answer (3)

Container I

Lowering in VP of solution I = $i_1\frac{2}{32}\times 760$

Lowering in VP of solution II = $i_2\frac{3}{33}\times 760$

If both are equal = $\frac{i_1}{16}=\frac{i_2}{11}\Rightarrow\frac{i_1}{i_2}=\frac{16}{11}$

$$\frac{\Delta T_{b_1}}{\Delta T_{b_2}}=\frac{i_1\times\frac{2\times 1000}{32\times 18}\times K_b}{i_2\times\frac{3}{33}\times\frac{1000}{18}\times K_b}$$

$$\frac{\Delta T_{b_1}}{\Delta T_{b_2}}=\frac{i_1}{i_2}\times\frac{11}{16}\Rightarrow 1$$

$\Delta T_{b_1}=\Delta T_{b_2}$ so same boiling point

2nd method

If lowering in vapour pressure is same then ΔT_b must be same (solvent is same)

$$\left[BP\propto\frac{1}{\text{Vapour pressure}}\right]$$

11. Which of the following aqueous solution have lowest freezing point?

(1) 0.1 m NaCl solution

($\alpha_{NaCl}=1$)

(2) 0.2 m NaCl solution

($\alpha_{NaCl}=0.7$)

(3) 0.1 m $MgCl_2$ solution

($\alpha_{MgCl_2}=1$)

(4) 0.2 m $MgCl_2$ solution

($\alpha_{MgCl_2}=1$)

Sol. Answer (4)

$\Delta T_f = iK_fm$

$\Delta T_f \propto im$

12. The correct statement is

[Given glucose and urea are non-volatile, nonelectrolytic solute]

(1) Osmotic pressure of 0.1 M aq urea solution is more than 0.05 M aq glucose solution at same temperature

(2) Osmotic pressure of 0.1 M aq urea solution is less than 0.05 M aq glucose solution at same temperature

(3) Osmotic pressure of 0.1 M aqueous urea solution is same as of 0.05 M aqueous glucose solution at same temperature

(4) Osmotic pressure of 0.01 M aq urea is more than 0.05 M aq glucose solution at same temperature

Sol. Answer (1)

π = ic.R.T.

$\pi \propto$ ic at constant temperature

$\pi \propto$ c for glucose and urea

13. Value of $\frac{\Delta T_b}{K_b}$ of 9% (w/w) of X_2Y and 6% (w/w) of XY_2 is 1 mole kg^{-1} in both cases. (Consider X_2Y and XY_2 are non-electrolytes). Hence, atomic masses of X and Y are respectively (approx.)

(1) 40, 40 (2) 44.6, 9.5 (3) 10, 40 (4) 9.5, 44.5

Sol. Answer (2)

For 9% X_2Y

$$\frac{\Delta T_b}{K_b} = ixm = 1 = \frac{9 \times 1000}{(2x+y) \times 91}$$

$$\Rightarrow (2x+y) = \frac{9000}{91}$$

For 6% XY_2

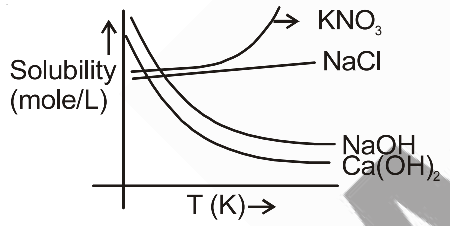
$$1 = \frac{6}{(x+2y)} \times \frac{1000}{94}$$

$$x + 2y = \frac{6000}{94}$$

Solving both equations

x = 44.6

y = 9.5

14. 

From the graph

(I) Solubility of NaCl is almost unaffected by temperature

(II) NaOH and Ca(OH)$_2$ show exothermic dissolution

(III) KNO_3 cannot be easily recrystallized

True statements from the above are

(1) (I) & (II) (2) (I), (II) & (III) (3) (II) & (III) (4) (I) & (III)

Sol. Answer (2)

15. The solubility of N_2(g) at 593 mm of Hg is 5.3×10^{-4} in water. Its solubility at 860 mm and at the same temperature in water is

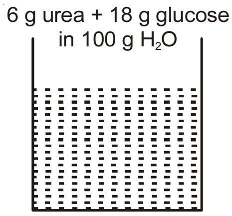
(1) 5.3×10^{-4} (2) 7.68×10^{-4} (3) 9.0×10^{-4} (4) 1.2×10^{-3}

Sol. Answer (2)

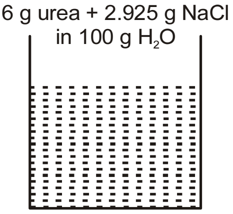
$P = K_H \cdot S$

$$\frac{P_1}{P_2} = \frac{S_1}{S_2} \Rightarrow S_2 = \frac{P_2}{P_1} \times S_1 = \frac{860}{593} \times 5.3 \times 10^{-4} = 7.68 \times 10^{-4} \text{ M}$$

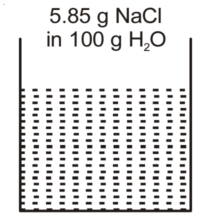
16.



Solution-I
Temperature - 100°C



Solution-II
Temperature - 100°C



Solution-III
Temperature - 100°C

[**Given:** All solutes are non-volatile and all solutions are ideal. NaCl is completely ionisable in solution, molar mass of NaCl is 58.5 g/mol].

Which of the following statements is incorrect?

(1) Boiling point of each solution is same

(2) Freezing point of each solution is same

(3) Osmotic pressure of each solution at 100°C is same [Assume m = M]

(4) Mole fraction of urea in solution-I is 0.1

Sol. Answer (4)

$$X_{urea} = \frac{0.1}{0.1 + 0.1 + \frac{100}{18}}$$

SECTION - B

Objective Type Questions (More than one options are correct)

1. 100 ml 20%(by mass) H_2SO_4(density = 1.2 gm/ml) and 100 ml 40% (by mass) H_2SO_4 (density = 1.4 gm/ml) are mixed together. Which are the correct concentration terms for this mixture?

(1) Molality = 2.54	(2) Molarity = 2.04
(3) Molality = 4.54	(4) Molarity = 4.08

Sol. Answer (3, 4)

ρ = 1.2 g/ml ; V = 100 ml and 20% by mass is H_2SO_4

$$\rho = \frac{m}{V} \Rightarrow m = \rho \times V = \frac{1.2}{ml} \times 100\ ml = 120\ g$$

$$\therefore\ W_{H_2SO_4} = \frac{20}{100} \times 120 = 24\ g$$

Secondly; ρ = 1.4 g/ml; V = 100 ml = 40% by mass

$$\Rightarrow\ \rho = \frac{m}{V} \Rightarrow m = 1.4 \times 100 = 140\ g$$

$$\therefore\ W_{H_2SO_4} = \frac{40}{100} \times 140 = 56\ g$$

$\Rightarrow$ On mixing both solutions

Final Molarity is

$$\frac{24}{98}+\frac{64}{98} \text{ moles in 200 ml}$$

$\therefore$ In 1000 ml $\Rightarrow \dfrac{24+56}{98} \times 5$

$\Rightarrow \dfrac{80}{98} \times 5 = 4.08$

$\therefore$ Final molarity is 4.08 M

Moles of H_2SO_4 is $\dfrac{24+56}{98}$

$W_{SOLVENT} = (120 - 24) + (140 - 56) = 180$ g

$\therefore$ In 180 g SOLVENT $\Rightarrow$ MOLES (H_2SO_4) = $\dfrac{80}{98}$

For 1000 g SOLVENT

$\dfrac{80}{98 \times 180} \times 1000 = 4.54$ m

2. Which are the correct statements?

(1) $CHCl_3 + CCl_4$ – Endothermic solution

(2) Acetic acid + Pyridine – Maximum boiling azeotrope

(3) HNO_3 + Water – Endothermic solution

(4) Water + HI – Minimum boiling azeotrope

Sol. Answer (1, 2)

It is a known fact that $CHCl_3/CCl_4$ forms endothermic solution as $\Delta H > 0$.

CH_3COOH and pyridine forms non-ideal solution due to negative deviation from Raoult's Law.

3. V litre decinormal solution of NaCl is prepared. Half of the solution is converted into centinormal and added to the left decinormal solution. Then

(1) Number of millimoles of NaCl are reduced by $\dfrac{1}{5}$

(2) Number of milliequivalents of NaCl do not change

(3) Normality of the final solution becomes 0.01 N

(4) Molarity of the final solution becomes 0.018 M

Sol. Answer (2, 4)

Given:

Initial volume = V ; Normality = $\dfrac{N}{10}$

Equivalents = $\dfrac{V \times 1}{10} = \dfrac{V}{10}$

50% solution is taken

$$\frac{V}{\alpha}\times\frac{1}{10} = \frac{V'\times 1}{100}$$

$$V' = \frac{100\times V}{20} = 5V$$

Final volume = (5V)

Now there are two solutions

I solution (Left solution)	II-Prepared solution
$\frac{V}{2}$; $\frac{N}{10}$	5V ; $\frac{N}{100}$

⇒ On mixing

$$N' = \frac{N_1V_1 + N_2V_2}{(V_1 + V_2)} = \left(\frac{V}{20}+\frac{V}{20}\right)\Big/\left(\frac{V}{2}+5V\right)$$

$$\therefore\ N' = \frac{V}{10}\times\frac{2}{11V} = \frac{2}{110} = 0.018\ N \equiv 0.018\ M$$

And no. of equivalent does not change on dilution.

4. At 300 K, the vapour pressure of an ideal solution containing 1 mole of A and 3 moles of B is 500 mm Hg. At the same temperature, 2 moles of B are added to this solution. The vapour pressure of solution increases by 10% of the original vapour pressure. Correct statements about the vapour pressure are

(1) Vapour pressure of A in the pure state is 50 mm Hg

(2) Vapour pressure of B in the pure state is 650 mm Hg

(3) Ratio of final vapour pressure to the initial vapour pressure is 1 : 0.5

(4) Ratio of vapour pressure of pure B to the vapour pressure of pure A is 13 : 1

Sol. Answer (1, 2, 4)

$n_A = 1$; $n_B = 3$; $P_T = 500$ mmHg

When ‘2’ moles of ‘B’ is added

$$n_B' = (3 + 2) = 5\ ;\ n_A = 1$$

$$P_T' = 500 + \frac{500\times 10}{100} = 50 + 500 = 550$$

By equation:

$$500 = P^\circ_A\left(\frac{1}{1+3}\right)+P^\circ_B\left(\frac{3}{1+3}\right)$$

$$(500 \times 4) = P^\circ_A + 3P^\circ_B \qquad \ldots \text{(i)}$$

Secondly we can write

$$550 = P^\circ_A\left(\frac{1}{6}\right)+P^\circ_B\left(\frac{5}{6}\right)$$

$\Rightarrow \quad P_A^\circ + 5P_B^\circ = 6 \times 550$ … (ii)

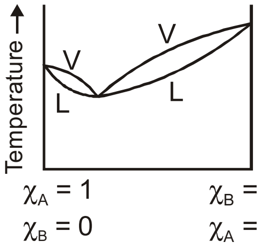
Subtracting (i) from (ii)

$2P_B^\circ = 3300 - 2000 = 1300 \qquad \therefore \quad P_B^\circ = \frac{1300}{2} = 650$ mmHg

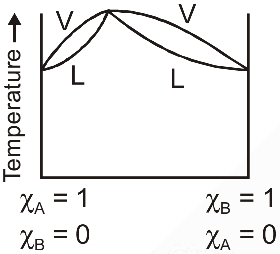
and $P_A^\circ = 2000 - (3 \times 650) \qquad \therefore \quad P_A^\circ = 2000 - 1950 = 50$ mm Hg

and $\frac{P_B^\circ}{P_A^\circ} = \frac{650}{50} = \frac{13}{1}$

5. Consider the following graphs.



Graph-I



Graph-II

Choose the correct statements

(1) According to both graphs mole fraction of A > mole fraction of B in condensate

(2) Graph I belongs to minimum boiling azeotrope

(3) Graph II belongs to maximum boiling azeotrope

(4) Graph II belongs to minimum boiling azeotrope while graph I belongs to minimum boiling azeotrope

Sol. Answer (1, 2, 3)

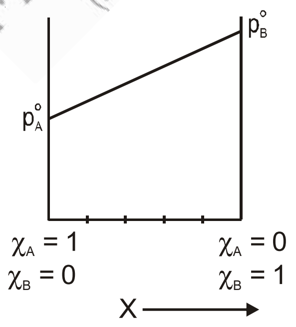
Graph (I) and graph (II) are the graphs of azeotropes and is clear from the above vapour-liquid equilibrium that

(1) is MINIMUM BOILING AZEOTROPES and

(2) is MAXIMUM BOILING AZEOTROPES

and it is also clear that $X_A > X_B$ in the condensate formed from the graph.

6. The following graph is plotted between the vapour pressures of two volatile liquids against their respective mole fractions



Which of the following combinations are correct?

(1) When $\chi_A = 1$, $P = P_A^\circ$

(2) When $\chi_B = 1$, $P > P_A^\circ$

(3) When $\chi_A = 1$, $P < P_A^\circ$

(4) When $\chi_B = 1$, $P = P_B^\circ$

Sol. Answer (1, 2, 4)

Fact.

7. A binary liquid (AB) shows positive deviation from Raoult's law when

(1) $P_A > P_A^o \chi_A^{liquid}$ and $P_B > P_B^o \chi_B^{liquid}$

(2) Intermolecular forces A – A, B – B > A – B

(3) $\Delta V_{mix} > 0$

(4) $\Delta H_{mix} > 0$

Sol. Answer (1, 2, 3, 4)

New forces are weaker.

8. In the depression of freezing point experiment, it is found that

(1) Vapour pressure of solution is less than that of pure solvent

(2) Vapour pressure of solution is more than that of pure solvent

(3) Only solute molecules solidify at the freezing point

(4) Only solvent molecules solidify at the freezing point

Sol. Answer (1, 4)

Addition of non-volatile solute lowers the vapour pressure of solvent.

9. At 27°C, the osmotic pressure of a non-volatile non-electrolyte solute is 47.7 mm Hg. The solution is diluted and heated upto 127°C, when the osmotic pressure becomes 19 mm Hg. Then

(1) Molality of solution becomes half

(2) Number of milli moles of solute remains same

(3) Extent of dilution of solution is 3.4 times

(4) Relative lowering in vapour pressure reduces

Sol. Answer (2, 3, 4)

Given : π = 47.7 mmHg

Solution is diluted and is heated upto 127°C, π = 19 mmHg

Hence, on dilution, no. of millimoles remains same and relative lowering in vapour pressure decreases.

10. Equimolal solutions of NaCl, $BaCl_2$ and Na_3PO_4 are prepared in water, then correct statements are

(1) Freezing point of NaCl solution is –2°C if freezing point of $BaCl_2$ solution is –3°C

(2) Freezing point of Na_3PO_4 is –4°C if freezing point of $BaCl_2$ is –3°C

(3) Elevation in boiling point for $BaCl_2$ solution is 1.5 times higher than NaCl solution

(4) Elevation in boiling point for NaCl is half of Na_3PO_4 solution

Sol. Answer (1, 2, 3, 4)

'm' for NaCl; $BaCl_{2-}$ and Na_3PO_4 is same

i (for NaCl) = 2

i (for $BaCl_2$) = 3

$(\Delta T_f)_1 = 2 \times K_f \times m$

$(\Delta T_f)_2 = 3 \times K_f \times m$

Hence (1) is correct answer

For Na_3PO_4 (i = 4) and for $BaCl_2$ (i = 3) $\therefore$ freezing point is – 4°C and – 3°C

For $BaCl_2$ (i = 3) and for NaCl (i = 2)

$\therefore$ Elevation in boiling point for $BaCl_2$ is 1.5 times higher than NaCl solution

and for NaCl (i = 2)

Na_3PO_4 (i = 4)

$\Rightarrow$ Elevation in BP for NaCl is half of Na_3PO_4 solution

11. Choose the pairs having identical value of van't Hoff factor.

(1) 0.05 M $K_4[Fe(CN)_6]$ (50% degree of dissociation) and 0.05 M Mohr salt (80% degree of dissociation)

(2) 0.2 M NaCl (80% degree of dissociation) and 0.2 M $BaCl_2$ (40% degree of dissociation)

(3) 0.05 M Na_3PO_4 (60% degree of dissociation) and 0.05 M $K_4[Fe(CN)_6]$ (45% degree of dissociation)

(4) 0.01 M $NaNO_3$ (90% degree of dissociation) and 0.01 M $FeCl_3$ (30% degree of dissociation)

Sol. Answer (2, 3, 4)

$NaCl \rightleftharpoons Na^+ + Cl^-$

$i = 1 + (2 - 1)(0.8) = 1.8$

$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$

$i = 1 + (3 - 1)(0.4) = 1.8$

$\therefore$ (2) is the correct answer because both have identical values of i.

$Na_3PO_4 \rightleftharpoons 3Na^+ + PO_4^{3-}$

$i = 1 + (3)(0.6) = 2.8$

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$

$i = 1 + (4)(0.45)$

$i = 1 + 1.8 = 2.8$

(3) is correct answer.

and $NaNO_3 \rightleftharpoons Na^+ + NO_3^-$

$1 + (2 - 1)\alpha = 1 + \alpha = 1 + 0.9 = 1.9$

and for

$FeCl_3 \rightleftharpoons Fe^{3+} + 3Cl^-$

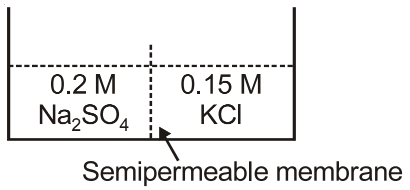
$1 + (4 - 1)\alpha = 1 + 3\alpha$

$= 1 + 3(0.3)$

$= 1.9$

So, (4) is the correct answer.

12. Consider the following arrangement and choose the correct options.



(1) O.P. of Na_2SO_4 solution is lesser than the O.P. of KCl solution

(2) Water will flow from KCl solution to Na_2SO_4 solution

(3) Water will flow from Na_2SO_4 solution to KCl solution

(4) O.P. of Na_2SO_4 solution is higher than the O.P. of KCl solution

Sol. Answer (2, 4)

For left hand compartment

0.2M Na_2SO_4; $\pi_1 = (0.2) \times (S) \times (T) \times 3$

$\pi_1 = (0.6)\,(S)\,(T)$

and for 0.15 M KCl

$\pi_2 = (2) \times (S) \times (T) \times (0.15)$

$= (0.3)\,(ST)$

$\therefore$ $\pi_1 > \pi_2 \Rightarrow$ Na_2SO_4 solution have higher osmotic pressure and water will flow from lower concentration to higher concentration.

$\Rightarrow$ Water will flow from RHC to LHC.

13. Which of the following pair of solutions can be expected to be isotonic at the same temperature?

(1) 0.1 M urea & 0.1 M NaCl

(2) 0.1 M urea & 0.1 M glucose

(3) 500 ml 0.2 M NaCl & 200 ml 0.2 N KCl

(4) 100 ml 0.05 N $Ca(NO_3)_2$ & 100 ml 0.15 M Na_2SO_4

Sol. Answer (2, 3)

Isotonic solutions have same osmotic pressures.

0.1M UREA ; 0.1M $C_6H_{12}O_6$

Same concentration and i = 1 for both

For NaCl and KCl n-factor is 1

$\therefore$ 0.2 M NaCl and 0.2 N KCl have same osmotic pressure.

14. A compound X undergoes 100% pentamerisation in a given solvent Y. Correct statements are

(1) van't Hoff factor of compound is 0.20

(2) Experimental elevation in boiling point = $\dfrac{\text{Calculated elevation in boiling point}}{5}$

(3) Observed molar mass of solute = $\dfrac{\text{Normal molar mass}}{5}$

(4) Observed freezing point × 5 = Normal freezing point

Sol. Answer (1, 2)

For pentamerization

$$5A \rightleftharpoons A_5$$

$$i = 1 - \alpha + \frac{\alpha}{5} = 1 + \alpha\left(\frac{1}{5} - 1\right) = \frac{5 - 4\alpha}{5}$$

$$0.2 = i = \frac{1}{5}; \qquad (\alpha = 1)$$

$\therefore$ van’t-Hoff factor is equal to 0.2 and 5 × (Experimental elevation in Boiling point) = Calculated elevation in B.P.

15. 100 ml of 3% (weight/volume) urea solution and 100 ml of 6.84% (weight/volume) of cane sugar are mixed at 20°C. The solution is heated upto 27°C after mixing 100 ml water into it. Correct statements for final solution are

(1) O.P. of solution is 4 atm

(2) O.P. of urea in the solution is 12.13 atm

(3) O.P. of cane sugar in solution is 1.64 atm

(4) O.P. of urea in the solution is 4 atm

Sol. Answer (3, 4)

UREA solution is 3% (w/v)

$$\therefore \quad n_{UREA} = \frac{3}{60} = \frac{1}{20} \text{ moles} = 0.05 \text{ mole in100 ml}$$

$$\text{and } n_{C_{12}H_{22}O_{11}} = \frac{6.84}{342} = 0.02 \text{ mole in 100 ml}$$

$$V_T = 300 \text{ ml}$$

$$\pi \text{ (UREA)} = \frac{(0.05 \times 10)\, ST}{3} = \frac{0.05 \times 10 \times 0.0821 \times 300}{3} = 4 \text{ atm}$$

$$p\ (C_{12}H_{22}O_{11}) = \frac{0.02 \times 10 \times 0.0821 \times 300}{3} = 1.64 \text{ atm}$$

So, Total O.P. = 4 + 1.64 = 5.64 atm

Hence, (3) & (4) options are correct.

16. Correct statements about the following solutions (Assuming equal amount of each solute is dissolved in 1 L solution)

1 L NaCl, 1 L $(NH_2)_2CO$, 1 L $BaCl_2$, 1 L $Ca_3(PO_4)_2$

(1) Osmotic pressure :

$NaCl > (NH_2)_2CO > Ca_3(PO_4)_2 > BaCl_2$

(2) Boiling point :

$NaCl > (NH_2)_2CO > Ca_3(PO_4)_2 > BaCl_2$

(3) Freezing point :

$NaCl > (NH_2)_2CO > Ca_3(PO_4)_2 > BaCl_2$

(4) Freezing point :

$(NH_2)_2CO < NaCl < Ca_3(PO_4)_2 < BaCl_2$

Sol. Answer (1, 2)

For (1)

NaCl (i = 2)

Urea (i = 1)

$Ca_3(PO_4)_2$ (i = 5)

$BaCl_2$(i = 3)

∴ Osmotic pressure and elevation in boiling point, both are colligative properties and order is same for both the cases.

17. Choose the correct statements.

(1) 1 M H_2SO_4 (d = 1 gm/ml) is more concentrated than 1 m H_2SO_4 (d = 1 gm/ml)

(2) Molality of solution is 1.136 if 2 gram-equivalents of H_2SO_4 is dissolved into 90.2 gm water

(3) Vapour pressure of solution becomes higher than ideal solution if there is a positive deviation (according to Raoult's law)

(4) When 0.1 M $K_4[Fe(CN)_6]$ solution and 0.1 M $FeCl_3$ solution is separated by a semi permeable membrane, water flows from $K_4[Fe(CN)_6]$ solution to $FeCl_3$ solution

Sol. Answer (1, 3)

Vapour pressure of the solution becomes higher than ideal solution when there is positive deviation from Raoult's law.

And 1 M solution is always more concentrated then 1 molal solution because molarity is w.r.t. volume of solution, but molality is defined w.r.t. weight of solvent.

18. Dimer of acetic acid in benzene is in equilibrium with acetic acid at a particular condition of temperature and pressure. If half of the dimer molecules are hypothetically separated out then

(1) Osmotic pressure of the solution reduces
(2) Freezing point of the solution reduces
(3) Boiling point of the solution reduces
(4) Vapour pressure of the solution reduces

Sol. Answer (1, 3)

Acetic acid undergoes dimerization as

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Since i < 1, ∴ Osmotic pressure decreases and boiling point also decreases as π and (ΔT_b) both are colligative properties.

19. In which of the following pair of solutions will the values of van't Hoff factor be same?

(assuming same dissociation)

(1) 0.05 M $K_4[Fe(CN)_6]$ and 0.10 M $FeSO_4$

(2) 0.10 M $K_4[Fe(CN)_6]$ and 0.05 M $FeSO_4(NH_4)_2SO_4.6H_2O$

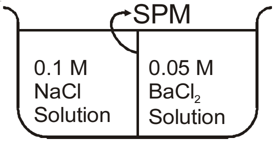
(3) 0.20 M NaCl and 0.10 M $BaCl_2$

(4) 0.05 M $FeSO_4.(NH_4)_2SO_4.6H_2O$ and 0.02 M KCl. $MgCl_2.6H_2O$

Sol. Answer (2, 4)

Number of particles dissociated are same.

20. Choose correct option about given figure.



(1) No movement of liquid from any solution across SPM

(2) $BaCl_2$ will flow towards NaCl solution

(3) NaCl will flow towards $BaCl_2$ solution

(4) Assuming 100% dissociation $\pi_{NaCl} > \pi_{BaCl_2}$

Sol. Answer (4)

Only solvent particles will move through SPM.

π = iCRT

SECTION - C

Linked Comprehension Type Questions

Comprehension-I

The experimental values of colligative properties of many solutes in solution resembles calculated value of colligative properties.

However in same cases, the experimental value of colligative property differ widely than those obtained by calculation. Such experimental values of colligative properties are known as **Abnormal values of colligative property. Cause for abnormal values of colligative properties are :**

(i) Dissociation of solute : It increases the colligative properties.

e.g. : Dissociation of KCl, NaCl etc. in H_2O.

(ii) Association of solute : It decreases the colligative properties

e.g. : Dimerisation of acetic acid in benzene

1. If degree of dissociation of an electrolyte A_2B_3 is 25% in a solvent, then

(1) Normal boiling point = Experimental boiling point

(2) Normal freezing point > Experimental freezing point

(3) Normal osmotic pressure = $\frac{1}{2}$ Experimental osmotic pressure

(4) Normal molecular weight = $\frac{1}{4}$ Experimental molecular weight

Sol. Answer (3)

Electrolyte A_2B_3 is 25% dissociated

$A_2B_3 \rightleftharpoons 2A^{3+} + 3B^{2-}$ (n = 5)

i = 1 + (5 – 1) (0.25) = 1 + (4 × 0.25) = 2 we know that

$$\frac{\pi_{OBS}}{\pi_{CAL}} = 2$$

$$\Rightarrow \ \pi_{CAL} = \frac{\pi_{OBS}}{2}$$

or normal osmotic pressure = $\frac{1}{2}$ (observed osmotic pressure)

2. 4 different 100 ml solutions are prepared by mixing 1 gram each of NaCl, $(NH_2)_2CO$, Na_2SO_4 and $K_4[Fe(CN)_6]$ at temperature T. Correct order of osmotic pressure is

(1) $(NH_2)_2CO$ solution > NaCl solution > Na_2SO_4 solution > $K_4[Fe(CN)_6]$ solution

(2) NaCl solution > Na_2SO_4 solution > $(NH_2)_2CO$ solution > $K_4[Fe(CN)_6]$ solution

(3) $K_4[Fe(CN)_6]$ solution > Na_2SO_4 solution > NaCl solution > $(NH_2)_2CO$ solution

(4) Na_2SO_4 solution > $(NH_2)_2CO$ solution > NaCl solution > $K_4[Fe(CN)_6]$ solution

Sol. Answer (2)

For I – Solution

$$n_{NaCl} = \frac{1}{58.5} \text{ in 100 ml}$$

$$\therefore \ \text{In 100 ml} \Leftrightarrow \text{MOLES} = \frac{1\times10}{58.5}$$

$$\pi_1 = \frac{10}{58.5} \times 2 \times ST = (0.341)\ ST$$

For II – Solution, UREA

$$= \frac{1}{60} \times 10 \times 1 \times ST = \frac{ST}{6}$$

$$\Rightarrow \ (0.16)\ ST$$

For III – Solution, Na_2SO_4

$$10 \times \left(\frac{1}{142}\right) \times (3) \times ST = \frac{3\times1\times ST}{142} = (0.02)\ ST \times 10$$

$$\Rightarrow \ (0.2)\ ST$$

For IV – Solution, ($K_4[Fe(CN)_6]$)

$$10 \times \frac{1}{368} \times (5) \times (S \times T) = (0.0135)ST \times 10 = (0.1355)\ ST$$

$\Rightarrow$ Order of osmotic pressure is NaCl sol^n > Na_2SO_4 sol^n > UREA sol^n > $K_4[Fe(CN)_6]$ sol^n

3. One mole I_2 (solid) is added in 1 M, 1 litre KI solution. Then

(1) Osmotic pressure of solution increases

(2) Freezing point of solution increases

(3) Relative lowering in vapour pressure decreases

(4) No change in boiling point of solution

Sol. Answer (4)

KI + $I_2 \rightarrow KI_3$, KI_3 dissociates as K^+ & I_3^-

So, numbers of ions are same. Hence, no change in boiling point of solution.

Comprehension-II

In non-ideal solutions, at one of the intermediate compositions, the total vapour pressure is highest and the boiling point is lowest. At this point, the composition of the liquid and vapour phase is same. So, if liquid mixture vapourises at this point and vapours are condensed, the condensate contains same composition as present in original liquid mixture. It means at this point liquid behaves like a pure liquid and is called an **Azeotropic mixture**.

1. Choose the correct statement.

(1) Ideal solutions cannot be separated into their components by fractional distillation

(2) For ideal solutions enthalpy of mixing is always greater than zero

(3) Only non-ideal solution showing positive deviation cannot be separated out by fraction distillation

(4) Non-ideal solution showing both positive and negative deviation cannot be separated out by fractional distillation

Sol. Answer (4)

Non-ideal solution showing +ve and –ve deviation cannot be separated by fractional distillation.

2. A and B forms non-ideal solution showing positive deviation. Boiling point of pure A and B is 350 K and 380 K respectively. The solution will boil at (approximate)

(1) 350 K (2) 380 K (3) > 380 K (4) < 350 K

Sol. Answer (4)

The solution will boil at a temperature less than 350 K, as it forms low boiling point azeotrope.

3. Which of the following cannot form low boiling point azeotrope?

(1) n-heptane & n-hexane (2) Acetone & aniline

(3) Both (1) & (2) (4) $CHCl_3$ & C_2H_5OH

Sol. Answer (3)

For a solution to form low boiling azeotrope, it is necessary that the solution shows positive deviation from Raoult's law. N-heptane & n-hexane is nearly an ideal solution while Acetone & Aniline show negative deviation from Raoult's law.

Comprehension-III

On mixing two components A and B to form a non-ideal solution, final solution becomes cold. (F = intermolecular force of attraction).

1. Correct statement about final solution is

(1) Evolution of some heat takes place (2) $F_{AB} > F_{AA}$ and $F_{AB} > F_{BB}$

(3) Intermolecular H-bonds may be broken out (4) Contraction of volume takes place

Sol. Answer (3)

Fact.

2. If final solution becomes hot, incorrect option

(1) Exothermic dissolution may takes place (2) Vapour pressure increases than expected value

(3) Maximum boiling azeotropes are formed (4) Negative deviations from Raoult's law

Sol. Answer (2)

Fact.

3. 0.5 M, 100 ml A and 0.2 M, 500 ml B are mixed at 27°C. Vapour pressure of pure A and pure B is 200 mm Hg and 50 mm Hg respectively at 27°C. Then the ratio of partial pressures of A and B (in vapour phase) after mixing is

(1) 2 : 1 (2) 1 : 2 (3) 2 : 3 (4) 4 : 1

Sol. Answer (1)

$$Y_A = \frac{P^o_A\chi_A}{P^o_A\chi_A + P^o_B\chi_B}$$

$$Y_B = \frac{P^o_B\chi_B}{P^o_A\chi_A + P^o_B\chi_B}$$

$$\frac{P_A}{P_B} = \frac{Y_A}{Y_B}$$

SECTION - D

Matrix-Match Type Questions

1. Match the following.

Column-I	Column-II
(A) Acetone + Carbon disulphide	(p) Vapour pressure measurement
(B) Acetone + Aniline	(q) Osmotic pressure
(C) Used in calculation of molar mass of polymer	(r) Maximum boiling azeotrope
(D) Ostwald-Walker's method	(s) Minimum boiling azeotrope

Sol. Answer A(s), B(r), C(q), D(p)

(A) Acetone and CS_2 forms minimum boiling point azeotrope.

(B) CH_3COCH_3 and $C_6H_5NH_2$ forms maximum B.P. azeotrope.

(C) Barkley's and Hartley method is used to determine osmotic pressure.

(D) Ostwald –Walker method are used to measure the vapour pressure.

2. Match the following.

Column-I **Solute (equimolar) (assuming $\alpha = 100\%$)**	**Column-II** **π (osmotic pressure) ratio**
(A) NaCl, $MgCl_2$, K_2SO_4	(p) 1 : 2 : 3
(B) $Al_2(SO_4)_3$, Na_3PO_4, $K_4[Fe(CN)_6]$	(q) 1 : 1 : 1
(C) Glucose, Rock salt, Glauber's salt	(r) 1 : 0.8 : 1
(D) Baryta water, lime water, washing soda	(s) 2 : 3 : 3

Sol. Answer A(s), B(r), C(p), D(q)

(A) $NaCl \rightarrow Na^+ + Cl^-$

$i = 1 + \alpha = 2$

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$

$i = 1 + 2\alpha = 3$

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$

$i = 1 + 2\alpha = 3$

$\therefore$ Ratio is 2 : 3 : 3

(B) $Al_2(SO_4)_3 \rightarrow 2Al^{3+}+3SO_4^{2-}$

For strong electrolyte $\alpha = 1$

$i = 1 + 4 = 5$

$Na_3PO_4 \rightarrow 3Na^{+}+ PO_4^{3-}$

$i = 1 + 3 = 4$

$K_4[Fe(CN)_6] = 1 + 4 = 5$

$\therefore$ Ratio is 5 : 4 : 5

$\Rightarrow$ 1 : 0.8 : 1

(C) $C_6H_{12}O_6$ $i = 1$

Rock Salt $i = 2$

Glauber's Salt (Na_2SO_4) $i = 3$

Ratio is 1: 2 : 3

(D) Baryta water $Ba(OH)_2$; $i = 3$

lime water $Ca(OH)_2$; $i = 3$

Washing Soda Na_2CO_3 ; $i = 3$

Ratio is 1 : 1 : 1

3. Match the following.

Column-I	**Column-II**
(A) 100 ml 1.2% $(NH_2)_2CO$ solution (wt./vol) at T temperature	(p) Isotonic with 100 ml 1M $K_3[Fe(CN)_6]$ at T temperature
(B) 250 ml 2 M $NaNO_3$ solution at T temperature	(q) Isotonic with 100 ml 6.84% (wt./vol) $C_{12}H_{22}O_{11}$ at T temperature
(C) 5.845% (by wt.) NaCl aqueous solution	(r) Boiling point = 100.052°C
(D) 1.8% (by wt.) $C_6H_{12}O_6$ aqueous solution	(s) Boiling point = 101.1°C

Sol. Answer A(q), B(p), C(s), D(r)

(Column – I)

(A) 1.2% UREA is at temp. T

M (UREA) = 60

$$\therefore \quad \eta_{UREA} = \frac{1.2}{60} \text{ in 100 ml}$$

$$\therefore \quad \text{In 1000 ml 'C'} = \frac{1.2}{60} \times 10 = \frac{12}{60} = \frac{1}{5}$$

$$\pi = 1 \times \frac{1}{5} \times 0.0821 \times T = \frac{ST}{5}$$

(B) $\pi = 2 \times 2 \times ST = 4ST$

(C) $\Delta T_b = \dfrac{(0.52) \times 5.845 \times 1000 \times 2}{58.5 \times 94.155} = 1.10°C$

(D) $\Delta T_b = \dfrac{(0.52) \times 1.8 \times 1000}{180 \times 98.2} = 0.05°C$

(Column – II)

(p) $\pi = 4 \times 1 \times ST = (4ST)$

(q) $\pi = \dfrac{1 \times 6.84 \times 10}{342} \times 0.0821 \times T$

$\Rightarrow (0.2\ ST) =$

Therefore it can be seen

(A) and (q) have same osmotic pressure *i.e.* $\left(\dfrac{ST}{5}\right)$

(B) and (p) are isotonic solution and have same osmotic pressure

(C) $\Leftrightarrow$ (s) as $\Delta T_b = 1.04°C$

(D) $\Leftrightarrow$ (r) as $\Delta T_b = 0.05°C$

4. Match the following.

Column-I	**Column-II**
(A) Benzene + Carbon tetrachloride	(p) Form maximum boiling azeotrope
(B) Chlorobenzene + Water	(q) $P_{Total} = p_A^o + p_B^o$
(C) Ethanol + Water	(r) Form minimum boiling azeotrope
(D) Acetone + Chloroform	(s) Does not form azeotrope

Sol. Answer A(r), B(q, s), C(r), D(p)

5. Match the following.

	Column-I			**Column-II**
	(Solute, degree of ionisation)			**(van't Hoff factor)**
(A)	K_2SO_4	; $\alpha = 0.85$	(p)	3.7
(B)	$SnCl_2$	; $\alpha = 0.7$	(q)	4.0
(C)	$Al(NO_3)_3$	; $\alpha = 0.9$	(r)	2.7
(D)	$Fe_2(SO_4)_3$	; $\alpha = 0.75$	(s)	2.4

Sol. Answer A(r), B(s), C(p), D(q)

SECTION - E

Assertion-Reason Type Questions

1. STATEMENT-1 : On cooling a mixture of ideal gases, an ideal solution can be obtained.

and

STATEMENT-2 : Ideal solution do not form azeotropes.

Sol. Answer (4)

It is the non-ideal solution which are having $(\Delta H)_{mix} \neq 0$, $(\Delta V)_{mix} \neq 0$ which form azeotropes and ideal solutions can not be obtained by cooling gases as the gases have different T_C.

2. STATEMENT-1 : Relative lowering of vapour pressure is equal to mole fraction of the solute.

and

STATEMENT-2 : Relative lowering of vapour pressure is a colligative property.

Sol. Answer (2)

$\frac{P^\circ - P_S}{P^\circ}$ is relative lowering of vapour pressure and is equal to mole fraction of solute because pressure of solution of non-volatile solute is proportional to mole fraction of solvent.

$\frac{P^\circ - P_S}{P^\circ}$ is a colligative property

$\therefore$ Both are correct but (2) is not correct explanation.

3. STATEMENT-1 : When HgI_2 is added to the aqueous solution of KI, the freezing point is raised.

and

STATEMENT-2 : Freezing point generally increases by adding non volatile solute in solvent.

Sol. Answer (3)

When HgI_2 is added it reacts with KI

$$HgI_2 + 2KI \rightarrow K_2(HgI_4)$$

$\therefore$ Solute particles decreases. ΔT_f is depression in FP and is decreased by adding non-volatile solute.

4. STATEMENT-1 : At low concentration benzene and toluene forms ideal solution.

and

STATEMENT-2 : Components with structural similarities form ideal solution.

Sol. Answer (1)

Benzene and Toluene form an ideal solution because their molecules are identical in shape, size and nature.

5. STATEMENT-1 : Molality and mole fraction are temperature independent quantity.

and

STATEMENT-2 : Molality and mole fraction are unit less quantity.

Sol. Answer (3)

Molality involves weight and mole fraction involves moles that's why they are temperature independent quantity.

Molality have units as 'molal' but mole fraction does not have units.

6. STATEMENT-1 : 0.1 M solution of Na_2SO_4 has greater osmotic pressure than 0.1 M solution of urea at same temperature.

and

STATEMENT-2 : The value of van't Hoff factor for Na_2SO_4 is less than urea.

Sol. Answer (3)

For Na_2SO_4 $i = 3$

and $\pi_1 = (0.1)\ (ST) \times 3$

and for UREA $i = 1$

and $\pi_2 = (0.1)\ (S)\ T$

$\Rightarrow\ \pi_1 > \pi_2$

i for Na_2SO_4 = 3 ; and for UREA, $i = 1$

$\therefore$ It can be concluded that osmotic pressure for Na_2SO_4 solution is more as compared to 'UREA' solution.

$\therefore$ Statement (1) is correct but statement (2) is wrong.

7. STATEMENT-1 : The equivalent mass of Mohr's salt is $\frac{M}{4}$ in non-redox reaction [If M is molecular mass of Mohr's salt].

and

STATEMENT-2 : The normality of Mohr's salt is higher than molarity for same amount and volume at constant temperature.

Sol. Answer (2)

Mohr's salt is $FeSO_4.(NH_4)_2\ SO_4.6H_2O$. So, Equivalent wt. = $\frac{M}{4}$.

Normality = Molarity × n-factor.

8. STATEMENT-1 : One molar solution is always more concentrated than one molal solution.

and

STATEMENT-2 : The amount of solvent in 1 M and 1 m aqueous solution is not equal.

Sol. Answer (4)

Fact.

9. STATEMENT-1 : Iodine is more soluble in CCl_4 than in water.

and

STATEMENT-2 : Non-polar solutes are more soluble in non-polar solvents

Sol. Answer (1)

Fact.

10. STATEMENT-1 : Henry's law and Raoult's law are not independent, *i.e.*, one can be derived from the other.

and

STATEMENT-2 : The partial pressure is directly proportional to the mole fraction of concerned species for ideal solutions.

Sol. Answer (2)

Raoult's law can be derived from Henry's law.

SECTION - F

Integer Answer Type Questions

1. For $[CrCl_3.xNH_3]$, elevation in boiling point of one molal solution is triple of one molal aqueous solution of urea. Assuming 100% ionisation of complex molecule and coordination number as six, calculate the value of x.

Sol. Answer (5)

ΔT_b (complex) = 3 × ΔT_b (area)

Thus, complex should furnish three ions. Therefore, complex is $[CrCl.xNH_3]Cl_2 \rightarrow [CrCl.xNH_3]^{2+} + 2Cl^-$

Also, co-ordination number of Cr is six

Thus, x = 5

2. An aqueous solution of an acid is so weak that it can be assumed to be practically unionised, boiled at 100.4°C 25 ml of this solution was neutralised by 38.5 ml of 1 N solution of NaOH. Calculate basicity of the acid if $k_b(H_2O)=0.52\ k\ mol^{-1}kg$. Assume molality is equal to molarity.

Sol. Answer (2)

$\Delta T_b = k_b \times m$

$0.4 = 0.52 \times m \quad \Rightarrow m = 0.77$

$25 \times 0.77 \times \text{'n'} = 38.5 \times 1 \quad \Rightarrow n = 2$

3. The vapour pressure of two pure liquids A and B that forms an ideal solution are 300 and 800 torr respectively at temperature T. A mixture of the vapours of A and B (for which the mole fraction of A is 0.25) is slowly compressed at temperature T. The vapour pressure of this condensate on 100% condensation of vapoure is measured to be 'P'. What is the value of 684 – P?

Sol. Answer (9)

$$\frac{X'_A}{X'_B} = \frac{p^o_A X_A}{p^o_B X_B} \qquad \Rightarrow \frac{X_A}{X_B} = \frac{X'_A}{X'_B} \times \frac{p^o_B}{p^o_A} = \frac{0.25}{0.75} \times \frac{800}{300} = \frac{8}{9}$$

$\Rightarrow X_B = 0.53$

$\Rightarrow P = 300 \times 0.47 + 800 \times 0.53 = 565$ torr

So, $574 - P = 9$

4. A compound X undergoes tetramerisation in a given organic solvent. The van't Hoff factor i is calculated as 0.05y. Find y. (Assuming 100% association)

Sol. Answer (5)

$4X \rightarrow (X)_4$

$$i = (1-\alpha) + \frac{\alpha}{n}$$

$$\alpha = 1, n = 4 \Rightarrow i = 1 - \frac{3}{4} = 0.25$$

$0.25 = 0.05\ y$

$\Rightarrow\ y = 5$

5. If $K_3[Fe(CN)_6]$ gets ionized completely in a solution, number of particles in the solution from 1 molecule of solute is________.

Sol. Answer (4)

$K_3[Fe(CN)_6] \rightarrow 3K^+ + [Fe(CN)_6)]^{3-}$

6. A sample of air (containing 20% O_2 and 80% N_2) is dissolved in water when total pressure of air is 1 atm. The solubility of N_2 and O_2 (in terms of mole fraction) is x and y. This sample is taken at a height of H above sea level where pressure of air is 0.4 atm and temperature is 300 K and solubility of N_2 and O_2 (in terms of mole fraction) is x′ and y′. Assume that value of Henry's constant remains same at sea level and H. The value of $2\left(\frac{x}{x'} + \frac{y}{y'}\right)$ is

Sol. Answer (10)

At sea level

$p_{N_2} = 0.8 \quad p_{O_2} = 0.2$

at height H, P = 0.4 atm

Mole fraction of N_2 and O_2 remain in ratio of 4 : 1 at any height.

$p_{N_2} = 0.4 \times 0.8 = 0.32$ atm

$p_{O_2} = 0.4 \times 0.2 = 0.08$ atm

$$x = \frac{0.8}{k_h}$$

$$x' = \frac{0.32}{k_h}$$

$$\therefore\ \frac{x}{x'} = 2.5$$

$$\text{and } \frac{y}{y'} = 2.5$$

$$\therefore\ 2\left(\frac{x}{x'} + \frac{y}{y'}\right) = 10$$

7. An electrically neutral ionic crystal contains metal ion M^{+x}, metal ion N^{+y} and oxide ions. Oxide ions form C.C.P. lattice while M^{+x} is present at $\frac{1}{8}$th of tetrahedral void and N^{+y} is present at $\left(\frac{1}{A}\right)$th of octahedral voids. If 0.1 M of $N(Cl)_y$ solution at 300 K has osmotic pressure 9.6 atm, then $(A^2 + 4xy)$ is

Given : i. $\frac{y \cdot x}{A}$ is odd number and y, x and A all are positive integers in which $A \le y$.

ii. $R = 0.08 \frac{\text{atm L}}{\text{mol K}}$ and $N(Cl)_y$ is 100% dissociated

Sol. Answer (28)

For electrical neutrality

total positive charge = total negative charge

$$1 \times x + \frac{4}{A} \times y = 8$$

$\pi = i \times C \times R \times T$

$9.6 = i \times 0.1 \times 0.08 \times 300$

$i = 4$

so y = 3 so possible value of A = 1, 2, 3

from eq.

If A = 1

$x + 4 \times 3 = 8 \Rightarrow x = -4$ (Not possible)

If A = 2

$x + 2 \times 3 = 8$

$x = +2$

so $\frac{y \cdot x}{A} = 3$ (possible because odd number)

If A = 3

$x + 4 = 8$

$x = 4$

then $\frac{y \cdot x}{A} = \frac{3 \times 4}{4} = 4$ (Not possible because even)

so possible value of A = 2

hence, $A^2 + 4xy = 4 + 4 \times 2 \times 3$

$= 28$

8. The osmotic pressure of two aqueous urea solutions-I and II are 2.1 atm and 1.8 atm respectively at 25°C. The osmotic pressure (in atm) of a solution at 25° prepared by mixing solution I and II in the volume ratio of 2 : 1 is

Sol. Answer (2)

$\pi_1 = C_1 RT \quad \Rightarrow \quad \pi_1 . v_1 = n_1 RT$

$\pi_2 = C_2 RT \quad \Rightarrow \quad \pi_2 . v_2 = n_2 RT$

In the final solution

Total moles of urea = $n_1 + n_2$

Final osmotic pressure = $\dfrac{(n_1 + n_2)}{v_1 + v_2} RT$

$$= \frac{\dfrac{(\pi_1 v_1 + \pi_2 v_2)}{RT} RT}{v_1 + v_2} = \frac{\pi_1 v_1 + \pi_2 v_2}{v_1 + v_2}$$

$$= \frac{2.1 \times 2v + 1.8 \times v}{3v} = \frac{6v}{3v} = 2 \text{ atm}$$

9. The boiling point elevation constant for toluene is 3.32 K kg mol^{-1}. The normal boiling point of toluene is 110.7ºC. The enthalpy of vaporisation of toluene (in kJ/mol) would be nearly.

Sol. Answer (34)

$$\Delta H_{vap.} = \frac{M_{solvent} \times R \times T_b^{o^2} \text{(solvent)}}{1000 \times K_b}$$

$$\therefore \; \Delta H_{vap.} = \frac{92 \times 8.314 \times (383.7)^2}{1000 \times 3.32} = 33.91 \text{ kJ/mol} \approx 34 \text{ kJ/mol}$$

10. Calculate the percentage degree of dissociation of an electrolyte XY_2 (normal molar mass = 164) in water if the observed molar mass by measuring elevation in boiling point is 65.6.

Sol. Answer (75)

	XY_2	$\rightleftharpoons$	X^{2+}	+	$2Y^-$
Initially	1		0		0
at equilibrium	$1 - \alpha$		α		2α

Total number of moles = $1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} ; \; \frac{1 + 2\alpha}{1} = \frac{164}{65.6}$$

$\therefore \; \alpha = 0.75; \; \% \, \alpha = 75\%$

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