

HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

1. Initial moles of KCl = $\frac{100}{1000} \times 0.1 = 0.01$

Let x moles of KCl are added, so

$$0.2 = \frac{0.01 + x}{100/1000} \quad \text{or} \quad x = 0.01$$

2. 10 µg per decilitre
⇒ 10×10^{-6} g in 100 mL

∴ 10^9 parts (1 billion) has = $\frac{10 \times 10^{-6}}{100} \times 10^9 \text{ g} = 100 \text{ g}$

5. Certain compounds combine with the moisture of atmosphere and are converted into hydroxides or hydrates. Such substances are called hygroscopic. e.g., anhydrous CuSO_4 , quick lime (CaO), anhydrous Na_2CO_3 etc.

6. (A) V.P. depends on temperature.

10. For two immiscible liquid ;

$$P_A^\circ = P_{\text{total}} - P_{\text{H}_2\text{O}}^\circ = 748 - 648 \Rightarrow 100$$

$$\frac{W_A}{W_B} = \frac{P_A^\circ M_A}{P_B^\circ M_B} ; M_A = \frac{1.25}{1} \times \frac{648 \times 18}{100} \Rightarrow 145.8$$

13. Let n_B mole of B present in 1 mole of mixture that has

been vaporized. Thus, $y_B = \frac{n_B}{1}$

Mole fraction of B in the remaining liquid phase will be

$$x_B = \frac{1 - n_B}{1}$$

$$x_B = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ} \quad \dots\dots (1)$$

$$[\because P = P_T^\circ + (P_B^\circ - P_T^\circ)x_B]$$

and $y_B = \frac{P_B}{P} \Rightarrow \frac{P_B^\circ x_B}{P} \quad \dots\dots (2)$

After substitution of values of x_B and y_B in (1) and (2)

we get $1 - n_B = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ} \quad \dots\dots (3)$

and $n_B = \frac{(1 - n_B)P_B^\circ}{P} \quad \dots\dots (4)$

or $n_B = \frac{P_B^\circ}{P + P_B}$

so $1 - \frac{P_B^\circ}{P + P_B} = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ}$

$$\Rightarrow P = \sqrt{P_B^\circ \cdot P_T^\circ} = \sqrt{100 \times 900}$$

$$\Rightarrow 300 \text{ torr}$$

15. $760 = 300 X_A + 800 (1 - X_A)$

$$\Rightarrow 760 = 800 - 500 X_A$$

$$\Rightarrow 500 X_A = 40$$

$$\therefore X_A = \frac{40}{500} = 0.08.$$

16. $x_A = \frac{1}{1+3} \Rightarrow \frac{1}{4} ; x_B = \frac{3}{4} ;$

$$\frac{y_A}{y_B} = \frac{P_A^\circ}{P_B^\circ} \times \frac{x_A}{x_B}$$

$$\frac{y_A}{(1 - y_A)} = \frac{1}{3} \times \frac{1}{3}$$

$$\Rightarrow \frac{1}{9} \text{ or } y_A = \frac{1}{10}$$

18. (A) An azeotropic mixture boil at particular temperature without changing its composition.

22. It shows negative deviation from Raoult's law

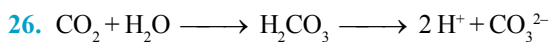
$$p_s (\text{actual}) = 580 \text{ torr}$$

$$p_s (\text{Raoult}) = 0.4 \times 300 + 0.6 \times 800 = 600 \text{ torr.}$$

23. Solubility \propto pressure

$$\frac{S_2}{S_1} = \frac{P_2}{P_1}$$

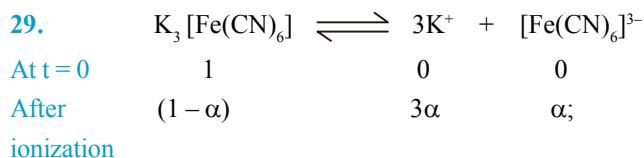
$$S_2 = 5.3 \times 10^{-4} \times \frac{760}{593} = 6.8 \times 10^{-4} \text{ M}$$



But CH_4 and H_2 are insoluble gases in water.

28. $i = \frac{C(1 - \alpha) + \frac{C\alpha}{n}}{C} \Rightarrow i = 1 - \alpha + \frac{\alpha}{n}$

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$$i = 1 + 3\alpha$$

Since, $i = \frac{M_{\text{normal}}}{M_{\text{abnormal}}}$

$$\therefore \frac{1 + 3\alpha}{1} = \frac{M_{\text{normal}}}{M_{\text{abnormal}}}$$

30. According to question according Raoult's law
- $$P_s = 0.95 P_0$$
- $$P_s = P_0 X_A$$
- given $M_A = 0.3 M_B$

$$0.95 P_0 = P_0 \left(\frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \right) \quad M_A = \text{molecular wt. of solvent}$$

$M_B = \text{molecular wt. of solute}$

$$0.95 = \frac{\frac{W_A}{0.3 M_B}}{\frac{W_A}{0.3 M_B} + \frac{W_B}{M_B}} \quad W_A = \text{gram wt. of solvent}$$

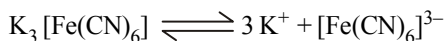
$W_B = \text{gram wt. of solute}$

on solving $\frac{W_A}{W_B} = 5.7$.

32. $\Delta T_b = i k_b m$

so $i = \frac{2.08}{0.52 \times 1} = 4$

so the complex is $K_3[Fe(CN)_6]$



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

$$0.2 = \frac{X \times 1000}{100} \times 1.86 \quad X = \frac{0.2}{10 \times 1.86}$$

after freezing

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

$$\Delta T_f = \frac{X \times 1000}{(100 - y)} \times 1.86 \quad \Delta \zeta T_f = 0.25$$

On solving, Amount of ice $y = 20$ g ice

34. $\Delta T_b = K_b \cdot m \cdot i$

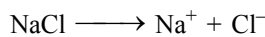
In 100 gm of solution

moles of NaCl = 0.1

$$(\alpha = 0.8)$$

moles of $MgCl_2 = 0.1$

$$(\alpha = 0.5)$$



$$i_{NaCl} = 1 + (2 - 1) 0.8 = 1.8$$

Effective no. of moles of NaCl = $0.1 \times 1.8 = 0.18$

$$i_{MgCl_2} = 1 + (3 - 1) 0.5 = 2$$

Effective no. of moles of $MgCl_2 = 0.1 \times 2 = 0.2$

Total no. of mole = $0.18 + 0.2 = 0.38$

$$\Delta T_b = \frac{0.38}{100} \times 100 \times 0.51 = 3.8 \times 0.51 = 1.938$$

$$\text{So, } T_b = 100 + 1.938 = 101.938$$

36. Boiling point of solution = boiling point + $\Delta T_b = 100 + \Delta T_b$
 Freezing point of solution = freezing point - $\Delta T_f = 0 - \Delta T_f$
 Difference in temperature (given) = $100 + \Delta T_b - (-\Delta T_f)$
 $104 = 100 + \Delta T_b + \Delta T_f = 100 + \text{molality} \times K_b + \text{molality} \times K_f$
 $= 100 + \text{molality} (0.52 + 1.86)$

$$\therefore \text{Molality} = \frac{104 - 100}{2.38} = \frac{4}{2.38} = 1.68 \text{ m}$$

$$\text{and molality} = \frac{\text{moles} \times 1000}{W_{\text{gm (solvent)}}}; 1.68 = \frac{\text{moles} \times 1000}{500}$$

$$\therefore \text{Moles of solute} = \frac{1.68 \times 500}{1000} = 0.84 \text{ moles.}$$

38. $\pi_1 = 2R \times 300 \times \left(1 + \left(\frac{1}{2} - 1 \right) 1 \right) = 300 R$

$$\pi_{II} = 0.5 R \times 300 \times 2 = 300 R$$

42. Pressure of air = $750 - 100 = 650$ mm of Hg
 on compressing $P_f = Hg 650 \times 3 \text{ mm of Hg} = 1950 \text{ mm of Hg}$
 so $P_T = (1950 + 100) = 2050$ mm of Hg

45. Molarity = $\frac{0.967 / 159.5}{20 / 1000} \left\{ \begin{array}{l} \text{Mol. wt. of } CuSO_4 \\ 159.5 \end{array} \right\}$
 $= 0.303 \text{ M}$

$$47. \frac{W_A}{W_B} = \frac{P_A^\circ}{P_B^\circ} \times \frac{M_A}{M_B} \Rightarrow \frac{0.7}{7} \times \frac{112.5}{18} \Rightarrow 0.625$$

$$\% \frac{W_A}{W_A + W_B} \times 100 = \frac{0.625}{1.625} \times 100 \Rightarrow 38.46$$

49. Possible vapor pressures are

$$\frac{75+22}{2}, \frac{75+10}{2}, \frac{22+10}{2} \text{ and } \frac{75+22+10}{3} = 48\frac{1}{2},$$

$$42\frac{1}{2}, 16, 35\frac{2}{3}.$$

52. According to Raoult's law

$$P_T = (0.08 \times 300 + 0.92 \times 800) \text{ torr} = (24 + 736) \text{ torr} = 760 \text{ torr} = 1 \text{ atm}$$

$$P_{\text{exp.}} = 0.95 \text{ atm} < 1 \text{ atm}$$

Hence solution shows -ve deviation

$$\text{so } \Delta H_{\text{mix}} < 0, \quad \text{and } \Delta V_{\text{mix}} < 0.$$

54. $P'_A = P_A^\circ X_A$ and $P'_B = P_B^\circ X_B$

$$P'_A = P_M \cdot Y_A \text{ and } P'_B = P_M \cdot Y_B$$

$$\therefore \frac{P'_A}{Y_A} = \frac{P'_B}{Y_B}$$

$$\text{or } \frac{P_A^\circ X_A}{Y_A} = \frac{P_B^\circ X_B}{Y_B} = \frac{P_B^\circ (1 - X_A)}{(1 - Y_A)}$$

$$\text{or } \frac{P_A^\circ X_A}{Y_A} (1 - Y_A) = P_B^\circ - P_B^\circ X_A$$

$$\text{or } \frac{P_B^\circ}{X_A} = \frac{P_A^\circ}{Y_A} + (P_B^\circ - P_A^\circ)$$

$$\text{or } \frac{1}{X_A} = \frac{1}{Y_A} \cdot \frac{P_A^\circ}{P_B^\circ} + \frac{(P_B^\circ - P_A^\circ)}{P_B^\circ}$$

$$\text{or } y = mx + C$$

$$\therefore \text{Slope} = m = \frac{P_A^\circ}{P_B^\circ} \text{ and intercept } C = \frac{(P_B^\circ - P_A^\circ)}{P_B^\circ}$$

61. $3S \rightleftharpoons S_3$

$$1 \quad 0$$

$$1 - \alpha \quad \frac{\alpha}{3} \quad \Rightarrow \quad i = 1 - \frac{2\alpha}{3}$$

$$\text{Now} \quad 0.1 \left(1 - \frac{2\alpha}{3} \right) = 0.08$$

$$\Rightarrow \quad \alpha = 0.3. \text{ Hence 30\% trimerization.}$$

$$63. \frac{\Delta P}{P} = \frac{ni}{ni + N}$$

$$0.5 = \frac{2i}{2i + 3}$$

$$i + 1.5 = 2i$$

$$i = 1.5$$

$$i = 1 + (y - 1)\alpha$$

$$1.5 = 1 + (2 - 1)\alpha$$

$$\alpha = 0.5$$

$$\text{mole of } Cl^- = 1.0$$

$$\text{mole of AgCl ppt.} = 1.0 \quad \text{Ans. (A)}$$

66. $\Delta T_f = i.m. K_f$

$$\Delta T_f = i_1 m_1 K_f + i_2 m_2 K_f + i_3 m_3 K_f = (m_1 + 2m_2 + m_3) K_f$$

$$\Delta T_f = \frac{3}{60} + \frac{7.45 \times 2}{74.5} + \frac{9}{180} \times 1000 \times 1.86$$

$$\Delta T_f = 3 \times 1.86 = 5.58$$

$$T_f \text{ of solution} = 273 - 5.58 = 267.42 \text{ K Ans.}$$

68. Mole of solute in first beaker = $\frac{0.05 \times 20}{1000} = 0.001$

$$\text{mole of solute (Na}^+ \text{ \& } Cl^-) \text{ in other beaker} = \frac{2 \times 0.03 \times 20}{1000} = 0.0012$$

conc. of IInd beaker is higher than Ist beaker so water flows from Ist beaker to IInd beaker till both beaker achieved equal conc. let v volume of water flows from Ist to IInd beaker

$$\text{so } \frac{0.001}{20 - v} = \frac{0.0012}{20 + v}$$

$$v = 1.8 \text{ ml}$$

$$\text{volume of Ist beaker} = 20 - 1.8 = 18.2 \text{ ml}$$

$$\text{volume of IInd beaker} = 20 + 1.8 = 21.8 \text{ ml.}$$

73. Solubility increases with decrease in temperature. But solubility increases with increase in pressure according to Henry's Law.

74. I. Melting of snow by salt : Depression in freezing point

II. Desalination of sea water : Reverse osmosis

III. Osmosis is used to determine the molar mass.

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75. When non volatile solute added to solvent. Due to elevation in boiling point, boiling point \uparrow and due to depression in freezing point, freezing temperature \downarrow

76. Given, In 150×10^3 gm of sample ———— 450 mg is present

$$\text{so in } 10^6 \text{ gm} \text{ ———— } \frac{450 \times 10^{-3}}{150 \times 10^3} \times 10^6$$

$$= 3 \text{ ppm}$$

77. Let volumes taken by 'x' & 'y' litres,

$$\text{so } \frac{0.1x + 0.4y}{x + y} = 0.34 \text{ \& } V_g = (x + y) \text{ (to be maximised)}$$

so $y = 4x$ so for maximum volume

$$y = 2L \text{ \& } x = \frac{1}{2}L$$

78. Mole of $H_2O = \frac{36}{18} = 2$

$$\text{Mole of glycerine} = \frac{46}{92} = 0.5$$

$$\text{total mole} = 2 + 0.5 = 2.5$$

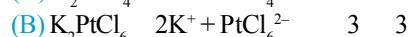
$$\text{Mole fractions of glycerine} = \frac{n_1}{n_1 + n_2} = \frac{0.5}{2.5}$$

$$\Rightarrow X_0 = 0.2 \text{ Ans.}$$

79. $i = \text{van't Hoff factor} = 1 + (y - 1)x$

($y = \text{number of ions, } x = \text{degree of ionisation}$)

$$y \quad i = 1 + (y - 1)x$$



In (A), oxidation number of Pt = 2

In (B) oxidation number of Pt = 4

80. i remains unchanged when number of ions before and after complex ion remains constant.

Solute	y	Complex	y
(A) $PtCl_4$	5	$K_2[PtCl_6]$	3
(B) $ZnCl_2$	3	$Zn[(NH_3)_4]Cl_2$	3

81. $HA \rightleftharpoons H^+ + A^-$

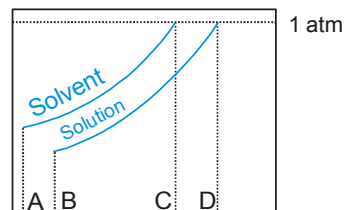
$$i = [1 + (y - 1)x] = 1 + x$$

$$pK_a = 4 = -\log K_a$$

$$\therefore K_a = 10^{-4} = Cx^2$$

$$1 \times 10^{-4} = 0.01 \times x^2 \Rightarrow x = 0.1 \quad \therefore i = 1 + x = 1.1$$

82.



Normal boiling point of the solution is that temperature at which vapour pressure of solution equals to 1 atm.

83. All are facts.

We should remember that, Entropy of solution is more than entropy of pure solvent. So the difference in entropy change will be less in case of solution.

$$84. \Delta T = \frac{1000 K_b w_1}{m_1 w_2}$$

$$\frac{\Delta T}{K_b} (AB_2) = \frac{1000 \times 6}{m_1 \times 100} = 1$$

$$\therefore m_1 (AB_2) = 60 = A + 2B$$

$$\frac{\Delta T}{K_b} (A_2B) = \frac{1000 \times 9}{m_1 \times 100} = 1$$

$$\therefore m_1 (A_2B) = 90 = 2A + B$$

$$\therefore A = 40, B = 10$$

85. As $\Delta T_b = i K_b m$

so $i K_b m$ can be expressed in degree (Unit of temperature)

and $K_b m$ can be expressed in degree (Unit of temperature)

and $\frac{\Delta T_b}{i}$ can be expressed in degree (Unit of temperature)

But unit of K_b is $\text{mol}^{-1} \text{ kg K}$

86. As $\Delta T_b = \text{molality} \times K_b$

$$0.52 = m \times 0.52$$

$$\text{molality} = 1 \text{ mol kg}^{-1}$$

$$\therefore \text{urea} = 1 \text{ mol}$$

$$\text{moles of water} = \frac{1000}{18} = 55.55$$

$$\text{mole fraction of urea} = \frac{1}{56.55} = 0.018$$

87. $\pi = CRT$

$$\pi = \frac{c}{M}RT \quad C = \text{moles/liter, } c = \text{kg/m}^3$$

$$\frac{\pi}{c} = \frac{RT}{M}$$

$$M = \frac{RT}{\pi/c} \quad [\pi/c = 8.314 \times 10^{-3}]$$

$$[T = 293 \text{ K}]$$

$$M = \frac{8.314 \times 293}{8.314 \times 10^{-3}} = 293 \times 10^3$$

88. Given $\Delta T_b = 1.08^\circ\text{C}$, $i = 2$ at boiling pt. of solution.

and $\Delta T_f = 1.80^\circ\text{C}$, and $\frac{k_b}{k_f} = 0.3$

so $\frac{\Delta T_b}{\Delta T_f} = \frac{i_b k_b m}{i_f k_f m}$

so $i_f = 1$

i.e., AB behaves as non-electrolyte at the f.p. of the solution.

89. 1M $\text{C}_6\text{H}_{12}\text{O}_6$ (molar mass = 180 g mol^{-1})

1000 mL solution has = 180 g solute

1180 g solution has = 180 g solute

1000 g solvent has = 180 g solute

Thus, molality = 1 molal

$$\therefore \Delta T_f = K_f \text{ molality} = 1.86 \times 1 = 1.86^\circ$$

$$\therefore \text{F.P.} = -1.86^\circ\text{C}$$

90. Firstly we have to convert mole fraction into molality.

$$\text{Molality} = \frac{x_{\text{solute}}}{x_{\text{solvent}} M_{\text{solvent}} / 1000} = \frac{0.07 \times 1000}{0.93 \times 18} = 4.18$$

Now, $\Delta T_f = k_f m$
 $= 1.86 \times 4.18 = 7.78^\circ$

91. $P = P_A^\circ X_A + P_B^\circ X_B$

$$\frac{100}{4} + \frac{60 \times 3}{4}$$

$$= 70 \text{ mm} < 75 \text{ mm (experimental)}$$

Thus, there is positive deviation (A) is true, mixture is more volatile due to decrease in b.p. Thus, (B) is true also force of attraction is decreased thus (C) is true.

92. $PV = nRT$

$$P_{\text{mix}} = 7.82 \times 10^4 \text{ Pa}$$

$$P_2 + P_1 = 7.82 \times 10^4 \text{ Pa}$$

$$P_1 = 7.03 \times 10^4 \text{ Pa}$$

$$\therefore P_2 = 0.79 \times 10^4 \text{ Pa}$$

$$P \propto n$$

$$\therefore \frac{w_2 m_1}{w_1 m_2} = \frac{p_2}{p_1}$$

$$w_2 = w_1 \frac{p_2 m_2}{p_1 m_1} = \frac{0.79 \times 10^4 \times 112.5}{7.03 \times 10^4 \times 18} = 0.70$$

93. $RLVP = i \frac{n}{n+V}$

so $0.167 = \frac{2 \times n}{n + \frac{180}{18}}$

so $n = 1$

 94. From given graph, we can say T_1 is that temp at which solid state and liquid (solution) are in equilibrium.

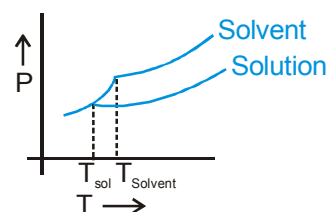
95. (A) Entropy of solution > Entropy of pure solvent

$$(\Delta S)_{\text{solution-solid}} > (\Delta S)_{\text{solvent-solid}}$$

In solution, number of particle is greater so solution have greater entropy.

(B) Only solvent involved in solid-liquid equilibrium.

(C) $\Delta T_f = T_{\text{solvent}} - T_{\text{solution}}$


 96. All $\Delta S_1, \Delta S_2, \Delta S_3$ and ΔS_4 are correct entropy changes.

97. On mixing non-volatile solute, elevation in boiling point takes place.

98. Colligative property of a solution depends on no. of particles of solute in solution.

99. Value of van't Hoff factor is least for urea solution, so there will be least depression in freezing point i.e., maximum freezing point.

100. $P_T = X_A p_A^0 + X_B p_B^0$
 $= \left(\frac{2}{4}\right) \times 80 + \left(\frac{2}{4}\right) \times 120 = 100 \text{ Torr}$
 Now mole fraction in vapour phase = $\frac{X_A p_A^0}{P_T} = \frac{40}{100} = 0.4$.

101. $\frac{268 - 167}{268} = x \Rightarrow$ So $x = 0.377$.

102. Boiling point get lowered when vapour pr. increases and it happens when there is a positive deviation from Raoult's law.

103. As van't Hoff factor increases RLVP increases

i.e., V.P. decreases $y > x > z$

Elevation in b.p. increases

i.e., b.p. increases $y < x < z$

Depression in f.p increases

i.e., f.p decreases $y > x > z$

Osmotic pressure increases so $y < x < z$.

104. In HF hydrogen bonding is present so there is association of molecules due to this van't huff factor is less, so depression in f.p decreases therefore f.p. value is larger than HCl. Similarly value of $i = 2$ for NaCl and $i = 1$ for Glucose.

105. $p_A = X_A p_A^0$
 $32 = X_A \cdot 40$

$\therefore X_A = \frac{32}{40} = 0.8$.

106. For urea, $\Delta T_f = k_f \times m$ or

$k_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86$

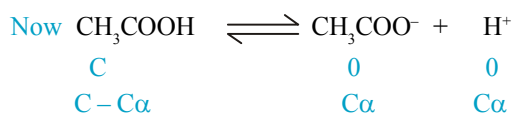
Now for CH_3COOH

$\Delta T_f = i k_f m$

so $i = \frac{0.02046}{1.86 \times 0.01} = 1.1$

Now $i = 1 + \alpha$

so $\alpha = 1.1 - 1 = 0.1$



$[\text{H}^+] = \text{C}\alpha = 0.01 \times 0.1 = 0.001$

so $\text{pH} = 3$.

107. $\text{RLVP} = \frac{i n_{\text{NaCl}}}{i n_{\text{NaCl}} + n_{\text{H}_2\text{O}}}$

$0.4 = \frac{i}{i + 3}$

so $i = 2$

$\therefore i = 1 + \alpha$ so $\alpha = 1$ or 100%

108. Mixtures of $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3COCH_3 shows positive deviation from Raoult's law, so vapour pr. increases and b.p decreases.

109. Wt. of $\text{CCl}_4 = 1.538 \times 100 = 153.8 \text{ gm}$

so moles of $\text{CCl}_4 = \frac{153.8}{154} \approx 1$

moles of solute = $\frac{0.5}{65} = 0.00769$

Now $\frac{P_0 - P_s}{P_s} = \frac{n}{N}$

or $\frac{143 - P_s}{P_s} = \frac{0.00769}{1}$

so $P_s = 141.9 \text{ mmHg}$.

110. $\Delta T_f = k_f m$
 $\Delta T_f = 1.86 \times 0.5 = 0.93$
 so $T_f = -0.93^\circ\text{C}$.

111. More the value of van't huff factor, more will be the depression in freezing point.

112. L indicates elevation in boiling pt. i.e., $k_b m$.

113. Osmotic pressure = CRT
 $= 0.30 \times 0.082 \times 298 = 7.34 \text{ atm}$

114. Due to high entropy of solution than pure solvent, f.p decreases.

115. $\pi = MRT$ i : $y \uparrow, i \uparrow, \pi \uparrow$

116. $(\text{B.P.})_{\text{mix}}$ is less than pure component, so intermolecular force is less so vapour pressure \uparrow and solution have positive deviation from Raoult's law.

117. Acetone and chloroform forms hydrogen bonding so volume decreases.

118. Mole fraction of more volatile substance is greater in vapour phase.

119. $M_{\text{observed}} = \frac{58.5}{i}$; $i > 1$.
120. Due to weak force of attraction more vapour will be formed so vapour pressure will be high.
121. Freezing point and boiling point are used in temperature scale.
122. Volatile nature \uparrow , vapour pressure increases, fraction in vapour phase increases.
123. This is due to cage like structure ice.
124. There is very weak attraction between benzene and methanol as compare to attraction between molecules of methanol.
125. $p = CRT$ order of conc is urea > glucose > sucrose
126. $9.3 = \frac{50}{62 \times (200 - w)} \times 1000 \times 1.86 \times 1$
 $w = 38.71 \text{ g.}$
127. In liquid \rightleftharpoons vapour equilibrium, molecule have same kinetic energy.
128. The order of force attraction and boiling point is $\text{CH}_3\text{OH} > \text{CH}_4 > \text{H}_2$.
129. At freezing point liquid solvent and solid solvent are in equilibrium.

EXERCISE - 2

Part # 1 : Multiple Choice

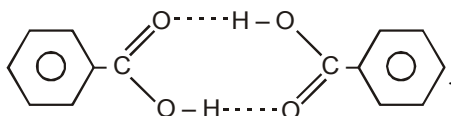
1. $A_x B_y \rightleftharpoons xA^{y+} + yB^{x+}$
- | | | | |
|---------------|---------------|------------|------------|
| Initial moles | n | 0 | 0 |
| At eq b. | $n(1-\alpha)$ | $nx\alpha$ | $ny\alpha$ |
- $$i = \frac{\text{Total mol at equilibrium}}{\text{Initial mol}} = \frac{n[(1-\alpha) + x\alpha + y\alpha]}{n}$$
- $$i = (1-\alpha) + x\alpha + y\alpha$$
- It can also seen that all other expressions imply the same thing.
- (A) $\alpha = \frac{i-1}{x+y-1}$ (B) $i = (1-\alpha) + x\alpha + y\alpha$.
- (C) $\frac{1-i}{1-x-y}$

2. $P = MST$
- $$P = \frac{n}{V} \times ST$$
- $$P = \frac{w}{V \times M} \times ST$$
- $$\frac{P}{d} = \frac{ST}{M}$$
4. For - ve deviation $A-B > A-A$
 $A-B > B-B$
 - ve deviation solution are non ideal solution.
6. Molality, Molarity, Percent by mass and Normality all can be related to mole fraction (by using density).
7. As concentration values are same for all solutions, so osmotic pr. will depend on van't hoff factor (i).
- | | I | II | III | IV |
|-----------------------------------|---|----|-----|-----|
| glucose (aq.) | | | | |
| NaCl (aq.) | | | | |
| $(\text{NH}_4)_3\text{PO}_4$ (aq) | | | | |
| Benzoic acid in benzene | | | | |
| Value of i | 1 | 2 | 4 | 0.5 |
- more the value of i, more is the osmotic pressure.
8. If intermolecular forces are weak then less amount of ΔH_{vap} is reqd. therefore high vapour pressure is obtained.
9. For ideal solutions :
 $\Delta V_{\text{mix}} = 0$ and $\Delta H_{\text{mix}} = 0$
 $\Delta S_{\text{mix}} = -ve$
10. Since intermolecular forces between solvent molecules are involved, so ΔH of solution and solvent is almost identical.
11. $X_A P_A^0 + X_B P_B^0 = 0.25 \times 512 + 0.75 \times 344 = 386 \text{ mm}$
 Now $P_A + P_B = 600 \text{ mm Hg}$ (Given)
 so $P_A + P_B > X_A P_A^0 + X_B P_B^0$
 therefore, there is positive deviation from Raoult's law
 $\Delta H > 0$ i.e., heat is absorbed.
12. When mixture is more volatile, total pressure increases so there is a positive deviation from Raoult's law, and vice-versa.
13. $P = 119x + 135$
 $x = 1$ for pure methanol.
 so $P_{\text{methanol}}^0 = 119 + 135 = 254 \text{ Torr}$
 But for pure ethanol $x = 0$
 so $P_{\text{ethanol}}^0 = 135 \text{ Torr}$
14. When solute added to the solvent, the vapour pressure of solution decreases.
15. $\Delta T_b = mK_b i$; $K_b = \frac{RT^2}{1000 \Delta H_{\text{vapour}}}$

16. Ideal gas equation, $PV = nRT$
Solute particle is similar as gas molecule.
17. $\Delta T_f = mK_f i$
18. Temperature \uparrow , vapour pressure \uparrow .
19. In solution, lesser number of solvent molecules have tendency to form vapour. Only solvent molecule under go phase transition.
20. $i = 1 + (x + y - 1)\alpha$

Part # II : Assertion & Reason

1. The benzoic acids forms a dimer due to H-bonding as



2. Extent of dissociation increases steadily with increasing dilution.
3. As degree of dissociation of HF increases on dilution.

EXERCISE - 3

Part # I : Matrix Match Type

2. (A) Acetone + CHCl_3 -ve deviation from Raoult's law $\Delta S > 0$
 $\Delta H < 0$ $\Delta V < 0$ Maximum Boiling Azeotropes.
- (B) Ethanol + Water +ve Deviation from Raoult's law $\Delta S > 0$
 $\Delta H > 0$ $\Delta V > 0$ Minimum Boiling Azeotropes
- (C) $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$ Ideal solution No Azeotropes
 $\Delta H = 0$ $\Delta V = 0$
- (D) Acetone + Benzene +ve Deviation from Raoult's law
 $\Delta H > 0$ $\Delta V > 0$ $\Delta S > 0$ Minimum Boiling Azeotropes

Part # II : Comprehension

Comprehension # 1 :

2. (1) $0.74 = \frac{0.0821}{250 \times 10^{-3}} \times 300 \left(\frac{x}{60} + \frac{1-x}{180} \right)$
 $x = 0.176$
 $\% \text{ urea} = \frac{0.176}{1} \times 100 = 17.6$

$$(2) \frac{dP}{P} = X_{\text{solute}} = \frac{\frac{0.176}{60} + \frac{0.824}{180}}{\frac{0.176}{60} + \frac{0.824}{180} + \frac{250}{18}} = 5.4 \times 10^{-4}$$

$$(3) \Delta T_b = mK_b = \left(\frac{0.176}{60} + \frac{0.824}{180} \right) \times \frac{1000}{250} \times 0.5 = 0.015$$

$\Delta T_b = 100.015.$

Comprehension # 2 :

1. B, C and D are the conditions and facts for positive deviation from Raoult's law.
(A) is incorrect.
Because A - B attractive force should be weaker than A - A and B - B attractive forces.
2. $X_A P_A^0 + X_B P_B^0 = \frac{1}{4} \times 100 + \frac{3}{4} \times 60 = 70 \text{ mm of Hg}$
Now $P_A + P_B > X_A P_A^0 + X_B P_B^0$
i.e., positive deviation from Raoult's law.
for positive deviation,
B.P. < expected value
 $F_{A..B} < F_{A..A}$
 $F_{A..B} < F_{B..B}$

EXERCISE - 4

Subjective Type

2. $\frac{P^0 - 21.85}{21.85} = \frac{30 \times 18}{90 \times m}$ for I case.....I
Now Weight of solvent = 90 + 18 = 108g
 $\frac{P^0 - 22.15}{22.15} = \frac{30 \times 18}{108 \times m}$ for II case.....II
- \therefore By eq. (i) $P^0 m - 21.85 m = 21.85 \times 6 = 131.1$
By eq. (ii) $P^0 m - 22.15 m = 22.15 \times 5 = 110.75$
- | | | |
|----------------------------------|---|---|
| - | + | - |
| 0.30 m = 20.35 | | |
| $m = \frac{20.35}{0.30} = 67.83$ | | |
- On substituting in Eq. (i), $\frac{P^0 - 21.85}{21.85} = \frac{30 \times 18}{90 \times 67.83}$
- $\therefore P^0 = 23.78 \text{ mm}$
3. $\Delta T_f = \frac{1000 K_f W_2}{M_2 W_1}$
 $M_2 = \frac{1000 \times 5.12 \times 2}{0.6 \times 100}$ $M_2 = 170.6 \text{ gm/mol}$

5. Given that,

$$P^{\circ} = 640 \text{ mm}, P_s = 600 \text{ mm}, w = 2.175 \text{ g}, W = 39.0 \text{ g}, M = 78$$

$$\therefore \frac{P^{\circ} - P_s}{P_s} = \frac{w \times M}{m \times W}$$

$$\therefore \frac{640 - 600}{600} = \frac{2.175 \times 78}{m \times W}$$

$$\therefore m = 65.25$$

6. Given

$$\Delta T = \frac{1000 \times K'_f \times w}{m \times W}$$

$$W = \text{wt. of benzene} = V \times d = 50 \times 0.879 \text{ g}$$

$$\therefore 0.48 = \frac{1000 \times 5.12 \times 0.643}{m \times 50 \times 0.879}$$

$$\Delta T = 5.51 - 5.03 = 0.48$$

$$\therefore m = 156.06$$

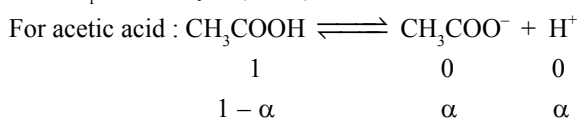
$$w = 0.643 \text{ g}, K'_f = 5.12 \text{ K mol}^{-1} \text{ kg}$$

$$11. \Delta T_b = i K_b m \quad 0.46 = i \times 0.52 \times \frac{0.011 \times 10^3}{0.1 \times 261}$$

$$i = 2.098 \quad \alpha = \frac{i-1}{n-1}$$

$$\Rightarrow \frac{2.098-1}{3-1} \quad \alpha \Rightarrow 0.55$$

13. $\Delta T = K_f \times \text{molality} \times (1 + \alpha)$



Given, $\alpha = 0.23$; Also, molality

$$= \frac{\text{mole of acetic acid}}{\text{weight of water in kg}}$$

$$= \frac{3 \times 10^{-3} \times 10^3}{60 \times \frac{500 \times 0.997}{10^3}} = 0.10$$

$$\Delta T = K_f \times \text{molality} (1 + \alpha)$$

$$\Delta T = 1.86 \times 0.1 \times 1.23 = 0.229$$

$$14. \Delta T_f = i K_f m \quad 0.062 = i \times 1.86 \times 0.01$$

$$i = 3.33 \quad \alpha = \frac{i-1}{n-1}$$

$$\alpha \Rightarrow \frac{3.33-1}{4-1} \quad \alpha \Rightarrow 0.777$$

25. For 0.01 M solution,

$$\pi_1 V_1 = n_1 S_1 T_1 \quad n_1 / V_1 = 0.01$$

$$\therefore \pi_1 = 0.01 \times 0.0821 \times 300 \quad T = 300 \text{ K}$$

$$= \mathbf{0.2463 \text{ atm}}$$

For 0.001 M solution,

$$\pi_2 V_2 = n_2 S T_2 \quad n_2 / V_2 = 0.001$$

$$\therefore \pi_2 = 0.001 \times 0.0821 \times 300 \quad T = 300 \text{ K}$$

$$= \mathbf{0.02463 \text{ atm}}$$

The movement of solvent particles occurs from dilute to concentrate solution, i.e., 0.001 M to 0.01M solution.

Thus, pressure should be applied on concentrated solution, i.e., **on 0.01 M solution** to prevent osmosis.

Also, magnitude of external pressure = $0.2463 - 0.0246 = 0.2217 \text{ atm}$ pressure on 0.01 M solution.

26. For initial solution,

$$\therefore \pi = \frac{500}{760} \text{ atm}, T = 283 \text{ K}$$

$$\frac{500}{760} \times V_1 = n \times S \times 283 \quad \dots \text{(i)}$$

After dilution, let volume becomes V_2 and temperature is raised to 25°C , i.e., 298 K

$$\pi = \frac{105.3}{760} \text{ atm}$$

$$\frac{105.3}{760} \times V_2 = n \times S \times 298 \quad \dots \text{(ii)}$$

\therefore By Eqs. (i) and (ii), we get

$$\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500} \quad \frac{V_1}{V_2} = \frac{1}{5}$$

$$\therefore V_2 = 5 V_1$$

i.e., solution was diluted to 5 times.

$$30. \pi = i c S T \quad \alpha = \frac{i-1}{n-1}$$

$$0.46 = \frac{i-1}{5-1} \quad i = 2.84$$

$$\pi = 2.84 \times 0.1 \times 0.082 \times 291$$

$$\pi = 6.785 \text{ atm}$$

32. Beaker A :-

$$\text{Mole fraction of urea} = \frac{\frac{12}{60}}{\frac{12}{60} + \frac{140.4}{18}} = \frac{0.2}{0.2 + 7.8} = 0.025$$

Beaker B :-

$$\text{Mole fraction of glucose} = \frac{\frac{18}{180}}{\frac{18}{180} + \frac{178.2}{18}} \Rightarrow 0.01$$

Mole fraction of glucose is less so vapour pressure above the glucose solution will be higher than the pressure above urea solution, so some H₂O molecules will transfer from glucose to urea side in order to make the solutions of equal mole fraction to attain equilibrium. Let x mole of H₂O transferred

$$\frac{0.2}{0.2 + 7.8 + x} = \frac{0.1}{0.1 + 9.9 - x} \Rightarrow x = 4$$

now mass of glucose solution = 196.2 - 18 × 4 = 124.2

$$\text{wt. \% of glucose} = \frac{18}{124.2} \times 100 \Rightarrow \mathbf{14.49\%}$$

33. Let n_B mole of B present in 1 mole of mixture that has been vaporized.

Thus, Y_B = n_B

X_B = 1 - n_B

$$P = P_A^\circ X_A + P_B^\circ X_B = P_A^\circ + X_B (P_B^\circ - P_A^\circ)$$

$$X_B = \frac{P - P_A^\circ}{P_B^\circ - P_A^\circ} = 1 - n_B \quad \dots(i)$$

$$Y_B = \frac{P_B^\circ X_B}{P} \Rightarrow n_B = \frac{P_B^\circ (1 - n_B)}{P}$$

$$n_B P = P_B^\circ - n_B P_B^\circ$$

$$n_B = \frac{P_B^\circ}{P_B^\circ + P} \quad \dots(ii)$$

from equation (i) and (ii)

$$1 - \frac{P_B^\circ}{P_B^\circ + P} = \frac{P - P_A^\circ}{P_B^\circ - P_A^\circ} \Rightarrow \frac{P}{P_B^\circ + P} = \frac{P - P_A^\circ}{P_B^\circ - P_A^\circ}$$

on solving

$$P = \sqrt{P_A^\circ P_B^\circ} = \sqrt{100 \times 900} \Rightarrow \mathbf{300 \text{ mm Hg}}$$

34. (A) $\frac{\Delta T_f}{\Delta T_b} = \frac{k_f}{k_b} = \Delta T_f = \frac{0.6 \times 31.8}{5.03} = \mathbf{3.793^\circ C}$

(B) Relative lowering of vapour pressure =

$$\frac{n}{n + N} = \frac{\frac{3}{251.5}}{\frac{3}{251.5} + \frac{100}{154}} = \mathbf{0.018}$$

(C) π = CRT

$$n = \frac{3}{251.5} = 0.012$$

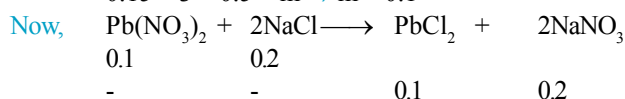
$$v = \frac{103}{1.64} = 62.8 \text{ mL}$$

$$\pi = \frac{0.012}{0.0628} \times 0.0821 \times 298 = \mathbf{4.65 \text{ atm}}$$

- (D) $0.6 = \frac{5.03 \times 3 \times 1000}{M_w \times 100} \Rightarrow M_w = \mathbf{251.5}$

35. ΔT_b = iK_bm

$$0.15 = 3 \times 0.5 \times m \Rightarrow m = 0.1$$



Now, this solution contains two salts

$$\Delta T_f = K_f \times m \quad 0.83 = 1.86 [2 \times 0.2 + 3s]$$

where s is molar solubility of PbCl₂.

$$s = 1.54 \times 10^{-3} \quad K_{sp} = 4s^3 = \mathbf{1.46 \times 10^{-5}}$$

36. ΔT_b = i × K_b × m

$$5.93 \times 10^{-3} = \frac{(x+1) \times 0.52 \times 0.25 \times 1000}{M \times 10}$$

$$\frac{(x+1)}{M} = 4.56 \times 10^{-4} \quad \dots(i)$$

$$\frac{M}{100} = 23x \quad \dots(ii)$$

From equation (i) and (ii)

Formula of protein = H₂₀P

$$M = 2300 \times 20 - 20 \times 23 + 23 = \mathbf{45563 \text{ amu}}$$

37. A + B → A_n + B

$$P_M = P_A^\circ X_A + P_B^\circ X_B$$

Let a mole of A are left due to polymerization after 100 min.

$$P_M = 300 \left(\frac{a}{12+a} \right) + 500 \left(\frac{12}{12+a} \right) \quad \dots(i)$$

$$k = \frac{2.303}{100} \log \frac{10}{a} \quad \dots(ii)$$

after 100 minute solute is added & final vapour pressure is 400 mm Hg i.e. P_s = 400

$$\frac{P_M - 400}{400} = \frac{0.525}{(a+12)} \quad \dots(iii)$$

from equation (i) and (iii) a = 9.9

$$\text{putting this in eq. (ii) } k = \frac{2.303}{100} \log \frac{10}{9.9} = \mathbf{1.0 \times 10^{-4}}$$

38. $C_2H_5OH \rightarrow V_1 = 20 \text{ mL}, d_1 = 0.7893 \text{ g/mL}$

$$m_1 = 15.786 \text{ g}$$

$$H_2O \rightarrow V_2 = 40 \text{ mL}, d_2 = 0.9971 \text{ g/mL}$$

$$m_2 = 39.884 \text{ g}$$

$$\text{Total mass} = 55.65 \text{ g}$$

$$d_{\text{sol.}} = 0.9571 \text{ g/mL}$$

$$V_{\text{sol.}} = 58.14 \text{ mL}$$

$$\% \text{ change} = \frac{60 - 58.14}{60} \times 100 = \mathbf{3.1 \%}$$

$$m = \frac{15.766 \times 1000}{46 \times 39.884} = \mathbf{8.6}$$

39. $P_T = P_A^\circ X_A + P_B^\circ X_B = P_A^\circ X_A + P_B^\circ (1 - X_A)$

$$P_T = P_B^\circ + X_A(P_A^\circ - P_B^\circ)$$

$$Y_A = \frac{P_A^\circ \times A}{P_T} = \frac{P_A^\circ \times A}{P_B^\circ + X_A(P_A^\circ - P_B^\circ)}$$

$$0.4 = \frac{0.4X_A}{1.2 - 0.8X_A}$$

$$1.2 = 1.8 \times A$$

$$X_A = \frac{2}{3}$$

so $X_B = \frac{1}{3}$

$$P_T = 0.4 \times \frac{2}{3} + 1.2 \times \frac{1}{3} = \frac{2}{3} = \mathbf{0.66 \text{ atm}}$$

40. $\frac{0.5}{M} = 3.75 \times 10^{-3} \Rightarrow M = 133.33$

$$0.165 = (1 + \alpha) \times \frac{1.86 \times 1.5 \times 1000}{133.33 \times 150}$$

$$1 + \alpha = 1.1827$$

$$\alpha = 0.1827 = \mathbf{18.27\%}$$

41. $CH_3OH \rightarrow V_1 = 30 \text{ mL}, d_1 = 0.798 \text{ g/mL}$

$$m_1 = 23.94 \text{ g}$$

$$H_2O \rightarrow V_2 = 70 \text{ mL}, d_2 = 0.9984 \text{ g/mL}$$

$$m_2 = 69.888 \text{ g}$$

$$m_T = 93.828 \text{ g}$$

$$d_{\text{solution}} = 0.9575 \text{ g/mL}$$

$$V_{\text{solution}} = 98 \text{ mL}$$

$$\Delta T_f = \frac{1.86 \times 23.94 \times 1000}{32 \times 69.888} = \mathbf{19.91}$$

$$T_f = -19.91^\circ\text{C}$$

$$M = \frac{23.94}{32 \times 0.98} = \mathbf{7.63 \text{ M}}$$

42. $P = 179X_B + 92$

$$P_B^\circ = 271, P_T^\circ = 92$$

$$n_B = \frac{936}{78} = 12, n_T = \frac{736}{92} = 8$$

$$X_B = \frac{12}{20} = 0.6 \quad X_T = 0.4$$

$$P_T = 271 \times 0.6 + 92 \times 0.4 = 199.4$$

$$Y_B = \frac{271 \times 0.6}{199.4} = 0.815$$

$$Y_T = 0.185$$

On further condensation

$$X_B = 0.815, X_T = 0.185$$

$$P_T = 271 \times 0.815 + 92 \times 0.185 = 237.844$$

$$Y_B = \frac{271 \times 0.815}{237.844} = \mathbf{0.9286}$$

43. For two immiscible liquids

$$\frac{w_1}{w_2} = \frac{P_1^\circ M_1}{P_2^\circ M_2} = \frac{3.6 \times 123}{97.7 \times 18} = 0.2518$$

$$\frac{w_2}{w_1} = 3.971$$

$$\frac{w_2 + w_1}{w_1} = 4.971$$

$$\frac{w_1}{w_2 + w_1} \times 100 = \mathbf{20.11\%}$$

44. $V_B = \frac{78}{0.877} \times 2750 \text{ mL} = 244.583 \text{ L}$

$$V_T = \frac{92}{0.867} \times 7720 \text{ mL} = 819.192 \text{ L}$$

$$P_B = \frac{1 \times 0.0821 \times 293 \times 760}{244.583} = 74.74 \text{ torr}$$

$$P_T = \frac{1 \times 0.0821 \times 293 \times 760}{819.192} = 22.317$$

$$46 = 74.74 X_B + 22.317 (1 - X_B)$$

$$52.423 X_B = 23.683$$

$$X_B = 0.451$$

$$Y_B = \frac{P_B^\circ \times X_B}{P_T} = \frac{74.74 \times 0.451}{46} = \mathbf{0.732}$$

$$45. i = 1 - \frac{\alpha}{2} = 1 - \frac{0.84}{2} = 0.48$$

$$\Delta T_b = \frac{0.48 \times 2.3 \times 0.61 \times 1000}{122 \times 50} = 0.1104$$

$$T_b = 46.2 + 0.1104 = 46.31^\circ\text{C}$$

$$46. P_A^\circ = 100, P_B^\circ = 300, X_A = X_B = \frac{1}{2}$$

$$P_T = 200$$

$$Y_A = \frac{100 \times \frac{1}{2}}{200} = \frac{1}{4}$$

$$\text{On condensation } X_A = \frac{1}{4}, X_B = \frac{3}{4}$$

$$P_T = 100 \times \frac{1}{4} + 300 \times \frac{3}{4} = 250$$

$$Y_A = \frac{25}{250} = 0.1$$

on further condensation

$$X_A = 0.1$$

$$47. \frac{d \ln P}{dT} = \frac{\Delta H}{RT^2} \quad \dots(i)$$

$$\log P = 3.54595 - \frac{313.7}{T} + 1.40655 \log T$$

$$\ln P = 3.54595 \times 2.303 - \frac{313.7}{T} \times 2.303 + 1.40655 \ln T$$

$$\frac{d \ln P}{dT} = \frac{313.7 \times 2.303}{T^2} + \frac{1.40655}{T} \quad \dots(ii)$$

Comparing equation (i) & (ii)

$$\Delta H = R[313.7 \times 2.303 + 1.40655 T]$$

at $T = 80 \text{ K}$

$$\Delta H = 1659.9 \text{ Cal.}$$

$$48. P_s = 20 \quad P^\circ = 20.0126$$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{0.0126}{20} = \frac{n}{n+N} \approx \frac{n}{N}$$

$$\frac{\text{moles of solute}}{\text{moles of H}_2\text{O}} = 0.0063$$

$$1 \text{ mole H}_2\text{O} = 18 \text{ g} = 18 \text{ mL}$$

$$18 \text{ mL solution} = 0.00063 \text{ mole}$$

$$1 \text{ L solution} = \frac{0.00063}{18} \times 1000 = 0.35 \text{ mole/L}$$

Let solubility of salt A_3B_4 is s then

$$7s = 0.035$$

$$s = 0.005 \text{ mole/L}$$

$$k_{sp} = 3^3 \cdot 4^4 (s)^7 = 27 \times 256 \times (0.005)^7$$

$$k_{sp} = 5.4 \times 10^{-13}$$

49. At 20°C :

$$\text{For } C_6H_6 \rightarrow V = \frac{78}{0.877} \times 2750 \text{ mL}$$

$$PV = 1 \times 0.0821 \times 293$$

$$P = 74.74 \text{ mm Hg}$$

Its vapour pressure of benzene at 27°C is P_1 then

$$\ln \frac{P_1}{P} = \frac{\Delta H_v}{R} \left[\frac{1}{T} - \frac{1}{T_1} \right]$$

$$\ln \frac{P_1}{74.74} = \frac{394.57 \times 78}{8.314} \left[\frac{1}{293} - \frac{1}{300} \right]$$

$$P_1 = 100.364 \text{ mmHg}$$

$$m = \frac{P^\circ - P_s}{P_s} \times \frac{1000}{M_{\text{solvent}}}$$

$$m = \frac{100.364 - 98.88}{98.88} \times \frac{1000}{78} = 0.1924$$

$$\Delta T_f = k_f \times m = 5.12 \times 0.1924 = 0.985^\circ\text{C}$$

$$T_f = 278.5 - 0.985 = 277.51^\circ\text{C}$$

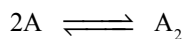
$$50. k_f = \frac{8.314 \times (278.4)^2 \times 78}{1000 \times 10042} = 5$$

$$m = \frac{0.02 \times 1000}{0.98 \times 78} = 0.2614$$

$$\Delta T_f = i \times k_f \times m$$

$$i = 1 - \frac{\alpha}{2} = 0.7643$$

$$\alpha = 0.4713$$



C



$$k = \frac{C\alpha/2}{(C - C\alpha)^2} = \frac{\alpha}{2C(1 - \alpha)^2}$$

$$k = \frac{0.4713}{2 \times 0.2614(1 - 0.4713)^2} = 3.225$$

$$51. P^T = 1.5 \Rightarrow [T^+] = 0.0316 = C\alpha \quad \dots(i)$$

$$0.372 = 1.86 \times C(1 + \alpha)$$

$$C + C\alpha = 0.2 \quad \dots(ii)$$

from equation (i) & (ii)

$$C = 0.1684, \alpha = 0.1876$$

$$k_a = \frac{C\alpha^2}{1 - \alpha} = \frac{0.1684(0.1876)^2}{(1 - 0.1876)} = 7.3 \times 10^{-3}$$

In 600 mL solution [TF] = $C - C\alpha = 0.1368$ mole/L
so moles = $0.1368 \times 0.6 = 0.08208$

$$\text{moles left after 24.8 years} = \frac{0.08208}{4} = 0.02052$$

moles disintegrated

$$= 0.08208 - 0.02052 = 0.06156$$

$$\text{moles of } \beta\text{-particle emitted} = 0.06156$$

$$\text{No. of } \beta\text{-particle emitted} = 0.06156 \times 6.023 \times 10^{23} \\ = 3.7 \times 10^{22}$$

$$52. \text{Initial moles of } H_2O = 0.9$$

$$\Delta T_f = 6 \text{ kJ}$$

$$k_f = \frac{RT_f^2 M}{1000 \Delta H_f} = \frac{8.314 \times (273)^2 \times 18}{1000 \times 6000} = 1.86$$

$$\Delta T_f = k_f \times m$$

$$m = \frac{2}{1.86} = 1.075$$

so in 1000 g $H_2O \rightarrow 1.075$ mole solute

$$\text{in 1 g } H_2O \rightarrow \frac{1.075}{1000} \text{ mole solute}$$

$$\text{in } 0.9 \times 18 \text{ g } H_2O \rightarrow \frac{1.075}{1000} \times 0.9 \times 18 \text{ mole solute}$$

$$\text{mole of solute (n)} = 0.017415$$

$$\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{760 - 700}{0.0851} = 0.0857$$

$$\text{moles of } H_2O (N) = \frac{0.017415}{0.0857} = 0.2032$$

$$\text{moles of Ice separate out} = 0.9 - 0.2032 = 0.6968$$

$$\text{mass of Ice separate out} = 0.6968 \times 18 = 12.54 \text{ g}$$

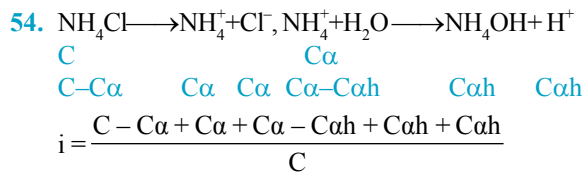
$$53. \Delta T_f = (1 + \alpha) k_f \times m$$

$$0.21 = (1 + \alpha) \times 1.86 \times 0.109$$

$$1 + \alpha = 1.0358$$

$$\alpha = 0.0358$$

$$k_a = \frac{C\alpha^2}{1 - \alpha} = \frac{0.109(0.0358)^2}{1 - 0.0358} = 1.44 \times 10^{-4}$$



$$= (1 + \alpha + \alpha h)$$

$$\Delta T_f = i \times k_f \times m$$

$$0.637 = \frac{(1 + \alpha + \alpha h) \times 1.86 \times 10}{53.5}$$

$$1 + \alpha + \alpha h = 1.832 \quad \&$$

$$\text{since } \alpha = 0.75, h = 0.109$$

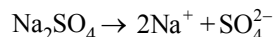
EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

$$1. \text{Moles of urea} = \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}} = 10^{-3} \text{ moles}$$

$$\text{Concentration (molarity) of solution} = \frac{10^{-3}}{100} \times 1000 \\ = 0.01 \text{ M.}$$

2. Elevation in boiling point is a colligative property which depends upon the number of solute particles. Greater the number of solute particles in a solution, higher the extent of elevation in boiling point.



3. According to Raoult's law equimolar solutions of all the substances in the same solvent will show equal elevation in boiling points as well as equal depression in freezing point.

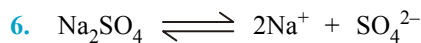
$$4. \text{Total millimoles of solute} = 480 \times 1.5 + 520 \times 1.2 \\ = 720 + 624 = 1344.$$

$$\text{Total volume} = 480 + 520 = 1000.$$

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

$$5. P_B = P_B^\circ X_B \quad P_B^\circ = 75 \text{ torr}$$

$$X_B = \frac{78/78}{(78/78) + (46/92)} = \frac{1}{1 + 0.5} = \frac{1}{1.5} P_B \\ = 75 \times \frac{1}{1.5} = 50 \text{ torr.}$$



$$\begin{array}{ccc} 1 & & 0 & & 0 \\ 1 - \alpha & & 2\alpha & & \alpha \end{array}$$

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

$$7. \text{Molality, } m = \frac{M}{1000d - MM_2} \times 1000$$

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

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

8. According to Raoult's law

$$P = P_A + P_B = P_A^0 x + P_B^0 x_B \quad \text{or}$$

$$290 = P_A^0 \times (0.6) + 200 \times (1 - 0.6)$$

$$\text{or } 290 = 0.6 \times P_A^0 + 0.4 \times 200 \quad \text{or } P_A^0 = 350 \text{ mm.}$$

9. Isotonic solutions have same osmotic pressure.

$$\pi_1 = C_1 RT, \pi_2 = C_2 RT$$

For isotonic solution, $\pi_1 = \pi_2$

$$\therefore C_1 = C_2.$$

$$\text{or } \frac{1.5/60}{V} = \frac{5.25/M}{V}$$

[where M = molecular weight of the substance]

$$\text{or } \frac{1.5}{60} = \frac{5.25}{M} \text{ or } M = 210.$$

$$10. P_A = P_A^0 x_A = 17.5 \times \frac{178.2/18}{\frac{178.2}{18} + \frac{18}{18}} = 17.325$$

$$11. P_{\text{total}} = P_A^0 x_A + P_B^0 x_B$$

$$760 = 520 x_A + 1000(1 - x_A)$$

$$760 = 520 x_A + 1000 - 1000 x_A$$

$$x_A = 0.5 \Rightarrow \text{mol \%} = 50\%$$

12. The solution is non-ideal, showing +ve deviation from Raoult's Law.

$$13. P_{\text{total}} = P_A^0 X_A + P_B^0 X_B = P_A^0 \times \frac{1}{4} + P_B^0 \times \frac{3}{4} = 550$$

$$\Rightarrow P_A^0 + 3P_B^0 = 550 \times 4 \quad \dots(i)$$

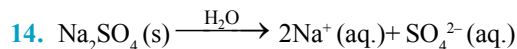
similarly

$$560 = P_A^0 \times \frac{1}{5} + P_B^0 \times \frac{4}{5} \Rightarrow P_A^0 + 4P_B^0 = 560 \times 5 \quad \dots(ii)$$

eq. (ii) - eq. (i)

$$P_B^0 = 560 \times 5 - 550 \times 4 = 600$$

$$\text{so } P_A^0 = 400.$$



$$\Delta T_f = i K_f m$$

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

$$15. P_T = X_{\text{Heptane}} P_{\text{Heptane}}^0 + X_{\text{Octane}} P_{\text{Octane}}^0$$

$$= \frac{0.25}{0.557} \times 105 + \frac{0.307}{0.557} \times 45$$

$$47.127 + 24.80 = 71.92 \approx 72 \text{ kPa}$$

$$16. \Delta T_f = i \times k_f \times m$$

$$2.8 = 1 \times 1.86 \times \frac{x}{62 \times 1} \Rightarrow x = \frac{2.8 \times 62}{1.86} = 93 \text{ gm}$$

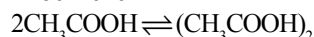
$$17. \frac{\Delta p}{P^0} = \text{mol fraction of glucose}$$

$$\frac{760 - P_{\text{soln.}}}{760} = \frac{18/180}{18/180 + \frac{178.2}{18}}$$

$$= \frac{0.1}{0.1 + 9.9} = \frac{1}{100} = 760 - P_{\text{soln}} = \frac{760}{100} = 706$$

$$P_{\text{soln.}} = 752.4 \text{ Ans.}$$

18. In benzene



$$i = 1 + \left(\frac{1}{2} + \alpha \right)$$

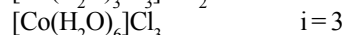
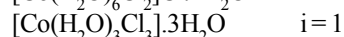
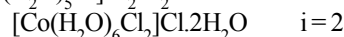
$$i = 1 - \frac{\alpha}{2} \text{ Here } \alpha \text{ is degree of association } \Delta T_f = i K_f m$$

$$0.45 = \left(1 - \frac{\alpha}{2} \right) (5.12) \frac{\left(\frac{0.2}{60} \right)}{1000}$$

$$1 - \frac{\alpha}{2} = 0.527 \Rightarrow \alpha = 0.945$$

% degree of association = 94.5%

19. $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ $i = 3$

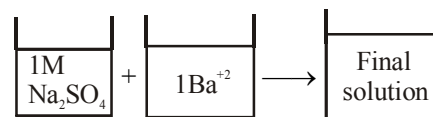


$$\Delta T_f \propto i \quad \text{where } \Delta T_f = (T_f - T_f')$$

$T_f' = \text{F.P. of solution}$

Freezing point of solution \uparrow as $i \downarrow$.

20.



50ml

450ml

500ml

Concentration of SO_4^{2-} in Ba^{+2} solution

$$M_1 V_1 = M_2 V_2$$

$$1 \times 50 = M_2 \times 500$$

$$M_2 = \frac{1}{10}$$

For just precipitation

$$I.P = K_{sp}$$

$$[\text{Ba}^{+2}][\text{SO}_4^{2-}] = K_{sp} (\text{BaSO}_4)$$

$$[\text{Ba}^{+2}] \times \frac{1}{10} = 10^{-10}$$

[Ba²⁺] = 10⁻⁹ M in 500ml solution
 For calculation of [Ba²⁺] in original solution (450 ml)

$$M_1 \times 450 = 10^{-9} \cdot 500$$

$$M_1 = \frac{500}{450} \times 10^{-9} = 1.11 \times 10^{-9} \text{ M}$$

[M₁ = molarity of Ba²⁺ in original solution(450ml)]

Part # II : IIT-JEE ADVANCED

1. $(\pi_{\text{obs}})_{\text{Na}_2\text{SO}_4} = \pi_{\text{glucose}}$

$$\text{or } \frac{10}{4} = \frac{1+2\alpha}{1} \quad \text{or } 10 = 4 + 8\alpha$$

$$\alpha = \frac{10-4}{8} = 0.75\% \quad \text{of } \alpha = 75\%$$

2. (i) In first case,

$$\Delta T_b = K_b \times m = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{wt. of solvent}}$$

$$\text{or } 0.17 = 1.7 \times \frac{1.22}{M \times 100 \times 10^{-3}}$$

or **M = 122 gm/mole**

Thus the benzoic acid exists as a monomer in acetone

(ii) In second case,

$$\Delta T_b = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{wt. of solvent}}$$

$$\text{or } 0.13 = 2.6 \times \frac{1.22}{M \times 100 \times 10^{-3}} \quad \mathbf{M = 224}$$

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

3. $\Delta T_b = i K_b m$ i (vant Haff factor) of CuCl₂ = 3

$$\Delta T_b = 3 \times 0.52 \times \frac{13.44}{134.4 \times 1} = 0.156 = 0.16.$$

4. $\Delta T_f = i \times K_f \times \text{molality}$

$$\Rightarrow 2 = i \times 1.72 \times \frac{20}{172} \times \frac{1000}{50}$$

$$\Rightarrow 2 = 4i \quad \Rightarrow i = 1/2 = 0.5$$

5. $\Delta T_f = K_f \cdot m$

$$= 2 \times \frac{0.1}{0.9 \times 46} \times 1000 = \frac{2000}{414} = \frac{1000}{207} = 4.83$$

$$\Delta T'_f = T_f - 4.83$$

$$\Delta T'_f = 155.7 - 4.83$$

$$\Delta T'_f = 150.9 \text{ K}$$

6. Total vapour pressure

$$P = P_A^0 X_A \quad (\text{considering solute to be non-volatile as given in the question})$$

$$P = 40 \times 0.9 = 36 \text{ mm Hg}$$

7. $\Delta T_b = K_b \cdot m$

$$= 0.52 \times \frac{0.1}{0.9 \times 18} \times 1000 = \frac{520}{9 \times 18} = 3.20$$

$$T_b = 373 + 3.20 \quad \Rightarrow \quad T_b = 376.2 \text{ K}$$

8. $P_{\text{N}_2} = K_H \times x_{\text{N}_2}$

$$x_{\text{N}_2} = \frac{1}{10^5} \times 0.8 \times 5 = 4 \times 10^{-5} \text{ per mole}$$

In 10 mole solubility is 4×10^{-4} .

9. $\Delta T_f = i \times K_f \times m$

$$= 4 \times 1.86 \times \frac{0.1}{329 \times 0.1} = 2.3 \times 10^{-2}$$

$$\Rightarrow T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2} \text{ } ^\circ\text{C}.$$

10. $\Delta T_b = 2^\circ\text{C}$; $m_a = 2.5 \text{ g}$

$$m_{\text{solvent}} = 100 \text{ g}$$

$$K_b = 0.76 \text{ K. kg. mol}^{-1}$$

$$P_{\text{solution}} = ?$$

$$\Delta T_b = K_b \times m$$

$$2 = 0.76 \times m \quad \therefore m = \frac{2}{0.76}$$

$$\frac{P^0 - P}{P} = m \times MM \times 10^{-3}$$

$$\therefore \frac{760 - P}{P} = \frac{2}{0.76} \times 18 \times 10^{-3}$$

$$760 - P = \frac{36}{760} P \quad \therefore 760 = \frac{796}{760} P$$

$$\therefore P = 760 \left(\frac{796}{760} \right) \text{ torr} = 725.6 \text{ torr} \approx 724 \text{ torr}$$

11. $\frac{X_{\text{solute}}}{X_{\text{solvent}}} = \frac{0.1}{0.9} = \frac{1}{9}$

$$\Rightarrow \frac{W_{\text{solute}}}{W_{\text{solvent}}} \times \frac{M_{\text{solvent}}}{M_{\text{solute}}} = \frac{1}{9} \quad \dots\dots (1)$$

$$W_{\text{solute}} + W_{\text{solvent}} = W_{\text{solution}} = \text{density} \times \text{volume}$$

$$W_{\text{solute}} + W_{\text{solvent}} = 2 \times V \quad \dots\dots (2)$$

Molarity = molality

$$\frac{n_{\text{solute}}}{V_{\text{solution}}} = \frac{n_{\text{solute}}}{W_{\text{solvent}}} \Rightarrow W_{\text{solvent}} = V_{\text{solution}} = \frac{W_{\text{solute}} + W_{\text{solvent}}}{2}$$

$$\Rightarrow 2W_{\text{solvent}} = W_{\text{solute}} + W_{\text{solvent}}$$

$$\Rightarrow W_{\text{solute}} = W_{\text{solvent}} \quad \dots\dots (3)$$

Using eq. (1) and (3), we get

$$\frac{M_{\text{solute}}}{M_{\text{solvent}}} = 9$$

13. $\Delta T_f = i k_f \times m$
 $= 1 \times 2 \times \frac{n_{\text{ethanol}}}{W_{\text{H}_2\text{O}}} \times 1000 = 2 \times \frac{34.5}{46 \times 500} \times 1000$
 $= \frac{34.5 \times 2}{23} = \frac{69}{23} = 3$

14. $P_T = P_A^\circ X_A + P_B^\circ X_B$
 $45 = 20(0.5) + P_B^\circ (0.5)$
 $P_B^\circ = 70$
 $22.5 = 20 X_A + 70(1 - X_A)$
 $50 X_A = 47.5$

$$X_A = \frac{4.75}{5} = 0.95$$

$$X_B = 0.05 \quad \Rightarrow \quad \frac{X_A}{X_B} = 19$$

15. $2 = 2(K_b)_x m$
 $1 = 2(K_b)_y m$

$$\frac{(K_b)_x}{(K_b)_y} = 2$$

$$\Delta(T_b)_x = \left(1 - \frac{\beta}{2}\right) (K_b)_x m \quad \dots(1)$$

$$\Delta(T_b)_y = \left(1 - \frac{0.7}{2}\right) (K_b)_y m \quad \dots(2)$$

On taking the ratio of eq. no (1) & (2)

$$\Rightarrow 3 = \frac{1 - \frac{\beta}{2}}{0.65} \times 2 \Rightarrow 1 - \frac{\beta}{2} = 1.5 \times 0.65 \Rightarrow \beta = 0.05$$

MOCK TEST

1. The loss in weight should be proportional to vapour pressure above that solution :

So, $P_{S_A} \propto 2\text{gm}$

$P_{S_B} \propto 1.5\text{gm}$

$P_{S_C} \propto 2.5\text{gm}$

So, maximum vapour pressure is above C solution hence, it is having minimum lowering and hence minimum mole fraction (hence minimum number of moles of solute) So max. molar mass of substance.

2. $\text{Ba}_{(x-2)}[\text{Co}(\text{CN})_x]_2 \rightarrow (x-2) \text{Ba}^{2+} + 2[\text{Co}(\text{CN})_x]^{-(x-2)}$
 $1-\alpha \qquad \qquad (x-2)\alpha \qquad \qquad 2\alpha$
 $i = 1 - \alpha + x\alpha - 2\alpha + 2\alpha$

$$(x-1)\alpha = 3 \quad x-1 = \frac{3}{\alpha}$$

$$\alpha = 0.75 \quad ; \quad x = 5.$$

\therefore formula of complex is $\text{Ba}_3[\text{Co}(\text{CN})_{5,2}]_2$ and hybridisation is dsp^3 as it is an inner orbital complex with strong field ligand.

3. Vapour pressure also depends on the nature of substance.

$$4. \quad \frac{\Delta P}{P} = \frac{i \cdot n}{i \cdot n + N} \quad \Rightarrow \quad \frac{1}{2} = \frac{i \cdot 2}{i \cdot 2 + 3}$$

$$\text{So, } i = \frac{3}{2} = 1.5 \quad \Rightarrow \quad 1 + (n-1)\alpha$$

$$\therefore \alpha = \frac{1}{2}$$

So, moles of Cl^- ions = $2 \times \frac{1}{2} = 1$ moles

So, moles of AgCl ppt = 1 moles

$$5. \quad (\text{molality})_i = \frac{x \times 1000}{100} = \frac{0.2}{K_f} \quad \dots(1)$$

$$(\text{molality})_f = \frac{x \times 1000}{w} = \frac{0.25}{K_f} \quad \dots(2)$$

(1)/(2)

$$\text{So, } \frac{0.2}{0.25} = \frac{w}{100}$$

$$\Rightarrow \text{so } w = 80 \text{ gm}$$

Hence ice separated = 20 gm

6. Pressure of air = $750 - 100 = 650$ mm of Hg on compressing
 $P_f = 650 \times 3$ mm of Hg
 $= 1950$ mm of Hg

So, $P_T = (1950 + 100) = 2050$ mm of Hg

7. Let volumes taken to be 'x' & 'y' litres, so

$$\frac{0.1x + 0.4y}{x + y} = 0.34 \quad \& \quad V_g = (x + y) \text{ (to be maximised)}$$

so $y = 4x$

so for maximum volume

$$y = 2L \quad \& \quad x = \frac{1}{2}L$$

8. $\pi = CRT$

$$C = [\text{Cl}^-] + [\text{Na}^+] + [\text{Ca}^{2+}]$$

$$C = \left(0.34 + \frac{0.1 \times 0.5}{2.5} + \frac{0.2 \times 2}{2.5}\right)$$

$$= 0.34 + 0.02 + 0.16 = 0.52$$

So, $\pi = 0.52 \times 0.082 \times 300 \text{ atm} = 12.792 \text{ atm}$

9. As $m \rightarrow 0$, NaHSO_4 will generate three particles while NaCl will generate only two particles.

$$10. P_T = \frac{1}{2} (75 + 22) = 48.5 \text{ torr}$$

$$P_T = \frac{1}{2} (75 + 10) = 42.5 \text{ torr}$$

$$P_T = \frac{1}{2} (22 + 10) = 16 \text{ torr}$$

$$P_T = \frac{1}{3} (75 + 22 + 10) = 35 \frac{2}{3} \text{ torr}$$

$$11. 0.0558 = i \times \frac{3.24}{324} \times 1.86$$

$$\Rightarrow i = 3 \quad (100\% \text{ dissociated})$$

$$0.0744 = i \times \frac{21.68}{271} \times \frac{1000}{2000} \times 1.86$$

$$\Rightarrow i \approx 1 \quad (\text{almost undissociated})$$

$$12. 1.24 = 34.3 \left[\frac{0.849}{\frac{M}{0.050}} \right] \Rightarrow M = 469.68$$

$$13. P_T (\text{at } 100^\circ\text{C}) = \frac{2}{3} \times 1350 + 300 = 900 + 100 = 1000 \text{ torr}$$

hence 100°C is boiling point.

14. Gain / loss in wt. should be proportional to vapour pressure above that solution.

15. Number of particles from $\text{K}_4[\text{Fe}(\text{CN})_6] = 5$
 number of particles from $\text{FeSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O} = 5$
 number of particles from $\text{KCl} \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O} = 5$

$$16. \frac{P - 20}{20} = \frac{6}{M} \times \frac{18}{180} = \frac{6}{M} \times \frac{1}{10} \quad \dots (1)$$

$$\frac{P - 20.02}{20.02} = \frac{6}{M} \times \frac{18}{198} = \frac{6}{M} \times \frac{1}{11} \quad \dots (2)$$

from (1) & (2) calculation gives $M \approx 54 \text{ gm/mole}$
 $P = 20.22 \text{ torr}$

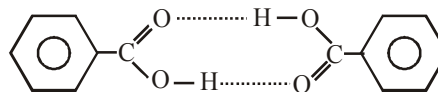
& on dilution ΔP decreases (lowering) so vapour pressure of solution increases.

17. 'S-1' is correct because fluids present inside the cell come out due to higher vapour pressure inside the cell than outside the cell.

'S-2' is correct because in reverse osmosis, solvent from saline water enters the pure solvent through semipermeable membrane.

18. Extent of dissociation increases steadily with increasing dilution.

19. The benzoic acids forms a dimer due to H-bonding as



20. As degree of dissociation of HF gets changed on dilution.

21. When liquid just starts forming vapours we have Raoult's law valid with $X_b \times X_c$ as mole fraction in liquid state so equation of curve obtained by collecting such points will be

$$P = X_B^l P_B^o + X_C^l P_C^o$$

$$= X_B^l P_B^o + (1 - X_B^l) P_C^o$$

$$= P_C^o + (P_B^o - P_C^o) X_B^l = P_C^o + (P_B^o - P_C^o) X_B$$

The second curve will not be a straight line having equation

$$P = \frac{P_B^o - P_C^o}{X_B^l (P_C^o - P_B^o) + P_B^o}$$

22. From solution of above question.

23. If initially in liquid there are x moles of A and y moles of

$$B \text{ then } X_A = \frac{x}{x+y}, X_B = \frac{y}{x+y}$$

$$\text{we have } 700 = X_A^l P_A^o + X_B^l P_B^o \quad \dots (1)$$

$$600 = X_A^l P_A^o + X_B^l P_B^o \quad \dots (2)$$

$$\text{Also } x = \frac{1}{3}(x+y) \times \frac{3}{10} + \frac{2}{3}(x+y) \times \frac{3}{4}$$

$$\text{which gives } \frac{x}{x+y} = 0.6$$

24. A \rightarrow p,r,s (+ve deviation from Raoult's law)

B \rightarrow p,r (ideal solution)

C \rightarrow p,q,r (+ve deviation from Raoult's law)

D \rightarrow p,r,s (-ve deviation from Raoult's law)

A \rightarrow p,r,s; B \rightarrow p,q,t; C \rightarrow p; D \rightarrow p,q,t

25. (A \rightarrow q); (B \rightarrow r); (C \rightarrow p); (D \rightarrow s)

$$26. P_{\text{cal}} = CRT = 0.01 \times 0.082 \times 300 = 0.246 \text{ atm}$$

$$\therefore \text{But } \alpha = 0.75$$

$$i = \frac{0.984}{0.246} = 4$$

$$\text{and } \alpha = \frac{i-1}{n-1} \therefore 0.75 = \frac{4-1}{n-1} \therefore n = 5$$

It means complex must provide 5 ions per molecule

\therefore complex can be $\text{Ba}_3[\text{Co}(\text{CN})_5]_2$

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27. $K_{IP} [BaF_2] = [Ba^{+2}][F^-]^2$
 $= 4 \times 10^{-3} \times (6 \times 10^{-3})^2 = 4 \times 36 \times 10^{-9} = 1.44 \times 10^{-7}$
 $K_{IP} < K_{sp}$ So no ppt. formation of BaF_2 + take place
 $[Ba^{2+}] = 0.01 \times \frac{2}{5} M = 0.004 M$
 $[Cl^-] = 0.02 \times \frac{2}{5} M = 0.008 M$
 $[Na^+] = 0.01 \times \frac{3}{5} M = 0.006 M$
 $[F^-] = 0.01 \times \frac{3}{5} M = 0.004 M$
 total conc = 0.024 M
 $p = 0.024 \times 0.082 \times 300 = 0.5904 \text{ atm} = 448.7 \text{ Torr}$

Ans. 448 or 449

28. $P_T = X_A P_A^0 + (1 - X_A) P_B^0$

$$\frac{1}{P_T} = \frac{Y_A}{P_B^0} + \frac{(1 - Y_A)}{P_B^0}$$

calculate $(X_A - Y_A)$ & maximise it

$$X_A = \frac{\sqrt{P_A^0 P_B^0} - P_B^0}{(P_A^0 - P_B^0)} \quad \& \quad P_T = \sqrt{P_A^0 P_B^0}$$

Ans. $X_A = \frac{\sqrt{P_A^0 P_B^0} - P_B^0}{(P_A^0 - P_B^0)}$, $P = \sqrt{P_A^0 P_B^0}$

29. According to Rault's law

$$\frac{\Delta p}{p^0} = x_2$$

Where $-\Delta p = (74.01 - 74.66) \text{ torr}$

And $p^0 = 74.66 \text{ torr}$

If M is the molar mass of hydrocarbon, then

$$X_Z = \frac{n_2}{n_1 + n_2} = \frac{\frac{8}{M}}{\left(\frac{100}{78}\right) + \left(\frac{2}{M}\right)}$$

Hence $\frac{74.66 - 74.01}{74.66} = \frac{\frac{2}{M}}{\frac{100}{78} + \frac{2}{M}}$

Solving for M, we get,

$$M = 177.6 \text{ mol}^{-1}$$

Given mass ratio is $m_C : M_H :: 94.4 : 5.6$

The atomic ratio is

$$N_C : N_H :: \frac{84.4}{12} : \frac{5.6}{1} \Rightarrow 7.87 : 5.6 \Rightarrow 1.4 : 1 \Rightarrow 7 : 5$$

Hence. Empirical formula is C_2H_5
 Molar Empirical mass = 89 g mol^{-1}

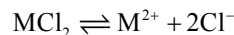
Number of C_2H_5 unit in the given molecule

$$= \frac{\text{Molar mass}}{\text{Molar empirical mass}} = \frac{177.6}{89} \cong 2$$

Thus molecular formula is $C_{14}H_{10}$.

30. $\frac{p^0 - p}{p^0} = x_2$

$$\frac{0.04}{32} = 0.00125 = \text{mole fraction of solute}$$



On dissociation, the salt produces 3 ions.

$$\therefore \text{mole fraction of undissociated salt} = \frac{0.00125}{3}$$

$$= 0.00042 \text{ moles}$$

$$\text{Mole fraction of water} = 0.99958 \text{ moles}$$

$$\text{Mass of solvent} = 0.9996 \times 18 = 17.993 \text{ g}$$

Solubility of the salt =

$$\frac{0.00042 \times 100}{17.993} = 0.2334 \text{ mol. lit}^{-1} = s$$

$$K_{sp} = s \times (2s)^2 = 4s^3$$

$$= 4 \times (2.334 \times 10^{-2})^3 = 5.08 \times 10^{-5}$$