

1. (b)  $P_{\text{total}} = P_A^\circ X_A + P_B^\circ X_B$

$$550 = P_A^\circ \times \frac{1}{4} + P_B^\circ \times \frac{3}{4}$$

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

In second case

$$P_{\text{total}} = P_A^\circ \times \frac{1}{5} + P_B^\circ \times \frac{4}{5}$$

$$P_A^\circ + 4P_B^\circ = 560 \times 5 \quad \dots(ii)$$

Subtract (i) from (ii)

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

$$\therefore P_A^\circ = 400$$

2. (c) Let vapour pressure of A =  $P_A^\circ$

Vapour pressure of B =  $P_B^\circ$

In first solution,

$$\text{Mole fraction of A}(x_A) = \frac{1}{1+2} = \frac{1}{3}$$

$$\text{Mole fraction of B}(x_B) = \frac{2}{1+2} = \frac{2}{3}$$

According to Raoult's law,

Total vapour pressure

$$= 250 = P_A^\circ x_A + P_B^\circ x_B$$

$$250 = \frac{1}{3} P_A^\circ + \frac{2}{3} P_B^\circ \quad \dots(i)$$

In second solution

$$\text{Mole fraction of A}(x_A) = \frac{2}{2+2} = \frac{2}{4} = \frac{1}{2}$$

$$\text{Mole fraction of B}(x_B) = \frac{2}{4} = \frac{1}{2}$$

$\therefore$  Total vapour pressure

$$= 300 = P_A^\circ x_A + P_B^\circ x_B$$

$$300 = \frac{1}{2} P_A^\circ + \frac{1}{2} P_B^\circ \quad \dots(ii)$$

Multiplying equation (i) by  $\frac{1}{2}$  and equation (ii) by  $\frac{1}{3}$

$$\frac{1}{6} P_A^\circ + \frac{2}{6} P_B^\circ = 125$$

$$\frac{1}{6} P_A^\circ + \frac{1}{6} P_B^\circ = 100$$

$$\frac{1}{6} P_B^\circ = 25$$

$$P_B^\circ = 25 \times 6 = 150 \text{ mm Hg}$$

On substituting value of  $P_B^\circ$  in equation (ii) we get

$$300 = P_A^\circ \times \frac{1}{2} + 150 \times \frac{1}{2}$$

$$P_A^\circ = 450 \text{ mm Hg}$$

3. (c) van't Hoff factor ( $i$ ) and the degree of association are related as below :

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

$$0.9 = 1 - 0.2 \left( 1 - \frac{1}{n} \right)$$

On solving,

$$\left( 1 - \frac{1}{n} \right) = \frac{1}{2}$$

$$\frac{1}{n} = 1 - \frac{1}{2} = \frac{1}{2}$$

$$\therefore n = 2$$

4. (a) Molarity =  $\frac{\% \times 10 \times d}{\text{GMM}} = \frac{22 \times 10 \times 1.253}{342} = 0.805 \text{ M}$

$$\text{Normality} = \frac{\% \times 10 \times d}{\text{GEM}} = \frac{22 \times 10 \times 1.253}{342/6} = 4.83 \text{ N}$$

$$\text{Molality} = \frac{22 \times 1000}{342(100 - 22)} = 0.825 \text{ m}$$

5. (a)  $K_H = 100 \text{ kbar} = 10^5 \text{ bar}$ ,  $P = 1 \text{ bar}$   
 $P = K_H \times x_A$

$$x_A = \frac{P}{K_H} = \frac{1}{100 \times 10^3} = 10^{-5}$$

$$\text{Moles of water} = \frac{1000}{18} = 55.5$$

$$\text{Weight of water} = 1000 \text{ g } (\because 1000 \text{ mL} = 1000 \text{ g})$$

$$\text{Mole fraction} = 10^{-5} = \frac{x}{55.5 + x}$$

As  $55.5 \gg x$ , thus neglecting  $x$  from denominator

$$10^{-5} = \frac{x}{55.5} \Rightarrow x = 55.5 \times 10^{-5} \text{ moles}$$

or 0.555 millimoles.

6. (c) For dilute solution,  $\frac{\Delta P}{P^\circ} \Rightarrow \frac{n_{\text{solute}}}{n_{\text{solvent}}}$

$$\text{For solution in A, } \frac{\Delta P_A}{P_A^\circ} = \frac{W/M}{W_A/M_A} = \frac{W}{M} \times \frac{M_A}{W_A} \quad \dots\dots(i)$$

$$\text{For solution in B, } \frac{\Delta P_B}{P_B^\circ} = \frac{W}{M} \times \frac{M_B}{W_B} \quad \dots\dots(ii)$$

$$\text{From (i) and (ii), } \frac{\Delta P_A/P_A^\circ}{\Delta P_B/P_B^\circ} = 2 = \frac{M_A W_B}{M_B W_A} = \frac{M_A}{M_B}$$

$$(W_A = W_B)$$

7. (a, b, c) when  $n_A = n_B$ , we have  $x_A = \frac{n_A}{n_A + n_B} = \frac{1}{2}$

$$\text{and } x_B = \frac{n_B}{n_A + n_B} = \frac{1}{2}$$

Using the given relation, we have

$$P_s = (110 \times \frac{1}{2} + 125 \times \frac{1}{2}) \text{ mm of Hg}$$

$$= 117.5 \text{ mm of Hg}$$

In case of pure A or pure B the mole fraction of other component will be zero, then

For pure A;  $x_A = 1, x_B = 0$

$$\therefore P_A = (110 \times 1 + 125 \times 0) \text{ mm of Hg}$$

$$= (110 + 0) \text{ mm of Hg}$$

$$= 110 \text{ mm of Hg}$$

Similarly,  $P_B^\circ = 125 \text{ mm of Hg}$  [ $x_B = 1, x_A = 0$ ]

From the above calculations it is clear that

when  $n_A = n_B$ :  $P_s < P_B^\circ$  [ $P_s = 117.5 \text{ mm}$  and

$$P_B^\circ = 125 \text{ mm}]$$

$n_A = n_B$ :  $P_s > P_A^\circ$  [ $P_s = 117.5 \text{ mm}$

and  $P_A^\circ = 110 \text{ mm}]$

Also  $P_A^\circ = 110 \text{ mm of Hg}$  and  $P_B^\circ = 125 \text{ mm of Hg}$

Statement (d) is incorrect.

8. (a, b, c)

Since the solute X behaves as univalent electrolyte in solution, so for this solute,  $i = 2$

Since the solute Y dimerises in solution, so for this

$$\text{solute } i = \frac{1}{2}$$

We know that

b.p.  $\propto i$ ,  $\therefore$  b.p. of X will be greater than that of Y

Osmotic pressure  $\propto i$ ,  $\therefore$  O.P. of X > O.P. of Y

Freezing point  $\propto \frac{1}{i}$ ;  $\therefore$  f.p. of X < f.p. of Y

and relative lowering of V.P. i.e.  $\frac{\Delta P}{P^\circ} \propto i$

$$\therefore \left( \frac{\Delta P}{P^\circ} \right)_X > \left( \frac{\Delta P}{P^\circ} \right)_Y$$

Thus statement (d) is incorrect. All other statements are correct.

9. (b, c) Vapour pressure of solution containing non-volatile solute is always smaller than that of solvent. Points a and b represent the boiling points of solvent and solution respectively (temperatures at which their V.P. = 1 atm each). Hence gap  $ab = K_b m$  = elevation of boiling point.

$$\begin{aligned} 10. (b) \quad P_{\text{Total}} &= X_A P_A^\circ + X_B P_B^\circ = X_A P_A^\circ + (1 - X_A) P_B^\circ \\ &= P_B^\circ + (P_A^\circ - P_B^\circ) X_A \end{aligned}$$

11. (2) Let x g be the mass of element in 51.0 g of saturated solution.

Mass of benzene in 51.0 g of saturated solution

$$= 51.0 - x \text{ g}$$

Total mass of benzene containing x g of solute = 50

$$+ 51 - x = (101 - x) \text{ g}$$

$$\Delta T_f = \frac{1000 K_f W_B}{M_B W_A} = \frac{1000 \times 5.5 \times x}{4 \times 25 \times (101 - x)} = 0.55 \text{ (given)}$$

$$\Rightarrow x = 1.0 \text{ g}$$

$$\text{Hence, solubility} = \frac{W_B \times 100}{W_A} = \frac{1}{(51 - 1)} \times 100 = 2.0 \text{ g}$$

12. (2)  $\Delta T = i K_f m$   
 $(273 - 269.28) = i \times 1.86 \times 1$   
 $3.72 = i \times 1.86$   
 $i = 2$

$$\alpha = \frac{i - 1}{n - 1}; (\alpha = 100\% = 1)$$

$$1 = \frac{2 - 1}{n - 1} \Rightarrow n = 2$$

13. (2) Let  $\pi_1 = 200 \text{ mm}$ ;  $T_1 = 283$   
 $\pi_2 = 105.3$ ;  $T_2 = 298$

$$\text{Now, } \pi = \frac{n}{V} RT$$

$$\text{At } T_1, 200 = \frac{n}{V_1} R \times 283$$

$$\text{At } T_2, 105.3 = \frac{n}{V_2} R \times 298$$

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{200}{105.3} = \frac{V_2}{V_1} \times \frac{283}{298} \Rightarrow V_2 = 2V_1$$

$$14. (4) \quad \pi = CRT = \left( \frac{W_2}{Mw_2} \right) \frac{RT}{V}$$

Given  $W_2 = 40 \text{ g}$

$$Mw_2 = 246$$

$$T = 27^\circ\text{C} = 300\text{ K}$$

$$V = 1\text{ L}$$

Substituting all the values, we get

$$\pi = \frac{40}{246} \times 0.082 \times 300 = 4\text{ atm}$$

15. (d) Molality of water in ethanol =  $\frac{0.1 \times 1000}{0.9 \times 46} = 2.41$

$$\Delta T_f = K_f m = 2.0 \times 2.41 = 4.82\text{ K};$$

$$\text{Hence, freezing point} = 150.7 - 4.82 = 150.9\text{ K}$$

16. (a) Vapour pressure of solution =  $X_A P_A^\circ + X_B P_B^\circ$   
 $= 0.9 \times 40 + 0.1 \times 32.8 = 39.3\text{ torr}$

17. (b) From the given data, we have

$$w = 0.5 \times 10^{-3}\text{ kg} \quad [0.5\% \text{ solution}]$$

$$W = 100 \times 10^{-3}\text{ kg}$$

[solvent in water, density =  $1\text{ g/cm}^3$ ]

$$\Delta T_f = 273 - 272.76 = 0.24$$

$$K_f = 1.86\text{ K kg mol}^{-1}$$

$$\therefore M = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

$$= \frac{1000 \times 1.86 \times 0.5 \times 10^{-3}}{0.24 \times 100 \times 10^{-3}} = 38.76$$

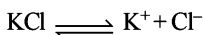
$\therefore$  The apparent molecular weight of KCl = 38.76

The molar mass of KCl =  $39 + 35.5 = 74.5$

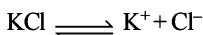
$$\therefore i = \frac{\text{Normal molecular weight}}{\text{Apparent molecular weight}}$$

$$= \frac{74.5}{38.76} = 1.92 \approx 2$$

18. (c) In solution KCl dissociates as follows



If  $\alpha$  is degree of dissociation, then



$$(1 - \alpha) \quad \alpha \quad \alpha$$

The number of effective particles is  $1 - \alpha + \alpha + \alpha$   
 $= (1 + \alpha)$

$$\therefore i = \frac{1 + \alpha}{1}$$

$$\text{or } \alpha = i - 1$$

$$= 1.92 - 1 \quad [i = 1.92]$$

$$= 0.92 \text{ or } 92.0\%$$

19. A-s; B-p; C-q; D-r

(A) All gases dissolve in water exothermically with decrease in randomness. Hence  $\Delta H < 0$ ,  $\Delta S < 0$ .

(B) Since solubility of the given solid in water increases on raising temperature, dissolution is endothermic. Hence  $\Delta H > 0$  and  $\Delta S > 0$  (Increase in disorder on dissolution).

(C) In a saturated solution, there is no further dissolution of solid. Hence  $\Delta H = 0$  and  $\Delta m = 0$ .

(D) On adding solid to super saturated solution, excess of solid dissolved separates out with the evolution of heat. Hence  $\Delta H < 0$  and  $\Delta m < 0$ .

20. A-r, s; B-p, q; C-r, s; D-p, q

$$(A) K_f = \frac{RT_f^{\circ 2}}{1000 L_f} = \frac{RT_f^{\circ 2} M}{1000 \Delta H_f};$$

$$T_f^\circ (\text{water}) = 273\text{ K}, M = 18$$

$$(B) K_b = \frac{RT_b^{\circ 2}}{1000 L_v} = \frac{RT_b^{\circ 2} M}{1000 \Delta H_f}$$

$$T_b^\circ (\text{water}) = 373\text{ K}, M = 18$$

$$(C) \Delta T_f = K_f \times m = K_f \times \frac{9 \times 1000}{180 \times 50} = K_f$$

$$(D) \Delta T_b = K_b \times m = K_b \times \frac{3 \times 1000}{60 \times 50} = K_b$$