

CHEMISTRY

1. As the solution in (1) is dilute, vapour pressure above it is more and hence vapours get transferred from (1) to (2). Hence, volume in (1) decreases.

2. $\pi_R = \frac{2.4 V_1 + 4.6 V_2}{V_1 + V_2} = 2.95 \text{ atm (assume temperature constant)} ; \quad \frac{V_1}{V_2} = 3.$

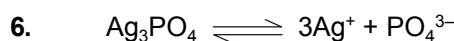
3. $P_T = 200 \times 0.5 + 300 \times 0.5 = 100 + 150 = 250 \text{ torr.}$; If $P_{ex} > 250$, no vapour exist.
 If $P_{ex} \leq 250$, vapour exist.

4. $\frac{2 \times (50 - V)}{50} \times 2 = 3.2 ; \quad V = 10 \text{ mL}$

5. $P_T = P_A^\circ + P_B^\circ \Rightarrow \frac{X_A}{X_B} = \frac{P_A^\circ}{P_B^\circ}$

$$\Rightarrow \frac{0.25}{0.75} = \frac{P_A^\circ}{740} = P_A^\circ = \frac{740}{3} = 246.67 \text{ torr}$$

$$\Rightarrow P_T = 740 + 246.67 = 986.67 \text{ torr.}$$



$$\Rightarrow (3s)^3 \times s = \left(\frac{3}{16}\right)^3 \times 10^{-12} \Rightarrow s^4 \times 27 = \frac{27}{2^{12}} \times 10^{-12} \Rightarrow s = \frac{1}{8} \times 10^{-3}$$

$$\Rightarrow \text{total ion concentration} = 3s + s = 4s = \frac{1}{2} \times 10^{-3} \text{ M}$$

As solution is very dilute $d = 1 \text{ g/ml}$

$$\text{If } 1 \text{ L water} = \text{then } \frac{1}{2} \times 10^{-3} \text{ moles of solute}$$

$$\Rightarrow n_{\text{water}} = \frac{1000}{18} \Rightarrow x_{\text{solute}} = \frac{10^{-3}}{2 \times 1000} \times 18 \Rightarrow 9 \times 10^{-6}$$

$$\Rightarrow \% \text{ decrease} = 9 \times 10^{-4}$$

7. $\Delta T_f + \Delta T_b + 100 = 105 \Rightarrow \Delta T_f + \Delta T_b = 5 \Rightarrow 5 = (K_f + K_b) \times m \Rightarrow m = 2$

Hence 2 moles of sucrose in 1 kg solvent.

$$\text{So } 0.2 \text{ moles sucrose in } 100 \text{ g solvent} \Rightarrow m_{\text{sucrose}} = 0.2 \times 342 = 68.4 \text{ g}$$

8. (C) Order of van't Hoff factor is $\text{BaCl}_2 > \text{KCl} > \text{HF}$ so order of π is also same.

(D) $\Delta T_b = K_f m$

K_f depend on nature of solvent.

$$9. \quad m = \frac{5}{900} \text{ i.e. } \frac{5}{900} \text{ moles in 1000 g water} \quad ; \quad X_{\text{gas}} = \frac{\frac{5}{900}}{\frac{5}{900} + \frac{1000}{18}} = \frac{\frac{5}{900}}{\frac{5}{900} + \frac{500}{9}} \approx \frac{5 \times 9}{900 \times 500}$$

$$\approx 10^{-4}$$

$$P_{\text{gas}} = 3 \times 10^4 \times X_{\text{gas}} = 3 \times 10^4 \times 10^{-4} = 3 \text{ atm}$$

10. Adding water result in dilution.

On dilution, reaction shifts in direction of increasing solute moles.

11. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$t = 0 \quad 1 \quad 0$$

$$t = \text{eq.} \quad 1 - 0.5 \quad 2 \times 0.5$$

$$P_{\text{N}_2\text{O}_4} = \frac{0.5}{1.5} \text{ atm} \quad P_{\text{NO}_2} = \frac{1}{1.5} \text{ atm} \quad ; \quad K_P = \frac{\left(\frac{1}{1.5}\right)^2}{\left(\frac{0.5}{1.5}\right)} = \frac{4}{3}$$

$$\Delta G^\circ = -2.3 \times 8.3 \times 330 \times \log\left(\frac{4}{3}\right) = -2.3 \times 8.3 \times 330 \times (0.6 - 0.48) = -756 \text{ J mol}^{-1}$$

12. At equilibrium,

$$P_{\text{CO}_2} = K_{\text{eq.}}$$

and so it depends on temperature.

13. $Q_P = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = 1000 \text{ torr}$

$Q_P < K_P$ reaction should occur in forward direction.

But since no $\text{NH}_4\text{HS}(\text{s})$ is present in the reaction vessel no reaction will occur & pressure will remain the same.

14. $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g})$
 $2 - 1.5 \quad 2 - 1.5 \quad 3$

$$K_C = K_P = \frac{3^2}{0.5 \times 0.5} = 36$$

15. $K_p > K_c$. So, $\Delta n_g > 0$. So, (A) is correct option.

16. At triple point, Vapour pressure of liquid A = Vapour pressure of solid A

$$3.5 - \frac{1500}{T} = 4 - \frac{2000}{T} \Rightarrow T = 1000 \text{ K}$$

$$\log_{10} P = \frac{-\Delta H^\circ}{2.303 RT} + \frac{\Delta S^\circ}{2.303 R} \quad ; \quad \text{Solid A} \rightleftharpoons \text{vapour of A } \Delta H_{\text{sub}}$$

$$\text{Hence } \frac{2000}{T} = \frac{\Delta H^\circ}{2.303 \times 2 T} \Rightarrow \Delta H_{\text{sub}}^\circ = 2.303 \times 4 \text{ kcal} = 9.212 \text{ kcal/mol}$$

liquid A \rightleftharpoons vapors of A ΔH_{vap}

$$\text{Hence } \frac{1500}{T} = \frac{\Delta H^\circ}{2.303 \times 2 \times T} \Rightarrow \Delta H_{\text{vap}}^\circ = 6.909 \text{ kcal/mol}$$



17. Let P_A° and P_B° be the vapor pressures of pure liquids and let n_A and n_B be the moles of A and B in starting liquid.

$$\text{Hence } 900 = P_A^\circ \times \frac{n_A}{n_A + n_B} + P_B^\circ \times \frac{n_B}{n_A + n_B} \quad \dots\dots(1)$$

$$\text{Total moles in residue} = \frac{1}{3} (n_A + n_B) ; n_A(\text{residue}) = 0.3 \times \frac{1}{3} (n_A + n_B) = \frac{1}{10} (n_A + n_B)$$

$$\text{Total moles in condensate} = \frac{2}{3} (n_A + n_B)$$

$$\Rightarrow n_A(\text{condensate}) = 0.6 \times \frac{2}{3} (n_A + n_B) = \frac{2}{5} (n_A + n_B)$$

$$\Rightarrow n_A(\text{total}) = \frac{1}{10} (n_A + n_B) + \frac{2}{5} (n_A + n_B)$$

$$\Rightarrow \frac{n_A}{n_A + n_B} = \frac{1}{2}$$

$$\Rightarrow \text{Initial } x_A = 0.5 ; x_B = 0.5$$

$$\Rightarrow 900 = \frac{P_A^\circ}{2} + \frac{P_B^\circ}{2} \quad \dots\dots(2)$$

$$P_T \text{ over residue} = 860$$

$$\Rightarrow 860 = P_A^\circ \times 0.3 + P_B^\circ \times 0.7 \quad \dots\dots(3)$$

solving (2) and (3) gives

$$P_B^\circ = 800 \text{ torr}$$

$$P_A^\circ = 1000 \text{ torr}$$

$$P_T \text{ over condensate} = 1000 \times 0.6 + 800 \times 0.4 = 600 + 320 = 960 \text{ torr}$$

18. $\text{FeC}_2\text{O}_4 + \text{KMnO}_4 \longrightarrow \text{Mn}^{2+} + \text{Fe}^{3+} + \text{CO}_2$.

$$\Rightarrow 10 \times 3 \times M = 30 \times 0.4 \times 5$$

$$M = 2$$

$$\Rightarrow \pi = 2 \times 0.82 \times 300 \times 2 = 49.2 \text{ atm} \times 2 = 98.4 \text{ atm}$$

$$\pi_{\text{KMnO}_4} = 0.4 \times 0.082 \times 300 \times 2 = 19.68 \text{ atm}$$

$$\text{In the new FeC}_2\text{O}_4 \text{ solution } n_{\text{FeC}_2\text{O}_4} = \frac{25}{1000} \times 2 = \frac{1}{20}$$

$$\text{RLVP} = \frac{\frac{1}{20} \times 2}{\frac{1}{20} \times 2 + \frac{900}{18}} = \frac{\frac{1}{10}}{\frac{1}{10} + 50} \approx \frac{1}{500}$$

$$\text{and } \Delta T_f = 1.8 \times \frac{20}{0.9} \times 2 = 2 \times 1.8 \times \frac{1}{18} = 0.2 \text{ K}$$

$$T_f = -0.2 \text{ K}$$

19. (I) : In equilibria like $\text{A(s)} \rightleftharpoons \text{A(vap)}$, an increase in pressure does not change equilibrium pressure of A(g) .
 (II) : on $P \uparrow$, equation shifts in a direction in which no. of moles of gases \downarrow
 (III) : $K_p = (P_B) (P_C)$ (constant at constant temp)
 (IV) : $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)} \quad \Delta H = +ve$
 on $T \uparrow$ forward reaction.



20. Osmosis from urea to NaCl.
21. Binary ideal solution boils at temperature which is higher than normal boiling point of more volatile component and lower than the normal boiling point of less volatile component.
24. $\Delta T_f = K_f \cdot m$

$$= 1.86 \times \frac{0.1}{0.9 \times 18} \times 1000 = 11.48 \quad ; \quad T_b = 273 - 11.48 = 261.52 \text{ K.}$$
25. For solution M : $P_{\text{vap}} = 32.8 \times 0.9 = 29.52 \text{ torr}$
 For solution N : $P_{\text{vap}} = 40 \times 0.9 = 36 \text{ torr} \Rightarrow \text{difference} = 36 - 29.52 = 6.48 \text{ torr}$
26. $\frac{1}{99} = \frac{10^{-3}}{N} \quad ; \quad N = 0.099 \text{ mol}$
27. 1 g NaCl has highest $i \times \text{mol}$.
31. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O(g)}$
 $K_p = (7.8)^2 = 60.84$
 $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O(g)} \quad ; \quad K'_p = (P_{\text{H}_2\text{O}})^2 = (5.6)^2 = 31.36$
 The ratio $\frac{K_p}{K'_p} = \frac{60.84}{31.36} = 1.9$
32. Dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is favourable at low humidity in air, high temperature and it decreases with increasing partial pressure of water vapours i.e. $P_{\text{H}_2\text{O}}$.
33. In this reaction, $\Delta n_g = 0$ and $\Delta H = +ve$.
 (a) On increasing temperature n_{CO_2} increases and so its concentration increases.
 (b) No shift, but due to decrease in volume, concentration increases.
 (c) No shift, but due to increase in volume, concentration decreases.
 (d) Adding CO , shifts reaction in forward. Hence concentration of CO_2 increases.
 (e) Removing H_2 shifts reaction in forward direction. So, concentration of CO_2 increases.
 (f) Adding inert gas at constant pressure increases volume but equilibrium does not shift. So, concentration of CO_2 decreases.
 (g) No change in concentration of CO_2 .
34. $\Delta T_f = i \times K_f \times \text{molality} \Rightarrow 0.5 \times 1.72 \times \frac{20}{172} \times \frac{1000}{50} = 2$
35. $\Delta T_f = iK_fm$
 $\Rightarrow 0.38 = 2 \times K_f \times 0.1 \dots\dots(1) \quad ; \quad \text{and } 0.285 = K_f \times \frac{(\text{total moles})}{1} \dots\dots(2)$
 $(2)/(1)$

$$\frac{0.285}{0.38} = \frac{\text{total moles}}{0.2}$$

 The reaction suggests that $x \text{ CN}^-$ get consumed to give $1 [\text{Hg}(\text{CN})_{x+2}]^{x-}$. As freezing point is increasing, $x > 1$.
 At maximum freezing point, all CN^- must have converted to $[\text{Hg}(\text{CN})_{x+2}]^{x-}$.
 So, total moles = $0.1 \text{ mol } \text{K}^+ + \frac{0.1}{x} \text{ mole } [\text{Hg}(\text{CN})_{x+2}]^{x-}$

$$\text{total moles} = \frac{0.285 \times 0.2}{0.38} \Rightarrow 0.1 + \frac{0.1}{x} \quad x = 2$$



36. Consider equimolar solution of A & B.

$$P_{\text{solution}} = x_A P_A^0 + x_B P_B^0 = 0.5 (400) + 0.5 (600) = 500 \text{ torr.}$$

Dissolving camphor to it does not change its vapor pressure. But P_{solution} now would be

$$P = x_A' P_A^0 + x_B' P_B^0 + x_C' P_C^0$$

$$x_A' = \frac{0.5}{0.5 + 0.5 + 1} = 0.25. \text{ Similarly, } x_B' = 0.25, x_C' = 0.50 \text{ mol.}$$

$$\therefore 500 = 0.25 (600) + 0.25 (400) + 0.5 P_C^0 = 250 + 0.5 P_C^0$$

$$\therefore P_C^0 = 500 \text{ torr} = 100 y \quad \therefore y = 5.$$

Also, after adding anthracene ($P^0 = 0$), $P = 200 \text{ torr}$ (given)

$$\text{Now, } \frac{P^0 - P}{P} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{x}{2}$$

$$\frac{500 - 200}{200} = \frac{x}{2}$$

$$\therefore x = 3$$

Thus, $x + y = 8$.

37. $X_B = 0.5 \quad X_T = 0.5$

$$p_{\text{total}} = P_B^0 X_B + P_T^0 X_T$$

$$80 = 0.5 P_B^0 + 0.5 P_T^0$$

$$160 = P_B^0 + P_T^0 \quad \dots\dots\dots(1)$$

$$y_B = \frac{P_B^0 X_B}{p_{\text{total}}} = \frac{P_B^0 \times 0.5}{80} = \frac{P_B^0}{160}$$

$$y_T = \frac{P_T^0 X_T}{p_{\text{total}}} = \frac{P_T^0 \times 0.5}{80} = \frac{P_T^0}{160}$$

$$p'_{\text{total}} = 100 = P_B^0 y_B + P_T^0 y_T$$

$$= 100 = P_B^0 \cdot \frac{P_B^0}{160} + P_T^0 \cdot \frac{P_T^0}{160}$$

$$P_B^{\circ 2} + P_T^{\circ 2} = 100 \times 160$$

From (1) Eq.

$$(P_B^0 + P_T^0) = 160$$

$$(P_B^0 + P_T^0)^2 = 160^2 = P_B^{\circ 2} + P_T^{\circ 2} + 2P_B^0 P_T^0$$

$$= P_B^{\circ 2} + P_T^{\circ 2} + 2P_B^0 P_T^0$$

$$= 100 \times 160 + 2P_B^0 P_T^0$$

$$2P_B^0 P_T^0 = 160^2 - 160 \times 100 = 160 \times 60$$

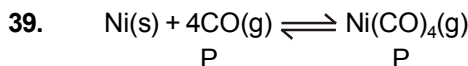
$$P_B^0 P_T^0 = 160 \times 30 \quad ; \quad P_B^0 + P_T^0 = 160$$

$$P_B^0 = 120 = x \quad ; \quad P_T^0 = 40 = y$$

$$\therefore \frac{x + 2y}{50} = \frac{120 + 2 \times 40}{50} = 4 \text{ Ans.}$$



38. $a = 10$; $b = 5$; $c = 10$; $(a + 2b + 3c) = 50$.



For backward reaction

$$Q_p \geq K_p$$

$$\frac{P}{P^4} \geq K_p$$

$$\therefore \frac{1}{P^3} \geq 0.125 \text{ atm}^{-3}$$

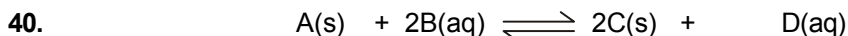
$$P^3 \leq 8 \text{ atm}^3$$

$$P \leq 2 \text{ atm}$$

$$P_{\text{Total}} = 2P = 4 \text{ atm.}$$

$$P = 4 \times 76 \text{ cm of Hg}$$

$$P/4 = 76$$



Initial	1	$\frac{1}{2}$	0	0
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At eq.	$1-x$	$\frac{1}{2}-2x$	$2x$	x
		$\approx a$		

$$x \approx 1/4$$

$$10^{20} = \frac{1}{[B]^2} \Rightarrow 10^{20} = \frac{1}{a^2} \Rightarrow a^2 = \frac{1}{4 \times 10^{20}} = \frac{10^{-20}}{4}$$

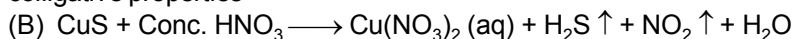
$$a = \frac{10^{-10}}{2} \approx 5 \times 10^{-11} \text{ M}$$

41.
$$\frac{p_{\text{eq}} \times M_0}{RT} = \frac{1.15 \text{ gm}}{V(L)} ; \frac{0.82 \times M_0}{0.082} = 1.15 \times 600 ; M_0 = 69$$

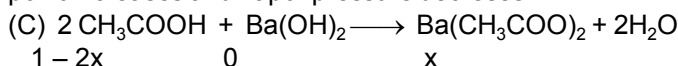
$$M_0 = \frac{M_{\text{th}}}{1+\alpha} = 69 \quad 1+\alpha = \frac{92}{69} = \frac{4}{3} ; \alpha = \frac{1}{3} = 0.33$$



Two particles reacting (K^+ and CN^-) and two particles are producing (K^+ and $[\text{Ag}(\text{CN})_2]^-$) Hence no change in colligative properties

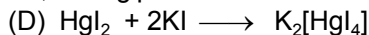


CuS is insoluble. Addition of HNO_3 produces ions Cu^{2+} , $(\text{NO}_3)^-$. Hence solute particles increases so boiling point increases and vapor pressure decreases.

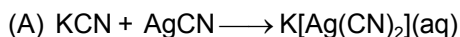


Hence $2x \times (1 + \alpha)$ are giving $3x$ moles of solute and $\alpha < 0.1$. Hence, moles of solute are increasing.

So, boiling point increases and vapor pressure decreases.



HgI_2 is insoluble. Adding KI produces $[\text{K}_2(\text{HgI}_4)]$. Hence, ions increase. So boiling point increases and vapor pressure decreases.



43. Use relation

$$K_p = K_c(RT)^{\Delta n_g}$$



44. (A) $\frac{1}{450} = \frac{i \times 0.1}{i \times 0.1 + 89.8}$

$$\Rightarrow \frac{1}{450} = \frac{i}{i + 898} \Rightarrow i + 898 = 450i \Rightarrow 898 = 449i \Rightarrow i = 2$$

$$\Rightarrow 2 = 1 + (4-1)\alpha \Rightarrow 2 = 1 + 3\alpha \Rightarrow \alpha = \frac{1}{3}$$

(B) $\pi = i \frac{0.1}{2} \times \frac{1}{12} \times 300$

$$1.5 = i \frac{0.1}{2} \times \frac{1}{12} \times 300$$

$$i = 1.2 = 1 + \alpha$$

$$\alpha = 0.2 = 1/5$$

(C) $0.025 = i \frac{40 \times 300}{20000 \times 1 \times 12}$

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

Nothing known about the solute so nothing can be said about α .

(D) $0.35 = i \times K_f \times \frac{0.1}{2} \quad 0.1 = 1 \times K_f \times \frac{0.1}{3} \quad 3.5 = i \times \frac{3}{2} \Rightarrow i = \frac{7}{3}$

$$\frac{7}{3} = 1 + (5-1)\alpha \Rightarrow \frac{4}{3} = 4\alpha \Rightarrow \alpha = \frac{1}{3}$$

45. (A) $P_A^\circ > P_B^\circ > P_C^\circ$ and $x_A = x_B = x_C = \frac{1}{3}$. So $y_A > y_B > y_C$ (volatility) and $y_A > x_A$; $y_C < x_C$

(B) $P_A^\circ < P_C^\circ$ and $x_A = x_C$; $y_C > y_A$ and $y_A < x_A$

(C) Azeotrope so $y_B = x_B$; $y_C = x_C$, $x_B = \frac{2}{3}$ so $y_B = \frac{2}{3}$. Hence $y_B > y_C$.

(D) $x_A = \frac{1}{4}$, $x_B = \frac{1}{4}$, $x_C = \frac{1}{2} \Rightarrow y_A = \frac{P_A^\circ}{4} / P_T$; $y_B = \frac{P_B^\circ}{4} / P_T$; $y_C = \frac{P_C^\circ}{2} / P_T$

$\Rightarrow p, s, t$ are possibilities.

