



## SOLUTIONS

## EXERCISE # O-I

1. vapour pressure depends only on Temp.
2. vapour pressure depends only on Temp.
3.  $v.p. \propto \frac{1}{\text{intermolecular force}}$
4. vapour pressure remains constant with constant temp

6.  $v.p. \propto \frac{1}{\text{force of attraction}}$

7. at higher altitudes  $P_{\text{atm}} < 1 \text{ atm}$  boiling point decreases as  $P_{\text{atm}}$  decreases

So if  $P_{\text{atm}} < 1 \text{ atm}$       B.P.  $< 100^\circ\text{C}$

8.  $P_{\text{ext}}$  increases so B.P. also increases

9.  $P_{\text{solvent}} = P^{\circ}_{\text{solvent}} X_{\text{solvent}}$

10.  $P_T = P^{\circ}_A X_A + P^{\circ}_B X_B$

$$P_T = (P^{\circ}_A - P^{\circ}_B)X_A + P^{\circ}_B$$

13.  $P_T = \frac{1}{5} \times 92 + \frac{4}{5} \times 31$

$$P_T = 43.2 \text{ mm of Hg}$$

14.  $P_T = P^{\circ}_A X_A + P^{\circ}_B X_B$

$$84 = 70 \times 0.8 + P^{\circ}_B \times 0.2$$

$$P^{\circ}_B = 140 \text{ torr}$$

18. for immiscible liquid

$$P_T = P^{\circ}_A + P^{\circ}_B = 100 + 200 = 300 \text{ torr}$$



19. Colligative properties depends only on number of solute particles.

33.  $\pi = CRT$

$$\pi = \frac{W}{\text{Molar mass}} = RT$$

$$\pi \propto \frac{1}{\text{Molar mass}}$$

34.  $\pi = CRT$

$$\pi = 0.3 \times 0.0821 \times 298$$

$$\pi = 7.33 \text{ atm}$$

35.  $\pi = CRT$

$$7.4 = C \times 0.0821 \times 300$$

$$C = 0.3 \text{ mole/L}$$

39.  $\pi_f = \frac{\pi_1 V_1 + \pi_2 V_2}{V_1 + V_2}$

$$\pi_f = \frac{1.2 + 2.5}{2} = 1.85 \text{ atm}$$

40. only solvent particles can move through SPM. So non blue colour formation

41.  $i = 1 + (n - 1)\alpha$

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

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

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

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



43.  $3A \rightarrow A_3$

$$i = 1 + \left(\frac{1}{3} - 1\right) = \frac{1}{3}$$

44.  $K_2[PtCl_6]$      $i = 3$

47. vapour pressure will be maximum for the solution which have min. no. of particles

51.  $\Delta T_f \uparrow, T_f \downarrow$

$$\Delta T_b \propto im$$

52.  $\pi_1 = \frac{1}{2} \times 2 \times RT = RT$

$$\pi_2 = 2 \times 0.5 \times RT = RT$$

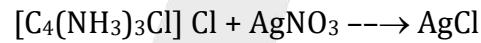
$\pi_1 = \pi_2$  (isotonic)

59.  $\frac{P^o - P_s}{P^o} = \frac{in}{in + N}$

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

$$i = 1.5 \quad \Rightarrow 1 + \alpha = 1.5$$

$$\Rightarrow \alpha = 0.5$$



2 mole

$2 \times 0.5 = 1$  mole

60.  $i = 1 + (n - 1)\alpha$

$$4 = 1 + (n - 1) \frac{3}{4}$$

$$n = 5$$

So. C.N. = 5 and compound should



62.  $C_2H_5Cl + C_6H_5OH$  is not ideal solution.

$$P_{theo.} = 80 \times 0.4 + 120 \times 0.6$$

$$32 + 72 = 104 \text{ mm}$$

$$P_{obs} < P_{theo.} \Rightarrow -ve \text{ deviation}$$



63. max. boiling azeotrope is formed by the solution which show -ve deviation.

64.  $\Delta V_{\text{mix}} < 0$

$$V < 50 \text{ mL}$$

65.  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \Rightarrow$  -ve deviation

66. for ideal solution

$$\Delta V_{\text{mix}} = 0 \quad \Delta H_{\text{mix}} = 0$$

$$\Delta S_{\text{mix}} > 0 \quad \Delta G_{\text{mix}} < 0$$

68.  $\Delta H = +\text{ve}$ ,  $\Delta S = +\text{ve}$ ,  $\Delta G = -\text{ve}$

69.  $P_{\text{obs}} = 580 \text{ torr}$

$$\begin{aligned} P_{\text{theo}} &= 300 \times 0.4 + 800 \times 0.6 \\ &= 120 + 480 = 600 \end{aligned}$$

$P_{\text{obs}} < P_{\text{theo}}$ .  $\Rightarrow$  -ve deviation



71.  $P_{\text{obs}} = 0.95 \text{ atm}$

$$\begin{aligned} P_{\text{theo}} &= 300 \times 0.08 + 800 \times 0.92 \\ &= 760 \text{ torr} = 1 \text{ atm} \end{aligned}$$

$P_{\text{obs}} < P_{\text{theo}}$

it will show -ve deviation

72. solubility of gas  $\propto$  Pressure  $\propto \frac{1}{T}$

73.  $P = K_H X$

$$K_H \uparrow, X \downarrow$$

$$T \uparrow, K_H \uparrow$$



74.  $X \propto P$

$$\frac{5.3 \times 10^{-4}}{C_2} = \frac{593}{760}$$

$$C_2 = \frac{760}{593} = 5.3 \times 10^{-4} = 6.8 \times 10^{-4} \text{ M}$$

76. Total mass of  $\text{HNO}_3 = 5000 \times 1.5 \times \frac{12.6}{100} + 5000 \times 1 \times \frac{6.3}{100} = 1260$

$$\text{Moles of } \text{HNO}_3 = \frac{1260}{63} = 20$$

$$M = \frac{20}{10} = 2$$

77.  $M = \frac{98 \times 1.8 \times 10}{98} = 18$

78.  $\frac{n_A}{n_{\text{H}_2\text{O}}} = \frac{0.2}{0.8} = \frac{1}{4}$

$$m = \frac{1000}{4 \times 18} = 13.9$$



## EXERCISE # S-I

2. Let The volume of 30% (W/w) H<sub>2</sub>SO<sub>4</sub> and 70% (W/w) H<sub>2</sub>SO<sub>4</sub> is 100 mL.

Total volume of solution = 0.2 L

$$\text{Total mass of H}_2\text{SO}_4 = 120 \times 0.3 + 160 \times 0.7$$

$$= 36 + 112 = 148 \text{ g}$$

$$\text{Mole of H}_2\text{SO}_4 = \frac{148}{98}$$

$$M = \frac{148/98}{0.2} = 7.55$$

$$M = \frac{148/98}{(280 - 148)} \times 1000 = 11.44$$

3. r.p. of H<sub>2</sub>O = 355 torr

$$P_{O_2} = 760 - 355 = 405 \text{ torr}$$

$$P'O_2 = 2 \times 405 = 810 \text{ torr}$$

(as volume is halved)

$$P_{\text{total}} = \text{v.p. of H}_2\text{O} + P'O_2$$

$$= 355 + 810 = 1165 \text{ torr}$$

4. PN<sub>1</sub> = 1 - 0.3 = 0.7 atm

$$P'N_2 = 3 \times 0.7 = 2.1 \text{ atm}$$

$$P_{\text{total}} = 2.1 + 0.3 = 2.4 \text{ atm}$$

$$5. P = \frac{2}{4} \times 100 + \frac{3}{5} \times 300$$

$$= \frac{1100}{5} = 220$$

$$7. P = P_{CH_3OH}^o X_{CH_3OH}$$

$$X_{CH_3OH} = \frac{23}{96} = 0.24$$



9.  $\frac{1}{P_T} = \frac{y_A}{P_A^o} + \frac{y_B}{P_B^o}$

$$= \frac{0.35}{577} + \frac{0.65}{390}$$

$$P_T = 440 \text{ torr}$$

$$y_A = \frac{P_A^o X_A}{P_{\text{total}}}$$

$$X_A = \frac{0.35 \times 440}{577} = 0.27$$

10.  $y_A = \frac{P_A^o \times A}{P_T} = 0.5$

$$P_A^o \times A = P_B^o \times B$$

$$\frac{X_A}{X_B} = \frac{n_A}{n_B} = \frac{P_B^o}{P_A^o} = \frac{75}{200} = \frac{3}{8}$$

$$X_A = \frac{3}{11}, X_B = \frac{8}{11}$$

$$\text{mole \% of A} = \frac{3}{11} \times 100 = 27.3\%$$

11.  $550 = P_A^o \times \frac{1}{4} + P_B^o \times \frac{3}{4}$

$$560 = P_A^o \times \frac{1}{5} + P_B^o \times \frac{4}{5}$$

$$P_B^o = 600 \text{ mm of Hg}$$

$$P_A^o = 400 \text{ mm of Hg}$$

12.  $1 = \frac{1}{4} \times P_A^o + \frac{3}{4} \times P_B^o \quad \dots\dots(i)$

$$1 = 0.2 \times P_A^o + 0.2 \times P_B^o + 0.6 \times 0.8 \quad \dots\dots(ii)$$

From (i) & (ii)  $P_B^o = 0.7 \text{ atm}$

$$P_A^o = 1.9 \text{ atm}$$

37.  $\frac{P^o - P_s}{P^o} = \frac{n}{N}$



$$\frac{760 - P_s}{P_s} = \frac{2.4 \times 7 / 164}{100 / 18}$$

$$P_s = \frac{760}{1.018} = 746.2 \text{ mm Hg}$$

38. moles of acid = moles of NaOH

$$200 \times M = 125 \times 0.1$$

$$M = 0.0625$$

$$DT_f = i K_f \times m$$

$$0.186 = i \times 1.86 \times 0.0625$$

$$i = 1.6$$

$$1.6 = 1 + \alpha \Rightarrow \alpha = 0.6$$

% dissociation = 60%

40. Solution of CHCl<sub>3</sub> and ethyl methyl ketone shows negative deviation

41. P<sub>exp</sub> = 90 mm Hg

$$P_{\text{The.}} = 100 \times \frac{1}{4} + 80 \times \frac{3}{4}$$

$$= 85 \text{ mm Hg}$$

P<sub>exp</sub> > P<sub>The.</sub>, It shows +ve deviation.

42. P = K<sub>H</sub>X  $\Rightarrow P \propto \alpha n_{\text{solute}}$

$$\frac{1}{P} = \frac{6.56 \times 10^{-3}}{5 \times 10^{-2}} \Rightarrow P = 7.62 \text{ bar}$$

43. P = K<sub>H</sub>X = K<sub>H</sub> ×  $\frac{nN_2}{nH_2O}$

$$0.987 = 76.48 \times 10^3 \times \frac{nN_2}{1000 / 18}$$

$$nN_2 = 0.717 \text{ m moles}$$

44. X = K<sub>H</sub>P =  $3.1 \times 10^{-2} \times 4$

$$X = 12.4 \times 10^{-2} \text{ m}$$



## EXERCISE # O-II

$$1. \quad y_A = \frac{P_A^o X_A}{P_T} = \frac{P_A^o X_A}{P_A^o X_A + P_B^o X_B}$$

$$y_A = \frac{P_A^o X_A}{(P_A^o - P_B^o)X_B + P_B^o}$$

$$\frac{1}{y_A} = \frac{P_A^o - P_B^o}{P_A^o} + \frac{P_B^o}{P_A^o} \cdot \frac{1}{X_A}$$

$$\frac{1}{X_A} = \frac{P_B^o}{P_A^o} \cdot \frac{1}{y_A} + \frac{P_B^o - P_A^o}{P_B^o}$$

$$2. \quad P_{ext} = 1000 \text{ torr}$$

B.P. is The temp. when v.p. =  $P_{ext}$  we have to check v.p. of solution at the given temp.

at  $90^\circ\text{C}$

$$P_T = 1000 \times \frac{2}{3} + 200 \times \frac{1}{3} = \frac{2200}{3}$$

$$P_T < P_{ext}$$

At  $100^\circ\text{C}$

$$P_T = 1350 \times \frac{2}{3} + 300 \times \frac{1}{3} = 1000$$

$$P_T < P_{ext}$$

So B.P. is  $100^\circ\text{C}$

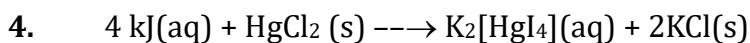
$$3. \quad x + y = 0.1$$

$$\text{If } y = 0, x = 0.1 \text{ (0.1 mole KCl)}$$

$$\Delta T_f = iK_f m = 2 \times 0.1 \times 1.85 = 0.37$$

$$\text{If } x = 0, y = 0.1 \text{ (0.1 mole KCl)}$$

$$\Delta T_f = iK_f m = 3 \times 0.1 \times 1.85 = 0.555$$



$$n_i \quad 5 \quad 1 \text{ (LR)} \quad 0 \quad 0$$

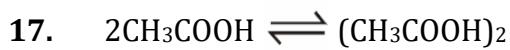
$$n_f \quad 1 \quad 0 \quad 1 \quad 2$$

$$\text{no. of particles initial} = 5 \times 2 = 10$$

$$\text{no. of particles finally} = 1 \times 2 + 1 \times 3 + 2 \times 2 = 9$$

no. of particles are decreasing

$$\Delta T_b \uparrow, T_b \downarrow$$



Initial 0.1 M 0

Eqn.  $(0.1 - 2x)$  M  $xM$

$$K = \frac{[(\text{CH}_3\text{COOH})_2]}{[\text{CH}_3\text{COOH}]} = \frac{x}{0.1 - 2x} = \frac{\frac{1}{24}}{0.1 - \frac{2}{24}} = \frac{5}{2} \quad \text{Ans.}$$



Initial 0.1 M 0

Eqn.  $(0.1 - 2x)$  M  $xM$

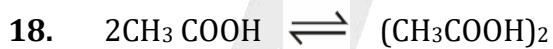
$$K = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOH}]^2}$$

$$\text{Or } 3.6 \times 10^{-2} = \frac{x}{(0.1 - 2x)^2} \approx \frac{x}{(0.1)^2}$$

$$\therefore x = 3.6 \times 10^{-4}$$

$$\frac{[(\text{CH}_3\text{COOH})_2]}{[\text{CH}_3\text{COOH}]} = \frac{x}{0.1 - 2x} \approx \frac{x}{0.1}$$

$$= \frac{3.6 \times 10^{-4}}{0.1} = \frac{9}{2500}$$



Eqn.  $(0.1 - 2x - y)$  M  $xM$

$\approx 0.1$  M



Eqn.  $(0.1 - 2x - y)$  M  $yM$   $yM$

$\approx 0.1$  M

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{or} \quad 2 \times 10^{-5} = \frac{y \cdot y}{0.1}$$

$$\therefore [\text{H}_3\text{O}^+] = y = \sqrt{2 \times 10^{-6}} \text{ M}$$

$$\text{and pH} = -\log (2 \times 10^{-6})^{1/2} = 2.85$$



## EXERCISE # S-II

1.  $P = 180 X_B + 90$

$$P_S = P^o_B X_B + P^o_T X_T = P^o_B X_B + P^o_T (1 - X_B)$$

$$= (P^o_B - P^o_T) X_B + P^o_T$$

$$P^o_T = 90 \text{ mm Hg}$$

$$P^o_B - P^o_T = 180$$

$$P^o_B = 270 \text{ mm Hg}$$

$$n C_6H_6 = \frac{936}{78} = 12 , \quad n C_6H_6 CH_3 = 8$$

$$P_T = P^o_B X_B + P^o_T X_T$$

$$= 270 \times \frac{12}{20} + 90 \times \frac{8}{20} = 330 \text{ mm Hg}$$

$$y_T = \frac{P^o_T X_T}{P_{\text{total}}} = \frac{36}{330} = X^1T$$

$$y_B = \frac{P^o_B X_B}{P_{\text{total}}} = \frac{162}{330} = X^1B$$

$$P'_{\text{total}} = 270 \times \frac{162}{330} + 90 \times \frac{36}{330} = 142.36$$

$$y'_B = \frac{P^o_B X_B}{P_{\text{total}}} = \frac{9.82}{142.36}$$



## EXERCISE # (JEE MAINS)

57. Due to presence of solute vapour pressure of solution will be less than V.P. of pure solvent. So, vapour move from higher pressure to lower pressure.

58. If both solutions are isotonic

$$\therefore \text{Molarity of A} = \text{Molarity of B}$$

$$\frac{0.73/M_A}{250} \times 1000 = \frac{1.65/M_B}{1000} \times 1000$$

$$\therefore \frac{M_A}{M_B} = \frac{0.73}{0.25 \times 1.65} = 1.77 = 177 \times 10^{-2}$$

So correct answer is 177.

60. Let mass of water initially present =  $x$  gm

$$\Rightarrow \text{Mass of sucrose} = (1000 - x) \text{ gm}$$

$$\Rightarrow \text{moles of sucrose} = \left( \frac{1000 - x}{342} \right)$$

$$\Rightarrow 0.75 = \frac{\left( \frac{1000 - x}{342} \right)}{\left( \frac{x}{1000} \right)} \Rightarrow \frac{x}{1000} = \frac{1000 - x}{342 \times 0.75}$$

$$\Rightarrow 256.5x = 10^6 - 1000x$$

$$\Rightarrow x = 795.86 \text{ gm}$$

$$\Rightarrow \text{moles of sucrose} = 0.5969$$

$$\text{New mass of H}_2\text{O} = a \text{ kg}$$

$$\Rightarrow 4 = \frac{0.5969}{a} \times 1.86 \Rightarrow a = 0.2775 \text{ kg}$$

$$\Rightarrow \text{ice separated} = (795.86 - 277.5) = 518.3 \text{ gm}$$

63.  $Y_A = 0.5 \Rightarrow Y_B = 0.5$

$$P_A = P_A^0 X_A$$

$$P_A^0 = 2$$



64. ∵ Dilute solution given:

$$\frac{P^0 - P_s}{P^0} \sim \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\frac{P^0 - P^0/2}{P^0} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$n_{\text{solute}} \sim \frac{n_{\text{solvent}}}{2} = \frac{100}{18 \times 2} = 2.78 \text{ mol}$$

More accurate approach:

$$\frac{P^0 - P_s}{P_s} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\frac{P^0 - P^0/2}{P^0/2} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$n_{\text{solute}} \sim n_{\text{solvent}} = \frac{100}{18} = 5.55 \text{ mol}$$

65.  $[\text{HCOOH}] = 0.5 \text{ ml l}^{-1}$

$\Rightarrow (0.5 \text{ ml} \times 1.05 \text{ g ml}^{-1}) \text{ HCOOH in 1L}$

$\Rightarrow 0.525 \text{ g HCOOH in 1L}$

$$m = \frac{(0.525 / 46)}{1 \text{ kg}} \text{ mol} \quad [\text{Assuming dilute solution}]$$

$$\therefore \Delta T_f = i K_f m \Rightarrow i = \frac{\Delta T_f}{K_f m} = \frac{0.0405 \times 46}{1.86 \times 0.525} = 1.9$$



## EXERCISE (JEE-ADVANCED)

21.  $P_T = P_A^\circ X_A + P_B^\circ X_B$

$$0.3 = P_A^\circ \times 0.25 + P_B^\circ \times 0.75$$

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

$$0.8 = P_A^\circ + P_B^\circ$$

on solving eq

$$P_A^\circ \text{ (i) } \& \text{ (ii)}$$

$$P_B^\circ = 0.2$$

22. Number of ions present per formula unit of ionic salt =  $x$

$$\text{Van 't Hoff factor (i)} = 0.9 \times x + 0.1 \times 1$$

(Assuming 90% dissociation)

$\therefore$  Relative lowering in vapour pressure = Mole fraction of solute

$$\Rightarrow \frac{60 - 59.724}{60} = \frac{i \times 0.1}{\frac{1800}{18} + 0.1}$$

$$\Rightarrow 0.0046 = \frac{i \times 0.1}{100 + 0.1}$$

$$0.0046 \approx \frac{(0.9x + 0.1) \times 0.1}{100}$$

$$\Rightarrow 0.9x + 0.1 = 4.6$$

$$\Rightarrow x = \frac{4.5}{0.9} = 5$$

$$x = 5$$

23. Mole of urea = 0.2

$$\text{Weight of urea} = 0.2 \times 60 = 12 \text{ g}$$

$$\text{Weight of solvent} = 1000 \text{ g}$$

$$\text{Weight of solution} = 1012 \text{ g}$$

$$\therefore \text{Volume of solution} = \frac{1012}{1.012} = 1000 \text{ ml}$$

$\because$  1000ml solution contain 0.2 mole

$$\therefore 50 \text{ ml solution contain} = \frac{0.2 \times 50}{1000} = 0.01$$

$$\text{Mole of urea in other solution} = \frac{0.01}{60} = 0.001$$



$$\therefore \text{Concentration of solution} = \frac{0.01 + 0.001}{\frac{300}{1000}} \\ = 0.0366$$

$$\therefore \pi = CRT \\ = 0.0366 \times 62 \times 300 \\ = 682$$

