

### # Numericals:

Q.4: What are the molality and molarity of a solution of ethanol in water if the mole fraction of ethanol is 0.05? Assume density of the molecule is  $0.997 \text{ gm/mol}$ .  
Soln:

Given,

$$\text{mole fraction of ethanol } (x_{e_1}) = 0.05$$

$$\text{Density } (D) = 0.997 \text{ gm/mol}$$

Now,

$$\begin{aligned}\text{mole fraction of water } (x_2) &= 1 - x_1 \\ &= 0.95\end{aligned}$$

Now, let the mass of water be  $1000 \text{ gm}$ .

So,

$$\text{no. of moles of water in } 1000 \text{ gm} = \frac{1000}{18} = 55.55 \text{ mole.}$$

Now,

$$x_2 = \frac{n_2}{n_1 + n_2}$$

$$\text{or } 0.95 = \frac{55.55}{n_1 + 55.55}$$

$$\text{or } 0.95 n_1 + 52.7725 = 55.55$$

$$n_1 = 2.92$$

$$\text{weight of water } (w_2) = \text{no. of moles of water} \times 18 = 1000 \text{ gm}$$

$$\text{weight of ethanol } (w_1) = 2.92 \times 46 = 134.32 \text{ gm}$$

$$\text{wt. of sol}^n = 1000 + 134.32 \\ = (1134.32) \text{ gm}$$

Sol,

$$\text{Volume of sol}^n = \frac{\text{mass of sol}^n}{\text{density}} = \frac{1134.32}{0.997} = 1137.73 \text{ ml}$$

Now,

$$\begin{aligned} \text{(i): Molality} &= \frac{\text{no. of moles of solute}}{\text{wt. of solute in gm}} \\ &= \frac{2.92}{1} = 2.92 \text{ m} \end{aligned}$$

$$\begin{aligned} \text{(ii): Molarity} &= \frac{\text{no. of moles of solute} \times 1000}{\text{volume of sol}^n \text{ in ml}} \\ &= \frac{2.92 \times 1000}{1137.73} \\ &= 2.57 \text{ M} \end{aligned}$$

Thus, molality is 2.92 m and molarity is 2.57 M.

Q.27: Concentrated nitric acid is 69% by weight of  $\text{HNO}_3$  and has density of 1.41 gm/ml. at 20°C. what volume and what wt of conc. nitric acid are needed to prepare 100 ml of 6 M acid?  
Sol<sup>n</sup>:

Given,

$$\%(\text{w/w}) \text{ of } \text{HNO}_3 = 69\%$$

$$\text{Density (D)} = 1.41$$

Now,

$$M = \frac{\%(\text{w/w}) \times \text{density} \times 10}{\text{mol. wt}}$$

$$= \frac{69 \times 1.41 \times 10}{63}$$

$$\therefore M = 15.443 \text{ M}$$

Here,

$$\text{no. of moles before N-acid before dilution} = \text{No. of moles of N-acid after dilution}$$

$$\text{or, } \left( \frac{\text{molarity} \times \text{volume}}{1000} \right)_b = \left( \frac{\text{molarity} \times \text{volume}}{1000} \right)_a$$

$$\text{or, } \frac{15.443 \times V}{1000} = \frac{69 \times 100}{1000}$$

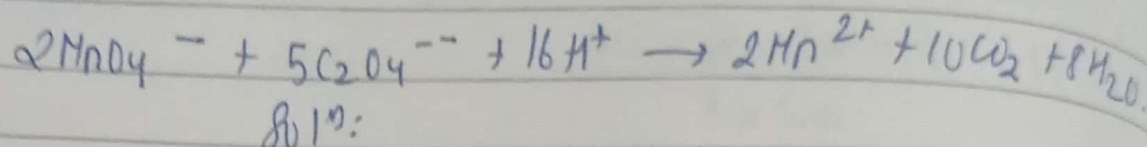
$$\text{Volume of conc. } \text{HNO}_3 = 38.853 \text{ ml}$$

Now,

$$\begin{aligned} \text{weight} &= \text{volume} \times \text{density} \\ &= 38.853 \times 1.41 = 54.782 \text{ gm.} \end{aligned}$$



Q.3): Calculate how many millilitres of 0.1 M  $\text{KMnO}_4$  are required to react completely with 0.01 mole of oxalate ion  $\text{C}_2\text{O}_4^{2-}$ , according to reaction.



Given,

no. of moles of oxalate ion = 0.01 moles

molarity of  $\text{KMnO}_4$  = 0.1 M.

Using stoichiometric relationship,

$$\frac{\text{no. of moles of } \text{KMnO}_4}{2} = \frac{\text{no. of moles of } \text{C}_2\text{O}_4^{2-}}{5}$$

$$\therefore, \text{no. of moles of } \text{KMnO}_4 = \frac{2}{5} \times \text{no. of moles of } \text{C}_2\text{O}_4^{2-}$$

$$= \frac{2}{5} \times 0.01 = 0.004 \text{ moles}$$

Sol

$$\text{molarity} = \frac{\text{no. of moles}}{\text{volume in ml}} \times 1000$$

$$\text{or } 0.1 = \frac{0.004}{V} \times 1000$$

$$\therefore V = 40 \text{ ml.}$$

40 ml of 0.1 M  $\text{KMnO}_4$  is required.

Q.4): Exactly 100 gm of certain solution containing 10 gm of NaCl. The density of the sol<sup>n</sup> is 1.071 gm/ml. What is the molality and molarity of NaCl.

Sol<sup>n</sup>:

Given,

$$\text{wt of NaCl} = 10 \text{ gm}$$

$$\text{wt of solution} = 100 \text{ gm}$$

$$\text{Density (D)} = 1.071 \text{ gm/ml}$$

We know, mol wt of NaCl =  $23 + 35.5 = 58.5$

Sol

$$\text{i) no. of moles of NaCl} = \frac{10}{58.5} = 0.171 \text{ moles.}$$

$$\text{wt of solvent} = 9(100 - 10) \text{ gm} = 90 \text{ gm}$$

$$\text{volume of sol}^n = \frac{\text{mass of sol}^n}{\text{density of sol}^n} = \frac{100}{1.071}$$

$$\therefore V = 93.37 \text{ ml}$$

Now,

$$\text{(i): Molality} = \frac{\text{no. of moles of solute} \times 1000}{\text{wt. of solvent in gm}} = \frac{0.171 \times 1000}{90} = 1.9 \text{ m}$$

$$\text{(ii) Molarity} = \frac{\text{no. of moles of solute} \times 1000}{\text{volume in ml}} = \frac{0.171 \times 1000}{93.37} = 1.83 \text{ M}$$

The molality is 1.9 m and molarity is 1.83 M.

Q.5: The boiling point of a sol<sup>n</sup> of 0.420 gm of naphthalene,  $C_{10}H_8$  in 26.6 gm of chloroform is  $0.455^\circ C$  higher than that of pure chloroform. What is the molal boiling point elevation constant for chloroform?

Sol<sup>n</sup>:

Given,

weight of solvent (chloroform) ( $W_1$ ) = 26.6 gm

weight of naphthalene ( $W_2$ ) = 0.420 gm

molar mass of naphthalene ( $MW_2$ ) = 128

Boiling point elevation ( $\Delta T_b$ ) =  $0.455^\circ C$

Molal BP elevation constant ( $K_b$ ) = ?

We know,

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

$$\text{or } \Delta T_b = K_b \cdot \frac{W_2 (W_2/MW_2)}{MW_2 \times W_1}$$

$$\text{or } \frac{\Delta T_b \times MW_2 \times W_1}{W_2} = K_b \quad \text{or} \quad \frac{\Delta T_b \times W_1}{(W_2/MW_2)} = K_b$$

$$\therefore K_b = 3688.53 \text{ gm mol}^{-1} \cdot K$$

$$= 3.69 \text{ kg mol}^{-1} \cdot K$$



Q.67: The v.p of dilute aq. sol<sup>n</sup> is 23.45 mm at 25°C whereas the v.p of pure water is 23.76 mm. Calculate the molal conc<sup>n</sup> of solute, use  $K_b$  value of water to find boiling point of sol<sup>n</sup>.

Given,

$$VP \text{ of sol}^n = 23.45 \text{ mm}$$

$$VP \text{ of water} = 23.76 \text{ mm}$$

$$K_b = 0.51$$

Here, using Raoult's law,

$$P_1 = P_1^0 \times x_1$$

$$\text{So } x_1 = \frac{P_1}{P_1^0} = \frac{23.45}{23.76} = 0.987$$

(mole fraction of water)

Now,

Let us take 1000 gm of water.

So,

$$\text{no. of moles of water } (n_1) = \frac{1000}{18} = 55.556 \text{ moles}$$

Now,

$$X_1 = \frac{n_1}{n_1 + n_2}$$

$$\text{on } 0.987 = \frac{55.556}{55.556 + n_2}$$

$$\therefore n_2 = 0.734$$

(No. of moles of solute)

= Molality of solute as  
1000 gm water is considered

We know,

$$\begin{aligned}\Delta T_b &= K_b \times m \\ &= 0.51 \times 0.734 \\ &= 0.374^\circ \text{C}.\end{aligned}$$

$$\begin{aligned}\therefore \text{BP of solvent sol}^\circ &= \text{BP of solvent} + \Delta T_b \\ &= 100.374^\circ\end{aligned}$$

Q.77: What weight of ethylene glycol,  $\text{C}_2\text{H}_6\text{O}_2$  must be included in each 1000 gm of aq. solvent to lower freezing point to  $-10^\circ\text{C}$ ?

Sol<sup>n</sup>:

Here,

solvent is water.

Weight of solvent ( $W_1$ ) = 1000 gm

Solute is  $\text{C}_2\text{H}_6\text{O}_2$ .

$$T_f = -10^\circ\text{C}$$

$$K_f = 1.86$$

Mol wt of solute = 62.

Now,

$$\begin{aligned}\Delta T_f &= T_f - T_{fs} \\ &= 10^\circ\text{C}.\end{aligned}$$

Now,

$$\Delta T_f = K_f \times \left( \frac{W_2}{M W_2} \right) \times 1000$$

$W_1$



$$10 = 1.86 \times \frac{(w_2/MW_2) \times 1000}{w_1}$$

$$\therefore w_2 = 333.7 \text{ gm.}$$

Q.8) When 1.00 gm of sulphur is dissolved in 20 gm of naphthalene ( $K_f = 6.8$ ), the resulting sol<sup>n</sup> freezes at a temp  $1.28^\circ\text{C}$  lower than pure naphthalene does. Calculate the mol. wt. of the sulphur.

Sol<sup>n</sup>.

Here, sulphur is solute and naphthalene is solvent.

Given,

$$\text{wt of sulphur } (w_2) = 1.00 \text{ gm}$$

$$\text{wt of solvent } (w_1) = 20 \text{ gm}$$

$$K_f = 6.8$$

$$\text{Depression in freezing point } (\Delta T_f) = 1.28^\circ$$

$$\text{Mol wt of sulphur } (MW_2) = ?$$

We know,

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

$$\text{or, } \Delta T_f = K_f \cdot \frac{(w_2/MW_2) \times 1000}{w_1}$$

$$\text{or, } \Delta T_f = K_f \cdot \frac{w_2}{MW_2} \times \frac{1}{w_1} \times 1000$$

$$\text{or, } MW_2 = \frac{K_f \times w_2 \times 1 \times 1000}{\Delta T_f \times w_1}$$

$$= \frac{6.8 \times 1.00 \times 1 \times 1000}{1.28 \times 20}$$

$$\therefore MW_2 = 265.625 \text{ gm/mol.}$$

Q9: The freezing point depression constant for mercuric chloride is  $HgCl_2$  is 34.3. For a solution of 0.849 gm mercurous chloride ( $HgCl$ ) in 50 gm  $HgCl_2$ , the freezing point depression is  $1.24^\circ C$ . What is the molecular wt of mercurous chloride? What is the molecular formula?

Sol<sup>n</sup>:

Given,

Solvent is  $HgCl_2$  and solute is ( $HgCl$ )<sup>em.</sup>

weight of solvent ( $W_1$ ) = ~~34.3~~ 50

weight of solute ( $W_2$ ) = 0.849

$K_f = 34.3$

$\Delta T_f = 1.24^\circ C$

Mol wt of mercurous chloride ( $MW_2$ ) = ?

Em-formula wt (EM wt) = 236

We know,

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

$$\Delta T_f = K_f \times \frac{W_2 \times 1000}{MW_2 \times W_1}$$

$$MW_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

$$= \frac{34.3 \times 0.849 \times 1000}{1.24 \times 50}$$

$$\therefore MW_2 = 469.698 \text{ gm/mol}$$

S<sub>2</sub>,

$$n = \frac{469.698}{236} = 1.99 \approx 2$$

S<sub>3</sub>, molecular formula =  $(HgCl)_2 = Hg_2Cl_2$

Q10: 10 litres of dry air were bubbled slowly through liquid water at  $20^{\circ}\text{C}$ , and the average weight loss of the liquid is ~~the~~  $0.172\text{ gm}$ . By assuming 10 litres of saturated water vapour were formed, calculate the vp of water at  $20^{\circ}\text{C}$ .

Sol<sup>n</sup>:

Given,

Volume of dry air = 10 litres

Absolute temp =  $20^{\circ}\text{C} = (20 + 273)\text{ K} = 293\text{ K}$

Saturated water vapour volume = 10 litres.

Weight loss of liquid =  $0.172\text{ gm}$ .

Now,

According to q,

The weight of water vapour = weight loss due to evaporation  
=  $0.172\text{ gm}$

No. of moles of water vapour =  $\frac{0.172}{18} = 0.0096\text{ moles}$

Let us assume water vapour to be an ideal gas. Then,

$$PV = nRT$$

$$\therefore P = \frac{nRT}{V} = \frac{0.0096 \times 0.0821 \times 293}{10}$$

$$= 0.023\text{ atm.}$$

Here,  $R = 0.0821\text{ lit atm mol}^{-1}\text{ K}^{-1}$

The vp of water vapour at  $20^{\circ}\text{C}$  is  $0.023\text{ atm}$ .



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Q.11) Ethanol and methanol form the solution that is very nearly ideal. The vapour pressure of ethanol is 44.5 mm and that of methanol is 88.7 mm at 20°C.

(a): Calculate the mole fraction of ethanol and methanol obtained by mixing 60 gm ethanol with 40 gm methanol.

(b) Calculate the partial pressure and the total v.p. of this solution and mole fraction of ethanol in vapour.

Sol<sup>n</sup>:

Given,

Let us take 1 as ethanol and 2 as methanol.

$$P_1^0 = 44.5 \text{ mm}$$

$$P_2^0 = 88.7 \text{ mm}$$

$$w_1 = 60 \text{ gm}$$

$$w_2 = 40 \text{ gm}$$

So,

$$n_1 = \frac{60}{46} = 1.3$$

$$n_2 = \frac{40}{32} = 1.25$$

So, For (a):

$$x_1 = \frac{n_1}{n_1 + n_2} = 0.51$$

$$x_2 = \frac{n_2}{n_1 + n_2} = 0.49$$

For (b):

Using Raoult's law,

$$P_1 = P_1^0 \cdot x_1 = 44.5 \times 0.51 = 22.70 \text{ mm}$$

(Partial pressure of ethanol)

$$P_2 = P_2^0 \cdot x_2 = 88.7 \times 0.49 = 66.16 \text{ mm}$$

(Partial pressure of methanol)

$$\begin{aligned}\text{Total pressure } (P_T) &= P_1 + P_2 \\ &= 22.70 + 66.16 = 88.86 \text{ mm}\end{aligned}$$

$$\text{Mole fraction of ethanol in vapour} = \frac{P_1}{P_T} = \frac{22.70}{88.86} = 0.254$$

Q.12: At  $20^\circ\text{C}$ , the vapour pressure of pure benzene is 75 mm and that of pure toluene is 22 mm. What is the composition of this solution of these two components that has a vapour pressure of 50 mm at this temp? What is the composition of vapour in equilibrium with this sol<sup>n</sup>.

Sol<sup>n</sup>:

Let us suppose 1 as benzene and 2 as toluene.

Given.

$$P_1^0 = 75 \text{ mm}$$

$$P_2^0 = 22 \text{ mm}$$

$$T = 20^\circ\text{C} = 293 \text{ K}$$

$$\text{VP of sol}^n = 50 \text{ mm}$$

Let ' $x_1$ ' be mole fraction of benzene and ' $x_2$ ' be mole fraction of toluene.

Using Raoult's law,

$$P_1 = P_1^0 \cdot x_1$$

$$\begin{aligned}P_2 &= P_2^0 \cdot (1 - x_1) \\ &= P_2^0 \cdot (1 - x_1)\end{aligned}$$

Similarly, sum of partial vp gives total vp of sol<sup>n</sup>

$$\text{VP}_{\text{sol}^n} = P_1 + P_2$$

$$\text{or } 50 = 75 \times x_1 + 22(1 - x_1) \quad \text{--- (i)}$$

$$\text{Solving (i), we get } x_1 = 0.53$$

$$x_2 = 0.47$$

So,

$$P_1 = P_1^0 \cdot x_1 = 75 \times 0.53 = 39.75 \text{ mm}$$

$$P_2 = P_2^0 \cdot x_2 = 22 \times 0.47 = 10.34 \text{ mm}$$

$$\therefore P_T = 50.09 \text{ mm} = P_1 + P_2.$$

So,

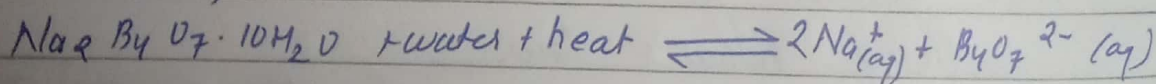
$$\begin{aligned} X_1' \text{ in vapour} &= \frac{P_1}{P_T} \\ &= \frac{39.75}{50.09} \\ &= 0.79 \end{aligned}$$

$$\begin{aligned} X_2' \text{ in vapour} &= \frac{P_2}{P_T} \\ &= \frac{10.34}{50.09} \\ &= 0.21 \end{aligned}$$

Q.13: The solubility of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) in water increases as the temperature increases. Is heat evolved or absorbed during this process? Is  $\Delta H$  positive or negative?

soln:

The reaction,



Here, the equilibrium shifts towards the solution side, so, the solubility increases.

The reaction shows heat is absorbed i.e., endothermic. So,  $\Delta H$  is positive.



Q.147: At  $55^\circ\text{C}$ , ethanol has  $p^\circ$  of 168 mm, and the  $p^\circ$  of methylcyclohexane is 280 mm. A solution of the two in which the mole fraction of ethanol is 0.68, has total  $p$  of 376 mm. Is the soln formed from its components by evolution of heat or by absorption?

Soln:

Given,

Let us consider 1 as ethanol and 2 as methylcyclohexane.

Given,

$$p_1^\circ = 168 \text{ mm}$$

$$x_1 = 0.68$$

$$p_2^\circ = 280 \text{ mm}$$

$$x_2 = 1 - x_1 = 0.32$$

Using Raoult's law,

$$p_1 = p_1^\circ \cdot x_1 = 168 \times 0.68 = 114.24 \text{ mm}$$

$$p_2 = p_2^\circ \cdot x_2 = 280 \times 0.32 = 89.6 \text{ mm}$$

$$\therefore p_T = p_1 + p_2 = 203.84 \text{ mm}$$

Here,  $p_{\text{exp.}} > p_T$  for ideal solution. This means the solution shows positive deviation from Raoult's law.

Thus, the formation of solution is accompanied by <sup>absorption</sup> ~~evolution~~ of heat i.e.  $\Delta H$  is positive