**1.** At 90°C, the vapour pressure of toluene is 400 torr and that of σ-xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?

Acc. to Raoult's Law;

$p_{Total} = p_A^\circ \chi_A + p_B^\circ \chi_B$; where

$p_A^\circ$; $p_B^\circ$ : vapour pressures of pure A & pure B

$\chi_A$; $\chi_B$ : mole fractions of A & B in liquid soln.

Cond$^n$ of boiling; $p_{Total} = p_{external} = 0.5$ atm

$\Rightarrow 0.5 \text{ atm} = p^\circ_{Toluene} \times \chi_{Toluene} + p^\circ_{\sigma\text{-xylene}} \times \chi_{\sigma\text{-xylene}}$

$\Rightarrow$ vapour pressures are divided by 760 $\frac{\text{torr}}{\text{atm}}$ to convert them into atm.

$\Rightarrow 0.5 = \left(\frac{400}{760}\right) \times \chi_{Toluene} + \left(\frac{150}{760}\right)\left(1 - \chi_{Toluene}\right)$

$\left(\because \chi_{Toluene} + \chi_{\sigma\text{-xylene}} = 1\right)$

**2.** The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

Acc. to relative lowering in vapour pressure;

$$\frac{\Delta p}{p^0} = \frac{n_{solute}}{n_{solute} + n_{solvent}} = \chi_{solute}$$

assuming 1 atm = 760 mm Hg ;

$$\left(\frac{760 - 750}{750}\right) = \left(\frac{1}{75}\right) = \frac{n_{solute}}{n_{solute} + n_{solvent}}$$

$$\Rightarrow \frac{n_{solute}}{n_{solvent}} \simeq \frac{1}{75} \quad ; \text{(solvent is water} \because \text{it is an aqueous solution & solute is very less)}$$

$$\Rightarrow \frac{n_{solute}}{\left(\frac{wt_{solvent}}{18}\right)} = \frac{1}{75}$$

$$\Rightarrow \frac{n_{solute}}{wt_{solvent}\,(\text{in gm})} = \frac{1}{75 \times 18}$$

-) molality $= \frac{n_{solute}}{wt_{solvent}\,(in\,kg)} = \frac{n_{solute} \times 1000}{wt_{solvent}\,(kg)}$

$= \frac{1000}{75 \times 18} = 0.741\ m.$

**3.** Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to –9.3°C. ($K_f$ for water = 1.86 K $mol^{-1}$ kg)

Acc. to depression in freezing point;

$\Delta T_f = T_f - T_f' = K_f \times$ molality; where

$T_f$ = freezing point of pure solvent;

$T_f'$ = " " " solution

$K_f$ = molal depression const.

substituting all variables;

$$0 - (-9.3) = 1.86 \times \frac{\left(\frac{50}{62}\right)}{\text{wt}_{\text{water}} \text{ (in kg)}}$$

$$\Rightarrow \text{wt}_{\text{water}} = \frac{1.86 \times 50}{62 \times 9.3} = 0.1612 \text{ kg}$$

$\Rightarrow$ mass of ice separated = 200g − 161.2g

= 38.7 g

**4.** How many grams of sucrose (mol.wt. = 342) should be dissolved in 100 gm water in order to produce a solution with 105°C difference between the freezing point & boiling point temperature at 1 atm?

**(Unit: $K_f$ = 2 K.kg mol$^{-1}$ ; $k_b$ = 0.5 K.kg mol$^{-1}$)**

Applying formula for elevation in boiling point;

$\Delta T_b = T_b' - T_b = K_b \times$ molality;

$T_b'$ = boiling point of solution;

$T_b'$ = " " " pure solvent

$K_b$ = molal elevation constant

molality = molality of solution

substituting values;

$\Delta T_b = T_b' - 100 = 0.5 \times m$ — ①

Applying formula of depression in freezing point;

$\Delta T_b$ = $k_b$ × molality ; where

$T_b'$ = freezing point of the solution ;

$T_b$ = " " " pure solvent .

$k_f$ = molal depression constant ;

molality = molality of solution

$\Delta T_f = 0 - T_f' = 2 \times m$ —— (2)

adding (1) & (2)

$(T_b' - T_f' - 100) = 2.5 \times m$

Given that ; $T_b' - T_f' = 105$

$\Rightarrow (105 - 100) = 2.5 \times m$

$\Rightarrow m = 2 = \dfrac{n_{glucose}}{wt_{water}\ (kg)}$

$\Rightarrow n_{glucose} = (2 \times 0.1) = 0.2$ mol

$\Rightarrow wt_{glucose} = 0.2 \text{ mol} \times 342 \dfrac{g}{mol} = 68.4$ gm

(5) An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.36°C at 1.00 atmospheric pressure. What is the molecular formula? $K_b(H_2O) = 0.52\ K\ mol^{-1}\ kg$

Applying formula for elevation in boiling point;

$\Delta T_b = T_b' - T_b = K_b \times$ molality;

$T_b'$ = boiling point of solution;

$T_b'$ = " " " pure solvent

$K_b$ = molal elevation constant

molality = molality of solution

substituting values;

moles of solute = $\frac{288\ gm}{(12x + 2x + 16x)\ g/mol} = \frac{288}{30x}\ mol$

molality = $\left(\frac{\frac{288}{30x}}{0.09}\right) \frac{mol}{kg}$

$\Rightarrow (101.36 - 100)\ K = 0.52\ \frac{K\text{-}kg}{mol} \times \left(\frac{288}{30x \times 0.09}\ \frac{mol}{kg}\right)$

$\Rightarrow x \cong 40 \Rightarrow$ formula = $C_{40}H_{80}O_{40}$

(6) A complex is represented as $CoCl_3 \cdot xNH_3$. It's 0.1 molal solution in a solution shows $\Delta T_f = 0.558°C$. $K_f$ for $H_2O$ is 1.86 K $mol^{-1}$ kg. Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

Applying formula of depression in freezing point;

$\Delta T_f = k_f \times \text{molality} \times i$; where

$T_f'$ = freezing point of the solution;

$T_f$ = " " " pure solvent.

$k_f$ = molal depression constant;

molality = molality of solution

$i$ = van't Hoff factor = $1 + (y-1)\alpha$.

$\alpha$ = degree of dissociation;

$y$ = no. of moles of product per mole of reactant

substituting values,

$0.558 = 1.86 \times 0.1 \times i$

$\Rightarrow i = 3 = 1 + (y-1)\alpha$;

assuming complete dissociation;

$y = 3$

$\Rightarrow$ including the co-ordination sphere; two other ions get released ; $\therefore$ a primary valency of 3 & secondary valency of 6 can be satisfied by $5\,NH_3$ & $3\,Cl^{\ominus}$ ; $\therefore$ formula $= [Co(NH_3)_5Cl]Cl_2$

**7.** Normal boiling point of diethyl ether is 327° and at 190 mmHg boiling points in 27°C. What is the value of $\Delta H^{\circ}_{vap.}$ in kJ/mole.

(Use : R = 8.3 J/K-mole, ln2 = 0.7)

Sol$^{n}$:-

$$\ln\left(\frac{K_{p_2}}{K_{p_1}}\right) = \frac{-\Delta H^{\circ}_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where; $K_{p_2}$ ; $K_{p_1}$ :: Equilibrium constants of boiling equilibrium at $T_2$ & $T_1$ temp. resp.

$T_2$ ; $T_1$ :: boiling points at 760 mm Hg & 190 mm Hg, resp.

$\Delta H_{vap.}$ = molar enthalpy of evaporation

$$\therefore \ln\left(\frac{760\,mm}{190\,mm}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{(327+273)} - \frac{1}{(27+273)}\right)$$