CHEMISTRY 311 PHYSICAL CHEMISTRY
Homework Assignment # 8

1. The partial molar volumes of acetone (MW = 58.08 g mol^{-1}) and chloroform (MW = 119.37 g mol^{-1}), respectively, 74.166 cm^3 mol^{-1} and 80.235 cm^3 mol^{-1} for a solution in which the mole fraction of chloroform is 0.4693. What is the volume of 1.000 kg of this solution?

   Answer

   Let us denote acetone by A and Chloroform by C. It is given that $0.4693 = n_A/n$, where $n = n_A + n_C$. In other words, $n_C = 0.4693n$ and $n_A = (1 - 0.4693)n$. The total number of moles present, n, can be found from the weight of the solution and the mole fractions as

$$\begin{aligned}1000 \text{ g} =& n_A \times 58.08 \text{ g mol}^{-1} + n_C \times 119.37 \text{ g mol}^{-1}\\ =& n(1 - x_C) \times 58.08 \text{ g mol}^{-1} + n x_C \times 119.37 \text{ g mol}^{-1}.\end{aligned}$$

   Substituting the molefractions and solving, we get

$$n = \frac{1000}{58.08 \times (1 - 0.4693) + 0.4693 \times 119.37} = 11.515 \text{ moles.}$$

   Therefore, $n_A = (1 - 0.4693) \times 11.515 = 6.111$ moles and $n_C = 0.4693 \times 11.515 = 5.404$ moles. The volume of the solution is, therefore, given by

$$\begin{aligned}V =& n_A \overline{V}_A + n_C \overline{V}_C\\ =& 6.111 \times 74.166 + 5.404 \times 80.235\\ V =& 886.82 \text{ cm}^3.\end{aligned}$$

2. Commercial antifreeze is mostly ethylene glycol, mixed with small amounts of rust inhibitors and a fluorescent dye which makes it easy to detect radiator leaks. Assuming that commercial antifreeze is pure ethylene glycol (MW=62.07 g/mol, density=1.1088g/mL), in what proportion by volume should water and antifreeze be mixed to make a coolant solution that freezes at −20°C? Enthalpy of fusion of water = 6.008 kJ/mol.

   Answer

   The change in the freezing point is given by $\Delta T_{fp} = -K_f m$, where

$$\begin{aligned}K_f =& \frac{R T_{fp}^{\circ 2} M_{\mathrm{H_2O}}}{\Delta H^\circ_{fus,\mathrm{H_2O}}} \qquad (1)\\ =& \frac{8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times (273.15 \text{ K})^2 \times 0.018016 \text{ kg mol}^{-1}}{6008 \text{ J mol}^{-1}}\\ K_f =& 1.8602 \text{ K kg mol}^{-1}\end{aligned}$$

   Therefore, the molality of ethylene glycol in a solution that freezes at −20°C ($\Delta T_{fp} = -20$ K) is

$$\begin{aligned}m =& -\Delta T/K_f\\ =& -(-20 \text{ K})/1.8602 \text{ K kg mol}^{-1}\\ m =& 10.752 \text{ mol kg}^{-1}.\end{aligned}$$

By definition, molality is the number of moles of solute in 1.0 kg of solvent. Therefore, 1.0 kg of water, which has a volume of 1.0 L, needs 10.752 moles of ethylene glycol if it is to freeze at $-20°$C. The volume of 10.752 moles of ethylene glycol is given by

$$V_{\mathrm{EG}} = 10.752 \times 62.07/1.1088 = 601.89 \text{ mL} = 0.602 \text{ L}.$$

Therefore, water and ethylene glycol must be mixed in the volume proportion of 1 : 0.602.

Of course, we could also solve this problem using the more accurate relationship (where subscript 1 refers to the solvent)

$$\begin{aligned} \ln x_{\mathrm{H_2O}} &= \frac{\Delta_{fus} H^\circ}{R}\left(\frac{1}{T_f^*} - \frac{1}{T}\right) \qquad (2)\\ &= \frac{6008 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{273.15} - \frac{1}{253.15}\right)\frac{1}{\text{K}} = -0.209 \\ x_{\mathrm{H_2O}} &= 0.8114; x_{\mathrm{EG}} = 0.1886 \end{aligned}$$

Tthe proportion of the number of moles of water to that of ethylene glycol is given by

$$\frac{n_{\mathrm{H_2O}}}{n_{\mathrm{tot}}} : \frac{n_{\mathrm{EG}}}{n_{\mathrm{tot}}} = 0.8114 : 0.1886 = n_{\mathrm{H_2O}} : n_{\mathrm{EG}}$$

Converting this to mass ratios, we get

$$\begin{aligned} w_{\mathrm{H_2O}} : w_{\mathrm{EG}} &= 0.8114 \text{ mol} \times 18.02 \text{ g mol}^{-1} : 0.1886 \text{ mol} \times 62.07 \text{ g mol}^{-1} \\ &= 14.625 \text{ g H}_2\text{O} : 11.706 \text{ g EG} \end{aligned}$$

Using densities, we can convert this to volume ratios: $\frac{11.706}{1.1088} = 10.557$

$$\begin{gathered} \frac{14.625 \text{ g}}{1.00 \text{ g mL}^{-1}} : \frac{11.706 \text{ g}}{1.1088 \text{ g mL}^{-1}} \\ 14.625 \text{ mL} : 10.557 \text{ mL} \\ 1.00 \text{ mL} : 0.722 \text{ mL} \end{gathered}$$

Therefore, the ratio is 0.722 L of EG per liter of water. This is slightly different from the first calculation we did using the simplified expression in Eq. (1). The difference is reflective of the approximations made in obtaining the simplified expression from the more accurate expression in Eq. (2).

3. One mole of benzene (component 1) is mixed with two moles of toluene (component 2). At 60°C, the vapor pressures of benzene and toluene are 51.3 and 18.5 kPa, respectively. (a) As the pressure is reduced, at what pressure will boiling begin (first appearance of bubbles)? (b) What will be the composition of the first bubble of vapor?

Answer

(a) From Eq. (6.9), the bubble-point line, we get the pressure at which the first bubble is formed.

$$\begin{aligned} P &= P_2^* + (P_1^* - P_2^*)x_1 \\ &= 18.5 + (51.3 - 18.5) \times (1/3) \text{ kPa} \\ &= 29.4 \text{ kPa} \end{aligned}$$

(b) From Eq. (6.18), we get the composition of the vapor:

$$\begin{aligned} y_1 &= \frac{x_1 P_1^*}{x_1 P_1^* + x_2 P_2^*} \\ &= \frac{(1/3) \times 51.3}{(1/3) \times 51.3 + (2/3) \times 18.5} \\ &= 0.581 \end{aligned}$$

4. At 1.013 bar pressure, propane boils at −42.1°C and n-butane boils at −0.5°C. The following vapor pressure data are available:

t (°C)	−31.2	−16.3
P (kPa) of propane	160.0	298.6
P (kPa) of n-butane	26.7	53.3

Assuming that these substances form ideal binary solutions with each other, (a) calculate the mole fractions of propane at which the solution will boil at 1.013 bar pressure at −31.2°C and at −16.3°C. (b) Calculate the mole fractions of propane in the vapor in equilibrium with the liquid at the two temperatures. (c) Plot the temperature-mole fraction diagram at 1.013 bar using these data, and label the regions.

Answer

(a) Let propane be component 1 and n-butane, component 2. The solutions will boil when the vapor pressure becomes equal to the applied pressure, $P = 1.013$ bar. From Eq. (6.9), we get

$$x_1 = \frac{P - P_2^*}{(P_1^* - P_2^*)}.$$

Therefore, at −31.2°C, we get

$$x_1 = \frac{101.3 - 26.7}{160.0 - 26.7} = 0.560$$

and at −16.3°C, we get

$$x_1 = \frac{101.3 - 53.3}{298.6 - 53.3} = 0.196$$

(b) At these compositions, the vapor compositions are given by Eq. (6.18) as

$$y_1 = \frac{x_1 P_1^*}{x_1 P_1^* + x_2 P_2^*} = \frac{x_1 P_1^*}{x_1 P_1^* + (1 - x_1) P_2^*}$$

Therefore, we get

t (°C)	−31.2	−16.3
y_1	0.884	0.577

so that the complete composition-boiling point data can be tabulated as

x_1	y_1	t (°C)
0.000	0.000	−0.5
0.196	0.577	−16.3
0.560	0.884	−31.2
1.000	1.000	−42.1

(c) The temperature-composition diagram is shown below: