

Chemistry 440 Problem set 5

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(Dated: due: 2 December 2011)

1. The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.3713 are $188.2 \text{ cm}^3/\text{mol}$ and $176.14 \text{ cm}^3/\text{mol}$, respectively. The molar masses of A and B are 241.1 g/mol and 198.2 g/mol . What is the volume of a solution of mass 1.00 kg?
2. At 310 K, the partial pressures of a substance B dissolved in liquid A are as follows: $x_B = 0.010, 0.015, 0.020$, with accompanying pressures, $p_B = (82.0, 122.0, 166.1) \text{ kPa}$. Show that the solution obeys Henry's law in this range of mole fractions and calculate the Henry's law constant.
3. The osmotic pressure of an aqueous solution at 288 K is 59.0 kPa . Calculate the freezing point of the solution.
4. The volume of an aqueous solution of NaCl at 298 K was measured at a series of molalities m , and was found to obey

$$V(m) = 1003 + 16.62m + 1.77m^{3/2} + 0.12m^2 \quad (1)$$

where V is the volume in cm^3 formed using 1.00 kg of solvent. Calculate the partial molar volumes of the salt and the solvent when $m = 0.2 \text{ mol/kg}$.

5. Label the regions of the phase diagram shown on the next page. State what substances exist in each region. Label each substance as solid, liquid or gas.
6. The vapor pressure of pure liquid A is at 293 K is 68.8 kPa , and that of pure liquid B is 82.1 kPa . These two compounds form ideal liquid and gaseous mixtures. Calculate the total pressure of the vapor and the composition of the liquid mixture when $y_A = 0.412$.
7. Benzene and toluene form nearly ideal solutions. Consider an equi-molar solution of benzene and toluene. At 20°C , the vapor pressures of benzene and toluene are 9.9 kPa

and 2.9 kPa , respectively. The solution is boiled by reducing external pressure below the vapor pressure. Calculate (a) the pressure when boiling begins; (b) the composition of each component in the vapor, and (c) the vapor pressure when only a few drops of liquid remain.

8. From Silbey, et. al, *Physical Chemistry*, Problem 6.9
9. Problem 6.13
10. Problem 6.17
11. Problem 6.26

Problem Set 5

$$1. V = n_A \bar{V}_A + n_B \bar{V}_B$$

$$\bar{V}_A = 188.2 \text{ cm}^3/\text{mol} \quad n_A/n = 0.3713$$

$$\bar{V}_B = 176.14 \text{ cm}^3/\text{mol} \quad n_B/n = 0.6287$$

$$\text{Total mass} = 1.00 \text{ kg} = n \left[241.1 \frac{\text{g}}{\text{mole}} \times 0.3713 + 198.2 \frac{\text{g}}{\text{mole}} \times 0.6287 \right]$$

$$\therefore n = 4.67 \text{ moles and}$$

$$n_A = 1.734, n_B = 2.936$$

$$\text{so that } V = 843.5 \text{ cm}^3$$

2. cheat (use one point)

$$\frac{P_B}{x_B} = k_B = \frac{82.0 \text{ kPa}}{0.01} = 8.2 \text{ MPa}$$

$$3. \pi = CRT = 59 \text{ kPa} = C(288 \text{ K}) \left(8.315 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right)$$

$$C = 24.6 \frac{\text{mol}}{\text{M}^3} \times \left(\frac{1 \text{ M}}{10^2 \text{ cm}} \right)^3 \times \frac{10^3 \text{ cm}}{\text{l}} = 2.46 \times 10^{-2} \frac{\text{moles}}{\text{l}}$$

$$\Delta T = k_f \cdot m = 1.86 \frac{\text{K}}{(\text{mol}/\text{kg})} \left(2.46 \times 10^{-2} \frac{\text{moles}}{\text{kg}} \right)$$

$$\sim 0.046 \text{ K} \quad \text{not much.}$$

4. Partial molar volumes

$$V = 1003 + 16.62M + 1.77M^{3/2} + 0.12M^2$$

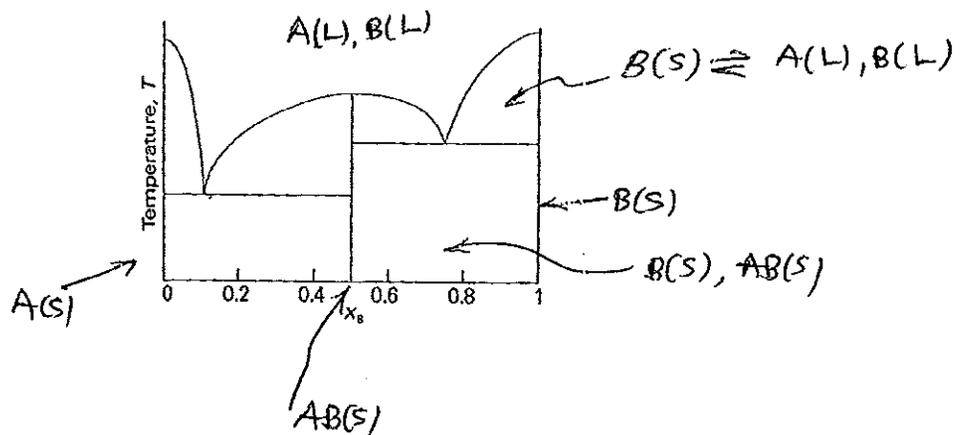
$$\bar{V}_{NaCl} = \left(\frac{\partial V}{\partial M}\right) = 16.62 + \frac{3}{2}(1.77M^{1/2}) + 0.24M$$

$$\bar{V}_{NaCl}(M=0.2) = 17.85 \text{ cm}^3/\text{mol}$$

$$\bar{V}_{H_2O} = (V - n_A \bar{V}_A) / n_B = 18.05 \text{ cm}^3/\text{mol}$$

$$\text{but } n_B = 1 \text{ kg solvent} \times \frac{1 \text{ mole}}{18 \text{ g}} = 55.5 \text{ moles}$$

5.

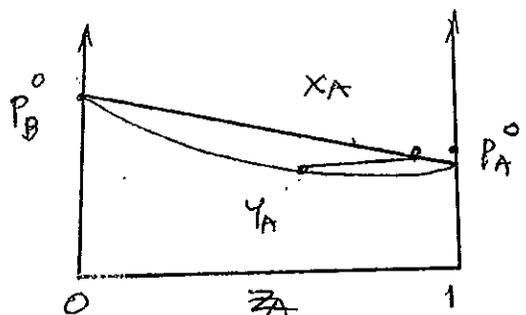


6.

$$P_A^0 = 68.8 \text{ kPa}$$

$$P_B^0 = 82.1 \text{ kPa}$$

$$y_A = 0.612$$



$$\left. \begin{aligned} P_A^0 x_A &= P y_A \\ P_B^0 x_B &= P(1-y_A) \end{aligned} \right\} \text{two eqns, two unks (P and } x_A)$$

$$\frac{P_A^0 x_A}{P_B^0 (1-x_A)} = \frac{y_A}{1-y_A} \Rightarrow \text{solve for } x_A$$

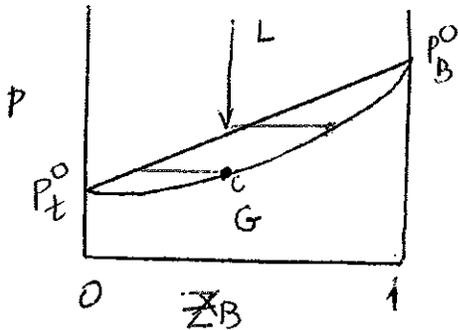
$$x_A = 0.653$$

$$P = x_A P_A^0 + x_B P_B^0 = 73.4 \text{ kPa}$$

7.

$$x_{ben} = 1/2 \quad p_B^0 = 9.9 \text{ kPa}$$

$$x_{tol} = 1/2 \quad p_t^0 = 2.9 \text{ kPa}$$



a) Boiling begins

$$\text{when } P = x_B p_B^0 + x_t p_t^0$$

$$= \frac{1}{2} (9.9 + 2.9) = 6.4 \text{ kPa}$$

b) composition in the vapor @ boiling

$$P y_B = x_B p_B^0 \Rightarrow y_B = \frac{(\frac{1}{2})(9.9)}{6.4} = 0.773$$

$$y_t = 1 - 0.773 = 0.227$$

c)

When only a few drops of liquid remain we are at point c, and $y_B = 1/2$. From PG.2 b

$$\frac{p_B^0 x_B}{p_t^0 (1-x_B)} = \frac{y_B}{1-y_B} \Rightarrow x_B = 0.2265$$

$$\text{and } P = x_B p_B^0 + (1-x_B) p_t^0 = 4.48 \text{ kPa}$$

8. Silbey, 6.9

$$\ln P_s = 29.411 - 5893.5/T$$

$$\ln P_L = 22.254 - 3479.9/T$$

Equate, solve for T, then $P_s = P_L$

$$T = 337.2 \text{ K}$$

$$\ln P = 11.93, \quad P = 1.52 \times 10^5 \text{ Pa}$$

9. Silbey, 6.13

$$\gamma = 0.0284 \text{ N/m}$$

$$\rho = 0.866 \text{ g/cm}^3$$

$$h = 2.0 \text{ cm}$$

but, $\gamma = \frac{1}{2} \rho g r h$ with $g = 980 \text{ cm/s}^2$

$$r = 2\gamma / (\rho \cdot g \cdot h) = 3.35 \times 10^{-2} \text{ cm}$$

10. $F = 2 + C - P$

$$C = 1, \quad F = 3 - P \Rightarrow P = 3$$

$$C = 2, \quad F = 4 - P, \Rightarrow P = 4$$

$$C = 3, \quad \Rightarrow P = 5$$

11. 6.26 $\mu_1 = \mu_1^0 + RT \ln x_1^2 + W x_2^2$

$$\Delta G_{\text{mix}} = n_1 \mu_1 + n_2 \mu_2 - [n_1 \mu_1^0 + n_2 \mu_2^0]$$

$$= n [x_1 \ln x_1 + x_2 \ln x_2 + W x_1 x_2^2 + W x_2 x_1^2]$$

$$= n [(x_1 \ln x_1 + x_2 \ln x_2) RT + W_1 x_1 x_2]$$

$$\Delta S_{\text{mix}} = - \left. \frac{\partial (\Delta G)_{\text{mix}}}{\partial T} \right| = - n \sum_i x_i \ln x_i$$

$$\Delta H_{\text{mix}} = W x_1 x_2 n$$