**Chemistry 230**
**Problem Set # 12 — 11/19/99**

Recommended Problems: Chapt. 9: 37, 43-45, 48
Chapt. 10: 1-4, 52, 53, 56
Chapt. 11: 30, 40, 41 (a,b,d,e,f)

1. A vapor pressure of 177.95 torr is measured for a solution of ethanol (eth) and chloroform (chl) at 45˚C having $x_{eth} = 0.9900$. The vapor pressure of pure ethanol at this temperature is 172.76 torr. [Hint: See problem 9.41 in Levine.]

   (a) Treating the solution as ideally dilute, determine the partial pressures and gas phase mole fractions of both components in the vapor phase.

   (b) Obtain the Henry's law constant for chloroform in ethanol at 45˚C.

   (c) Calculate $\mu^\circ_{chl,l} - \mu^\circ_{chl,v}$ for chloroform in ethanol at 45˚C.

   (d) The vapor pressure is 183.38 torr when $x_{eth}$ is decreased to 0.9800, and the mole fraction of ethanol in the vapor phase is 0.9242. Calculate the Convention II activity coefficients for both components in this solution. (Is there a problem with these results?)

2. A *simple* binary solution is one for which

$$\Delta G_{mix} = RT\,(n_A \ln x_A + n_B \ln x_B) + (n_A + n_B)\, x_A\, x_B\, W(T,P)$$

   at constant $T$ and $P$, where $W(T,P)$ is a function of $T$ and $P$. Theory shows that when the A and B molecules are approximately spherical and have similar sizes, the solution should be approximately simple. For a simple solution,

   (a) Find expressions for $\Delta H_{mix}$, $\Delta S_{mix}$, and $\Delta V_{mix}$.

   (b) Show that $\mu_A = \mu_A^* + RT \ln x_A + W x_B^2$, with a similar equation for $\mu_B$.

   (c) Obtain expressions for the vapor partial pressures $P_A$ and $P_B$, assuming ideal vapor.

3. The following data are available for solutions of acetone (ace) and chloroform (chl) at 50.0˚C:

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_{ace,l}$ | 0.00 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 1.000 |
| $x_{ace,v}$ | 0.00 | 0.071 | 0.165 | 0.279 | 0.408 | 0.550 | 0.684 | 0.789 | 0.890 | 0.955 | 1.000 |
| $P_{tot}$(torr) | 521 | 495 | 474 | 463 | 460 | 469 | 489 | 511 | 540 | 576 | 612 |

   (a) For the case $x_{ace,l} = 0.70$, calculate (i) $\mu_i - \mu_i^*$ for each component; (ii) $\Delta G_{mix}$ for preparing 2.34 mol of this solution; and (iii) $\Delta G_{mix}$ for 2.34 mol of the corresponding ideal solution.

   (b) Calculate and plot $\gamma_I$ for both components, over the full range of composition.

   (c) Calculate $\gamma_{II}$ for both components, taking acetone as the solvent. [**Hint:** See problem 10.8 in Levine.]

4. Use your data and results just above for acetone/chloroform solutions at 50˚C to calculate $G^E/n$ as a function of composition. Compare your results with Fig. 10.3b for 35.2˚C. [**Hint:** See Problem 10.7 in Levine.]