Exam #3

Instructions: There are 6 questions worth a total of 100 points on this exam. Answer all questions in the exam book provided. Partial credit will only be given if I can understand your reasoning, so show and explain your analysis.

1. (15 points) Consider the phase diagram of water shown below and the enlarged region shown at the right.

(a) Describe the state of the system at the point marked “a”.

(b) Describe the changes that occur along the path marked “b”.

(c) What, if anything, can be said about the relative densities of the phases encountered along path b?

2. (15 points) The vapor pressure of a certain non-associated liquid is 10 torr at 298 K. Use Trouton’s rule to estimate its standard boiling point.

3. (15 points) The vapor pressures of liquid and solid Cl₂ are given by:

\[ \ln(P / \text{torr}) = 10.560 - 1640(K / T) \]  
\[ \ln(P / \text{torr}) = 7.769 - 1159(K / T) \]

(a) Calculate the temperature and pressure at the triple point of Cl₂.

(b) Calculate the enthalpy of sublimation (kJ/mol) at the triple point.
4. (15 points) At 25 °C and the vapor pressure of Hg(l) is 2.0×10⁻³ torr, its molar volume is 14.76 cm³ mol⁻¹, and its activity is defined to be unity. Assuming Hg(l) to be incompressible (and to remain a liquid), determine the fugacity and activity at a pressure of 1 kbar and 25 °C.

5. (20 points) The Gibbs excess of a particular binary solution is given by

\[ G^{\text{ex}}(T,P,n_1,n_2) = a \frac{n_1 n_2}{n_1 + n_2} \]  \hspace{1cm} (5-1)

where \( a \) is independent of composition.

(a) Show that this expression is equivalent to \( \overline{G}^{\text{ex}}(T,P,x_i) = a x_i x_2 \).

(b) Show that, in general, excess chemical potentials and activity coefficients are related by:

\[ \mu_i^{\text{ex}} = RT \ln \gamma_i \]

(c) Beginning with the definitions \( G^{\text{ex}} = G - G^{\text{IS}} \) and \( \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{\neq i}} \), use the results of part (b) to show that the activity coefficient \( \gamma_1 \) in a system obeying Eq. 5-1 can be written:

\[ \gamma_1 = \exp(ax_2^2 / RT) \]

(d) Show that the excess volume in such a system is given by:

\[ V_x^{\text{ex}} = x_1 x_2 \left( \frac{\partial a}{\partial P} \right)_{T,x} \]

6. (20 points) The vapor pressure \( P_{\text{tot}} \) and vapor composition \( y \) of a particular binary liquid mixture varies with liquid mole fraction \( x \) in the manner tabulated below.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( P_{\text{tot}} ) / torr</th>
<th>( y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>1000</td>
<td>0.60</td>
</tr>
<tr>
<td>1</td>
<td>800</td>
<td>1</td>
</tr>
</tbody>
</table>

(a) Show that, assuming an idea vapor phase, the activity coefficients can be expressed in terms of the vapor pressures of the pure components \( P_i^* \) by:

\[ \gamma_i = \frac{y_i P_{\text{tot}}}{x_i P_i^*} \]

and calculate the activity coefficients of the two components at \( x = 0.5 \).

(b) Are these activity coefficients consistent with a single-term Redlich-Kister expansion (i.e. with the simple Margules form)? Explain.

(c) Use the simplest representation consistent with these data to estimate the activity coefficients in the infinite dilution limit, i.e. \( \gamma_1(x_1 \to 0) \) and \( \gamma_2(x_1 \to 1) \) and \( \overline{G}^{\text{ex}} / RT \) at \( x = 0.5 \). Explain your reasoning. [Hint: It is easier to use the RK expansion than the van Laar equations for this problem.]