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?

(a) At the (triple) point labeled “a” in this figure three solid phases of ice, phases “II”, “III”, and “V” coexist in equilibrium.
(b) Below ~220 K the system is pure ice II. At some transition temperature near 220 K the system transforms to ice V, where it remains until ~280 K at which point it melts to form liquid water.
(c) The Clapeyron equation says that the slopes coexistence curves are given by:

\[
\left( \frac{dP}{dT} \right)_{trs} = \frac{\Delta_{trs} S}{\Delta_{trs} V} \text{ lines}
\]

curves indicate the sign of the volume change in the transitions. Entropy always increases with increasing \( T \) which means that the sign of \( (dP/dT)_{trs} \) is determined by the sign of \( \Delta_{trs} V \). A negative slope means that the transition proceeds with a decreasing volume (increasing density) and vice versa. The slopes of the II \( \rightarrow \) V and V \( \rightarrow \) L transitions indicate that the relative densities of the phases are ordered \( \rho(V) > \rho(II) \) and \( \rho(V) > \rho(L) \) at their respective transition temperatures. It is reasonable to guess that over the full \( T \) range shown \( \rho(V) > \rho(II) > \rho(L) \).

2. (15 points) The vapor pressure of a certain nonassociated liquid is 10 torr at 298 K. Use Trouton’s rule to estimate its standard boiling point.
Trouton’s rule (Topic Summary 9) states that the entropy of vaporization of simple non-associated liquids at their standard (or normal) boiling points is approximately 10.5 R. The Clausius-Clapeyron equation in integrated form relates the vapor pressure and temperature at two points along the L-V coexistence curve as:

\[
\ln \left( \frac{P_{vap}(T_2)}{P_{vap}(T_1)} \right) \approx -\frac{\Delta_{vap}H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Denoting the boiling point by \( T_b \), and using the relation \( \Delta_{vap}H(T_b) = T_b \Delta_{vap}S(T_b) \)

\[
\ln \left( \frac{760 \text{ torr}}{10 \text{ torr}} \right) \approx -\frac{\Delta_{vap}H}{R} \left( \frac{1}{T_b} - \frac{1}{298 \text{ K}} \right)
\]

\[
= -\frac{T_b \Delta_{vap}S}{R} \left( \frac{1}{T_b} - \frac{1}{298 \text{ K}} \right)
\]

\[
\approx 10.5 \left( \frac{T_b}{298 \text{ K}} - 1 \right)
\]

or

\[
T_b \approx \left( \frac{1}{10.5} \ln \left( \frac{760 \text{ torr}}{10 \text{ torr}} \right) + 1 \right) 298 \text{ K}
\]

\[
= 421 \text{ K}
\]

3. (15 points) The vapor pressures of liquid and solid Cl\(_2\) are given by:

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

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

(a) Calculate the temperature and pressure at the triple point of Cl\(_2\).

(b) Calculate the enthalpy of sublimation (kJ/mol) at the triple point.

(a) At the triple point the free energies of all three phases must be equal, which will only occur when the vapor pressures of the solid and liquid are equal. Equating the two pressure equations yields:

\[
10.560 - 1640(K/T) = 7.769 - 1159(K/T)
\]

\[
2.791 = 481(K/T) \quad \text{or} \quad T_{tp} = 172.3 \text{ K}
\]

Plugging this value of \( T \) into the 1st equation I find a pressure of \( P_{tp} = 2.83 \text{ torr} \).

(b) The integrated form of the Clausius-Clapeyron equation can be written:

\[
\ln \{P(T)\} = a - \frac{\Delta_{sub}H}{R} \frac{1}{T}
\]

which means that the coefficient of the \( 1/T \) term in the empirical equation \( \ln P = a + b/T \) is related to the sublimation enthalpy by \( \Delta_{vap}H = -Rb \). For the sublimation curve this relation provides

\[
\Delta_{sub}H = 13.6 \text{ kJ mol}^{-1}
\]
4. (15 points) At 25 °C and the vapor pressure of Hg(l) is $2.0 \times 10^{-3}$ torr, its molar volume is 14.76 cm$^3$ mol$^{-1}$, and its activity is defined to be unity. Assuming Hg(l) to be incompressible (and remain a liquid), determine the fugacity and activity at 25 °C and a pressure of 1 kbar.

The fugacity of a condensed phase at a temperature $T$ and any pressure $P$ is related to the fugacity at $T$ and the vapor pressure of the phase $P_{\text{vap}}$ by:

$$f^L (T, P) = f^L (T, P_{\text{vap}}) \exp \left\{ \frac{1}{RT} \int_{P_{\text{vap}}}^{P} V^L dP \right\}$$

$$\approx P_{\text{vap}} \exp \left\{ \frac{1}{RT} \int_{P_{\text{vap}}}^{P} V^L dP \right\}$$

The first relation is exact. The second relation comes from recognizing that, for $P_{\text{vap}}$ as small at $2.0 \times 10^{-3}$ torr, the vapor that coexists with the liquid at $T$ will behave ideally so that $f^L (T, P_{\text{vap}}) = f^V (T, P_{\text{vap}}) \approx P_{\text{vap}}$. If the liquid is considered incompressible, the integral in the Poynting correction becomes:

$$\int_{P_{\text{vap}}}^{P} V^L dP' \approx V^L (P - P_{\text{vap}}) \approx V^L P$$

and the fugacity can be written:

$$f^L (T, P) \approx P_{\text{vap}} \exp \left\{ \frac{P V^L}{RT} \right\}$$

Substituting values I find:

$$f^L (T, P) \approx (2.0 \times 10^{-3} \text{ torr}) \exp \left\{ \frac{(10^8 \text{ Pa})(14.76 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} \right\}$$

or

$$f^L (25 ^\circ \text{C}, 1 \text{ kbar}) = 3.6 \times 10^{-3} \text{ torr} = 4.8 \times 10^{-6} \text{ bar}$$

The activity at this pressure (relative to atmospheric pressure) is equal to the Poynting correction:

$$a^L (25 ^\circ \text{C}, 1 \text{ kbar}) = 1.81$$

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

$$G^{ex}(T, P, n_1, n_2) = a \frac{n_1 n_2}{n_1 + n_2} \quad \text{(5-1)}$$

where $a$ is independent of composition.

(a) Show that this expression is equivalent to $\overline{G}^{ex}(T, P, x_1) = ax_1 x_2$.

(b) Show that, in general, excess chemical potentials and activity coefficients are related by:
\( \mu_i^{ex} = RT \ln \gamma_i \)

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

\[
\gamma_i = \exp(\alpha x_2^2 / RT)
\]

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

\[
V^{ex} = x_1 x_2 \left( \partial a / \partial P \right)_{T,i}.
\]

(a) \( \bar{G}^{ex} = \frac{G^{ex}}{n_1 + n_2} = a \frac{n_1 n_2}{(n_1 + n_2)^2} = a \frac{n_1}{n_1 + n_2} - \frac{n_2}{n_1 + n_2} = ax_1 x_2 \)

(b) Activity coefficients are related to chemical potentials via:

\[
\mu_i = \mu_i^o + RT \ln \gamma_i, x_i
\]

The excess chemical potential is the difference between the chemical potentials in the real and ideal solutions:

\[
\mu_i^{ex} = \mu_i - \mu_i^{IS}
\]

In an ideal solution \( \gamma_i = 1 \) for all \( i \) so that:

\[
\mu_i = \mu_i^o + RT \ln x_i
\]

Inserting Eqs. 5-2 and 5-4 into Eq. 5-3 and canceling like terms yields the desired result:

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

(c) Given the definitions of \( G^{ex} \) and \( \mu^{ex} \) it is clear that

\[
\mu_i^{ex} = (\partial G^{ex} / \partial n_i)_{T,P,n_{j\neq i}}
\]

Differentiating the form provided wrt \( n_1 \):

\[
\mu_i^{ex} = a \left( \frac{\partial}{\partial n_1} \left( \frac{n_1 n_2}{(n_1 + n_2)^2} \right) \right)_{n_2}
\]

\[
= a \left( \frac{n_2}{(n_1 + n_2)^2} - \frac{n_1 n_2}{(n_1 + n_2)^2} \right)
\]

\[
= a \left( x_2 - x_1 x_2 \right)
\]

\[
= ax_2^2
\]

Thus,

\[
\gamma_i = \exp(\mu_i^{ex} / RT)
\]

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

(d) The differential of the Gibbs energy is:

\[
dG = -SdT + VdP - \Sigma_i \mu_i dn_i \]
Because a similar equation will hold for the ideal solution an equivalent expression applies to the Gibbs excess:
\[ dG^{ex} = -S^{ex}dT + V^{ex}dP - \sum_i \mu_i^{ex}dn_i \]
The excess volume is therefore given by the partial derivative:
\[ \left( \frac{\partial G^{ex}}{\partial P} \right)_{T,\bar{n}} = V^{ex} \]
or, dividing by the total number of moles
\[ \left( \frac{\partial \bar{G}^{ex}}{\partial P} \right)_{T,\bar{n}} = \bar{V}^{ex} \].

Differentiating the form of \( \bar{G}^{ex} \) derived in part (a), one has the desired result:
\[ \bar{V}_{ex} = x_1x_2 \left( \frac{\partial a}{\partial P} \right)_{T,\bar{n}} . \]

6. (20 points) The vapor pressure \( P_{tot} \) 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_1 )</th>
<th>( P_{tot} ) / torr</th>
<th>( y_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>0.50</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:
\[ \gamma_i = \frac{y_i P_{tot}}{x_i P_i^*} \]
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. \( \gamma_1(x_1 \rightarrow 0) \) and \( \gamma_2(x_1 \rightarrow 1) \) and \( \frac{\bar{G}^{ex}}{RT} \) at \( x = 0.5 \). Explain your reasoning. [Hint: It is easier to use the RK expansion than the van Laar equations for this problem.]

(a) The activity coefficients in solution are related to solution-phase fugacities by
\[ f_{i,i}^{(sol)} = x_i \gamma_i f_i^* \]
The solution fugacities are equal to the vapor phase fugacities, which for these low pressures can be assumed to be equal to the partial pressures:
\[ f_i^{(v)} \approx P_i^{(v)} = y_i P_{tot} \]

Equating \( f_i^{(sol)} = f_i^{(v)} \), calling the vapor pressures of the pure components \( P_i^* \) and solving for the solution activity coefficients provides:

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

Evaluating for the two components at a mole yields: \( \gamma_1 = 1.50, \gamma_2 = 1.33 \) (at \( x=0.5 \))

(b) No. The activity coefficients in the Margules equation must be equal at a mole fraction of 0.5 so these data are not accurately represented by this equation.

(c) Try the next simplest representation, the RK expansion keeping the first two terms (i.e. \( A, B \neq 0, C=D=\ldots=0 \)):

\[ G_{ex} = x_1 x_2 \{ A + B(x_1 - x_2) \} \]

According to the Topic Summary 10, activities coefficients in such a case can be expressed:

\[ \ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_1^3 \]
\[ \ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3 \]

For a composition of \( x_1=x_2=0.5 \), this pair of equations becomes:

\[ 4 \ln \gamma_1 = A + B \]
\[ 4 \ln \gamma_2 = A - B \]

which is easily solved for \( A \) and \( B \):

\[ A = 2 \{ \ln \gamma_1 + \ln \gamma_2 \} \]
\[ B = 2 \{ \ln \gamma_1 - \ln \gamma_2 \} \]

Inserting the values of \( \gamma_1 \) and \( \gamma_2 \) yields: \( A = 1.386, B = 0.236 \). Using these constants in the two limits desired gives the final results:

\[ \ln \gamma_1 (x_2 \to 1) = A - B; \gamma_1 = 3.16 \]
\[ \ln \gamma_2 (x_1 \to 1) = A + B; \gamma_2 = 5.06 \]

The Gibbs excess at \( x=0.5 \) is \( G_{ex}(0.5) / RT = \frac{1}{4} A = 0.347 \)