1. (6 + 6 points) Two quick questions:
   (a) The *Handbook of Chemistry and Physics* tells us, correctly, that CCl₄ boils normally at 76.7 °C, but its molar enthalpy of vaporization is listed in one place as 34.6 kJ mol⁻¹ and in another as 31.9 kJ mol⁻¹. This handbook also says the CCl₄ vapor pressure is 0.0987 atm at 15.8 °C. Which enthalpy value does this vapor pressure support?

   Let’s stick to atm pressure units here: “boils normally” means $P = 1$ atm. We convert the temperatures to K units, and the Clausius-Clapeyron equation gives us the answer:

   $$\ln \frac{0.0987 \text{ atm}}{1.0 \text{ atm}} = -\frac{\Delta H_{\text{vap}}^0}{R} \left( \frac{1}{288.95 \text{ K}} - \frac{1}{349.85 \text{ K}} \right)$$

   or $\Delta H_{\text{vap}}^0 = 31.96$ kJ mol⁻¹

   (b) A chemist was given a small cylinder of gas by her colleague. The label on the cylinder read: “$P = 23.5$ atm, $V = 0.010$ L, 0.81 g of CF…,” but at that point, a drop of acetone had obscured the label. The chemist knew that the gas was either CF₄ or CF₃H. She used the ideal gas relationship (with $T = 300$ K, the lab’s temperature) and calculates $V_m = RT/P = 1.05$ L mol⁻¹, which let her calculate the molar mass as $(0.81 \text{ g})(1.05 \text{ L mol}^{-1})/(0.010 \text{ L}) = 85$ g mol⁻¹. This is closer to the molar mass of CF₄ (88 g mol⁻¹) than to that for CF₃H (70 g mol⁻¹), and CF₄ is what she assumed she has. Was she justified? Use the van der Waals equation of state’s CF₄ and CF₃H parameters below to find out.

   $$a/\text{atm L}^2 \text{ mol}^{-2} \quad b/\text{L mol}^{-1}$$

<table>
<thead>
<tr>
<th></th>
<th>CF₄</th>
<th>CF₃H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>3.57</td>
<td>5.44</td>
</tr>
<tr>
<td>$b$</td>
<td>0.056</td>
<td>0.064</td>
</tr>
</tbody>
</table>

   We know the mass of the gas, and thus we can calculate the number of moles, $n$, of gas. We calculate $n = 0.81 \text{ g}/88 \text{ g mol}^{-1} = 9.205$ mmol for CF₄ or $n = 0.81 \text{ g}/70 \text{ g mol}^{-1} = 11.57$ mmol for CF₃H. Next, we calculate the pressure the van der Waals equation predicts for each of these possibilities. We find $P = 20.87$ atm for CF₄ (not very close to the observed 23.5 atm) and $P = 23.48$ atm for CF₃H, which is in very good agreement! The sample must have been CF₃H.

2. (3 points each) For each pair of quantities below, the one on the left is either greater than (>), less than (<), or equal to (=) the one on the right. Enter the appropriate symbol (> <, =) in the blanks provided in the middle.

   (a) $\mu(\text{H}_2\text{O(s)}, \ T = 270 \text{ K}) \underline{\quad} \mu(\text{H}_2\text{O(l)}, \ T = 270 \text{ K})$

   Solid water is in equilibrium with liquid water at 273.15 K. Below this temperature, solid water (ice) is the stable phase. That is the phase with the smaller chemical potential.

   (b) $K$ for $\text{I}_2(g) \Leftrightarrow 2\text{I}(g)$ at 400 K $\underline{\quad} K$ for $\text{I}_2(g) \Leftrightarrow 2\text{I}(g)$ at 600 K
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This reaction must be endothermic; a bond is broken. For endothermic reactions, \( K \) increases with \( T \).

(c) \[
\left( \frac{\partial G}{\partial T} \right)_{P} (\text{Ar, 100 K}) \succ \left( \frac{\partial G}{\partial T} \right)_{P} (\text{Ar, 300 K})
\]

\((\partial G/\partial T)_{P} = -S\), and \( S \) increases with \( T \) (for anything).

(d) \[
\Delta G_{f}^{0}(\text{N}_2(g), T = 298 \text{ K}) \equiv \Delta G_{f}^{0}(\text{H}_2(g), T = 298 \text{ K})
\]

These species are both elements in their most stable form at 298 K. Thus, the both have \( \Delta G_{f}^{0} = 0 \).

(e) van der Waals \( b \) const. for He \( \leq \) van der Waals \( b \) const. for SF\(_6\)

The \( b \) constant represents the molar volume of a real gas occupied by the molecules themselves. SF\(_6\) is much bigger than He.

(f) \( \Delta G \) of mixing (ideal solution) \( \leq \) zero

Ideal solutions spontaneously mix in all compositions. (It’s an entropy thing!) Spontaneous means negative free energy change.

3. (12 points) Solid copper(II) bromide, \( \text{CuBr}_2(s) \), vaporizes via the following reaction:

\[
2\text{CuBr}_2(s) \rightleftharpoons 2\text{CuBr}(s) + \text{Br}_2(g)
\]

Studies of the vapor pressure \( P \) of \( \text{Br}_2(g) \) in equilibrium with \( \text{CuBr}_2(s) \) and \( \text{CuBr}(s) \) show that it follows the expression

\[
P = (1.35 \times 10^9 \text{ bar}) e^{-(11,642 \text{ K})/T} \quad 320 \text{ K} \leq T \leq 380 \text{ K}
\]

Find the equilibrium constant \( K \), the reaction free energy change \( \Delta G_{R}^{0} \), the reaction enthalpy change \( \Delta H_{R}^{0} \), and the reaction entropy change \( \Delta S_{R}^{0} \) for this reaction at \( T = 350 \text{ K} \).

At this temperature, 350 K, the expression for \( P \) tells us that \( P = P_{\text{Br}_2} = 4.83 \times 10^{-6} \) bar. But the reaction has an equilibrium constant expression \( K = P_{\text{Br}_2} \) because the other two species in the reaction are pure solids (with unit activity). Thus, \( K = 4.83 \times 10^{-6} \). Next, we use \( \Delta G_{R}^{0} = -RT \ln K \) to find \( \Delta G_{R}^{0} = 35.6 \text{ kJ mol}^{-1} \). We then use

\[
\frac{d\ln K}{dT} = \frac{d\ln P_{\text{Br}_2}}{dT} = \frac{d}{dT} \left[ \ln \left( 1.35 \times 10^9 e^{-(11,642 \text{ K})/T} \right) \right]
\]

\[
= -11,642 \text{ K} \frac{d(1/T)}{dT} = \frac{11,642 \text{ K}}{T^2} = \frac{\Delta H_{R}^{0}}{RT^2}
\]
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or \( \Delta H_{R}^o = (11,642 \text{ K})R = 96.8 \text{ kJ mol}^{-1} \). Finally, we have \( \Delta S_{R}^o = (\Delta H_{R}^o - \Delta G_{R}^o)/T = 175 \text{ J mol}^{-1}\text{K}^{-1} \) (which we note is positive, as expected, for a reaction that produces one mole of gaseous product from no gaseous reactants).

4. (4 + 2 + 4 points) A few more quick questions:
(a) For He\((g)\) at 25 °C, one of the four values in the table below is 126 J mol\(^{-1}\) K\(^{-1}\). Fill in the table with numerical values for all four quantities.

<table>
<thead>
<tr>
<th>Molar enthalpy of formation</th>
<th>Molar standard entropy</th>
<th>Molar free energy of formation</th>
<th>Constant pressure molar heat capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>126 J mol(^{-1}) K(^{-1})</td>
<td>0</td>
<td>( C_P = 2.5R = 20.8 \text{ J mol}^{-1}\text{K}^{-1} )</td>
</tr>
</tbody>
</table>

He is an ideal gas element. Thus, its formation enthalpy and free energy are both zero, and its \( C_P \) is \( 5R/2 = 2.5R = 20.8 \text{ J mol}^{-1}\text{K}^{-1} \). All that’s left is the entropy! (Dimensional analysis would have told you that the value you were given had to be either \( C_P \) or \( S \).)

(b) The gas-phase reaction
\[
3 \text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2 \text{NH}_3(g)
\]
is held at equilibrium at a constant temperature. He\((g)\) is added to the mixture while keeping the total pressure constant. When equilibrium is attained again, the amount of \( \text{NH}_3(g) \) will have (circle one)

- increased
- decreased
- stayed the same

If the total pressure is held constant, the volume of the system must increase as we add helium! This perturbation will drive the reaction back to reactants (to make more moles of gas), meaning some \( \text{NH}_3 \) has been lost.

(c) Explain the trend in entropies of fusion (i.e., of melting), \( \Delta S_{fuss}^o \), for the five linear hydrocarbons, methane through n-octane, listed below in J mol\(^{-1}\) K\(^{-1}\) units.

- methane 10.4
- ethane 31.8
- n-butane 34.6
- n-hexane 73.3
- n-octane 95.9

This increase in \( \Delta S_{fuss}^o \) as the hydrocarbons get “longer and longer” reflects the strong order in the solids (long molecules packed like drinking straws in a box) versus the ever-increasing freedom afforded to the molecules in the liquid phase (where the molecules are free to bend and wiggle around).
5. (20 points) Sketch in the graphs below, as accurately as you can, the qualitative behavior of the chemical potential, $\mu$, the entropy, $S$, the enthalpy, $H$, and the heat capacity, $C_P$, for a pure substance raised in temperature at 1 atm pressure through the normal boiling point, $T_{vap}$.

Plot by plot: the $\mu(T)$ plot has the two curves for the two phases in question cross at the vaporization temperature, and the gas curve has the more negative slope since $(\partial \mu/\partial T)_P = -S$ and $S(g) > S(l)$. The $S(T)$ plot reflects the facts that (1) $S$ always increases with $T$, (2) $S$ increases more rapidly with $T$ for the liquid because $(\partial S/\partial T)_P = C_P/T$ and $C_P(l) > C_P(g)$, and (3) there is a discontinuous jump up in $S$ at the vaporization temperature reflecting the (positive) entropy change on vaporization: $\Delta S_{vap} = \Delta H_{vap}/T_{vap}$. The $H(T)$ plot has similarities to the $S(T)$ with a discontinuous
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jump up due to the enthalpy change on vaporization. The $C_p(T)$ plot reflects (1) the generally larger liquid heat capacity (compared to the gas), (2) the spike to an infinite heat capacity at the phase transition temperature, and (3) the fairly constant value of heat capacity as temperature changes.

6. (10 points) Pyridine ($py$) and acetone ($ac$) are completely miscible as liquids in all proportions near room temperature. Their vapor pressures when pure are (at 300 K, the temperature you may assume throughout this problem)

$$P^*_{py} = 27 \text{ torr} \quad P^*_{ac} = 281 \text{ torr}$$

(a) The partial pressure of acetone over a $py/ac$ solution is 17 torr in a solution for which $x_{ac}$, the mole fraction of acetone in the liquid phase, is $x_{ac} = 0.05$. How can you tell that this solution is not ideal?

Ideal solutions follow Raoult’s law for both components. If acetone followed Raoult’s law, its partial pressure would be

$$P_{ac} = x_{ac}P^*_ac = 0.05(281 \text{ torr}) = 14 \text{ torr}$$

which is not the observed vapor pressure of 17 torr.

(b) While not ideal, this solution follows Henry’s law at and below this acetone concentration. One can show that in a binary solution in the ideal dilute region (which is what we have here), if one component follows Henry’s law, the other component must follow Raoult’s law. With this in mind, tell me two things:

(i) What is the Henry’s law constant for acetone in pyridine?

(ii) What is the total equilibrium pressure of a $py/ac$ solution with $x_{ac} = 0.05$?

(i) Henry’s law (with Henry’s law constant $k_H$) tells us

$$P_{ac} = x_{ac}k_H = 0.05k_H = 17 \text{ torr} \quad \text{or} \quad k_H = (17 \text{ torr})/0.05 = 340 \text{ torr}$$

(ii) If acetone follows Henry’s law, then pyridine follows Raoult’s law, making the total pressure equal to

$$P = P_{ac} + P_{py} = 17 \text{ torr} + x_{py}P^*_py = 17 \text{ torr} + (1 - 0.05)(27 \text{ torr}) = 42.7 \text{ torr}$$

7. (18 points) At 100 °C, the vapor pressures of hexane and octane are 2.416 atm and 0.466 atm. Solutions of these are ideal, i.e., they follow Raoult’s law. One particular solution is mixed and held at 100 °C and 5.00 atm, where it is all in the liquid phase. The pressure is slowly reduced to 1.50 atm, where the system is found to exist as a two-phase (gas-liquid) system.

(a) What is the liquid-phase hexane mole fraction?
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Let’s call hexane component 1. Then, Raoult’s law tells us how the total pressure $P$ is related to the liquid phase mole fraction $x_1$ and the pure component vapor pressures:

$$P = P^*_2 + (P^*_1 - P^*_2)x_1 = 2.416 \text{ atm} + (0.466 \text{ atm} - 2.416 \text{ atm})x_1 = 1.50 \text{ atm}$$

and we find $x_1 = 0.530$.

(b) What is the gas-phase hexane mole fraction?

Now we solve for the gas phase composition mole fraction $y_1$ as follows:

$$P = \frac{P^*_1 P^*_2}{P^*_1 + (P^*_2 - P^*_1)y_1} = \frac{(2.416 \text{ atm})(0.466 \text{ atm})}{2.416 \text{ atm} + (0.466 \text{ atm} - 2.416 \text{ atm})y_1} = 1.50 \text{ atm}$$

which yields $y_1 = 0.854$

(b) It is further found that the ratio of the total number of moles in the liquid phase, $n(l)$, to the total number of moles in the gas phase, $n(g)$, is 1.10. What is the total system composition, i.e., the isopleth composition?

We use the lever rule expression to find the system isopleth composition mole fraction $x$:

$$n(l)[x - x_1] = n(g)[y_1 - x] \quad \text{or} \quad \frac{n(l)}{n(g)} = 1.10 = \frac{y_1 - x}{x - x_1} = \frac{0.854 - x}{x - 0.530}$$

from which we find $x = 0.684$. Here’s the full phase diagram: