1. (25) Given the data below calculate $\Delta G^\circ$ for the phase transition

$I_2(s) \rightarrow I_2(g)$

at 273.15 K (or, 0.00°C) as accurately as possible.

Then use that value to calculate the equilibrium sublimation pressure, in torr, of $I_2(s)$ at 273.15 K.

<table>
<thead>
<tr>
<th>at 25.00°C</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$S^\circ$ (J/mol-K)</th>
<th>$C_p^\circ$ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_2(s)$</td>
<td>0</td>
<td>116.135</td>
<td>54.44</td>
</tr>
<tr>
<td>$I_2(g)$</td>
<td>62.44</td>
<td>260.69</td>
<td>36.90</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\Delta H_{273}^\circ &= (62.44 \text{ kJ/mol}) + (-0.01754 \text{ kJ/mol-K})(-25.00 \text{ K}) \\
&= 62.44 + 0.44 = 62.88 \text{ kJ/mol} \\
\Delta S_{273}^\circ &= 144.56 \text{ kJ/mol-K} + (-17.54 \text{ kJ/mol-K}) \ln \frac{273.15 \text{ K}}{298.15 \text{ K}} \\
&= 144.56 + 1.54 = 146.10 \text{ kJ/mol-K} \\
\Delta C_p^\circ &= (62.88 \text{ kJ/mol}) - (273.15 \text{ K})(0.146 \text{ kJ/mol-K}) \\
&= 62.88 - 39.91 = 22.97 \text{ kJ/mol} \\
P^\circ &= (1 \text{ bar}) \exp \left( \frac{-22.97 \times 10^3 \text{ J/mol}}{(8.3145 \text{ J/mol-K})(273.15 \text{ K})} \right) \\
&= (1 \text{ bar}) \exp (-10.116) \\
&= 4.04 \times 10^{-5} \text{ bar} \left( \frac{750 \text{ torr}}{\text{ bar}} \right) = 0.00703 \text{ torr}
\end{align*}
\]
2. (25) For the following reaction the value of $K_p^\circ$ is 3.42 at 727 K:

$$2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$$

If the initial pressures are $P_{\text{SO}_2} = 0.600$ bar, $P_{\text{O}_2} = 2.000$ bar, and $P_{\text{SO}_3} = 0.000$ bar, what is the equilibrium pressure of $\text{SO}_3$?

This problem must be solved to two significant digits by the method of successive approximations. *Enough intermediate results must be given to show how the problem was solved.*

\[
\begin{align*}
\text{2SO}_2 + \text{O}_2 & \rightleftharpoons 2 \text{SO}_3 \quad (\text{all gases}) \quad K_p^\circ = 3.42 \\
\text{ini} & \quad 0.600 \quad 2.000 \quad 0.000 \quad \text{bar} \\
\Delta & \quad -2x \quad -x \quad +2x \\
\text{equil} & \quad 0.600-2x \quad 2.000-x \quad 2x \\
3.42 = & \quad \frac{(2x)^2}{(0.600-2x)^2 \cdot (2.000-x)} \\
3.42 = & \quad \frac{x^2}{(0.700-x)^2 \cdot (2.000-x)}
\end{align*}
\]

\[
\begin{align*}
\text{if } x & \text{ is too small, then } Q < K_p^\circ \\
0.2 & \quad 2.22 \quad \text{too small} \\
0.22 & \quad 4.25 \quad \text{too large} \\
0.21 & \quad 3.04 \quad \text{too large, but not by much} \\
0.215 & \quad 3.58 \quad \text{too large, but not by much} \\
\text{x closer to 0.215 than to 0.21} \\
\text{so } P_{\text{SO}_3} = 2x = 0.43 \text{ bar}
\end{align*}
\]
3. (25) The normal melting point of 1,1,2,2-tetrachloroethane (167.8 g/mol) is -43°C and its Δ\text{fus}\text{H}^o = 9.3 kJ/mol. The density of the liquid is 1.595 g/mL. What must the pressure be if the melting point is to be raised to 20°C? The density of the solid is 1.955 g/mL.

(When doing this problem it is safe to assume that Δ\text{fus}\text{H}^o and the densities do not change with temperature or pressure).

\[
\frac{-dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}
\]

\[
\int \frac{dP}{\Delta P} = \int \frac{\Delta H}{\Delta V} \frac{dT}{T} \Rightarrow \frac{P_{\text{liq}}}{P_{\text{sol}}} \leq \frac{T_{\text{fus}}}{T_{\text{fus}}} \text{ increases with } P
\]

\[
\Delta P = \frac{-\Delta_{\text{fus}} \text{H}}{-\Delta_{\text{fus}} \text{V}} \ln \frac{T_2}{T_1}
\]

\[
\Delta V = \frac{n}{\Delta_{\text{fus}} \text{V}} = V_{\text{sol}} - V_{\text{liq}}
\]

\[
= \left( \frac{n}{1.955} - \frac{1}{1.595} \right) \frac{\text{mL}}{\text{g}} \left( 10 \frac{\text{L}}{\text{mL}} \right) (167.8 \frac{\text{g}}{\text{mol}}) = -0.0194 \text{ L/mol}
\]

\[
\Delta P = -9.3 \times 10^3 \text{ J/mol} \left( \frac{8.314 \text{ J/mol-k}}{0.08314 \text{ bar-L/mol-k}} \right) \ln \frac{293K}{230K}
\]

\[
1.6 \times 10^3 \text{ bar} = P - 1 \text{ bar} \quad \text{so} \quad P = 1.16 \times 10^3 \text{ bar}
\]

\[
\Delta P = \frac{\Delta H}{\Delta V} \frac{1}{T} \Delta T
\]

\[
= \frac{-9.3 \times 10^3 \text{ J/mol}}{-1.94 \text{ J/mol-bar}} \frac{63K}{230K} = 1.31 \times 10^3 \text{ bar}
\]

\[
\left( \frac{63}{\frac{1}{2} (230 + 293)} \right) = 1.15 \times 10^3 \text{ bar}
\]
4. (25) The Antoine equation is often used to describe the change in vapor pressure with temperature. The equation has the form

\[ \ln\left(\frac{P}{1 \text{ torr}}\right) = A - B \left(T + C\right)^i \]

where the temperature must be given in K. The constants A, B, and C are assumed to be independent of temperature. The Antoine equation is very reliable for 10 torr < P < 1500 torr.

(a) For H_2O the values of the constants are


What is the predicted pressure at 373 K? By how much is that value in error?

(b) What is the expression for the heat of vaporization of the liquid expressed in terms of the constants A, B, and C?

[It may help to remember that vaporization is the equilibrium between a liquid and its vapor. Depending on which version of the formula you have learned for the variation of the equilibrium constant with temperature (which in this case is also the Clausius-Clapeyron equation) it may help to remember that dy/d(1/x) = -x^2(dy/dx)]