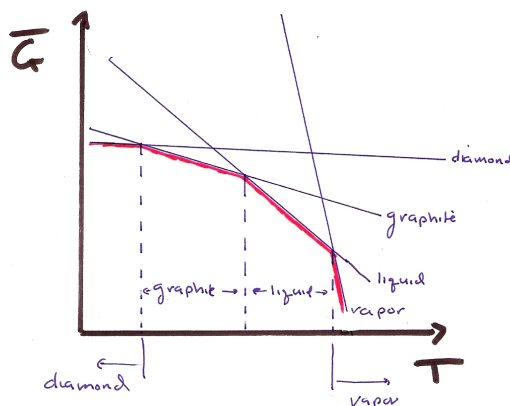


CHEM 3410: Physical Chemistry I — Fall 2009

Homework 7 — Model Solutions

- A triple point is any point where three phases are in equilibrium. There are 2 triple points on the given diagram:
 - Graphite/Vapor/Liquid
 - Graphite/Diamond/Liquid
 - Diamond has a larger density. This can be seen by considering what would happen if you increase the pressure of graphite at constant temperature. The increase in pressure would favor the phase with a lower molar volume (or greater density). According to the diagram, the phase stable would be diamond, meaning it has a larger density.
 You can also reason the same answer by considering the slope of the diamond-graphite equilibrium line. The slope is positive, meaning that $\Delta \bar{V}_{\text{graphite} \rightarrow \text{diamond}} > 0$.
 - To make synthetic diamond, you would want to be a low temperature (below 330°C) and increase the pressure significantly.
 - The stable phase (the one present on the phase diagram) must have the lowest chemical potential. Therefore, the four phases would have the following free energy curves (this is a sketch, not a calculation):



- We have the vapor pressure of the solid (dry ice) at two different temperatures. Using the Clausius-Clapeyron equation we can solve for the enthalpy of sublimation:

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{sub}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{2}{1} = \frac{-\Delta H_{sub}}{R} \left(\frac{1}{203.9 \text{ K}} - \frac{1}{200.8 \text{ K}} \right)$$

$$\Delta H_{sub} = 76.1 \text{ kJ/mol}$$

- The enthalpy of sublimation would be temperature dependent since the heat capacities of the solid and gas phases are different. To determine the temperature dependence you would need to know the different in heat capacities of the solid and gas phase (ΔC_p).
- Much like problem 3, we have the vapor pressure of the solid and liquid at two different temperatures. We can solve for the enthalpy of sublimation and vaporization.

$$\ln \frac{352}{35} = \frac{-\Delta H_{sub}}{R} \left(\frac{1}{161 \text{ K}} - \frac{1}{146.5 \text{ K}} \right)$$

$$\boxed{\Delta H_{sub} 31.22 \text{ kJ/mol}}$$

(b)

$$\ln \frac{1590}{7890} = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{173 \text{ K}} - \frac{1}{193 \text{ K}} \right)$$

$$\boxed{\Delta H_{vap} 22.13 \text{ kJ/mol}}$$

(c)

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

$$\Delta H_{fus} = \Delta H_{sub} - \Delta H_{vap} = 31.22 \text{ kJ/mol} - 22.13 \text{ kJ/mol}$$

$$\boxed{\Delta H_{fus} = 9.09 \text{ kJ/mol}}$$

(d) At the triple point the vapor pressure of the solid equal that of the liquid.

$$\ln \frac{P_{tp}}{35} = \frac{-\Delta H_{sub}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{146.5 \text{ K}} \right)$$

$$\ln \frac{P_{tp}}{7830} = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{193 \text{ K}} \right)$$

$$\ln \frac{7830}{35} = \frac{-\Delta H_{sub}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{146.5 \text{ K}} \right) - \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{193 \text{ K}} \right)$$

Solving for T_{tp} :

$$\boxed{T_{tp} = 170.03 \text{ K and } P_{tp} = 1215 \text{ Pa}}$$

4. To determine the enthalpy of vaporization graphically, we need to plot $\ln P$ vs $1/T$. This comes from the integral form of the Clausius-Clapeyron equation:

$$\frac{dP}{P} = \frac{\Delta H_{vap}}{R} \frac{dT}{T^2}$$

If we do an indefinite integral we get:

$$\ln P = \frac{-\Delta H_{vap}}{R} \frac{1}{T} + \text{constant}$$

A plot of $\ln P$ versus $1/T$ will yield a straight line with a slope of $\frac{-\Delta H_{vap}}{R}$. Using the plot shown below, the best-fit line yields a slope of -2443.7.

$$\Delta H_{vap} = 2443.7 * 8.314 = 20317 \text{ J/mol}$$

$$\boxed{\Delta H_{vap} = 20.3 \text{ kJ/mol}}$$

Enthalpy of vaporization determination (Engel & Reid 8.10)

