Chemistry 311

Physical Chemistry

Homework Assignment # 6

Due: Monday, October 25, 2004

1. For uranium hexafluoride, the vapor pressure (in Pa) for the solid and liquid are given by

$$\ln p_s = 29.411 - 5893.5/T$$

$$\ln p_l = 22.254 - 3479.9/T$$

where T is in units of Kelvins. Calculate the temperature and pressure of the triple point.

2. The heats of vaporization and of fusion for water are 2490 J g^{-1} and 333.5 J g^{-1}, respectively, at 0 °C. The vapor pressure of water at 0 °C is 611 Pa. Calculate the sublimation pressure of ice at −15 °C, assuming that the enthalpy changes are independent of temperature.

3. Water is one of the very few substances (in fact, I don't know of another) for which the slope of the solid-liquid boundary on the phase diagram (see Fig. 5.1), dP/dT, is negative. Make a sketch of this diagram to answer the questions below. (Note that the temperature axis is not at all to scale. The distance between 273.15 and 273.16 K is greatly exaggerated while the distance between 273.16 and 373.15 K is greatly compressed.) Consider a system of liquid water and ice in equilibrium at a temperature of 273.155 K and 0.611 kPa.

   (a) Mark the position of the system on the phase diagram.

   (b) What do you expect to see when pressure is increased gradually to 101.325 kPa, holding temperature constant. Draw the variation of the system's position on the phase diagram as a result of this process.

   (c) Recall Le Chatelier's principle for chemical equilibria. Can you relate this principle to what is happening in this example, even though no reaction is taking place? [Hint: the answer may have something to do with why ice floats on water.]

   (d) The solid-liquid equilibrium for carbon dioxide has a positive slope. Will solid CO_2 float on liquid CO_2? Why, or why not?