Physics 408 Problem Set 10 Due Tues, Nov 23 at beginning of class

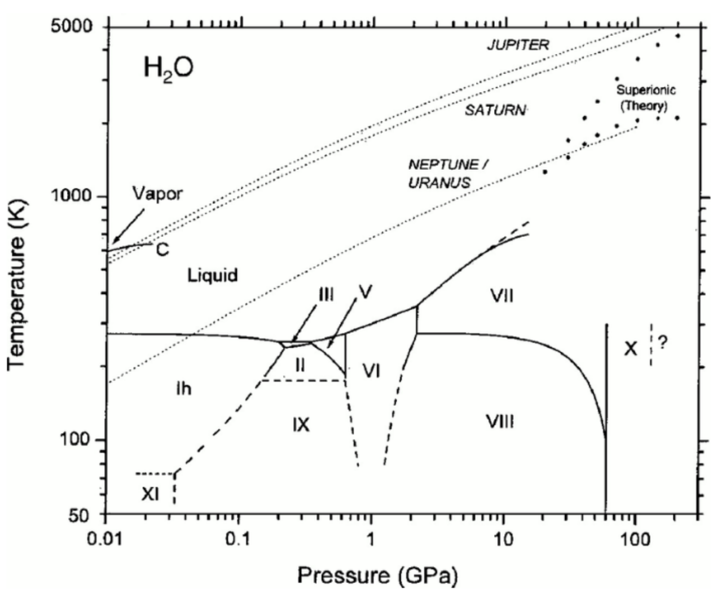
1) Callen problem 9.3.5.

2) Callen problem 9.2.1

3) Callen problem 9.4.7, with the addition:
Once having calculated the reduced pressure and volume for the condition $T = 0.95\ T_c$, calculate the difference, at the pressure where the transformation occurs, between the chemical potential of the stable liquid (& gas) at the transformation point and that of the unstable continuation of the van der Waals equation at the same pressure and temperature. (This is the difference from D to K in fig. 9.10 of the text.) You will have to do a numerical integral to get this, however note that the *VdP* integration is more easily treated by a difference of *PdV* integrations, see example 2 in that section of the text.

4) Sulfur exists has two solid forms at ambient pressure, rhombic and monoclinic. Rhombic is stable at low temperatures, and transforms to monoclinic at 95° C. The monoclinic solid melts at 120° C.
a) Make a plot showing the Gibbs free energy per mole of these three phases vs. temperature.
b) Assuming that the two solid phases can exist as metastable supercooled and superheated forms, which has the higher melting point?
c) Which solid has the higher entropy?
d) Assuming that the Debye model applies to both solids, which has the larger Debye temperature?
e) The monoclinic solid form has the larger molar volume. If the pressure is increased above 1 atm, will the 95° C transformation increase or decrease in temperature, or stay the same?

5) The figure shows a phase diagram for H_2O (from Hemley, Ann. Rev. Phys. Chem. (2000) 51, 763. The figure also shows conditions within the dense atmospheres of some outer planets.). The dashed curves are not known with great accuracy, it can be difficult to establish equilibrium between solid phases.



(a) Which phase has the largest density, ice VIII or ice VII?
(b) Which phase has the largest entropy, under conditions where they can coexist in equilibrium, ice VIII or ice VII?
(c) Will crystals of any of the solid phases sink when formed from liquid water? (ref: *Cat's Cradle*, Kurt Vonnegut).
(d) The phase boundaries between Ice VIII & X, and XI & IX, appear vertical at the lowest temperatures. Explain why these curves are

required to be vertical, extrapolated to $T = 0$ (or at least expected to have this property under most conditions).
(e) Ice Ih is the familiar form of ice that occurs at ambient pressure. The boundary between this phase and ice IX has a large slope in the PT diagram; what property of ice that I discussed earlier in the term is responsible for this result?

6) A single-component substance such as the van der Waals gas will exist at a stable equilibrium at a constant pressure and temperature. The condition for such an equilibrium is that the Gibbs free energy is a minimum.
a) Consider the case that a small fraction α of a substance experiences a spontaneous small change in volume, with the temperature held fixed. In order that the substance would return to its stable equilibrium, with the volume fluctuation decaying to zero, write down the expected conditions on the first and second derivatives of G. Show that the first derivative condition reproduces the familiar criterion for mechanical equilibrium between α and the rest of the system.
b) Show that the second derivative condition leads to a specification that the compressibility must have a positive value. Note that this also reproduces a condition obtained in chapter 8 (see page 210).
c) From the stability criterion obtained in part b, identify a region of the van der Waals PV diagram inside of which the curves obtained from the equation of state are locally unstable against fluctuations. Explain by sketching an isotherm and showing where this boundary crosses. The metastable supercooled or superheated phases cannot extend inside this unstable region, the boundary of which is called the *spinodal*. Which points in figure 9.10 correspond to points on the spinodal boundaries? Explain how you identify these points.