Problem Set 6
(due Monday, March 9)

1. **For formal written solution:** Problem 5.32, page 174. Remember that L in this section of the book represents the *total* heat needed to accomplish the phase transformation (for a given amount of the substance), not the heat per unit mass. As usual, please compose a self-contained narrative that goes through the steps of this problem, introducing each idea in your own words. Parts (c) and (d) ask you to apply the result in two very different situations. Please choose whichever of these two parts seems more interesting to you; you needn't do both (although you're welcome to if you like).

Additional problems:

2. Problem 5.1, page 152. This problem is mostly tedious arithmetic, but it's important to help give a concrete feel for these abstract quantities. Don't worry that the free energies come out to be negative.

3. Problem 5.5, pages 155–156. (Please assume that the water comes out of the cell in liquid form.)

4. Problem 5.8, page 158.

5. Fuel cells ordinarily become hot as they operate. To see how this can affect their efficiency, consider a hydrogen fuel cell (as described in the text) that is operated at $90°C$ instead of room temperature. Thanks to the thermodynamic identity for G, you can still use the room temperature data at the back of your textbook to make an estimate of this fuel cell's maximum efficiency. It is convenient to first establish a zero-point of G for each substance. Please take G for both H_2 and O_2 to be zero at $25°$, so that G for one mole of H_2O is -237 kJ at $25°C$.

   (a) Using these conventions, estimate the Gibbs free energy of a mole of H_2 at $90°C$. Repeat for O_2 and H_2O.

   (b) Using the results of part (a), calculate the maximum electrical work done by the cell at $90°C$, for one mole of hydrogen fuel. Compare to the ideal performance of the cell at $25°C$.

6. The tendency of F to decrease applies even to microscopic systems, as long as we remember that it's true only on average, thanks to thermal fluctuations. Consider, then, a system consisting of a single cyanogen (CN) molecule, which has a single ground state and *three* degenerate rotational first-excited states, whose energies are higher than the ground state by 4.7×10^{-4} eV. We can then assign the first excited level a multiplicity of 3 and an entropy of $k \ln 3$. Given these values, for what range of temperatures is F for the first excited level less than F for the ground state? Discuss the implications briefly, for CN molecules in cold interstellar molecular clouds.

7. Use the Interactive Molecular Dynamics simulation to map out a portion of the phase diagram for this two-dimensional Lennard-Jones fluid. I suggest keeping N fixed at 500 or more, then adjusting the temperature and volume to find the various conditions under which two phases can coexist in equilibrium. It's probably easiest to start at a large volume and low temperature, so the system consists of a single solid crystal surrounded by a low-density gas. Then add energy gradually, letting the system equilibrate at various temperatures and noting the temperature and pressure after each equilibration. (You can use the Data panel to record the temperature and pressure data in a format that can be copied into a spreadsheet for plotting. Be sure to let the system equilibrate at each setting before recording your data, using the Reset button as appropriate.) Map out as much of the vapor pressure curve as you can, making a note of the approximate triple point temperature at which the solid crystal melts into a liquid. For extra credit, you might also try to locate the critical point (which occurs only at a precise density value) and/or explore the solid/liquid phase boundary line (which shoots up to very high pressures, but is easier to plot on the same diagram if you keep the pressures reasonably low). Plot all your phase boundary data in a spreadsheet and label the various phases and special points on your graph. Turn in a table of your numerical data as well, and add complete explanations of your methods and observations. This numerical "experiment" is surprisingly rich and subtle, so consider it an opportunity to exercise your creativity and thinking skills!

8. Problem 5.28, page 171.

9. Problem 5.30, page 172. This question looks like it should be easy, but isn't. Take your time and think carefully about which of the three curves must be lower at each temperature, as well as the slopes and curvatures of the curves.

10. Problem 5.35, page 175. (Again, remember that L in this section is the total heat required for the transformation, not the heat per unit mass.)

11. Problem 5.36, page 175, parts (a) and (b). Please use a computer to make a quantitatively accurate plot—not just a sketch. I suggest using Mathematica. Use the data at either $50°$ or $100°$ to determine and plot the curve, and then see how accurate your prediction is at the other end.