1. Can you identify in the two figures below what are all the symmetry operations that transform the collection of blue motifs into itself ? Using your textbook, can you label them according to the international notation ? (Note: in the left figure, there are 6 spirals; the top 3 lie at the same height, and the bottom 3 lie at another, common height).
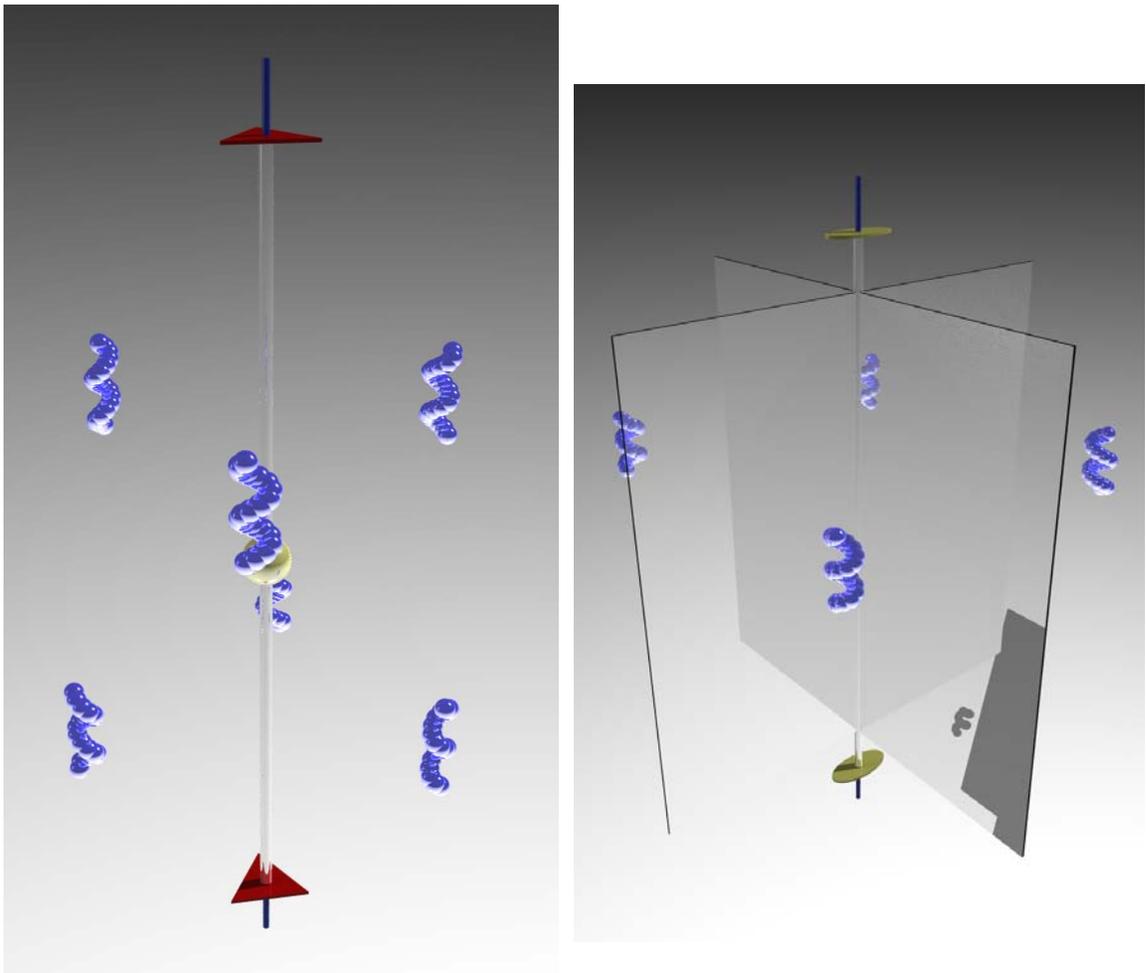
Courtesy of Marc De Graef. Used with permission.

2. Allen-Thomas Problem 3.5 (pag. 202), excluding question (f).

3. Allen-Thomas Problem 3.12 (pag. 205).

4. For a given primitive cell volume V, which monoatomic crystal will have its nearest neighbours furthest away, between simple cubic, bcc, and fcc ?

5. **Electrochemistry**.

   a. What voltage is measured across the electrodes of a Zn/Cu Daniell galvanic cell once its electrochemical reaction comes to equilibrium? (Show why).

   b. Engel and Reid, problem P11.13.

6. **Thermodynamics of a car battery**. The standard lead-acid rechargeable battery used throughout the automotive industry is shown schematically below. It consists of a lead and lead oxide electrode immersed in aqueous sulfuric acid. The reactions at each electrode are:

$$Pb_{(s)} + H_2SO_{4(aq)} \leftrightarrow PbSO_{4(s)} + 2H^+_{(aq)} + 2e^-$$

$$PbO_{2(s)} + H_2SO_{4(aq)} + 2H^+_{(aq)} + 2e^- \leftrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$
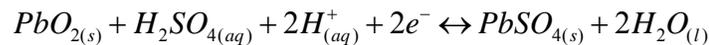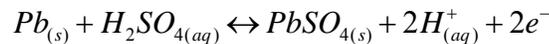
The overall reaction for this galvanic cell is:

$$PbO_{2(s)} + Pb_{(s)} + 2H_2SO_{4(aq)} \leftrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$
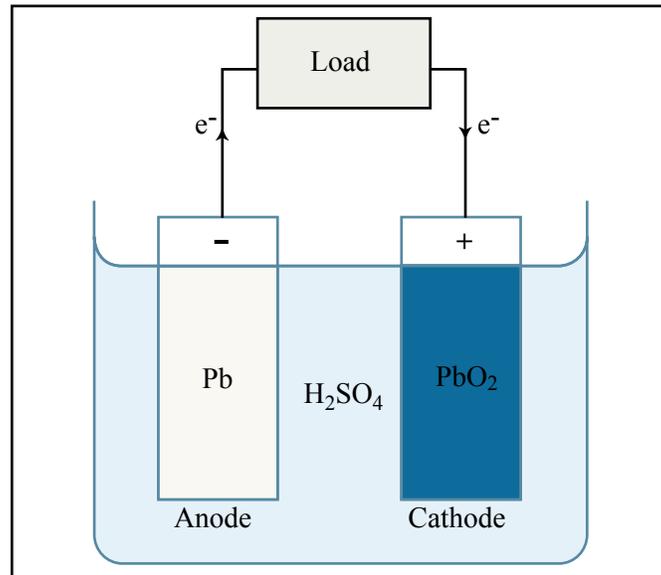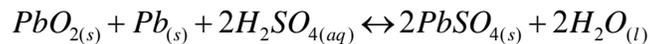
Figure by MIT OCW.

   a. Write an expression for the EMF of the lead acid battery as a function of physical constants, temperature, and the activities of components.

   b. The standard potential of the lead-acid battery E^o = 2.09V at 298 K. If the activity coefficient of 0.1 M H_2SO_4 is 0.0329 and the water present in the sulfuric acid solution can be assumed to have an activity ~1, determine the voltage expected across the terminals of a battery containing 0.1 M sulfuric acid as the liquid electrolyte.

7. **Stability of a closed system at constant temperature and pressure**.

a. Let's determine the shape of G (Gibbs free energy) vs. P (pressure) curves. What thermodynamic parameter(s) are related to $\left(\dfrac{\partial G}{\partial P}\right)_{T,n}$? From this relationship, what is the slope of G vs. P?

b. Now, what about the curvature of G vs. P: What thermodynamic parameters are related to $\left(\dfrac{\partial^2 G}{\partial P^2}\right)_{T,n}$, and what can you say about the curvature of G vs. P, based on your knowledge of property requirements for stability? Draw a qualitative sketch of what G vs. P must look like using your information from (a) and (b).

c. What are the two inequalities that must be satisfied by the Gibbs free energy for a system to be at a stable equilibrium with respect to fluctuations in temperature (all other variables held constant) or pressure (all other variables held constant)?

d. For the system to be stable against arbitrary simultaneous fluctuations in both temperature and pressure, what inequality must the second derivative of Gibbs free energy, d^2G satisfy?

e. Write out the expression for d^2G and show that the stability requirement on d^2G is equivalent to the condensed expression:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)\left(\frac{\partial^2 G}{\partial P^2}\right) - \left(\frac{\partial^2 G}{\partial T \partial P}\right) \geq 0$$

8. **Understanding single-component phase diagrams**. The phase diagram of carbon is shown below, along with some physical data for two different forms of carbon, diamond and graphite. Use this data to answer the questions below.

a. The phase boundary between diamond and graphite at T = 298 K occurs at P = 14,300 atm. What is the free energy change to transform 1 mole of graphite to diamond at this temperature and pressure?

b. Recall that $\left(\dfrac{\partial G}{\partial P}\right)_{T,n} = V$, and thus $\left(\dfrac{\partial \Delta G}{\partial P}\right)_{T,n} = \Delta V$ for a process where volume change occurs. Calculate the free energy change to transform 1 mole of graphite to diamond at 298 K, assuming the volume change in transforming from graphite to diamond is approximately independent of pressure at this temperature.

c. Using the information provided in the phase diagram, draw a qualitatively correct diagram G vs. T of the molar free energies of all relevant phases of carbon at a fixed pressure of 100 atm over the temperature range 1000-5000 K.

d. Does liquid carbon have a greater molar volume than graphite at the melting point of graphite at 1 atm pressure? Does liquid carbon have a greater molar volume than graphite at the melting point of graphite at 100 atm? Show why.
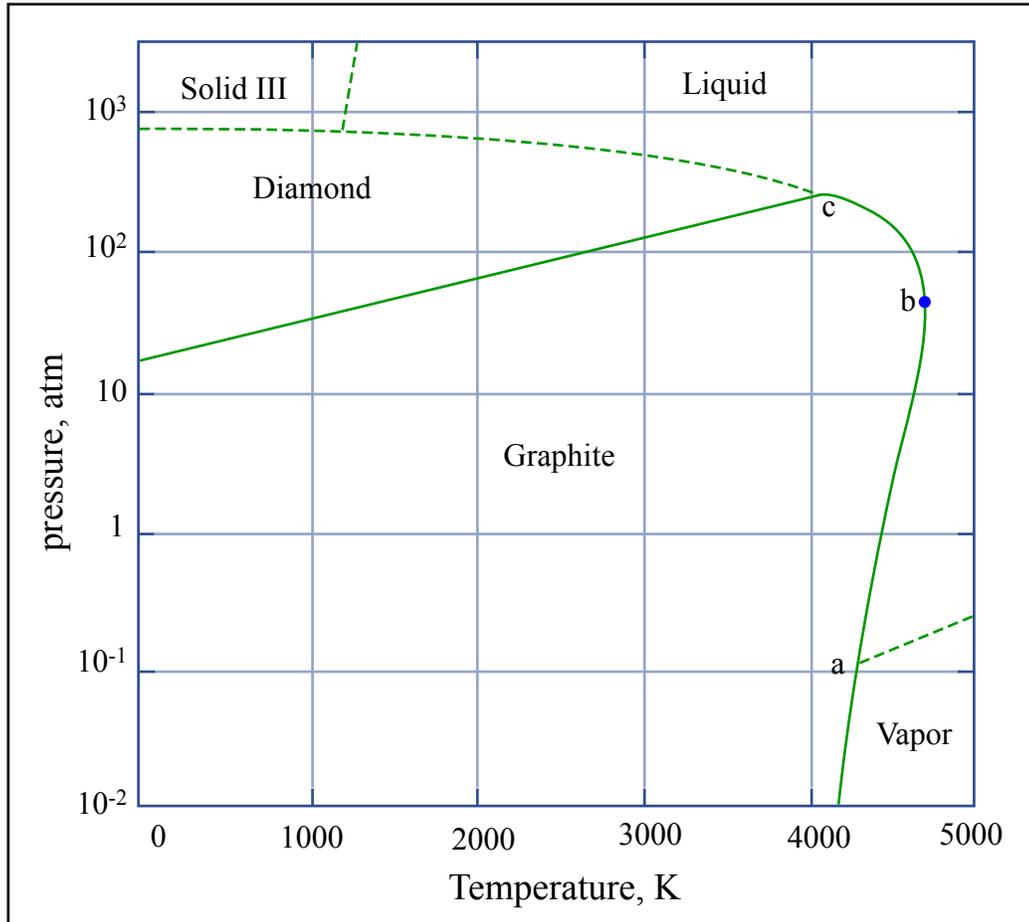
Figure by MIT OCW.

(Gaskell)

$$\rho_{graphite}(298K) = 2.22 \frac{g}{cm^3}$$

$$\rho_{diamond}(298K) = 3.515 \frac{g}{cm^3}$$

Modified from Gaskell, Introduction to Metallurgical Thermodynamics (Hemisphere, New York, 1981) Ch. 7 p. 185