

1. **Point Group Symbols.** There exist four two-dimensional point groups that are derived by the addition of a mirror line through one of the four crystallographic rotation axes 2, 3, 4, and 6. The symbols used to name the result are  $nmm$  except when  $n$  is a 3-fold axis. The symbol used is then only  $3m$ . What is the reason for this?
  
2. **Group Theory.** Let's consider the point group  $4mm$ .
  - a. Sketch the arrangement of symmetry elements in the group and a representative pattern of motifs that conforms to this symmetry.
  - b. Identify the set of operations that is present in this group, labeling the rotation operations  $A_{\pi/2}$ ,  $A_{\pi}$  and so on, as needed. Similarly, label the reflection loci  $\sigma_1$ ,  $\sigma_2$ , ... as needed. Show, by construction of the group multiplication table, that this set of operations constitutes a group.
  - c. Show that the number of motifs in the pattern is the same as the rank of the group. In addition, show that if one adds an initial motif to the point group, that the elements of the group specify how that initial motif is related to all of the other motifs that are present.
  
3. **Tensor properties.** A particular crystal is orthorhombic with a lattice in which the three orthogonal lattice translations have values  $a = 10.2 \text{ \AA}$ ,  $b = 12.5 \text{ \AA}$ ,  $c = 4.8 \text{ \AA}$ . The electrical conductivity tensor relates the current density vector,  $J$  (charge/unit area unit time) to an applied electric field  $E$  (volts/meter):

$$J_i = \sigma_{ij} E_j$$

The electrical conductivity tensor for the crystal described above is:

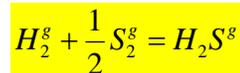
$$\sigma_{ij} = \begin{bmatrix} 6 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 10 \end{bmatrix} 10^{-6} \text{ ohm}^{-1} \text{ m}^{-1}$$

Relative to a coordinate system in which  $x_1$ ,  $x_2$ ,  $x_3$  are taken along the directions of  $a$ ,  $b$ , and  $c$  respectively.

- a. What current density vector is produced by the application of a field of  $10^2$  volts/m along  $[111]$  of the crystal?

- b. What is the angle between  $\vec{J}$  and  $\vec{E}$ ?
- c. What is the magnitude of the conductivity of the crystal along [111]?

4. **Gas-phase reactions.** Free energy changes can be measured experimentally by measuring the concentrations of reactants/products at equilibrium (or partial pressures, in the case of gases). Let's demonstrate this. Suppose a (closed) container initially containing one mole of hydrogen gas and one mole of disulfide gas is allowed to equilibrate at various temperatures (at constant pressure  $P = 1$  atm), and the mole fraction of hydrogen sulfide formed is measured at each temperature.  $H_2S$  gas forms from the reaction of hydrogen and sulfur according to the reaction:



The following measurements were taken in the range of  $T = 1000$ - $2000$  K:

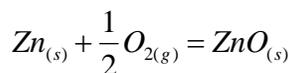
T (K)	$n_{H_2S}$
1200	0.94
1300	0.905
1400	0.814
1500	0.72
1600	0.675
1700	0.57
1800	0.455

- a. What is the relationship between the moles of each gas present as the reaction proceeds? Write an expression for the equilibrium constant of the reaction in terms of  $n_{H_2S}$ , the moles of hydrogen sulfide present for the case of initial conditions as given above.
- b. Using the measured data, determine an expression for molar free energy of formation of hydrogen sulfide as a function of temperature, and plot this quantity vs. temperature over the temperature range given above.
- c. What is the total free energy change in the system if 1 mole of  $H_2$  and 1 mole of  $S_2$  at  $T = 1400$  K reacts to form 0.5 moles  $H_2S$ ? Is this the final equilibrium state of the system? (Explain why or why not).

5. **Oxidation/reduction of materials during processing and fabrication.**

- a. You have a sample of zinc oxide exposed to an atmosphere containing oxygen at a pressure of 0.02 atm and an initial temperature of 1200 K. Would this sample spontaneously reduce to pure zinc at this temperature and oxygen pressure? (Show why). If the ZnO is stable at this temperature, to what temperature would we need to heat the oxide to begin reducing ZnO to pure zinc metal? The following thermodynamic data is available:

For the reaction:

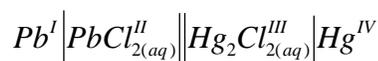


...the standard state reaction free energy  $\Delta \bar{G}_{rxn,o}$  in the forward direction is:

$$\Delta \bar{G}_{rxn,o} = -482,920 - 18.8T \ln T + 344.7T \quad T = 1170-2200 \text{ K}$$

- b. The oxide form of many metals is the thermodynamically favored state of the metal when exposed to oxygen atmospheres. This explains why studies of pure metals are often carried out in vacuum ovens: to lower the oxygen partial pressure and avoid oxidation reactions that can change the state of the sample of interest. Consider again the reaction above: if we have a sample of pure zinc metal at  $T = 1200 \text{ K}$ , to what value would the oxygen pressure need to be reduced to avoid oxidation of the sample?

6. **Electrochemical cells.** A Daniell electrochemical cell is prepared with the structure:



...where the vertical lines designate separations between the phases I-IV of the cell; the double line represents the membrane separating the two aqueous electrolyte solutions (phases II and III). The EMF of the cell is 0.5357 volts at 25°C.

- What are the half-cell reactions for this battery?
- What is the maximum amount of work that can be extracted from this battery at 25°C?
- The mercury electrode in the cell is replaced by an Hg-**X** alloy in which  $X_{\text{Hg}} = 0.3$  and **X** is an inert component that *does not participate* in the cell reactions. The EMF of the cell is

found to increase by 0.0089 volts. Calculate the activity and activity coefficient of Hg in the alloy at 25°C.

7. **Stability requirements in materials.** We showed in lecture 15 that by expanding the internal energy in a Taylor series around the equilibrium point, we could derive constraints on the values of certain materials properties that must be met for a material to be in a stable state. We can derive additional materials constraints from our other primary thermodynamic functions as well. Let's do this for the Helmholtz free energy:

- a. For a system where there is no molecule transfer or reaction, the Helmholtz free energy is:

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dF = -PdV - SdT$$

The Helmholtz free energy of a system is minimized at equilibrium. Write the first few terms of the Taylor expansion  $\delta F(\mathbf{T}, \mathbf{V})$  at the equilibrium point of a system as a function of T and V as we did in class for the internal energy, and show that one of the requirements for stable equilibrium is:

$$\left( \frac{\partial^2 F}{\partial V^2} \right) \geq 0 \text{ for stable equilibrium}$$

- b. Given the stability requirement in part (a), show that this requirement means that the isothermal compressibility of materials,  $\kappa$ , must be positive:

$$\kappa \geq 0$$