3.012 PS 5 **3.012**

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Optional problems:

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 ***n****mm* 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_{π} and so on, as needed. Similarly, label the reflection loci σ_1, σ_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 Å, *b* = 12.5 Å, *c* = 4.8 Å. 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. Write the direction cosine schemes for a transformation of axes that corresponds to:

   a. Rotation by $\pi/2$ about the x_2 axis.

   b. Reflection in the x_1-x_2 plane.

   c. Rotation by $2\pi/3$ about the [111] direction of a cubic crystal.

5. Show that the operation of inversion imposes no restrictions on the form of a second-rank tensor property.

6. **Gas-phase reactions**. What is the equilibrium state of a CO-CO_2-H_2-H_2O gas mixture produced by mixing CO_2 and H_2 in the molar ratio 1:1 at 1000 K and a total pressure of 1 atm? The reaction which occurs is:

$$CO_2 + H_2 = CO + H_2O$$

The standard state free energy change for the reaction as a function of temperature is:

$$\Delta\overline{G}_{rxn,o} = 36{,}000 - 32T \text{ Joules/mole CO or } H_2O \text{ produced}$$

7. **Preventing oxidation.**

   a. The following data have been obtained for the oxygen potentials corresponding to the coexistence of the two oxides CuO and Cu_2O:

T (K):	1173	1223	1273	1303	1350
P_{O2} (atm):	0.0208	0.0498	0.1303	0.225	0.504

In general, the standard state free energy change of a reaction can be expressed as:

$$\Delta\overline{G}_{rxn,o} = \Delta\overline{H}_{rxn,o} - T\Delta\overline{S}_{rxn,o}$$

Using the data given above, estimate $\Delta\overline{H}_{rxn,o}$ and $\Delta\overline{S}_{rxn,o}$ of the reaction:

$$2CuO_{(s)} = Cu_2O_{(s)} + \frac{1}{2}O_{2(g)}$$

…and express its $\Delta\overline{G}_{rxn,o}$ as a function of temperature.

b. A sample of copper sheet has to be annealed (incubated at a high temperature, which allows the atoms in the sample to re-arrange, e.g. to improve crystal perfection). In order to prevent oxidation of the copper during the heat treatment, it must be performed in a vacuum (which is produced by pumping air out of the gas-tight heat-treatment furnace). If it is required that the heat treatment be carried out at 650°C, calculate the maximum total pressure (i.e., the poorest vacuum) that can be tolerated. Could a vacuum of 10^{-4} atm be used at any temperature? The standard state free energy of reaction of the reactants is:

$$2Cu_{(s)} + \frac{1}{2}O_{2(g)} = Cu_2O_{(s)}$$

$\Delta G_{rxn,o} = -169{,}000 - 7.12T\ln T + 123T$ (valid for T=298K to 1356 K)

8. Mortimer problem 8.28.

9. Mortimer problem 8.29.

10. **Decomposition of silica**. Consider the reduction of SiO_2 to Si by heating at P = 1 atm. At what temperature will the reduction take place, and what will the pressure of CO (gas) be if the reaction takes place at 740°C? The reaction of interest is:

$$3SiO_{2(s)} + 4C_{(s)} = 2CO_{(g)} + 2CO_{2(g)} + 3Si_{(s)}$$

The following data have been measured:

$$Si(s) + O_{2(g)} = SiO_{2(g)} \qquad \Delta\overline{G}_{rxn,o} = -94,556 + 174T \frac{J}{mole\_O_2} \quad \text{(700-1700K)}$$

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \qquad \Delta\overline{G}_{rxn,o} = -394,100 - 0.84T \frac{J}{mole\_O_2} \quad \text{(298-2000K)}$$

$$2C_{(s)} + O_{2(g)} = 2CO_{(g)} \qquad \Delta\overline{G}_{rxn,o} = -223,400 - 175.3T \frac{J}{mole\_O_2} \quad \text{(298-2500K)}$$