THERMODYNAMICS (4 problems, 50 points total).

Physical Constants:
Gas constant: R = 8.3144 J/mole-K = 0.082057 L-atm/mole-K
Faraday constant F = 96,485 C/mole
Unit conversion: C * V = Joules

1. **Thermodynamic logic. [3 parts, a-c]** Answer the questions below with brief statements and/or equations as necessary.

    a. Explain why using the Gibbs free energy to solve for equilibrium states of a system (under appropriate conditions) is easier than directly applying the second law and considering entropy changes only.

The second law is satisfied for systems at constant temperature and pressure if the Gibbs free energy of the system is minimized. Calculating the minimum in free energy for the system **only** is significantly simpler than determining the maximum in entropy for the system **and** its surroundings (which is required to determine equilibrium from the entropy point of view).

    b. If a closed binary system of gold and nickel at fixed temperature and pressure comes to two-phase equilibrium with 40 mole% of the system as a liquid solution and 60 mole% as a solid solution, what equations must the chemical potentials of gold and nickel satisfy?

The chemical potential of each component must be the same in each phase:

$$\mu_{Au}^{liquid} = \mu_{Au}^{solid}$$
$$\mu_{Ni}^{liquid} = \mu_{Ni}^{solid}$$

c. Suppose two components A and B form an ideal solid solution. At P = 1 atm and T = 400 K, the free energy of the solution has the shape shown below. For a composition $X_B = 0.3$, is the chemical potential of A in the solution greater than, less than, or equal to the chemical potential of B? Mark the chemical potentials of A and B in the solution for $X_B = 0.3$ on the diagram.
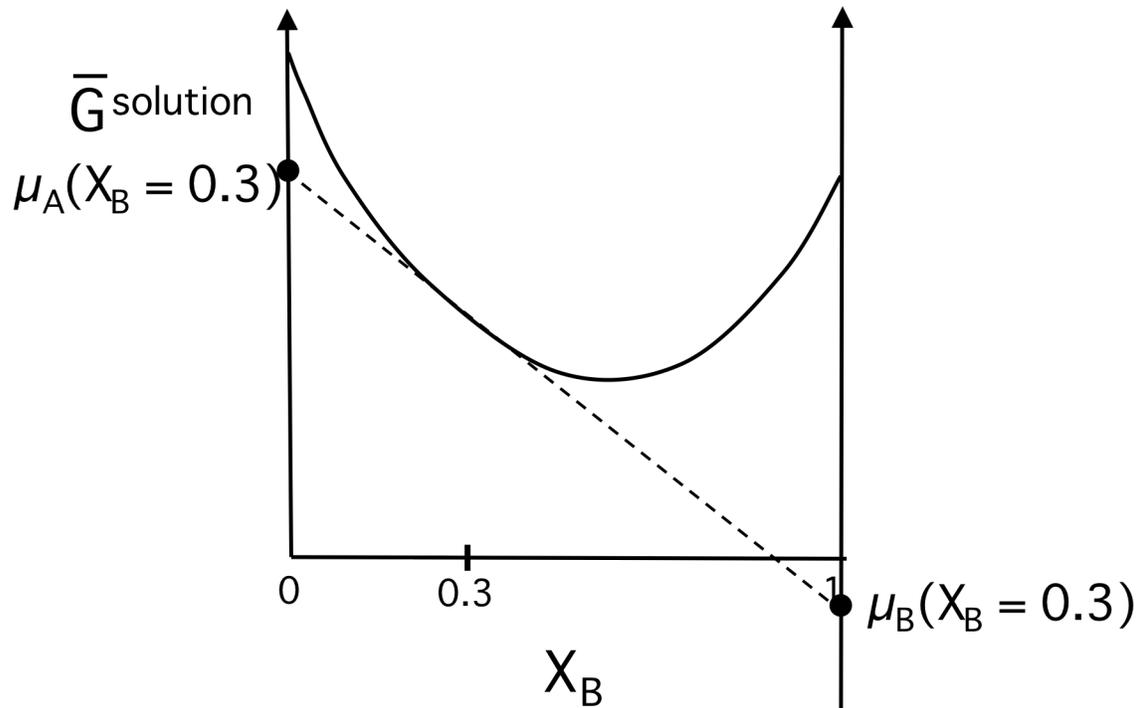
SOLUTION:

The chemical potentials are graphically obtained as the $X_B = 0$ and $X_B = 1$ intercepts of the tangent to the solution free energy curve at $X_B = 0.3$ (below). From this graphical construction and the fact that $\overline{G}^{solution}$ and the chemical potentials are typically < 0, we would have $\mu_A > \mu_B$ or $|\mu_B| > |\mu_A|$.

2. **Oxidation of silicon. [2 parts, a and b]** Crystals of pure silicon grown at high temperature as large cylinders are cut into thin 'wafers' that are the starting materials for modern microelectronics. When pure silicon crystals are exposed to air at room temperature, they rapidly react with oxygen to form a thin (~1-2 nm-thick) oxide layer at their surface. The free energy of this reaction has been empirically measured, and has the following linear dependence on temperature:

$$Si_{(s)} + O_{2(g)} \leftrightarrow SiO_{2(s)}$$

$$\Delta \overline{G}^o_{rxn} = -902,000 + 174T \, \frac{J}{mole}$$
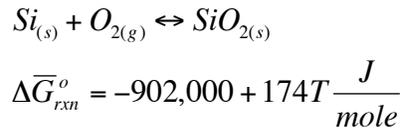
…where T in the above equation is temperature in K.

a. Assume that the air is to first order a mixture of 80 mole% nitrogen and 20 mole% oxygen behaving as ideal gases (P = 1 atm). Show that the oxidation of silicon is spontaneous at 25°C in air.

SOLUTION:

a. For the oxidation to be spontaneous, the free energy change for the reaction must be less than zero:

$$\Delta \overline{G}_{rxn} < 0$$

$$\Delta \overline{G}_{rxn} = \Delta \overline{G}^o_{rxn} + RT \ln \frac{a_{SiO_2}}{a_{Si} \left(\dfrac{P_{O_2}}{P^o} \right)}$$

Using the standard approximation that the activities of the **pure** solids are 1 (remember that the activity of solids/liquids in general is not 1 if they are not pure, single-component materials!), we have:

$$\Delta \overline{G}_{rxn} = \Delta \overline{G}^o_{rxn} + RT \ln \frac{P^o}{P_{O_2}}$$

Using the definition of partial pressure, we can determine P_{O2}:

$$P_{O_2} = X_{O_2} P = 0.2(1atm) = 0.2atm$$

At T = 298 K and P = 1 atm:

$$\Delta \overline{G}_{rxn} = \Delta \overline{G}^o_{rxn} + RT \ln \frac{P^o}{P_{O_2}} = -902,000 + 174(298) + (8.3144)(298) \ln \left(\frac{1atm}{0.2atm} \right) = -846 \frac{kJ}{mole}$$

Thus, the reaction is spontaneous.

b. In order to preserve the native Si surface without oxidation, your colleague suggests placing the Si crystal in a vacuum chamber that can lower the oxygen partial pressure to $P_{O2} = 1\times10^{-8}$ atm. Would this condition be sufficient to block spontaneous oxidation of the crystal at T = 500 K?

SOLUTION:

b. Oxidation will be stopped if the oxygen partial pressure is low enough to tip the free energy of reaction from negative to positive (the balancing point occurs when the free energy change for the reaction is exactly zero):
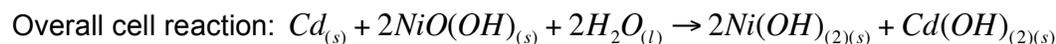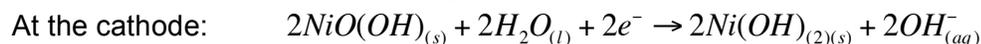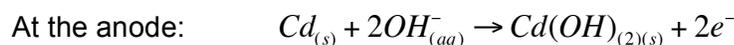
$$\Delta\overline{G}_{rxn} = \Delta\overline{G}_{rxn}^{o} + RT\ln\frac{P^o}{P_{O_2}} = 0$$

$$-815,000\,\frac{J}{mole} + (8.3144)(500)\ln\frac{1}{P_{O_2}} = 0$$

$$\therefore P_{O_2} = 7.22\times10^{-86}\,atm$$

…thus, the oxygen partial pressure reached by the vacuum will be far greater than the level required to stop oxidation thermodynamically. Alternatively, we can simply test the free energy of reaction at 500 K under the vacuum oxygen partial pressure:

$$\Delta\overline{G}_{rxn} = \Delta\overline{G}_{rxn}^{o} + RT\ln\frac{P^o}{P_{O_2}} = -815,000\,\frac{J}{mole} + (8.3144)(500)\ln\frac{1}{(1\times10^{-8}\,atm)} = -738\,\frac{kJ}{mole}$$

…which is still very negative, indicating oxidation will still occur spontaneously.

3. **Thermodynamics of a rechargeable battery. [2 parts, a-b]** 'NiCad' rechargeable batteries are galvanic cells that utilize electrochemical reactions on nickel and cadmium electrodes, with an aqueous solution of KOH as the electrolyte:

At the anode: $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{(2)(s)} + 2e^-$

At the cathode: $2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{(2)(s)} + 2OH^-_{(aq)}$

Overall cell reaction: $Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow 2Ni(OH)_{(2)(s)} + Cd(OH)_{(2)(s)}$

The standard EMF of the NiCd battery is 1.299 V at 25°C.

a. Write an expression that shows how the EMF of the NiCd cell depends on the activities of the components, and then simplify this expression as much as possible.

SOLUTION:

Note that there was a typo in the overall cell reaction given (O was missing from NiO(OH) on left side)- this is corrected above.

$$E = -\frac{\Delta G_{rxn}}{2F} = E^o - \frac{RT}{2F}\ln Q$$

$$E = E^o - \frac{RT}{2F}\ln \frac{a_{Cd(OH)_2}\left(a_{Ni(OH)_2}\right)^2}{a^2_{NiO(OH)}a^2_{H_2O}a_{Cd}}$$

Using the standard approximation that the activities of pure solids are ~1, this reduces to:

$$E = E^o - \frac{RT}{2F}\ln \frac{1}{a^2_{H_2O}} = E^o + \frac{RT}{F}\ln a_{H_2O}$$

b. In a NiCd battery with a concentrated KOH electrolyte, the EMF is found to be 1.2 V at 25°C. Determine the activity of water in the electrolyte at 25°C.

SOLUTION:

$$E = 1.2V = -\frac{\Delta \overline{G}_{rxn}}{2F}$$

$$\therefore \Delta \overline{G}_{rxn} = -(1.2V)(2)(96,485\frac{C}{mole}) = -232\frac{kJ}{mole}$$

$$E = E^o + \frac{RT}{F} \ln a_{H_2O}$$

$$1.2V = 1.229V + \frac{(8.3144 \frac{J}{mole \cdot K})(298K)}{96,485 \frac{C}{mole}} \ln a_{H_2O}$$

$$\therefore a_{H_2O} = 0.021$$

4. **Phase equilibria of sulfur**. **[4 parts, a-d]** Answer the questions below using the phase diagrams and physical data given on the following two pages.

    a.   **Three of the 4** putative phase diagrams for sulfur given on the following pages are incorrect. Using your understanding of single-component phase diagrams and the given physical data, identify the correct phase diagram, **mark the error** in each of the 'wrong' diagrams, and underneath the incorrect diagrams **provide a brief explanation** of why the diagram is wrong (you can use equations or sentences as appropriate).

The two key tests of these phase diagrams are:

(i)   Do they obey the Gibbs phase rule?

           For a single-component phase diagram: $D + P = C + 2$
           The degrees of freedom can be no less than zero, and must be consistent with the designation given to regions of the phase diagram (is it a phase field, a coexistence curve, a triple point): $D = 3 - P$

(ii)   Are the slopes of coexistence curves consistent with the Clausius Clapeyron equation?

           The slope dP/dT of a coexistence curve is dictated by the sign on the molar volume change at the phase transition, because the enthalpy change and temperature are always positive for stability:

$$\left.\frac{dP}{dT}\right|_{coexistence} = \frac{\Delta\overline{H}_{trans}}{T_{trans}\Delta\overline{V}_{trans}}$$

           Notably, the densities of the given phases of sulfur fall in the order $\rho_{orthor\,hom\,bic} > \rho_{monoclinic} > \rho_{liquid} > \rho_{vapor}$, thus the molar volumes

$$(\overline{V}_i = \frac{(\text{molecular weight})_i}{\rho_i})$$ have the ordering

$$\overline{V}_{vapor} > \overline{V}_{liquid} > \overline{V}_{monoclinic} > \overline{V}_{orthor\,hom\,bic}.$$

    b. For your choice of the correct phase diagram, mark the triple points on the diagram with a diamond.

    c. For your choice of the correct phase diagram, at a constant temperature T_1, draw a qualitatitively correct plot of the molar Gibbs free energy of sulfur vs. pressure over the range $P = P_1$ to $P = P_2$ (make your drawing large as we will make some annotations on it). It is probably easiest to draw your free energy plot underneath the phase diagram. *Suggestion: sketch out the diagram in some of the 'extra workspace' first; it is tricky to draw it correctly on the first try*.

d. On your free energy diagram, show graphically why the liquid phase of sulfur spontaneously transforms to monoclinic solid sulfur at temperature T_1 when the pressure resides within the 'M' region of the phase diagram.
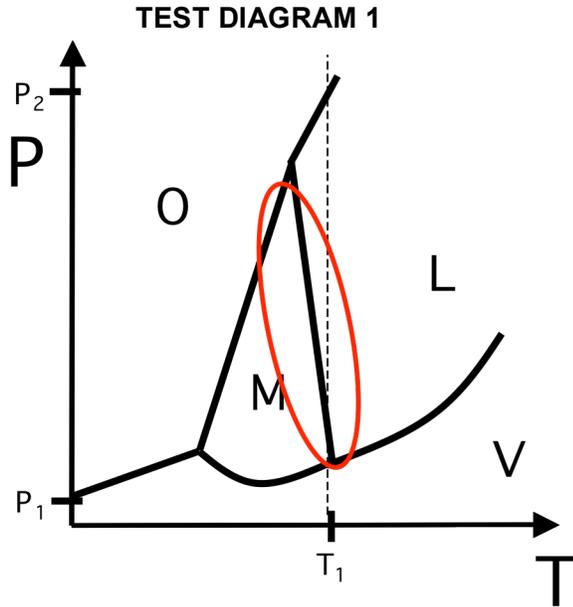
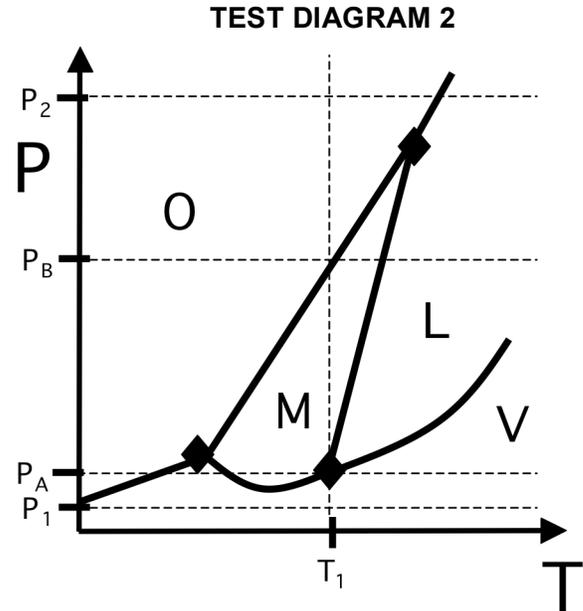**Putative Phase diagrams for sulfur 1 and 2**

Sulfur physical data:

$$\rho_{orthor\,hom\,bic} = 5.4\frac{g}{cm^3} \qquad \rho_{monoclinic} = 2\frac{g}{cm^3} \qquad \rho_{liquid} = 1.82\frac{g}{cm^3}$$

$\overline{V}_{vapor} > \overline{V}_{liquid}$ for all conditions where vapor is stable

O = orthorhombic solid phase; M = monoclinic solid phase; L = liquid phase; V = vapor phase
Diagrams not drawn to scale; P_1 ~ 1 atm, P_2 ~ 1200 atm, T_1 ~430 K

This diagram is incorrect as it shows a negative slope at the M->L transition, where $\overline{V}_{liquid} > \overline{V}_{monoclinic}$.

This is the correct diagram. The triple points are marked with diamonds.

## Putative Phase diagrams for sulfur 3 and 4

Sulfur physical data (THE SAME INFORMATION AS PREVIOUS PAGE, REPEATED FOR CONVENIENCE):

$$\rho_{orthor\,hom\,bic} = 5.4\frac{g}{cm^3} \qquad \rho_{monoclinic} = 2\frac{g}{cm^3} \qquad \rho_{liquid} = 1.82\frac{g}{cm^3}$$

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TEST DIAGRAM 3

TEST DIAGRAM 4
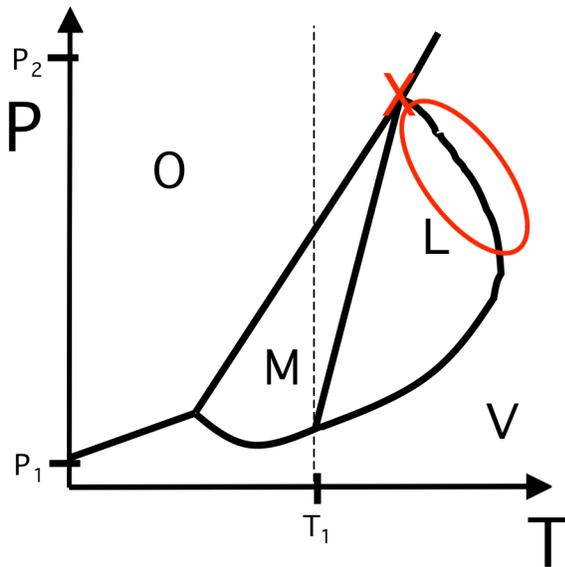
This diagram actually shows two errors—the point Marked with an 'X' shows a 'qaudruple point'-O-M-L-V four-phase equilibrium, which would phase rule (D = -1). In addition, the slope (marked with the oval) shows an incorrect sign for the volume change at the liquid--to-vapor phase transition.
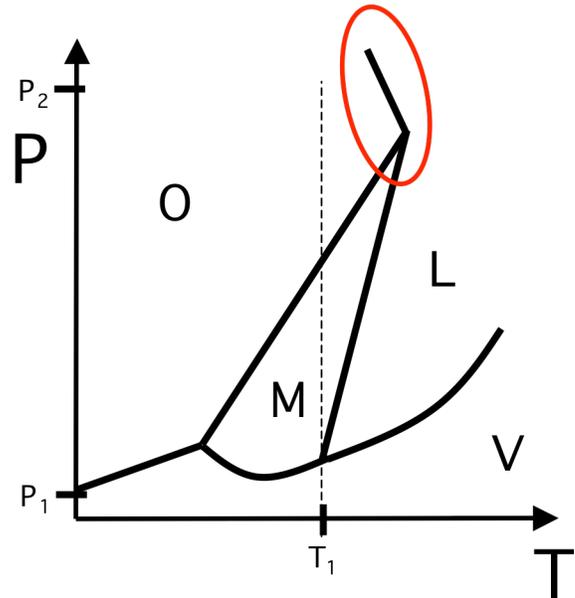
This diagram shows a negative slope at the orthorhombic->L transition at high pressures, in conflict with violate $\overline{V}_{liquid} > \overline{V}_{orthor\,hom\,bic}$.

The free energy diagram for the correct phase diagram along the given path is:
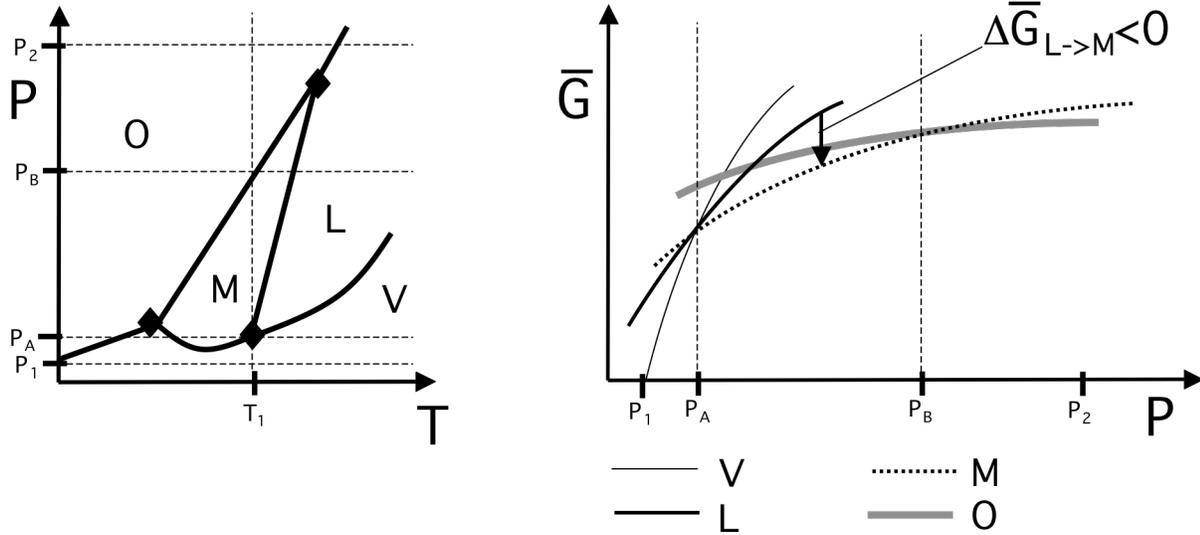
Note that the slopes should have the order V > L > M > O, to match the order of the densities of the materials, since the slope is the molar volume of the material in each phase. The three molar free energy curves for L, V, and M meet at the triple point (P_A) on the graph above.

EXTRA WORKSPACE: