

**3.012 Quiz 2**

11.14.05

100 points total (50 in thermo + 50 in bonding)

**3.012**

**Fall 2005**

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***Give as much written explanation as possible of your reasoning, and write clearly and legibly. There is plenty of space in between questions, and more blank space at the end.***

*Time yourself carefully – do not spend most of your time on a single question. Remember, you have close to two hours (from 1.05pm to 2.55pm). You can start with thermo, or start with bonding.*

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**Write your name here:** \_\_\_\_\_

**BONDING (2 problems, 50 points total)**

**1) Homonuclear bonding [7 questions, a) to g)]** In this problem we'll investigate molecular bonding in simple cases, ranging from the hydrogen molecular ion  $\text{H}_2^+$  to the carbon dimer  $\text{C}_2$ , to ethene ( $\text{C}_2\text{H}_4$ , also called ethylene).

a. The hydrogen molecular ion  $\text{H}_2^+$  has only one electron in the field of two hydrogen nuclei (i.e. in the field of two protons). What is the Hamiltonian acting on this single electron? State clearly where the hydrogen nuclei are, in your coordinate system.

b. What trial wavefunction can we write for this problem, as a linear combination of atomic orbitals? Explain how the variational principle would allow us to determine the coefficients for the atomic orbitals in this LCAO trial wavefunction.

- c. What is then the LCAO ground-state wavefunction for the single electron in this hydrogen molecular ion ? What is the LCAO wavefunction for the first excited state ?
- d. How does the energy of the hydrogen molecular ion depends on the distance between the two protons, when the electron is in its ground-state ? And when it is in its first excited state ? What are the different contributions that determine the stability of this system in the ground state ?

- e. Suppose we have a carbon dimer  $C_2$ ; what will be its occupied molecular orbitals? Label them as  $\sigma$  or  $\pi$ , and as g (for *gerade*) or u (*ungerade*).

f. Suppose I have a molecule of ethene  $C_2H_4$  (also called ethylene). What will be the geometry of this molecule? Describe the hybridization for each of the four electrons on one carbon atom.

g. Describe the Huckel model. How would you apply it to the two  $p_z$  electrons present in this system? Can you obtain the HOMO and the LUMO of the molecule? Use the symbol  $\alpha$  for the matrix element  $\langle p_z | \hat{H}_{ethene} | p_z \rangle$  between a  $p_z$  orbital and itself (also called Coulomb integral by your textbook), and  $\beta$  for the matrix element between a  $p_z$  orbital on one carbon and a  $p_z$  orbital sitting on a neighboring carbon (also called resonance integral – remember that  $\beta$  is negative).

**2) Symmetry operations [4 questions, a) to d)]**

- a. What are the symmetry operations present in the ethene molecule  $C_2H_4$  ? Show them together with a drawing of the molecule.

**b.** The symmetry operations above form a group – i.e. they verify the properties of closure, associativity, identity, and inverse. Choose one of these four properties, and show that it is satisfied using some of the symmetry operations that you just described in a.

**c.** The presence of a rotation axis and a mirror plane that contains that axis gives rise to another mirror plane: can you explain this, and how it relates to ethene ?

- d.** Now, a more general question, not related to the ethene molecule discussed before. What are the rotations operations that are compatible with translations ? Can you prove your statement ?



**THERMODYNAMICS (4 problems, 50 points total).**

**Physical Constants:**

Gas constant:  $R = 8.3144 \text{ J/mole-K} = 0.082057 \text{ L-atm/mole-K}$

Faraday constant  $F = 96,485 \text{ C/mole}$

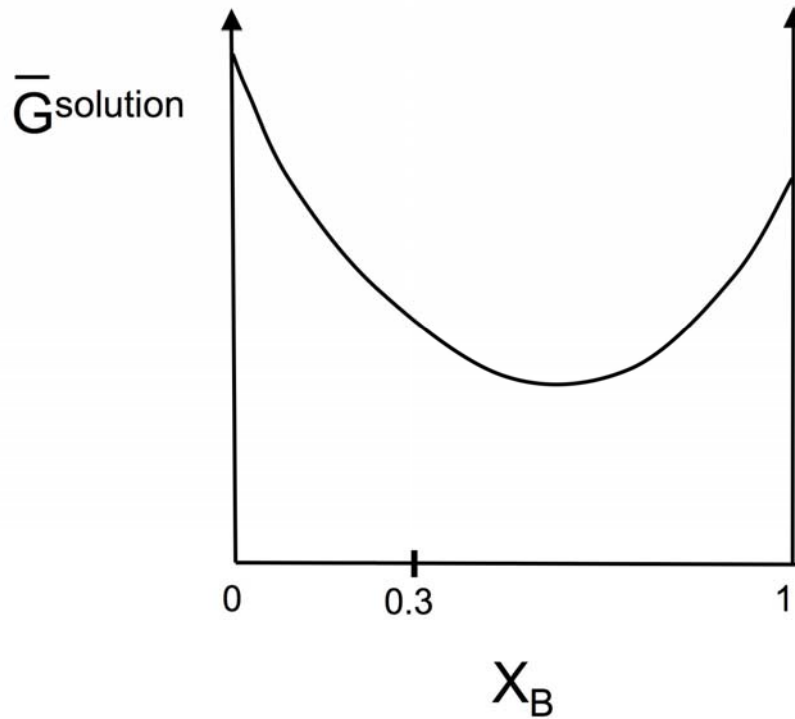
Unit conversion:  $C * V = \text{Joules}$

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

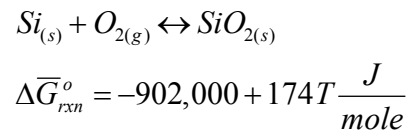
a. Explain why using the Gibbs free energy to solve for equilibrium states of a system (under appropriate conditions) is easier than directly applying the second law and considering entropy changes only.

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?

- c. Suppose two components A and B form an ideal solid solution. At  $P = 1 \text{ atm}$  and  $T = 400 \text{ K}$ , 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.



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:

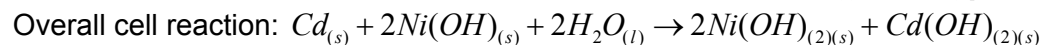
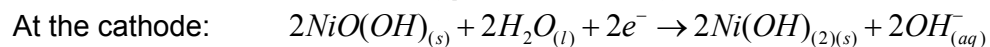
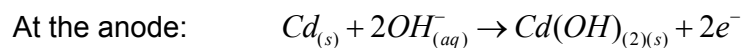


...where T in the above equation is temperature in K.

- 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.

- 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  $P_{O_2} = 1 \times 10^{-8}$  atm. Would this condition be sufficient to block spontaneous oxidation of the crystal at  $T = 500$  K?

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:



**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.

- 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.

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.
- 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).
  - For your choice of the correct phase diagram, mark the triple points on the diagram with a diamond.
  - For your choice of the correct phase diagram, at a constant temperature  $T_1$ , draw a qualitatively 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.*
  - 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

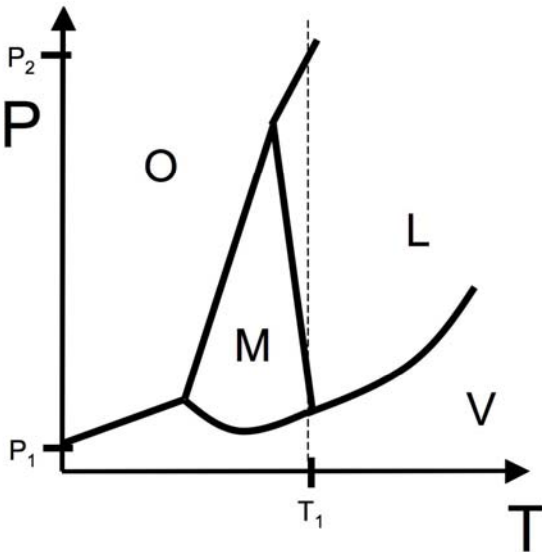
**Sulfur physical data:**

$$\rho_{orthorhombic} = 5.4 \frac{g}{cm^3} \quad \rho_{monoclinic} = 2 \frac{g}{cm^3} \quad \rho_{liquid} = 1.82 \frac{g}{cm^3}$$

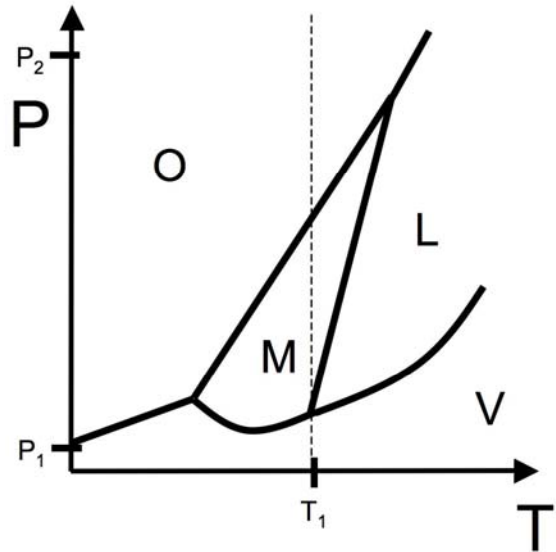
$\bar{V}_{vapor} > \bar{V}_{liquid}$  for all conditions where vapor is stable

O = orthorhombic solid phase; M = monoclinic solid phase; L = liquid phase; V = vapor phase  
Diagrams not drawn to scale;  $P_1 \sim 1 \text{ atm}$ ,  $P_2 \sim 1200 \text{ atm}$ ,  $T_1 \sim 430 \text{ K}$

**TEST DIAGRAM 1**



**TEST DIAGRAM 2**



Putative Phase diagrams for sulfur 3 and 4

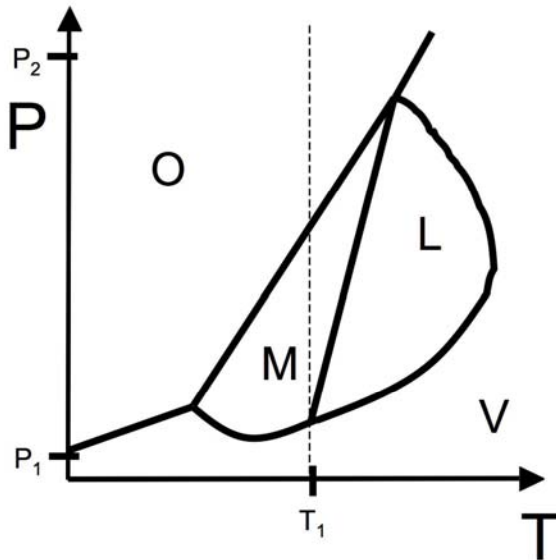
Sulfur physical data (THE SAME INFORMATION AS PREVIOUS PAGE, REPEATED FOR CONVENIENCE):

$$\rho_{orthorhombic} = 5.4 \frac{g}{cm^3} \quad \rho_{monoclinic} = 2 \frac{g}{cm^3} \quad \rho_{liquid} = 1.82 \frac{g}{cm^3}$$

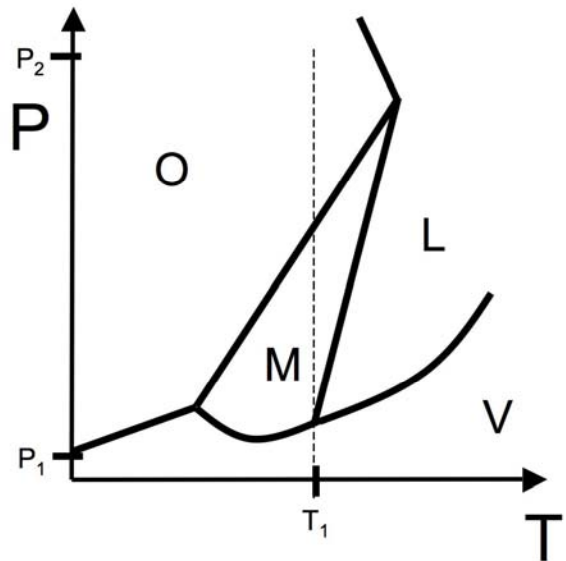
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TEST DIAGRAM 3



TEST DIAGRAM 4





EXTRA WORKSPACE:

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