ME-351 THERMODYNAMICS AND ENERGETICS II

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SPRING 2025

NAME :

SCIPER :

Question	Points	Score
1	10	
2	10	
3	10	
4	15	
5	15	
6	10	
7	15	
8	15	
Total:	100	

Answer the questions in the space provided. Please ensure you show all your work and your answers are legible. If you need additional space, continue on the back of the page. You have 3 hours to complete the exam. **Good Luck!**

Difficult to remember formulas

1. Reciprocal Rule : $\left(\frac{\partial x}{\partial y}\right) = \frac{1}{\left(\frac{\partial y}{\partial x}\right)}$
2. Cyclical Relation : $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$
3. Chain Rule : $\left(\frac{\partial x}{\partial z}\right)_\phi = \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial z}\right)_\phi$
4. $\left(\frac{\partial x}{\partial \phi}\right)_z = \left(\frac{\partial x}{\partial \phi}\right)_y + \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial \phi}\right)_z$
5. Maxwell relations : $\left(\frac{\partial A}{\partial B}\right)_{\text{conjugate}(A)} = \pm \left(\frac{\partial(\text{conjugate}(B))}{\partial(\text{conjugate}(A))}\right)_B$

1. An engine is extracting work from an ideal gas in a steady state process. The gas enters the engine at a temperature and pressure of T_1, p_1 and exits from the engine at T_2, p_2. The inlet and outlet temperatures and pressure are such that $T_1 > T_2$ and $p_1 > p_2$. The gas flow rate into the engine is $\dot{m}$. The engine is adiabatically insulated from the environment.

   (a) (2 points) What is the rate of entropy change for the engine?

   (b) (6 points) What is the entropy change per mole of the gas?

   (c) (2 points) What is the rate of entropy change for the universe? You can ignore any entropy generated during the production of the steam.

   Heat capacity of one mole of an ideal gas is $C_p = \frac{5}{2}R$, $C_V = \frac{3}{2}R$

2. A system has its characteristic potential given by:

$$\Lambda = C\frac{S^3 p}{N_A N_B}$$

where S, p, N_A, N_B are the entropy, pressure, number of A atoms, and number of B atoms respectively. C is a constant.

(a) (3 points) What are the natural variables of the characteristic potential? Express the characteristic potential as a Legendre transform of the internal energy

(b) (4 points) Compute all equations of state for the characteristic potential

(c) (3 points) Are the equations of state extensive or intensive? Justify your answer with mathematical arguments.

3. (a) (6 points) Derive the equilibrium criteria for two-phase coexistence (say between an α and β phase) in a binary A-B alloy at constant temperature, and pressure. The total number of A and B atoms, N_A and N_B are constant.

   (b) (4 points) Show that the chemical potential of A is equal to $\mu_A = G_m + (1 - x_A)\frac{\partial G_m}{\partial x_A}$, where $G_m = G/(N_A + N_B)$

4. The phase diagram for a binary A-B alloy is shown in fig. 1

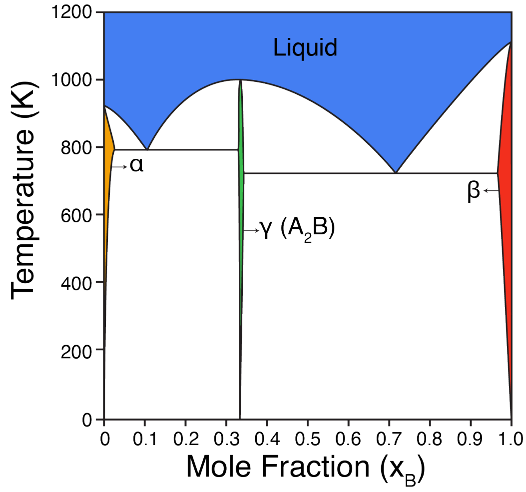
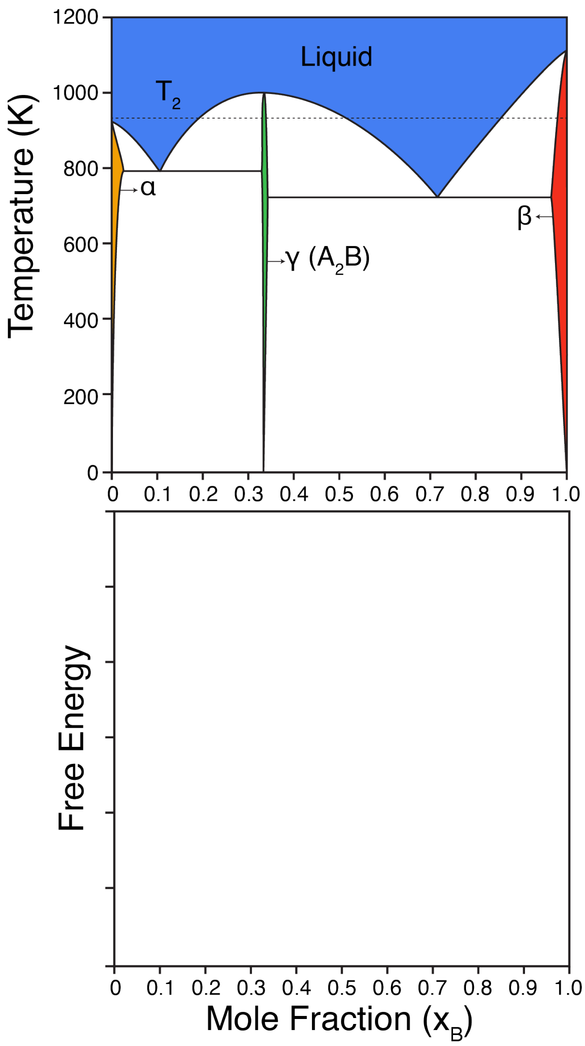
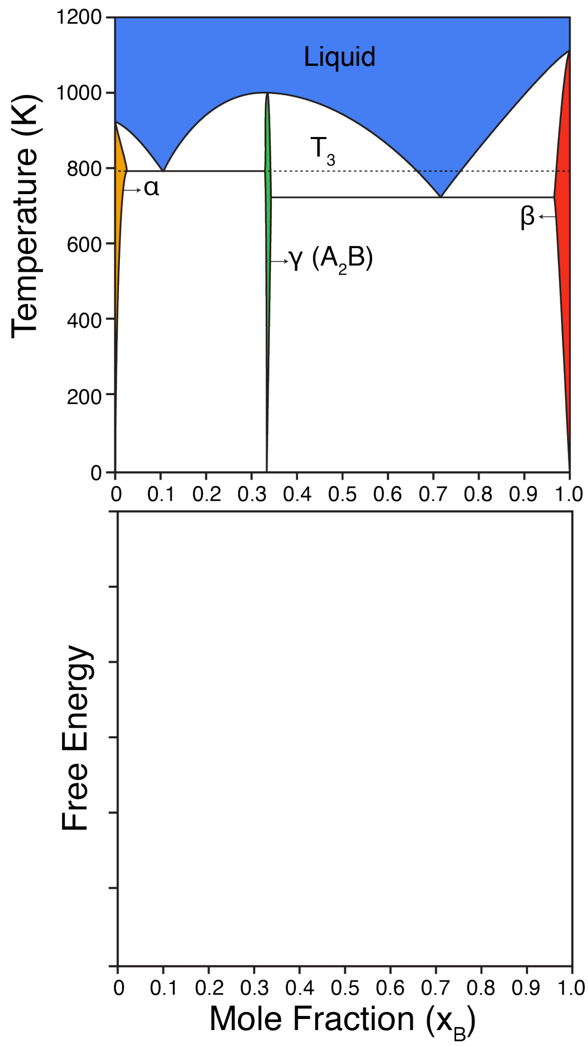


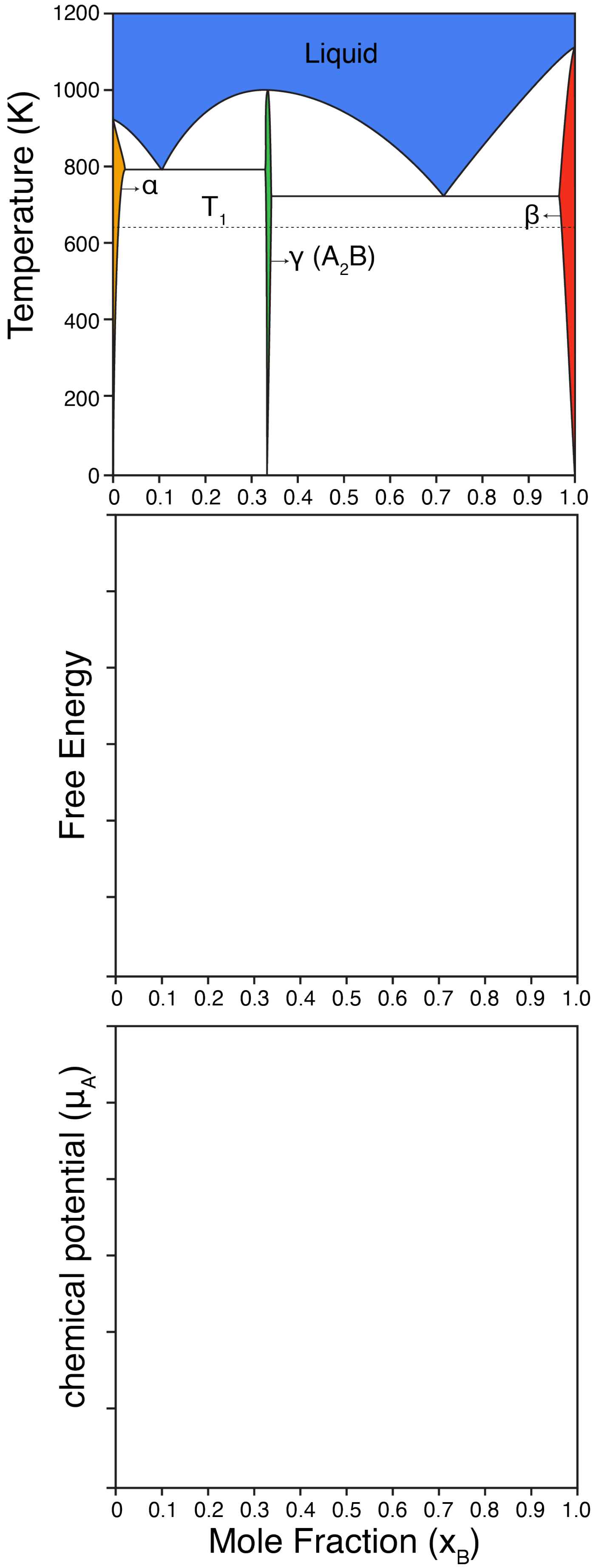
Figure 1

(a) (2 points) Consider an alloy with 50% A. If this alloy is held at 800K, which phases are present and what is their composition?

(b) (9 points) Sketch the free energies and chemical potentials of all the phases on the phase diagram at the indicated temperatures. Pay attention to the slopes, tangents, intercepts etc.

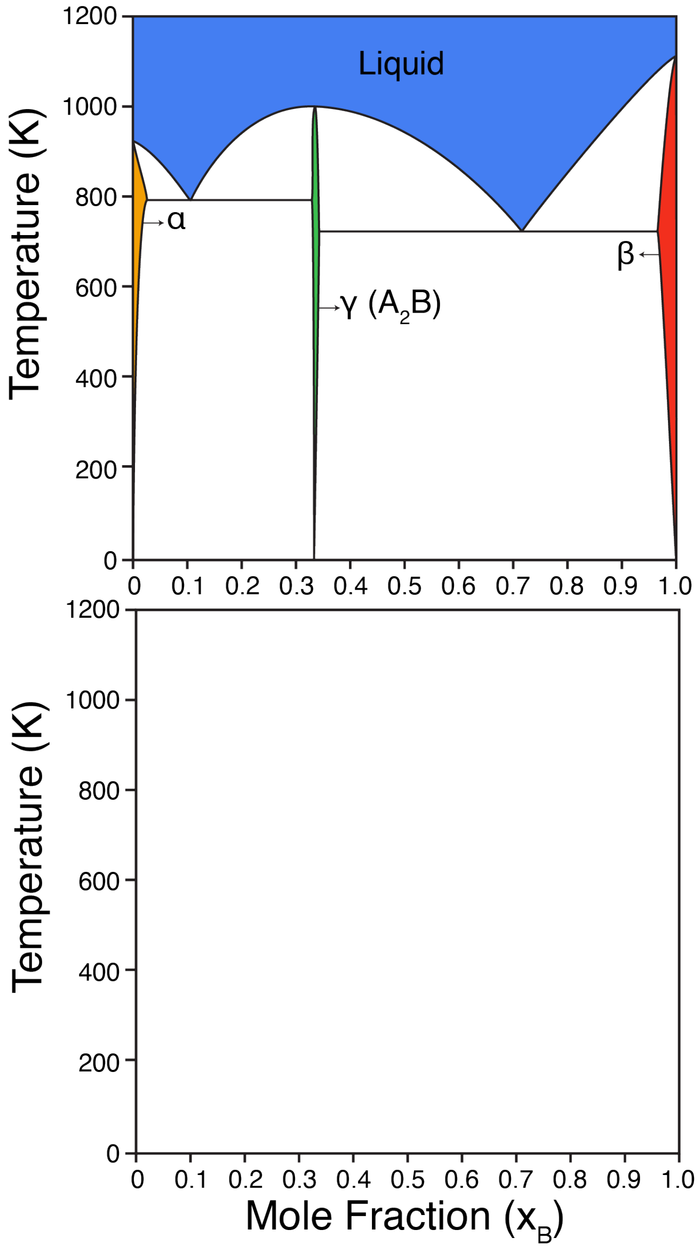






Liquid
Temperature (K)
1200
1000
800
600
400
200
0
α
T_1
β
γ (A_2B)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Free Energy
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
chemical potential (μ_A)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Mole Fraction (x_B)

(c) (4 points) Schematically draw the phase diagram if the γ (A_2B) phase is prevented from forming.



5. A rod of length l and surface area A is stretched as shown in fig. 3.

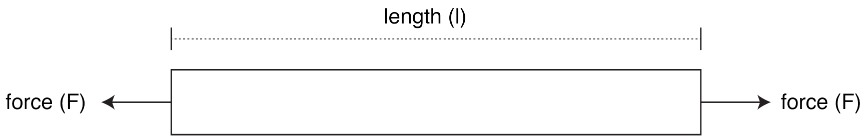


Figure 3

(a) (4 points) Write down an expression for the characteristic potential of the rod as a Legendre transform of the internal energy when the rod is placed in an isothermal environment. What is the characteristic potential when the rod is maintained in an isentropic environment?

(b) (8 points) The Young's modulus of the material is defined as $l\left(\frac{\partial \sigma}{\partial l}\right)$. Relate the isothermal Youngs modulus to the isentropic Young's modulus. Express your answer in terms of "well-known" material properties such as the thermal expansion, compressibility, and heat capacities of the material.

(c) (3 points) Based on the expression you derived in the previous part of the question, which of the modulii would you expect to be larger - the isentropic or isothermal modulus?

6. (10 points) A colleague has asked you to verify a phase diagram (fig. 4) that they constructed based on some experiments that they conducted on a metal substrate. The metal substrate was exposed to a gaseous environment of oxygen and your collaborator ran a series of experiments to construct the phase diagram shown in fig. 4. The α phase is found to be a *disordered* phase where that oxygen atoms are randomly distributed on the surface of the metal while the β phase is an ordered phase comprising of a well-defined arrangement of oxygen atoms on the surface of the metal. You also know that the ordered β phase is not tolerant to any defects - leading to very high energies for any arrangement other than the ordered state. Could the phase diagram in fig. 4 be correct? Justify your answer with thermodynamic arguments.

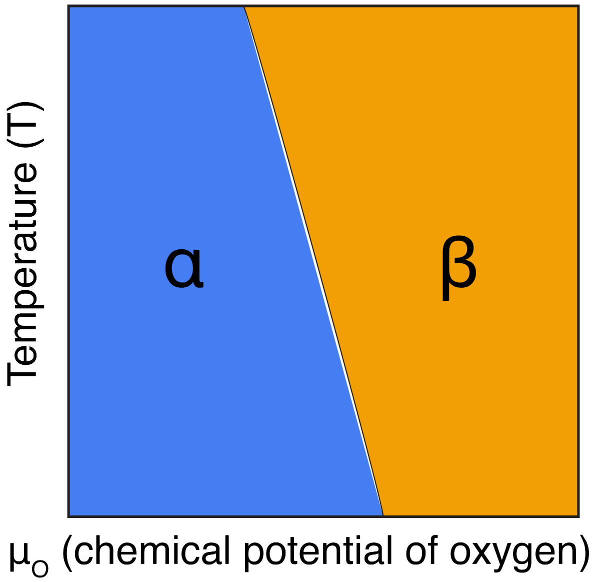


Figure 4

7. (15 points) Polymers are substances that consist of repeating subunits called *monomers*. Consider a one-dimensional polymer chain with M monomers. Each monomer can exist in two states. The lowest energy state has energy ϵ_0, and length l_0 while the higher energy state has energy ϵ_1 and length l_1. The polymer chain is held at fixed temperature (T), force (F) and number of monomer units (M). Each monomer unit and bond between neighboring monomer units are inifinitely stiff. This means that the length of the monomer units do not change elastically under the application of a force. Derive an expression for the average length of the chain as a function of the external force F.

8. Two elements (A and B) form an ideal solid solution in the liquid phase. They are also found to form a compound with stoichiometry AB The Gibbs free energy of the AB compound, relative to solid A and solid B is given by:

$$\Delta G_{AB} = C_1 + TC_2$$

where $C_1 < 0, C_2 < 0$ are constants and T is the temperature. The free energies of liquid A and liquid B relative to the solid phases is given by:

$$\Delta G^l_A = \alpha_1 + T\alpha_2$$

$$\Delta G^l_B = \beta_1 + T\beta_2$$

where $\alpha_1, \alpha_2, \beta_1, \beta_2$ are all constants. The units of all free energies are J/mole. The liquid phase is found at high temperatures, while the solid phases are stable at lower temperatures

(a) (4 points) What are the signs of the constants, $\alpha_1, \alpha_2, \beta_1, \beta_2$? Use thermodynamic arguments to justify your answer.

(b) (2 points) Compute the melting temperature of pure A and pure B. Express your answer in terms of $\alpha_1, \alpha_2, \beta_1, \beta_2$.

(c) (2 points) Draw a schematic (one-dimensional) phase diagram at 0K with respect to the composition (x_A) of the A-B mixture.

(d) (4 points) Compute the melting point of the AB compound.

(e) (3 points) Experimental measurements in this A-B alloy show that the liquid phase is better described as a regular solution with a negative mixing enthalpy. Will the melting temperature you computed for the AB compound in the previous question be higher or lower than the experimentally measured melting point in a real system?

The entropy of mixing of an ideal solid solution is given by:

$$\Delta S = -R(x_A \log(x_A) + x_B \log(x_B))$$