MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Thermodynamics of Materials
3.00 Fall 2001

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Final Exam: Friday Dec. 21, 2001 (9AM-12 noon)

NAME: ______________________________

This exam is composed of seven questions. Please read them carefully and thoughtfully before you answer.

The first two questions consist of a sets of conceptual exercises for which good answers will require a short, carefully-worded, sentence.

The last five questions require some analytic work and manipulation of formulas, or graphical constructions. You will not need a calculator and notes are not permitted.

Your answers should fit in the space provided in the exam. If you find that the provided space is insufficient, use the back of the previous page and clearly indicate that your answer continues.

You may wish to work your answer out on scratch paper before writing on the exam. Your answers will be graded on their accuracy, physical insight, and clarity. A concise clear answer will get a better score than with a longer answer with the same content. You may supplement your answer with a figure, a plot, or equations. Your answers will be graded in their entirety—extraneous or irrelevant equations or remarks may reduce the clarity or accuracy of your answer.

Some questions ask that you to make a plot. When producing plots, you do not need to make your numerical scales and positions precisely. Rather, the plots should be qualitatively correct and labeled carefully so that the grader of the exam is able to determine whether you have demonstrated sufficient understanding. Of course, neat plots are better than sloppy ones.

The questions are not necessarily ordered according to their difficulty—it would be prudent to read them all before you start. Finally, each question is not weighted equally in the grading; the weights are given below.

Question 1: 14 points possible ______________________________

Question 2: 18 points possible ______________________________

Question 3: 18 points possible ______________________________

Question 4: 14 points possible ______________________________

Question 5: 10 points possible ______________________________

Question 6: 12 points possible ______________________________

Question 7: 14 points possible ______________________________

Total: 100 points possible ______________________________

Exam Question 3.1

Read *carefully* and determine whether (and why) the following statements are true or false and indicate your thermodynamic reasoning. If you claim that a statement is false, you may state which law or laws of thermodynamics it violates or you may employ a physical counter-example or any other plausible physical reason. You may wish to amend any false statement with a clarifying phrase that makes the statement true.

3-1-i If the total Gibbs free energy of two phases are equal at constant pressure and temperature, then the two phases are in equilibrium with each other.

3-1-ii The internal energy of a system and its surroundings is not conserved during an irreversible process, but it is conserved for reversible processes.

3-1-iii If a system has no constraints other than being in equilibrium with a constant pressure reservoir and constant temperature reservoir, then that system is in equilibrium if every process increases its Gibbs free energy.

3-1-iv The heat capacity of one mole of a single stable phase is positive if all of its intensive variables are held fixed.

3-1-v The internal energy of a system, U, is an extensive function and therefore $U(\lambda S, \lambda V, \lambda N_i) = \lambda U(S, V, N_i)$ where λ is a positive constant, S is the entropy of the system, V is the volume of the system, and the N_i are the number of moles of the chemical components of the system.

3-1-vi The Gibbs free energy of a system, G, is an extensive function and therefore $G(\lambda T, \lambda P, \lambda N_i) = \lambda G(T, P, N_i)$ where λ is a positive constant, T is the temperature of a reservoir in equilibrium with the system, P is the pressure of a reservoir in equilibrium with the system, and the N_i are the number of moles of the chemical components of the system.

3-1-vii Consider two systems that can exchange volume and heat. If it is also possible for the systems to exchange a chemical species A, then species A will move from the system with the lower value of chemical potential for that species (μ_A) to the system with higher chemical potential.

Exam Question 3.2

The following questions require a single sentence, and/or a single equation, and/or a simple graphical illustration for their solution.

3-2-i What is the difference between heat and work?

3-2-ii Describe the difference between a state function and a quantity like heat.

3-2-iii What is the difference between heat and temperature?

3-2-iv Write down one of Maxwell's relations.

3-2-v Suppose that an alloy is produced with three pure chemical components by sealing a closed rigid container (fixed volume) and heated to temperature $T = 500\mathrm{K}$ for 250 years. Observation of this alloy with X-ray diffraction indicates the presence of a BCC-phase, an FCC-phase, an HCP-phase, a monoclinic phase, and a simple cubic phase. What nontrivial conclusion can you make about the sample?

3-2-vi A mole of isotropic linear elastic material is reversibly stressed so that its volume is decreased by 3%, the stress is then instantaneously (i.e., irreversibly) removed and the volume increases back to its original value. Will the net change of entropy of the elastic material be positive, negative, or zero?

3-2-vii List three ways that the molar internal energy of a body can be increased.

3-2-viii Why is a small amount of any chemical species B, always soluble in a phase composed purely of another species A?

3-2-ix Describe some relevant material properties that are required for a solution that has complete solubility as a liquid at high temperatures, and has a miscibility gap separating liquids at differing compositions at low temperatures.

Exam Question 3.3

Consider a closed chamber of fixed volume that is divided into two parts by a rigid membrane as illustrated in the figure below.

Initially, each part contains an ideal gas mixture of Helium and Xenon with partial pressures specified in the figure.

The membrane allows Helium to pass through it, but does **not** allow Xenon to pass through it. In other words, the membrane that divides the closed chamber is permeable only to Helium.

Assume the temperature is constant and that Helium and Xenon are the only species present.

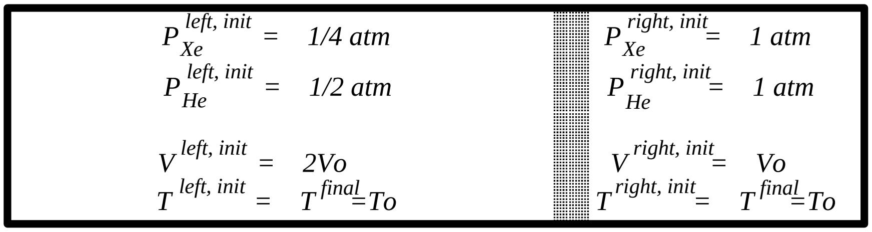


Figure 1: Chamber with a rigid osmotic membrane that allows only transport of He and no transport of Xe. The temperature is constant and uniform. Work out the problem for two cases: **(A)** the membrane is affixed to the chambers so that the volumes on each side remain constant, and **(B)** the membrane can freely move so that the two volumes can vary.

Show your reasoning and equations for your method of solution for partial credit.

(A) Fixed Membrane The final volumes for each side are the same as their initial volume, what are the equilibrium partial pressures of He and Xe within the left and right sides?

(B) Free Membrane The volumes of the chambers may vary freely, what are the equilibrium partial pressures of He and Xe within the left and right sides?

Exam Question 3.4

Consider an isolated system consisting of a kilogram of lead and a kilogram of water illustrated below.

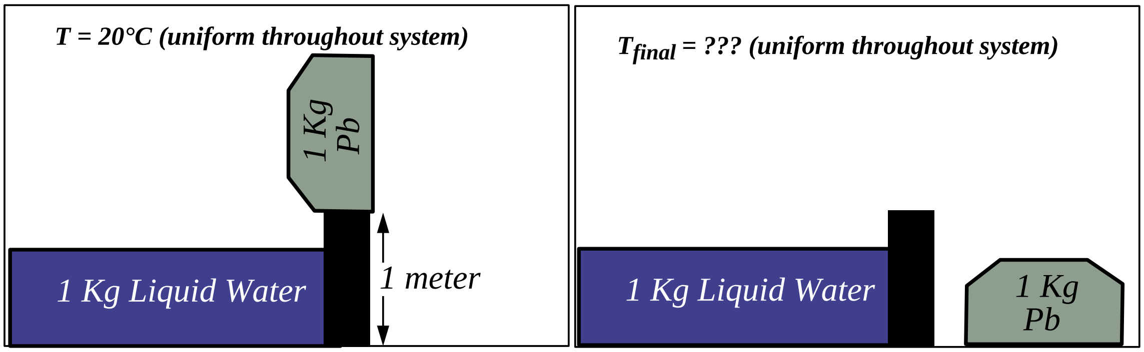


Figure 2: Isolated system illustrated before and after.

The heat capacity of 1 kilogram of Pb is given by C_{Pb}; the heat capacity of 1 kilogram of water is given by $C_{\mathrm{H_2O}}$; all other heat capacities in the isolated system (including the pedestal with finite width that initially supports the Pb) can be neglected. C_{Pb} and $C_{\mathrm{H_2O}}$ may be considered independent of any constraints (e.g., constant pressure or constant volume) and to be independent of temperature.

3-4-i Derive an expression for the final temperature after a process leading to the figure on the right of the illustration.

3-4-ii Would the temperature be larger or smaller if the block of lead had fallen to the left (i.e., into the water) in the same configuration (i.e., with the longest side of the block on the bottom)?

3-4-iii Illustrate *four* local or global equilibrium states of this system and rank them from least to most stable.

3-4-iv Illustrate *one* unstable equilibrium state of this system.

Exam Question 3.5

3-5-i On the diagram below, construct a two-component phase diagram that obeys Gibbs phase rule and has one **eutectic** point and one **peritectoid** point.

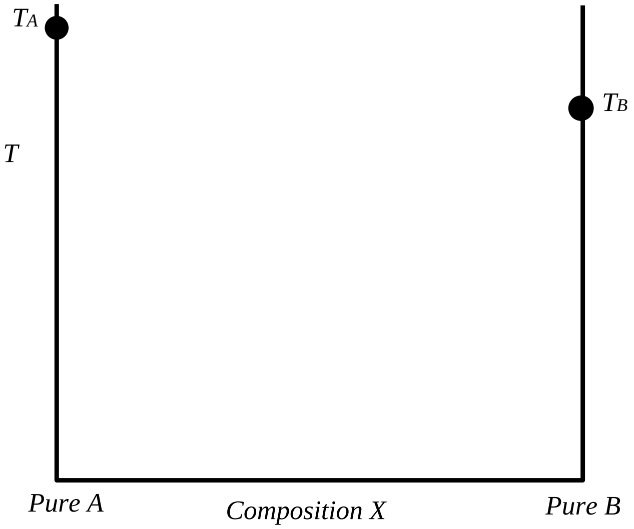
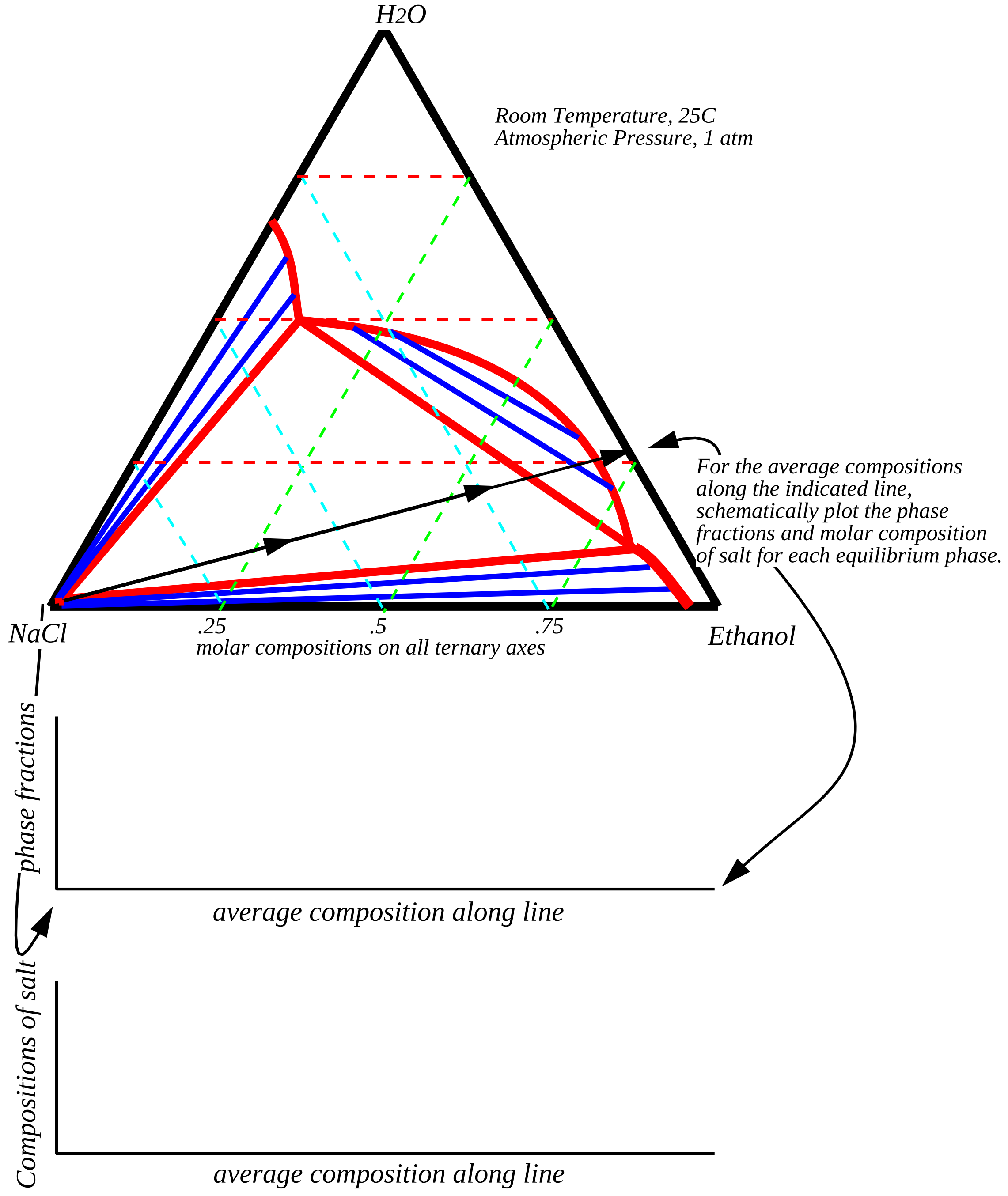


Figure 3: Coordinate axes for constructing a binary phase diagram with one **eutectic** point and one **peritectoid** point. Pure A is a simple cubic solid at all temperatures below its melting point which is indicated by T_A. Pure B is a hexagonal close packed solid at all temperatures below its melting point which is indicated by T_B.

3-5-ii Below, construct molar Gibbs free energy curves of solution that are **consistent** with your phase diagram at the eutectic temperature and at the peritectoid temperature.

Exam Question 3.6

For the ternary phase diagram of components H_2O, NaCl and ethanol that is illustrated below at room temperature and pressure, make two qualitatively correct plots. In the upper set of coordinate axes, make a plot of equilibrium phase fractions as a function of the average alloy composition indicated by the arrow-line in the phase diagram. In the lower set of coordinate axes, make a plot of the molar NaCl composition as a function of the same average alloy composition.



For the average compositions along the indicated line, schematically plot the phase fractions and molar composition of salt for each equilibrium phase.

Figure 4: The salt-water-ethanol phase diagram.

Exam Question 3.7

Indicate your answer by drawing on the following two plots and labeling your answer clearly.

3-7-i Describe and illustrate the equilibrium condition if the alloy composition is fixed at X_o.

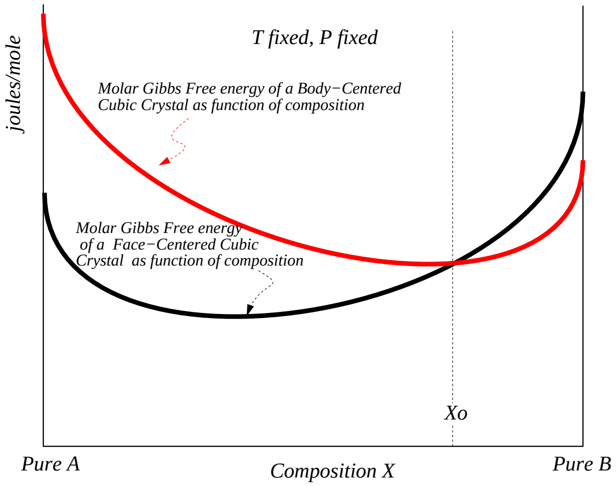


Figure 5: Molar Gibbs free energy curves and a fixed binary alloy composition.

3-7-ii Describe and illustrate the equilibrium compositions if the alloy can exchange chemical species A with an ideal gas reservoir of fixed partial pressure P_A. If there is more than one equilibrium composition, indicate which is most stable.

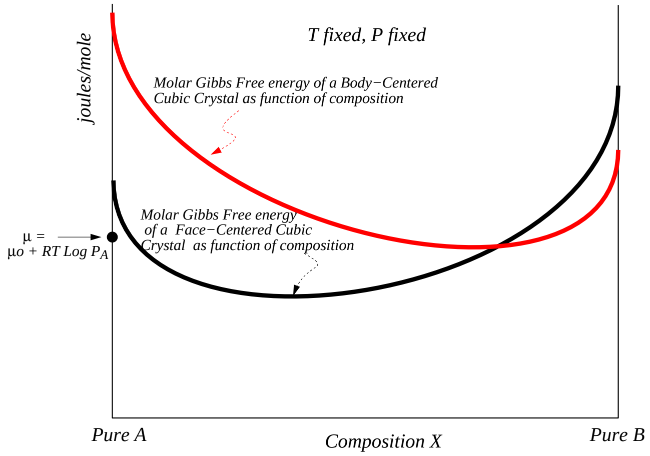


Figure 6: Molar Gibbs free energy curves and a fixed chemical potential of one of its components.