

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Thermodynamics of Materials

3.00 Fall 2002

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Exam 2: Wed. 13 Nov, 2002 (11:05-11:55AM)

SOLUTIONS: _____

This exam is composed of three questions. Please read them carefully and thoughtfully before you answer. The first question consists of a set of conceptual exercises for which a good answer will require a short, carefully worded sentence. The second question has two parts and probes your ability to give an accurate definition and write a short theme for its explanation. The last question requires some analytic work and manipulation of formulas. You will not necessarily 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 out your answer 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 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.

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.

There are six pages in this exam, including this cover page.

Question 2.1: 5600 points possible _____

Question 2.2: 2000 points possible _____

Question 2.3: 2400 points possible _____

Total: 10000 points possible _____

Exam Question 2.1

Read *carefully* and answer the following questions.

The first five statements are true-or-false type; for these, state your conclusion and thermodynamic reasoning. If you claim that a statement is false, you may state which thermodynamic principles 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.

The last two questions require a thermodynamic prediction or explanation that can be satisfactorily answered with a few short sentences.

2-1-i The total entropy of a system at constant volume and temperature is never observed to decrease spontaneously.

False. However, this would be true, according to the second law, if the statement referred to the universe or a system of constant internal energy and volume.

Common Errors	
Symbol	Error Description
α	Didn't specify which sign the entropy change would be for a suitably defined system .
β	Used entropy of a non-isolated system as a corrected statement—to which generic statements are not applicable.
γ	Failed to realize that system as stated had an environment that could have entropy changes that would need to be summed for application in a universal statement.
δ	Failure to relate sign change of entropy of a material when used in counter-example.
ϵ	Thought statement was true which is incorrect.
μ	Unnecessary assumption of ideal gas or fluid system.
ν	Incorrect or misleading supporting statement.

2-1-ii At global equilibrium, the Gibbs free energy of an isolated system attains its lowest possible value.

False. However, the statement would be true if the system were specified to be closed and in equilibrium with a constant pressure and constant temperature reservoir—and therefore not isolated..

Common Errors	
Symbol	Error Description
α	Amended statement to include constant P and T correctly, but failed to realize that system could not be isolated.
β	Claimed statement to be true, but did not amend conditions of constant pressure and temperature reservoirs.
γ	Claimed false, but with incorrect reasoning or supporting statement.

2-1-iii At one atmosphere pressure, a solution composed of Iron and Ruthenium can have three possible equilibrium crystal structures: FCC, BCC, and HCP.

Consider a reservoir with a fixed pressure of one atmosphere and a fixed temperature of T^{res} .

Suppose one closed system of BCC Fe-Ru solution is in thermal and mechanical equilibrium with the reservoir (at $P = 1\text{atm}$ and $T = T^{\text{res}}$) and a second closed system of FCC Fe-Ru solution is also in thermal and mechanical equilibrium with the same reservoir.

At equilibrium, the closed system of BCC Fe-Ru solution must have the same pressure and temperature as the closed system of FCC Fe-Ru solution.

True. Equilibrium¹ requires that each system must have a uniform pressure and temperature that is equal to that of the reservoir; thus the temperatures and pressures of any subsystem must be the same under these conditions.

Common Errors	
Symbol	Error Description
α	Gave an equivocal answer or included irrelevant explanations.
β	Failure to realize that each system is closed and therefore no other conditions beyond mechanical and thermal equilibrium applied.

2-1-iv At one atmosphere pressure, a solution composed of Iron and Ruthenium can have three possible equilibrium crystal structures: FCC, BCC, and HCP.

Consider a reservoir with a fixed pressure of one atmosphere and a fixed temperature of T^{res} that is simultaneously in equilibrium with FCC, BCC, and HCP solutions of Fe-Ru.

If the FCC and BCC solutions can freely exchange both iron and ruthenium atoms, then their Gibbs free energies must be equal at equilibrium.

False. The Gibbs Free energy is an extensive quantity and the statement does not imply that the FCC and BCC system is composed of the same number of moles.

Common Errors	
Symbol	Error Description
α	Misleading supporting statement indicating misunderstanding of the concept.

2-1-v At one atmosphere pressure, a solution composed of Iron and Ruthenium can have three possible equilibrium crystal structures: FCC, BCC, and HCP.

Consider a reservoir with a fixed pressure of one atmosphere and a fixed temperature of T^{res} that is simultaneously in equilibrium with FCC, BCC, and HCP solutions of Fe-Ru.

If the FCC and BCC solutions can freely exchange both iron and ruthenium atoms, then the composition of the two solutions must be the same at equilibrium.

False. The condition of equilibrium is that the chemical potential of Fe and that of Ru must be uniform and equal in each phase. Equality of chemical potential does not restrict equality of composition.

Common Errors	
Symbol	Error Description
α	Answer indicates no understanding of chemical equilibrium.
β	Correct answer, but incorrect reasoning.
γ	Answer indicating incomplete understanding of chemical equilibrium.

2-1-vi If one mole of material of phase α , in thermal and mechanical equilibrium with a reservoir of fixed $P = P^{\text{res}}$ and $T = T^{\text{res}} = 500\text{K}$, is observed *spontaneously* to absorb 1000 Joules of heat as it transforms to phase β , what are the *maximum* and *minimum* values of $\Delta \overline{S}^{\alpha \rightarrow \beta}$?

¹In the absence of effects of capillarity, which have not been discussed at this point of the course.

$$\begin{aligned}
 -T\Delta S_{\text{universe}} = \Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} &\leq 0 \\
 &= 1000 - 500S_{\text{system}} \leq 0
 \end{aligned}
 \tag{1}$$

Therefore, $2 \frac{\text{J}}{\text{K mole}} \leq \overline{\Delta S^{\alpha \rightarrow \beta}} < \infty$

Common Errors	
Symbol	Error Description
α	Assumed that the initial state of the system was determined, and because entropy is a state function reasoned that the entropy change was single-valued.
β	Incorrect reasoning for determination of bounds.
γ	Made sign error.
δ	Gave answer, but didn't specify units of answer.
ϵ	Applied a ΔS statement, but did not specify an applicable system.

2-1-vii Please answer the question by drawing and annotating the diagram below.

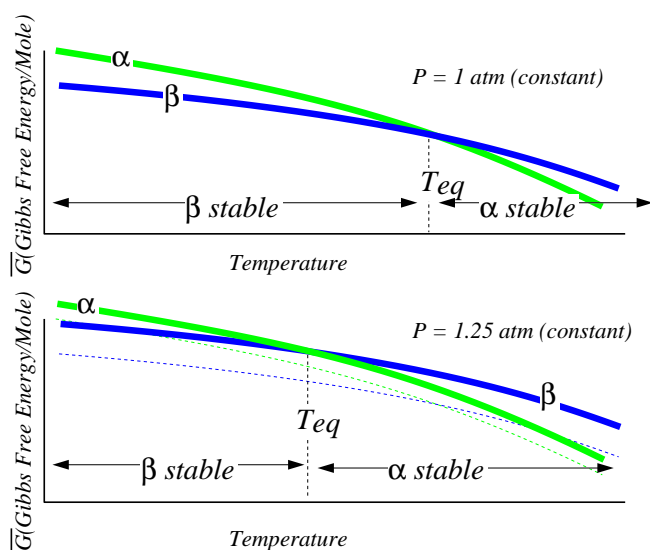


Figure 1: On the top diagram, the molar Gibbs free energy is plotted for two phases, α and β at fixed pressure (1 atm) and composition. On the top diagram, annotate the temperature ranges where each phase is most stable. For the bottom diagram at pressure 1.25 atm, illustrate (schematically) how the curves and ranges of stability will change if $\overline{V}^{\alpha}/\overline{V}^{\beta} = 1/100$.

The motion of the curves with pressure can be determined from

$$d\overline{G} = \overline{V}dP - \overline{S}dT \tag{2}$$

Both curves will move upwards, but the one with the greatest molar volume will move the most.

Common Errors	
Symbol	Error Description
α	Drew motion of β -curve in wrong direction relative to α -curve.
β	Drew curves but gave no further rationalization.
γ	Draw curves correctly, but gave a misleading supporting statement.
δ	Reversed sense of volume with regard to rationalization of curve motion whether by utilization of $d\bar{G} = \bar{V}dP$ or by LeChatelier's statement reasoning.
ϵ	Wrote statement that seemed to imply everything is composed of ideal gases.

Each of the two parts of Question 2.2 requires a precise statement and a short theme of two or three sentences about the statement.

Problem was graded by ranking answers from best to worst. Lower case roman numerals indicate ranking.

Exam Question 2.2

2-2-i Write a precise and accurate statement that expresses a condition of global equilibrium. If you use equations, be sure to define each term or symbol.

There are many alternative statements of global equilibrium. Here is one:

$$(\delta U)_{\delta S=0, \delta V=0} \geq 0 \quad (3)$$

where δ is a virtual change of U , the internal energy of a system at global equilibrium; S , V the system's total entropy and volume of a system which are constrained to have zero variation.

If any conceivable change in the total internal energy of a system with constant total entropy and volume is greater than or equal to zero, then the total internal energy is at its global minimum and that system is in global equilibrium.

2-2-ii Define chemical potential and produce a statement of a condition of equilibrium that exemplifies the use of chemical potential.

One definition is:

$$\mu_i \equiv \left(\frac{\partial G}{\partial N_i} \right)_{P, T, N_j \neq N_i} \equiv \left(\frac{\partial U - TS + PV}{\partial N_i} \right)_{P, T, N_j \neq N_i} \quad (4)$$

The chemical potential of species i is the rate of increase of G with the addition of the i -th species when all other independent variables are fixed.

For any two systems (that are in equilibrium with the same temperature and pressure reservoirs) that can exchange a chemical species, the systems are in equilibrium with respect to exchange of that chemical species if the chemical potentials are uniform and equal in the two systems.

Exam Question 2.3

In this problem, the equilibrium for ideal gas reactions between monatomic oxygen ($O_{(gas)}$), diatomic oxygen ($O_{2(gas)}$), and ozone ($O_{3(gas)}$) are considered for room temperature $T = 300K$ as a function of pressure.

The production of **one mole of monatomic oxygen** from **diatomic oxygen** has an associated increase in Gibbs Free energy of $\Delta G = 227$ kilojoules (or $\exp(-\Delta G/RT) = 3 \times 10^{-40}$ at $T = 300K$).

The production of **one mole of ozone** molecules from **diatomic oxygen** has an associated increase in Gibbs Free energy of $\Delta G = 163$ kilojoules (or $\exp(-\Delta G/RT) = 4 \times 10^{-29}$ at $T = 300K$).

Consider a closed system containing only oxygen with a piston that can be used to fix the total pressure. Assume that the only reactions are between species of monatomic oxygen, diatomic oxygen, and ozone.

At what total pressure will the concentrations of monatomic oxygen, diatomic oxygen, and ozone be equal? In other words, calculate the pressure at which the composition is equal parts monatomic oxygen, diatomic oxygen, and ozone.

This problem has no solution. It is overconstrained, meaning there are more independent equations than independent variables. This was unintentional—as I finished the question, it seemed easily soluble by the method that I show below. However, upon working the solution out in detail I learned that I had given one too many constraints.

I am sorry. I graded very liberally on this problem. If you wrote something that indicated that you knew how to approach such problems, you received all or nearly full credit.

Let $\Delta G_{mon} = 227\text{kJ}/(\text{mole monatomic oxygen})$ and let $\Delta G_{oz} = 163\text{kJ}/(\text{mole ozone})$

Then for $\frac{1}{2}\text{O}_2(\text{gas}) \rightleftharpoons \text{O}(\text{gas})$,

$$\frac{X_{\text{O}}}{X_{\text{O}_2}^{1/2}} = P_{\text{total}}^{-1/2} \exp(-\Delta G_{mon}/RT) \quad (5)$$

and for $\frac{3}{2}\text{O}_2(\text{gas}) \rightleftharpoons \text{O}_3(\text{gas})$,

$$\frac{X_{\text{O}_3}}{X_{\text{O}_2}^{3/2}} = P_{\text{total}}^{1/2} \exp(-\Delta G_{oz}/RT) \quad (6)$$

Furthermore, equal compositions imply

$$X_{\text{O}_3} = X_{\text{O}} = X_{\text{O}_2} = \frac{1}{3} \quad (7)$$

There are already five equalities for the four unknowns (X_{O_3} , X_{O} , X_{O_2} , and P_{total})

We could divide the first two equations to get:

$$\frac{X_{\text{O}_3}}{X_{\text{O}_2} X_{\text{O}}} = P_{\text{total}} \frac{\exp(-\Delta G_{mon}/RT)}{\exp(-\Delta G_{oz}/RT)} \quad (8)$$

which would give $P_{\text{total}} = 4 \times 10^{11} \text{atm}$, but plugging this solution into either of the first two equations indicates the over constraint.