

MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
**Thermodynamics of Materials**

3.00 Fall 2001

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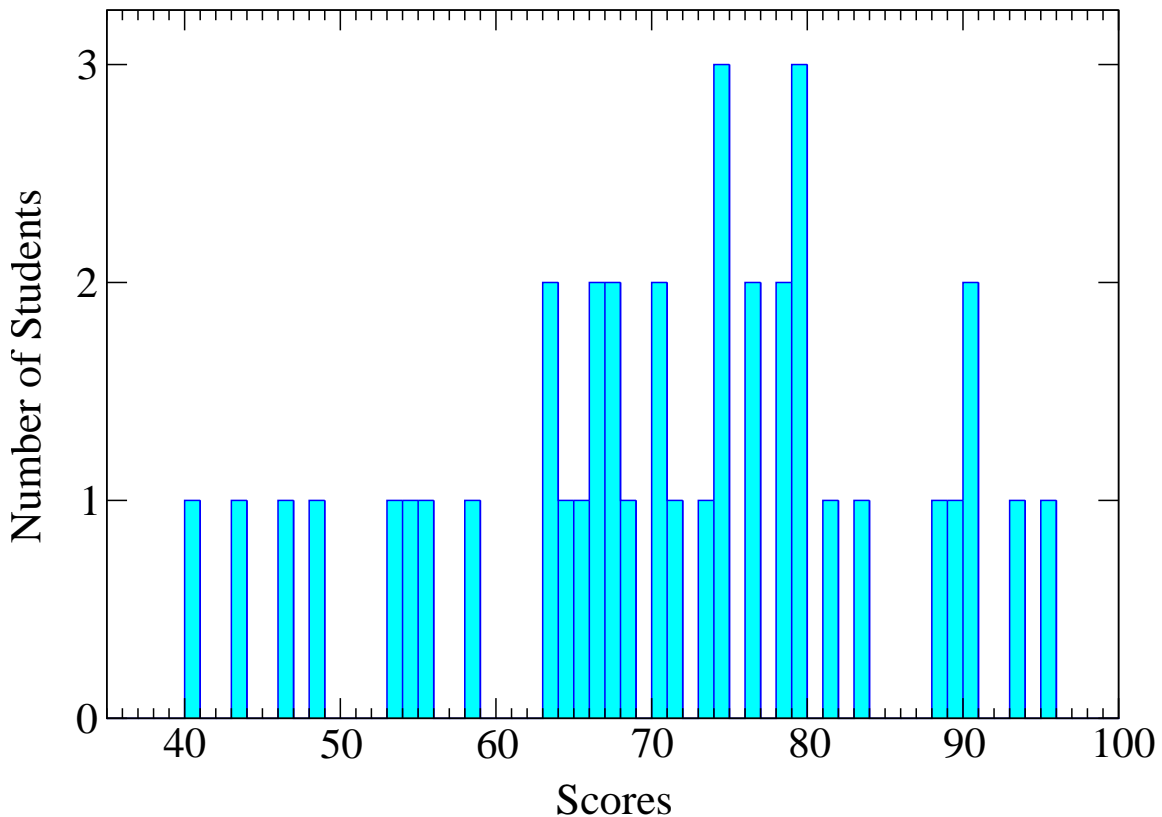
Cambridge, MA 02139

Exam 2: Friday Nov. 9, 2001 (11:05-11:55AM)

## Solutions and Results

### F2001 3.00 Exam 2 Results

Average 71.5      Average Dev. 13.6



Question 2.1: 40 points possible \_\_\_\_\_  
Question 2.2: 30 points possible \_\_\_\_\_  
Question 2.3: 30 points possible \_\_\_\_\_  
Total: 100 points possible \_\_\_\_\_

## Exam Question 2.1

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.

2-1-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.

False as written, but the statement would be true if the molar Gibbs free energy was specified. It would also be true if it were specified that the two phases had the same *extent*—in other words, one phase could be *completely* converted to the other.

Common Errors	
Symbol	Error Description
$\alpha$	Failure to recognize that equality of extensive $G$ is not necessarily meaningful.
$\beta$	Wrote a correct answer, but included extraneous and/or incorrect information.
$\gamma$	Wrote an incorrect statement.

2-1-ii The chemical potential of any species that can be exchanged between two phases will always be equal.

False as written, but the statement would be true if it were specified that the system was in equilibrium. Chemical potentials can vary spatially if the system is not at equilibrium.

Common Errors	
Symbol	Error Description
$\alpha$	Failure to specify equilibrium.
$\beta$	Wrote a correct answer, but included extraneous and/or incorrect information.
$\gamma$	Wrote an incorrect statement.

2-1-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 there is at least one process that increases its Gibbs free energy.

The statement is not necessarily true. For equilibrium, **all** imaginable processes would have a positive change in the Gibbs free energy at equilibrium. The existence of a **single** process is not sufficient to specify equilibrium.

Common Errors	
Symbol	Error Description
$\alpha$	Failure to recognize a single increasing process is insufficient.
$\beta$	Wrote a correct answer, but included extraneous and/or incorrect information.
$\gamma$	Failed to read statement carefully, but wrote a statement that was substantially correct.

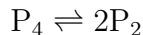
2-1-iv A mole of pure carbon in a graphite crystalline lattice has about twice the entropy content as a mole in a pure carbon diamond cubic crystalline lattice. Therefore, pure carbon-graphite is more disordered than pure carbon-diamond.

Because a crystalline lattice is highly ordered, it is difficult to correlate differences in the entropy of two lattices of a same pure component with a concept of disorder. Entropy can be thought of as a measure of the different ways that a system can store a fixed amount of energy—and this includes, but is not limited to, standard notions of disorder. The statement is misleading and therefore should be considered false.

Common Errors	
Symbol	Error Description
$\alpha$	Claimed that entropy and disorder are synonymous.
$\beta$	Wrote a correct answer, but included extraneous and/or incorrect information.
$\gamma$	Wrote statement that had no direct bearing on solution.
$\delta$	Wrote statement that erroneously indicated that a large value of entropy was indicative of stability .

## Exam Question 2.2

Consider the gaseous reaction:



For a system that has **only** the gases  $P_4$  and  $P_2$  present, it is determined that at  $T=1430\text{K}$  and  $P_{\text{total}}=1\text{ atm}$ , the mole fractions of  $P_4$  and  $P_2$  are equal ( $X_{P_4} = X_{P_2}$ ).

Approximating the system as an ideal gas mixture, find the mole fraction of  $P_4$  at the same temperature ( $T=1430\text{K}$ ) and at a total pressure  $P_{\text{total}} = \frac{3}{8}\text{ atm}$ .

$$\frac{P_{P_2}^2}{P_{P_4}} = K_{eq}(T)$$

Let  $x$  be the mole fraction of  $P_4$ , therefore  $(1-x)$  is the mole fraction of  $P_2$ . Because the mole fraction times the total pressure is the partial pressure,

$$\frac{(1-x)^2 P_{\text{total}}^2}{x P_{\text{total}}} = K_{eq}(T)$$

therefore,

$$\frac{(1-x)^2}{x} = \frac{K_{eq}(T)}{P_{\text{total}}}$$

As stated, the mole fractions of  $P_4$  and  $P_2$  are equal, so  $x = 1/2$  at  $P_{\text{total}} = 1\text{atm}$  implies that  $K_{eq} = 1/2$  at  $1430\text{K}$ .

If  $P_{\text{total}} = \frac{3}{8}\text{atm}$ , then

$$\frac{(1-x)^2}{x} = \frac{8}{(3)(2)}$$

or

$$x^2 - \frac{10}{3}x + 1 = 0 = \left(x - \frac{1}{3}\right)(x - 3)$$

and  $x = 1/3$  is the only solution that makes sense for a mole fraction.

Common Errors	
Symbol	Error Description
$\alpha$	Failure to write down a reaction equilibrium equation that is a function only of temperature.
$\beta$	Wrote a $K_{eq}$ but with incorrect exponents.
$\beta'$	Wrote a $K_{eq}$ but with incorrect pressure relationship.
$\gamma$	Failure to realize that sum of mole fractions must be one.
$\delta$	Algebra error.
$\epsilon$	Couldn't find an expression for mole fractions.

If you can't find either an expression or a numerical answer for the above, you may get partial credit by stating what the mole fractions are in the initial state ( $T=1430\text{K}$  and  $P_{\text{total}}=1\text{ atm}$ ) and whether and why  $X_{P_4}$  should be larger or smaller at  $P_{\text{total}} = \frac{3}{8}\text{ atm}$ .

- a If the initial mole fractions are equal and they sum to one,  $X_{P_4} = X_{P_2} = 1/2$ .
- b Lower pressure should favor reactants because they occupy twice the volume, therefore the mole fraction of  $P_4$  should decrease with decreased pressure.

Common Errors	
Symbol	Error Description
$\eta$	Got the volume-pressure relationship backwards.
$\lambda$	Didn't realize which side had the lowest volume.
$\mu$	Incorrect reasoning.

### Exam Question 2.3

Consider a closed chamber of fixed volume that is divided into two equal parts by a rigid membrane.

Initially, each part contains an ideal gas mixture of Helium and Xenon with partial pressures specified in the figure. (n.b., the membrane cannot move so that there are always two chambers each at 1 cubic meter).

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.

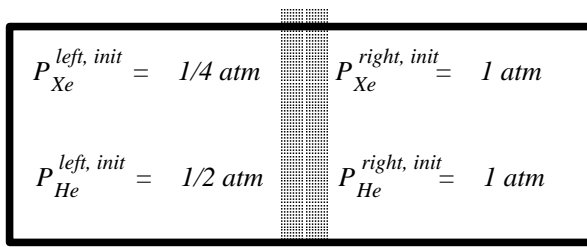


Figure 1: Chamber with a rigid osmotic membrane that allows only transport of He and no transport of Xe. The temperature is constant and uniform.

What are the partial pressures of Xe and He in the left and right chambers at equilibrium?

The following steps are included to help your reasoning. You may use them if you think they help—otherwise, any method that will lead you to the correct answer is acceptable.

2-3-i Write equations expressing the condition(s) for equilibrium. Only the chemical potential of He must be equal across the membrane because the amount of He is the only exchangeable extensive quantity.

$$\begin{aligned} \mu_{\text{He}}^{\text{left, final}} &= \mu_{\text{He}}^{\text{right, final}} \\ \mu_{\text{He}}^{\circ} + RT \log P_{\text{He}}^{\text{left, final}} &= \mu_{\text{He}}^{\circ} + RT \log P_{\text{He}}^{\text{right, final}} \\ P_{\text{He}}^{\text{left, final}} &= P_{\text{He}}^{\text{right, final}} \end{aligned}$$

2-3-ii Write equations expressing any constraint(s) on the system. The total number of He atoms in the system are fixed:

$$N_{\text{He}}^{\text{left, final}} + N_{\text{He}}^{\text{right, final}} = N_{\text{He}}^{\text{left, init}} + N_{\text{He}}^{\text{right, init}} =$$

Multiply both sides of the equation by  $RT/V_{\text{chamber}}$  (we can do this step because the volumes on both sides are equal), then

$$P_{\text{He}}^{\text{left, final}} + P_{\text{He}}^{\text{right, final}} = P_{\text{He}}^{\text{left, init}} + P_{\text{He}}^{\text{right, init}} =$$

Therefore,

$$P_{\text{He}}^{\text{left, final}} = P_{\text{He}}^{\text{right, final}} = \frac{P_{\text{He}}^{\text{left, init}} + P_{\text{He}}^{\text{right, init}}}{2} = \frac{3}{4} \text{ atm}$$

Common Errors	
Symbol	Error Description
$\alpha$	An incorrect equilibrium expression for this problem.
$\beta$	Didn't utilize the fact that the total amount of He is fixed.
$\gamma$	Concluded, incorrectly, that the total pressures must be equal on both sides
$\delta$	Assumption that He and Xe are reacting, or assumption of reaction equilibrium.
$\epsilon$	A correct guess at the solution without apparent demonstration.
$\mu$	Substantially correct assumptions, but couldn't find an expression.
$\eta$	Irrelevant or incorrect information.

If you can't find either an expression or a numerical answer for the above, you may get partial credit by stating whether (and why) you expect the pressure of He to increase or decrease in the left chamber.

Partial pressure should increase in the left chamber because it is initially lower there.