3.020, Spring 2021
Thermodynamics of Materials
Problem Set 2

Massachusetts Institute of Technology
Department of Materials Science and Engineering

Due March 5, 2021 at 10am EST

We encourage you to work in groups. If you do so, please note the names of your groupmates on the first page of your solutions.

Remember to clearly present your solutions, including intermediate steps. We have provided a lot of space for each problem in this document, so please make use of it. Failure to show your work may result in reduced credit. Sloppy presentation may result in reduced credit.

2.1: Conditions for equilibrium [15 pts]

For this problem you're going to rationalize the conditions for equilibrium for a system held at isothermal and isobaric conditions. On the following page you'll find a helpful description of a similar argument, but for a system held at isothermal and isochoric conditions; the case for isothermal and isobaric is an extension of this argument.

   Recommended to use extra paper if needed!

(a) [1 pt] State the condition for equilibrium for an isolated system.

(b) [1 pt] State the condition for equilibrium for a system held at isothermal and isobaric conditions.

(c) [11 pt] Prove that the Gibbs free energy of a closed system with nonrigid, diathermal boundaries, in contact with a temperature and pressure reservoir, cannot increase in an isothermal isobaric process. *Please work on a blank page, you'll likely need plenty of space.*

(d) [2 pt] Explain in words (e.g. 1-3 sentences) how your result implies the Gibbs free energy minimum criterion for equilibrium.

The following is a worksheet for the case of isothermal and isochoric conditions, meant to help you construct your agurment for isothermal and isobaric conditions.

To solve this problem, we'll construct an arbitrary closed system with diathermal, rigid boundaries, enclosed in a huge closed system with fixed volume and insulated boundaries:
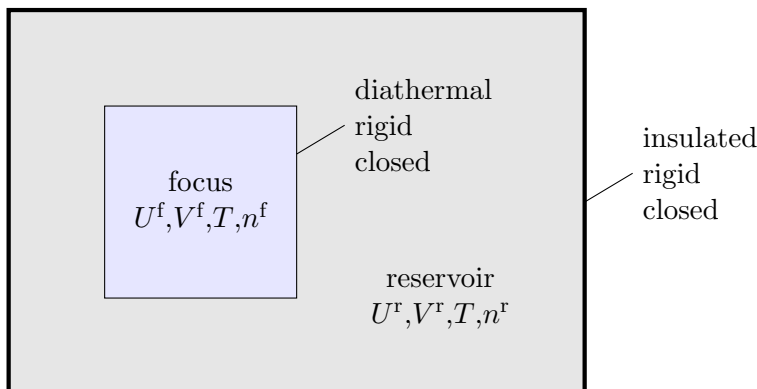
The enclosing system is called a "thermal reservoir" and we conceptualize it as being so massive, its temperature cannot change no matter how much heat energy it exchanges with the smaller, focus system. We'll denote properties relating to the reservoir using a superscript r and we'll denote properties relating to the enclosed "focus" system using the superscript f. We'll denote properties relating to the composite of the two using the superscript c.

Let the reservoir be at temperature T. Suppose that the focus system is initially in state 1, which is at temperature T, and undergoes an isothermal process to state 2. We'll use subscripts to denote states.

We'll start by applying the first law to the composite system for process $1 \to 2$:

$$\Delta U^{\mathrm{c}}_{1\to 2} =$$

where $Q^{\mathrm{c}}_{1\to 2}$ is the heat that flows into the composite system during the process, and $W^{\mathrm{c}}_{1\to 2}$ is the work performed on the composite system during the process. We are able to immediately evaluate the right-hand-side of this equation (how?):

$$\Delta U^{\mathrm{c}}_{1\to 2} = \tag{1}$$

Now, because internal energy is (intensive or extensive?) we are able to express $\Delta U^{\mathrm{c}}_{1\to 2}$ in terms of $\Delta U^{\mathrm{f}}_{1\to 2}$ and $\Delta U^{\mathrm{r}}_{1\to 2}$:

$$\Delta U^{\mathrm{c}}_{1\to 2} =$$

from which, using Eqn (1), we are able to relate $\Delta U^{\mathrm{f}}_{1\to 2}$ and $\Delta U^{\mathrm{r}}_{1\to 2}$:

$$\Delta U^{\mathrm{r}}_{1\to 2} = \tag{2}$$

Now we apply the first law to the reservoir alone for process $1 \to 2$:

$$\Delta U^{\mathrm{r}}_{1\to 2} =$$

where $Q^{\mathrm{r}}_{1\to 2}$ is the heat that flows into the reservoir during the process, and $W^{\mathrm{r}}_{1\to 2}$ is the work performed on the reservoir during the process. Again, we are able to eliminate a term on the right (how?):

$$\Delta U^{\mathrm{r}}_{1\to 2} =$$

3

from which, using Eqn (2), we are able to express $Q^r_{1\to2}$ in terms of $\Delta U^f_{1\to2}$:

$$Q^r_{1\to2} = \tag{3}$$

Now that we've applied the First Law to the reservoir and the composite system, it's time to apply the Second Law. When heat Q flows reversibly into a system at constant temperature T, the entropy of the system changes:

$$\Delta S = \frac{Q}{T}$$

This definition applies readily for the thermal reservoir; the following relationship holds:

$$\Delta S^r_{1\to2} = \frac{Q^r_{1\to2}}{T}$$

We can apply Eqn (3) to get the reservoir's entropy change in terms of the focus system's internal energy change:

$$\Delta S^r_{1\to2} = \tag{4}$$

Because entropy is (intensive or extensive?) we can express $\Delta S^c_{1\to2}$ in terms of $\Delta S^f_{1\to2}$ and $\Delta S^r_{1\to2}$:

$$\Delta S^c_{1\to2} = \tag{5}$$

Now, we're going to use a simple mathematical trick: we're going to express the entropy change of the focus system as follows (multiplying by 1):

$$\Delta S^f_{1\to2} = \frac{T\Delta S^f_{1\to2}}{T} \tag{6}$$

Now we're going to substitute Eqn (4) and Eqn (6) into Eqn (5) to obtain the following expression:

$$\Delta S^c_{1\to2} = \frac{(\quad\quad\quad\quad\quad\quad)}{T} \tag{7}$$

Now, the change in Helmholtz free energy for an isothermal process is:

$$\Delta F = \Delta U - T\Delta S$$

so we can rewrite Eqn (7) express the entropy change of the composite system in terms of $\Delta F^f_{1\to2}$:

$$\Delta S^c_{1\to2} = \tag{8}$$

We know that the following inequality holds for the change in entropy of the composite system (why? justify this step...):

$$\Delta S^c_{1\to2} \ (\ \leq \ \text{or} \ \geq \ ? \ ) \ 0$$

so (using Eqn (8)) the following inequality holds:

$$-\frac{\Delta F^f_{1\to2}}{T} \ (\ \leq \ \text{or} \ \geq \ ? \ ) \ 0$$

and so, since $T > 0$ we can multiply though by $-T$ to obtain:

$$\Delta F^f_{1\to2} \ (\ \leq \ \text{or} \ \geq \ ? \ ) \ 0$$

which proves that the Helmholtz free energy of the focus system cannot have increased in the process from state 1 to state 2.

2.2: Heats of reaction [2 pts]

Show that for an isobaric reversible process, the change in enthalpy is equal to the heat. This justifies the phase "heat of reaction" commonly used to describe enthalpy changes.

2.3: Using the general strategy (a.k.a. fun with multi) [6 pts]

(a) [3 pts] Calculate the coefficients that describe the change in G with P and S, written as A and B in this differential form:

$$dG = AdP + BdS$$

(b) [3 pts] Draw a curve representing $G(S)$ at constant P. Your curve may not be accurate - you don't even need to put numbers on the axes - but it should have the correct slope and curvature.

2.4: Find the Why! [7 pts]

A spontaneous process is one which takes a system towards equilibrium by optimizing the relevant thermodynamic potential. In materials processing, this is most often the Gibbs free energy. In the following you will estimate certain thermodynamic quantities based on observation of spontaneous processes.

Some context: *Proteins are the biological modules responsible for regulating most of life's physiological processes. These molecules are long chains of small amino acids. Proteins typically need to be folded into a particular 3D structure in order to function properly.*

Leventhal's Paradox: MIT professor Cyrus Levinthal noted that proteins fold rather quickly based on the astronomical number of potential configurations of the bond angles. For example: a small sized protein consisting of 101 amino acids would have 100 petite bonds, and thus 200 phi and psi bond angles consisting of 3 possible confirmations each. This theoretical protein would have 3^{200} or 2.7×10^{95} possible confirmations. If this protein can sample one conformation each picosecond would still take 2.7×10^{86} seconds. By comparison the age of the universe is only 4.3×10^{17} sec-

onds. For perspective, the largest protein complex isolated is Photosystem I with 6,771 amino acids!

So, how does life even work? As you may have guessed, protein folding is governed by thermody-namics. The interaction between the side chains of the amino acid sequence as well as with the sur-rounding water will make the functional conformation of the protein thermodynamically favorable. Gibbs free energy can describe the spontaneity of this protein folding. Understanding this process on the molecular level and being able to predict protein folding outcomes has long been considered a holy grail of biochemistry. In late-2020, a team at Deepmind announced a major advance in the field using methods of artificial intelligence and deep learning, taking home the Critical Assessment of Structure Prediction challenge prize. Read all about it: https://www.nature.com/articles/d41586-020-03348-4

(a) [2 pts] Cytochrome C is a fairly ubiquitous protein used in electron transfer in cellular metabolism. The change in enthalpy of folding is given for 2 different temperatures in the following table. At each temperature calculate the minimum possible change in entropy for the folding process to be spontaneous.

Temperature (Celsius)	ΔH of folding (kJ/mol)
-5	-8117
15	-7501

(b) [1 pt] Describe in a few words why protein folding results in a decrease in entropy.

(c) [2 pts] Moving on from protein folding, now consider mercury (Hg), the Roman messager god, the Greek Hermes, and a liquid metal at ambient conditions. Assume that the latent heat of fusion is 2.295 kJ/mol and can be treated as a constant. What's the minimum entropy change upon melting such that the liquid phase is more stable than the solid for all $T > 300$ K?

(d) [2 pts] An aqueous $CaCl_2$ solution has higher entropy than equivalent amounts of crystalline $CaCl_2$ and liquid water. Assume that heat of dissolution is a constant, $\Delta H_{soln} = 82.8$ kJ/mol. What is the minimum entropy change of solution forming required for $CaCl_2$ to dissolve spontaneously for all $T > 350$ K?

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