

Homework Assignment 8

PHYSICS 314 - THERMODYNAMICS & STATISTICAL PHYSICS (Spring 2018)

Due Friday, April 13th, by noon, Noyce 1135

I cannot award full credit for work that I am unable to read or follow. For my benefit and for yours, please:

- Write neatly
- Show and EXPLAIN all steps
- Make diagrams large and clearly-labeled

You are welcome to collaborate with others on this assignment. However, the work you turn in should be your own. Please cite collaborators and outside sources. See the syllabus for details.

Regardless of the number of parts, all homework problems are weighted equally. Regardless of the number of questions, all homework assignments are weighted equally.

- 1) State whether the following quantities are *extensive* or *intensive*. Explain your answer both in words and using the mathematics of extensive and intensive variables discussed on pages 163-164 of Schroeder.

- a) Heat capacity, C_V

Heat capacity is **extensive**; it is the amount of heat needed to raise the temperature of a substance by a given amount. The amount of heat needed is directly proportional to how much of the substance there is.

Heat capacity at a constant volume is the derivative of energy with respect to temperature with the volume fixed.

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V$$

Energy is an extensive quantity, and temperature is an intensive quantity. Extensive divided by intensive yields extensive.

- b) Specific heat, c_V

Specific heat is **intensive** because it is the amount of heat needed to raise the temperature of a substance by a given amount *divided by the amount of the substance*. Thus the amount of substance is factored out by definition.

Furthermore, the specific heat is the ratio of two extensive quantities, heat capacity and mass. Dividing one extensive quantity by another yields an intensive quantity.

$$c_v = \frac{C_V}{m}$$

- 2) Four new thermodynamic potentials can be obtained by subtracting μN from the four thermodynamic potentials that we have been discussing in class, U , H , F , and G . Probably the most useful of the four is the *grand free energy* (also known as the *grand potential*), Φ .

$$\Phi \equiv F - \mu N$$

- a) Derive the thermodynamic identity for the grand free energy. From this identity, find the related formulas for the partial derivatives of grand free energy with respect to T , V , and μ .

Use the product rule to write an expression for a differential change in grand free energy.

$$d\Phi = dF - \mu dN - d\mu N$$

This can be simplified by subbing in the expression for a differential change in Helmholtz free energy (Schroeder (5.20)).

$$d\Phi = (-S dT - P dV + \mu dN) - \mu dN - d\mu N$$

$$d\Phi = -S dT - P dV - N d\mu$$

Hold two variables constant at a time to find the partial derivative expression for the third.

Fix volume and chemical potential.

$$d\Phi = -S dT$$

$$S = -\left.\frac{\partial\Phi}{\partial T}\right|_{V,\mu}$$

Fix volume and temperature.

$$d\Phi = -d\mu N$$

$$N = -\left.\frac{\partial\Phi}{\partial\mu}\right|_{V,T}$$

Fix chemical potential and temperature.

$$d\Phi = -P dV$$

$$P = -\left.\frac{\partial\Phi}{\partial V}\right|_{\mu,T}$$

- b) Is grand free energy *extensive* or *intensive*? Explain your answer both in words and using the mathematics of extensive and intensive variables discussed on pages 163-164 of Schroeder.

Grand free energy, like the other energies discussed, is **extensive**. If we double the amount of stuff, we add the individual energies of the old and the new, and get double the original energy.

Furthermore, from the problem above, grand free energy can be written as the difference between an extensive quantity, F , and the product of an intensive (μ) and extensive (N) quantity.

$$\Phi \equiv F - \mu N$$

The product of an intensive and extensive quantity is an extensive quantity. Thus, grand free energy is the difference between two extensive quantities and thus is extensive.

3) Examine the following partial derivative relationships for chemical potential that we derived in class.

$$\mu = \left. \frac{\partial G}{\partial N} \right|_{T,P} \quad \mu = \left. \frac{\partial F}{\partial N} \right|_{T,V}$$

Carefully explain *in your own words* why the first equality implies that the chemical potential is equal to the Gibbs free energy per particle: $G = N\mu$, yet the second does **NOT** imply that the chemical potential is equal to the Helmholtz free energy per particle: $F = N\mu$. (Remember that we are free to define $F = 0$ and $G = 0$ wherever we choose.)

Suppose we originally have a system at temperature T_0 and pressure P_0 . The first relationship above implies that when a particle is added to the system while holding the temperature and pressure constant, the Gibbs free energy increases by the current chemical potential, μ_0 .

$$\mu_0 = \left. \frac{\partial G}{\partial N} \right|_{T_0, P_0}$$

If another particle is added, the Gibbs free energy again increases by the *new* chemical potential, μ_{new} .

$$\mu_{new} = \left. \frac{\partial G}{\partial N} \right|_{T_{new}, P_{new}}$$

The question is: Are these chemical potentials the same, or is the chemical potential changed by the addition of the particle?

Temperature and pressure are *intensive* variables, so the number of particles does not change them. With the addition of a particle, the temperature and pressure remain T_0 and P_0 . This implies that the two chemical potentials are the same.

$$\mu_{new} = \left. \frac{\partial G}{\partial N} \right|_{T_{new}, P_{new}} = \left. \frac{\partial G}{\partial N} \right|_{T_0, P_0} = \mu_0$$

Thus, any time another particle is added, the Gibbs free energy increases by the same amount, μ_0 . This implies a linear relationship; the slope of G as a function of N is a constant, μ_0 .

$$G = N\mu_0 + \text{offset}$$

Since the reference point of Gibbs free energy is arbitrary, choose it to be where there are zero particles. This eliminates the offset.

$$G = N\mu_0$$

There is only one chemical potential, so let it be simply μ .

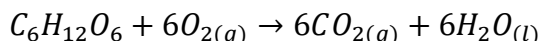
$$G = N\mu$$

The same argument cannot be made for Helmholtz free energy. In the second partial derivative relationship above, temperature and *volume* are held constant. In contrast to pressure, volume is an *extensive* quantity. When a new particle is added, the volume would normally change. However, since volume is fixed, it cannot change with the addition of a new particle. Thus, something else about the system must change. In this case, it is the density, which increases as an additional particle is added to a fixed volume. This increase in density changes the chemical potential. (Consider two otherwise identical systems with different densities. The denser of the two will tend to give up particles to the less dense.) A changing chemical potential means the change to the Helmholtz free energy changes with every new particle added.

$$\mu_{new} \neq \mu_0$$

Thus, no simple linear relationship exists between Helmholtz free energy and number of particles. We cannot conclude that $F = N\mu$.

- 4) Work is produced by muscle when glucose is metabolized through the reaction below.



- a) Use the tables in the back of Schroeder to calculate ΔH and ΔG for this reaction. Assume that there is one mole of glucose ($C_6H_{12}O_6$) and that the reaction takes place at room temperature and atmospheric pressure.

For each substance, the enthalpies of formation from the table are shown below.

$$\Delta H_f(C_6H_{12}O_6) = -1273 \text{ kJ}$$

$$\Delta H_f(O_{2(g)}) = 0 \text{ kJ}$$

$$\Delta H_f(CO_{2(g)}) = -393.5 \text{ kJ}$$

$$\Delta H_f(H_2O_{(l)}) = -285.8 \text{ kJ}$$

To find the change in enthalpy, subtract the enthalpy of formation of the reactants from the enthalpy of formation of the products.

$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

$$\Delta H = [6 \times \Delta H_f(CO_2) + 6 \times \Delta H_f(H_2O_{(l)})] - [\Delta H_f(C_6H_{12}O_6) + 6 \times \Delta H_f(O_2)]$$

$$\Delta H = [6 \times -393.5 \text{ kJ} + 6 \times -285.8 \text{ kJ}] - [-1273 \text{ kJ} + 6 \times 0 \text{ kJ}]$$

$$\Delta H = -2803 \text{ kJ}$$

For each substance, the Gibbs free energy of formation from the table are shown below.

$$\Delta G_f(C_6H_{12}O_6) = -910 \text{ kJ}$$

$$\Delta G_f(O_2) = 0 \text{ kJ}$$

$$\Delta G_f(CO_2) = -394.4 \text{ kJ}$$

$$\Delta G_f(H_2O_{(l)}) = -237.1 \text{ kJ}$$

To find the change in Gibbs free energy, subtract the Gibbs free energy of formation of the reactants from the Gibbs free energy of formation of the products.

$$\Delta G = \Delta G_f(\text{products}) - \Delta G_f(\text{reactants})$$

$$\Delta G = [6 \times \Delta G_f(CO_2) + 6 \times \Delta G_f(H_2O_{(l)})] - [\Delta G_f(C_6H_{12}O_6) + 6 \times \Delta G_f(O_2)]$$

$$\Delta G = [6 \times -394.4 \text{ kJ} + 6 \times -237.1 \text{ kJ}] - [-910 \text{ kJ} + 6 \times 0 \text{ kJ}]$$

$$\Delta G = -2879 \text{ kJ}$$

- b) What is the maximum amount of work that the muscle can perform for each mole of glucose consumed?

The maximum amount of work that can be performed (the “usable work”) is equal to the decrease in the Gibbs free energy.

From part a), $\Delta G = -2879 \text{ kJ}$. The negative sign means that this much energy can be expelled as work.

$$W = -\Delta G = 2879 \text{ kJ}$$

- c) Assuming maximum work output, is heat absorbed or expelled by the chemicals during the metabolism? For one mole of glucose, calculate the amount of heat absorbed or expelled during the metabolism.

By conservation of energy, the energy output of the system is equal to the energy input. In a perfectly efficient process, the energy output is equal to the work output of the system; this is the maximum work output. The energy input to the system is the heat released by the chemical reaction plus any heat added to the system.

The process takes place at constant pressure, and thus the heat from the chemical reaction is equal to the loss of enthalpy during the reaction. From part a), the amount of enthalpy of the system changes by $\Delta H = -2803 \text{ kJ}$. Thus, the heat expelled in the chemical reaction is $Q_{\text{reaction}} = -\Delta H = 2803 \text{ kJ}$.

From part b), the maximum amount of work that can be output is $W = 2879 \text{ kJ}$.

Since the heat released in the chemical reaction is smaller than the work output, **heat must be absorbed by the system** during the reaction to make up for the difference. The difference between the

maximum work output and the heat released by the chemical reaction is the heat that must be absorbed.

$$Q_{\text{absorbed}} = 2879 \text{ kJ} - 2803 \text{ kJ}$$

$$Q_{\text{absorbed}} = 76 \text{ kJ}$$

- d) Explain your answer about the direction of heat flow using the concept of entropy. The table at the back of Schroder has the entropy values needed.

Consider the change in entropy. For each substance, the entropies from the table are shown below.

$$S(C_6H_{12}O_6) = 212 \text{ J/K}$$

$$S(O_2) = 205.1 \text{ J/K}$$

$$S(CO_2) = 213.7 \text{ J/K}$$

$$S(H_2O_{(l)}) = 69.91 \text{ J/K}$$

To find the change in entropy, subtract the entropies of the reactants from the entropies of the products.

$$\Delta S = \Delta S(\text{products}) - \Delta S(\text{reactants})$$

$$\Delta S = [6 \times S(CO_2) + 6 \times S(H_2O_{(l)})] - [S(C_6H_{12}O_6) + 6 \times S(O_2)]$$

$$\Delta S = [6 \times 213.7 \text{ J/K} + 6 \times 69.91 \text{ J/K}] - [212 \text{ J/K} + 6 \times 205.1 \text{ J/K}]$$

$$\Delta S = 259 \text{ J/K}$$

The entropy of the system increases. Thus, heat can flow into the system from the constant temperature environment.

$$Q = T\Delta S$$

$$Q = 298 \text{ K} (259 \text{ J/K})$$

$$Q \approx 77.2 \text{ kJ}$$

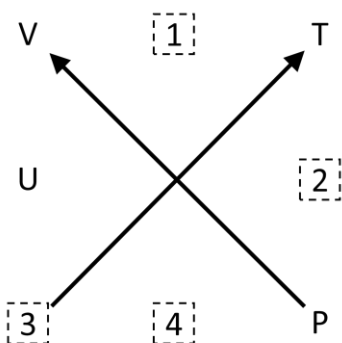
This is close to the 76 kJ found in part c). The difference comes mostly from rounding and uncertainties in the data values from the table.

- e) Now suppose that the operation of the muscle is not ideal. Assume that there are inefficiencies, and the work output is less than the maximum possible work found in part b). Explain *qualitatively* how this changes your answers to parts a), c), and d).

Part a) is unchanged. The enthalpy change and the Gibbs free energy change are independent of how efficiently energy is turned into work.

Inefficiencies mean new entropy must be created somewhere in the system. This new entropy leaves less entropy available to be gained through heat as described in part d). This means less heat can be gained by the system. If the efficiencies create enough new entropy (more than the $\Delta S = 259 \text{ J/K}$ from the reaction), then to get rid of the excess entropy, the system will have to expel heat (rather than absorb it).

- 5) Figure 5.2 on page 151 of Schroeder is one way to visualize the connections between thermodynamic quantities. Another way to visualize the connections is shown below. Your task is to fill in the four numbered squares with the correct thermodynamic quantities.



To understand how the chart works, consider an example. On the left side of the square is the energy, U . The chart indicates the connections between energy and the two adjacent quantities, the one on the top left and the one on the bottom left. The top left position is volume, V , which is connected *against the direction of the arrow* on the diagonal to pressure, P . The bottom left position is the unknown quantity 3, which is connected *with the direction of the arrow* to temperature, T . These connections are to be interpreted as follows:

$$P = -\left.\frac{\partial U}{\partial V}\right|_{(3)} \quad \text{and} \quad T = +\left.\frac{\partial U}{\partial (3)}\right|_V, \quad \text{or}$$

$$dU = -P dV + T d(3).$$

The direction of the arrow determines the sign. *The number of particles is assumed to be held constant.*

Redraw the chart with the numbered squares replaced with the proper thermodynamic quantities. Provide partial differential formulas like the ones above to justify your answers.

First consider unknown 3. Comparing the formula for dU above to Schroeder (3.46), unknown 3 is entropy, S .

$$dU = -P dV + T dS$$

Entropy also correctly completes the derivative formulas.

$$P = -\left.\frac{\partial U}{\partial V}\right|_S \quad \text{and} \quad T = +\left.\frac{\partial U}{\partial S}\right|_V$$

Next consider unknown 4 in a similar manner to how U was treated.

The bottom left position is entropy, S , which is connected *with the direction of the arrow* on the diagonal to temperature, T . The bottom right position is the pressure, P , which is connected *with the direction of the arrow* to volume, V . These connections are to be interpreted as follows:

$$T = +\left.\frac{\partial(4)}{\partial S}\right|_P \quad \text{and} \quad V = +\left.\frac{\partial(4)}{\partial P}\right|_S, \quad \text{or}$$

$$d(4) = T dS + V dP.$$

Comparing the formula for $d(4)$ above to Schroeder (5.18) with fixed N , unknown 4 is enthalpy, H .

Next consider unknown 2 in a similar manner.

The bottom right position is pressure, P , which is connected *with the direction of the arrow* on the diagonal to volume, V . The top right position is the temperature, T , which is connected *against the direction of the arrow* to entropy, S . These connections are to be interpreted as follows:

$$V = +\left.\frac{\partial(2)}{\partial P}\right|_T \quad \text{and} \quad S = -\left.\frac{\partial(2)}{\partial T}\right|_P, \quad \text{or}$$

$$d(2) = V dP - S dT.$$

Comparing the formula for $d(2)$ above to Schroeder (5.23, 5.24) with fixed N , unknown 2 is Gibbs free energy, G .

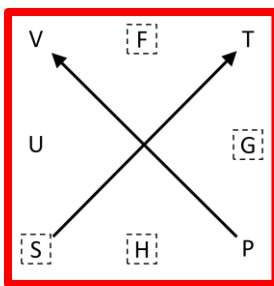
Finally consider unknown 1 in a similar manner.

The top left position is volume, V , which is connected *against the direction of the arrow* on the diagonal to pressure, P . The top right position is the temperature, T , which is connected *against the direction of the arrow* to entropy, S . These connections are to be interpreted as follows:

$$P = -\left.\frac{\partial(1)}{\partial V}\right|_T \quad \text{and} \quad S = -\left.\frac{\partial(1)}{\partial T}\right|_V, \quad \text{or}$$

$$d(1) = -P dV - S dT.$$

Comparing the formula for $d(1)$ above to Schroeder (5.20) with fixed N , unknown 1 is Helmholtz free energy, F .



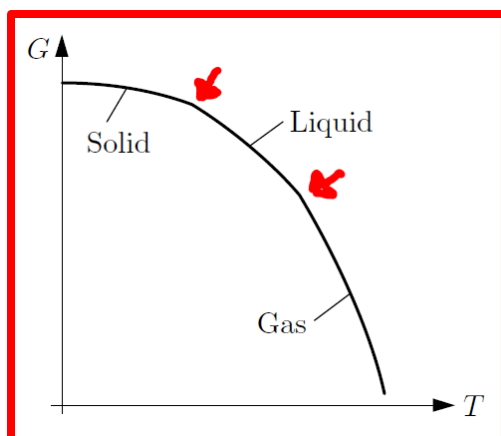
- 6) Sketch a *qualitatively* accurate graph of Gibbs free energy as a function of temperature for a pure substance as it changes from a solid to a liquid to a gas *at fixed pressure*. Assume the number of molecules is also fixed. On your plot, be sure to label the phases and the phase transition points. Briefly explain the main features of your plot. *Hint: Consider the relative entropies of the three phases.*

With fixed pressure and molecule number, the entropy is the negative of the slope of a G vs. T plot.

$$S = - \left. \frac{\partial G}{\partial T} \right|_{P,N}$$

(Schroeder 5.24)

The entropy is always positive, so the slope is always negative. Entropy increases as the substance transitions from a solid to a liquid to a gas. (The solid is more strictly ordered than the liquid or gas, and thus has fewer possible arrangements.) Thus, the magnitude of the slope increases as the substance moves from a solid to a liquid to a gas. Each phase transition (marked with an arrow) corresponds to an abrupt change in entropy, and therefore an abrupt change in slope.



- 7) Read the following material discussing recent topics from class.

Hydrogen-powered vehicles: A chicken and egg problem

<https://physicstoday.scitation.org/doi/full/10.1063/PT.3.3690>

What separates a liquid from a gas?

<https://physicstoday.scitation.org/doi/full/10.1063/PT.3.1796>

Write a short response to the two articles. One paragraph per article is sufficient.

- Summarize the main points of each article in a sentence or two.
- For each article, discuss in a few sentences the connections between the science discussed in the article and the material covered in this course.

- Which article did you feel better conveyed the relevant science? Why? (Keep in mind the intended audience of each piece.)
- Fulfilling the above requirements will earn you a $3.25/4$. The rest of the points will be awarded based on the depth and quality of your explanations of the connections. (For example, a response that discusses the energy flow of a negative temperature system will earn more points than a response that simply states that negative temperature is something we saw in class.)

8) List three main ideas from this homework assignment. For example, you could write a few-sentence explanation of a concept, or list an equation and explain the variables and in what circumstances the equation applies.

The goal is for you to review and to reflect on the big picture. Think about what you might want to remember when you look back at this homework before the test. I hope that this will be useful for your studying. I am not looking for anything specific here; you will be graded on effort and completion.