Physics 114 Statistical Mechanics Spring 2021

Week 3 Reading and Problem Assignment

Overview:

This week we take on *thermodynamic potentials* or *free energies.* Nature chooses to minimize different types of free energy given different constraints. Free energy is also defined as how much energy in a system is available to do useful work. We derive the functional forms of these free energies: F, G, H, Ω, and see how they are used in practical calculations. By considering the differential forms for these free energies and equating mixed partial derivatives, we derive "Maxwell relations". Why play this game? Because sometimes one expression, like $(\frac{\partial S}{\partial V})_T$ could never be realized practically in the lab. But the fact that it is equal to $(\frac{\partial P}{\partial T})_V$ makes it the basis of a real experiment: change temperature with volume held fixed; and measure the change in pressure. Partial derivatives like this allow us to define practical quantities like thermal expansivity, bulk moduli, and specific heats.

Suggested Reading:

G&T Sections

- Chapter 2.21, 2.22, 2.23.2 and 2.24.2

B&B Sections

- Chapter 16
- Ch. 26.1 to middle of p. 299
- Chapter 27

Optional Reading:

Note: You do not have to read any part of Schroeder. But in this week's problems, I may ask you to look up values for free energies or entropies which are conveniently located in his Reference data table found on our Moodle page :-)

- Schroeder's Sections 5.1 and 5.2 do a nice job with free energies. I'll put scans of these, plus his free energy Reference data table, under the "Resources" area of our Moodle site.
- Callen's Chapters 5, 6 & 7 Go over Legendre transformations, thermodynamic potentials, and Maxwell relations in great detail. Again, scans will be under our "Resources" area.

Warmup Problems:

1: Using Maxwell Relations

The isobaric thermal expansion coefficient (what a mouthful!) is called α in

G&T and β in B&B. Sigh!

a) Describe in words what this expansion coefficient tells you about a substance.
b) Use a Maxwell relation together with the third law of thermodynamics to show that $\alpha \to 0$ as $T \to 0$.

2: Deriving Maxwell Relations
Please give a (brief!) derivation of the Maxwell relation which you used in Problem 1.

Problems to discuss in our meeting

Note: The * means that these problems are to be handed in. They are due the day after we meet.

1: Enthalpy is a free energy G&T problem 2.65

2*: Change in Gibbs free energy with temperature You have a piston at 72^oF with 10^{-2} mole of Argon gas inside. If you keep the pressure constant at $P = 1\ atm$ but raise its temperature to 90^oF, how much does its Gibbs free energy change? (Please use the value for S given in Schroeder's data table pp. 404-405.) If you wanted to keep its temperature at 90^oF but change the Gibbs free energy back to the original value by changing its pressure, what would the final pressure be?

3: Legendre transforms G&T problem 2.32

4: The Landau potential G&T problem 2.66

5*: Helmholtz free energy of hydrogen
The first excited energy level of a hydrogen atom has an energy of *10.2* eV, if we take the ground state energy to be zero. However, the first excited state is really four independent states all with the same energy. We can assign it (as we'll see in a week very soon) as having entropy $S = kln4$.

a) For what temperatures is the Helmholtz free energy of a hydrogen atom in the first excited state positive, and for what temperatures is it negative?

b) The surface of the sun has a temperature of about $6000K$. Do hydrogen atoms like to be in their ground state at the sun's surface?

6: Thermodynamic identities for compressibility G&T problem 2.68

7: Using Maxwell relations to describe expansions B&B problem 16.2

8: A natural gas fuel cell (A guided exploration of Schroeder Prob. 5.5)
Background: To form any molecule from its conventional starting state requires "heat of formation". For example, Schroeder's free energy data table tells us that the enthalpy to form a mole of ammonia gas, NH_3, is $\Delta_f H = -46.11kJ$. The minus sign means energy is released when ammonia forms from nitrogen and hydrogen gas ... that the process is "exothermic". The table also lists the Gibbs free energy required at atmospheric pressure as $\Delta_f G = -16.45kJ$. When we talk about the heat for a chemical reaction, by convention we subtract Δ_f of the reactants from Δ_f for the products.

Consider a fuel cell that uses this reaction:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$$

a) Use the Schroeder data table to find ΔH and ΔG for one mole of methane, CH_4, undergoing this reaction at room temperature and atmospheric pressure.
b) Under idealized lab conditions, all of ΔG becomes useful electrical work. What is the electrical work output of this methane fuel cell for each mole of methane?
c) The decrease in enthalpy is the sum of electrical work and the waste heat. How much waste heat is produced for each mole of methane?
d) The whole point of a fuel cell is to produce a voltage. The voltage is equal to *electrical work done / total charge leaving one electrode and arriving at the other*. What is the voltage of this fuel cell if the reaction at each electrode is as shown below?

$$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^- \quad (\textit{oxidation at the cathode})$$

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O \quad (\textit{reduction at the anode})$$

9*: Enthalpy and the Joule-Kelvin (aka Joule-Thompson) process
a) Put into your own words the argument that explains why in a Joule-Kelvin process, the enthalpy does not change ... and thus how we thus derive G&T Eq. (2.218).
b) Do G&T problem 2.30. Suppose that for Helium we have $\frac{a}{bR} = 19K$. What is the inversion temperature of Helium?

10: Helmholtz and Gibbs:
a) The Helmholtz F and Gibbs G free energies are two important thermodynamic potentials. Each of these is minimized by a system under certain circumstances - what are these circumstances?

b) Each of F and G represent "available work", so which one is preferable to use for

i) calculating the energy needed to materialize a rabbit on a table ?

ii) finding the chemical potential μ ?

iii) determining if the following chemical reaction will go at a temperature of $500K$?

$$H_2O \to H_2 + \frac{1}{2}O_2$$

c) Please say which potential is best to use, and then use it to solve this problem: A cylinder contains an internal piston on each side of which is one mole of a monatomic ideal gas. The cylinder walls are diathermal, and the system is immersed in a heat reservoir at temperature 0^oC. The initial volumes of the two gaseous subsystems (on either side of the piston) are 10 L and 1 L, respectively. The piston is now moved reversibly, so that the final volumes are 6 L and 5 L, respectively. How much work is delivered?