Homework 8

Due by 10pm on Wednesday, November 11th, 2020

Reading: Schroeder Ch. 4, Sec 4.3 and Chap. 5, Secs. 5.1-3. Class notes.

1. A heat pump is an electrical device that heats a building by pumping heat in from the cold outside. In other words, it's the same as a refrigerator, but its purpose is to warm the hot reservoir rather than to cool the cold reservoir (even though it does both). Let us define the following standard symbols, all taken to be positive by convention:

T_h = temperature inside building
T_c = temperature outside
Q_h = heat pumped into building in 1 day
Q_c = heat taken from outdoors in 1 day
W = electrical energy used by heat pump in 1 day

(a) Explain why the "coefficient of performance" (COP) for a heat pump should be defined as Q_h/W.
(b) What relation among Q_h, Q_c, and W is implied by energy conservation alone? Will energy conservation permit the COP to be greater than 1?
(c) Use the second law of thermodynamics to derive an upper limit on the COP, in terms of the temperatures T_h and T_c alone.
(d) Explain why a heat pump is better than an electric furnace, which simply converts electrical work directly into heat. (Include some numerical estimates.)

2. Derive Schroeder's Equation (4.10) that gives the efficiency of the Otto cycle.

3. Consider a system made up of one mole of argon gas at room temperature and atmospheric pressure. Compute the total energy (kinetic only, neglecting atomic rest energies), entropy, enthalpy, Helmholtz free energy, and Gibbs free energy. Express all answers in SI units.

4. A muscle can be thought of as a fuel cell, producing work from the metabolism of glucose:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O.$$

(a) Use the data at the back of this book to determine the values of ΔH and ΔG for this reaction, for one mole of glucose. Assume that the reaction takes place at room temperature and atmospheric pressure.
(b) What is the maximum amount of work that a muscle can perform, for each mole of glucose consumed, assuming ideal operation?
(c) Still assuming ideal operation, how much heat is absorbed or expelled by the chemicals during the metabolism of a mole of glucose? (Be sure to say which direction the heat flows.)
(d) Use the concept of entropy to explain why the heat flows in the direction it does.
(e) How would your answers to parts (a) and (b) change, if the operation of the muscle is not ideal?

5. Functions encountered in physics are generally well enough behaved that their mixed partial derivatives do not depend on which derivative is taken first. Therefore, for instance,

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right),$$

where each $\partial/\partial V$ is taken with S fixed, each $\partial/\partial S$ is taken with V fixed, and N is always held fixed. From the thermodynamic identity (for U) you can evaluate the partial derivatives in parentheses to obtain

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V,$$

a nontrivial identity called a **Maxwell relation**. Go through the derivation of this relation step by step. Then derive an analogous Maxwell relation from each of the other three thermodynamic identities we have discussed (for H, F, and G). Hold N fixed in all the partial derivatives; other Maxwell relations can be derived by considering partial derivatives with respect to N, but after you've done four of them the novelty begins to wear off. We'll explore applications of these Maxwell relations in the next homework.

6. 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 level is really four independent states, all with the same energy. We can therefore assign it an entropy of $S = k \ln 4$, since for this given value of the energy, the multiplicity is 4. Question: For what temperatures is the Helmholtz free energy of a hydrogen atom in the first excited level positive, and for what temperatures is it negative? (Comment: When F for the level is negative, the atom will spontaneously go from the ground state into that level, since $F = 0$ for the ground state and F always tends to decrease. However, for a system this small, the conclusion is only a probabilistic statement; random fluctuations will be very significant.)

7. By subtracting μN from U, H, F, or G, one can obtain four new thermodynamic potentials. Of the four, the most useful is the **grand free energy** (or **grand potential**),

$$\Phi = U - TS - \mu N.$$

(a) Derive the thermodynamic identity for Φ, and the related formulas for the partial derivatives of Φ with respect to T, V, and μ.
(b) Prove that, for a system in thermal and diffusive equilibrium (with a reservoir that can supply both energy and particles), Φ tends to decrease.
(c) Prove that $\Phi = -PV$.
(d) As a simple application, let the system be a single proton, which can be "occupied" either by a single electron (making a hydrogen atom, with energy -13.6 eV) or by none (with energy zero). Neglect the excited states of the atom and the two spin states of the electron, so that both the occupied and unoccupied states of the proton have zero entropy. Suppose that this proton is in the atmosphere of the sun, a reservoir with a temperature of 5800 K and an electron concentration of about 2.2×10^{19} per cubic meter. Calculate Φ for both the occupied and unoccupied states, to determine which is more stable under these conditions. To compute the chemical potential of the electrons, treat them as an ideal gas. At about what temperature would the occupied and unoccupied states be equally stable, for this value of the electron concentration? (As in the previous problem, the prediction for such a small system is only a probabilistic one.)