Problem 7.3. Neglecting both spin (which cancels out of the final result) and the excited states of the hydrogen atom (which contribute negligibly even at 10,000 K), this system has just two states:

$$\text{unoccupied:} \quad E = 0, \quad N = 0, \quad \text{Gibbs factor} = e^0 = 1;$$
$$\text{occupied:} \quad E = -I, \quad N = 1, \quad \text{Gibbs factor} = e^{-(-I-\mu \cdot 1)/kT}.$$

The ratio of the probabilities of these two states is the same as the ratio of partial pressures of ionized to un-ionized atoms:

$$\frac{P_p}{P_H} = \frac{\mathcal{P}(\text{unoccupied})}{\mathcal{P}(\text{occupied})} = \frac{1}{e^{-(-I-\mu)/kT}} = \frac{e^{-I/kT}}{e^{\mu/kT}}.$$

Here μ is the chemical potential for electrons. Treating the electrons as an ideal gas and again neglecting spin,

$$\mu = -kT \ln\left(\frac{V Z_{\text{int}}}{N v_Q}\right) = -kT \ln\left(\frac{kT}{P_e v_Q}\right),$$

so $e^{\mu/kT} = P_e v_Q / kT$, which yields the Saha equation,

$$\frac{P_p}{P_H} = \frac{kT}{P_e v_Q} e^{-I/kT}.$$

Problem 7.4. Taking electron spin into account, the hydrogen atom now has two occupied states, each with the same energy, so the ratio of unoccupied to occupied atoms is

$$\frac{P_p}{P_H} = \frac{\mathcal{P}(\text{unoccupied})}{\mathcal{P}(\text{occupied})} = \frac{1}{2e^{-(-I-\mu)/kT}} = \frac{e^{-I/kT}}{2e^{\mu/kT}}. \tag{1}$$

But now, a free electron has two degenerate states, so the chemical potential of the electron gas is

$$\mu = -kT \ln\left(\frac{V Z_{\text{int}}}{N v_Q}\right) = -kT \ln\left(\frac{2kT}{P_e v_Q}\right),$$

implying that $e^{\mu/kT} = P_e v_Q / 2kT$. When we plug this into equation 1, the factors of 2 cancel, yielding the Saha equation exactly as derived in the previous problem.

Problem 7.5. (Ionization of donors in a semiconductor.)

(a) Taking the system to be a single donor ion, there are three possible states: one ionized state (no electron present), and two un-ionized states (with one electron present, either spin-up or spin-down). The energies and Gibbs factors of these states are

$$\text{ionized:} \quad E = 0, \quad N = 0, \quad \text{Gibbs factor} = e^0 = 1;$$
$$\text{un-ionized:} \quad E = -I, \quad N = 1, \quad \text{Gibbs factor} = e^{-(-I-\mu \cdot 1)/kT}.$$

For our parameters, this works out to

$$y = (10^{23} \text{ m}^{-3}) \left(\frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2\pi (9.11 \times 10^{-31} \text{ kg})(7.04 \times 10^{-21} \text{ J})} \right)^{3/2} \frac{e^{1/t}}{t^{3/2}} = (0.0036) \frac{e^{1/t}}{t^{3/2}}$$

(where I've converted N_d/V and I to SI units before doing the arithmetic). To plot x as a function of t I used *Mathematica*, first defining the function $y(t)$ with the instruction y[t_] := 0.0036 * Exp[1/t] / t^1.5. Then, to draw the actual plot, I typed

Plot[(Sqrt[1+4y[t]]-1)/(2y[t]),{t,.01,1}];

This produced the following plot:
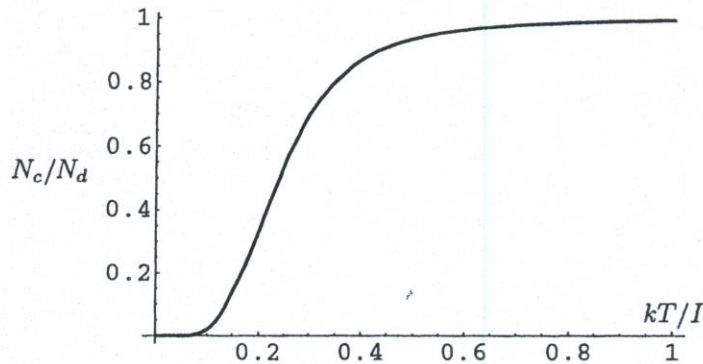
As expected, the fraction of ionized donors goes to zero at low temperature and to 100% at high temperature. Interestingly, the steep increase occurs when kT is substantially less than the ionization energy. To convert the horizontal scale to kelvins, note that $I/k = (0.044 \text{ eV})/(8.62 \times 10^{-5} \text{ eV/K}) = 511$ K. At room temperature, kT/I is about 0.59, and more than 95% of the donors are ionized.

Problem 7.6. It's easiest to start from the right-hand side of the desired relation and work backwards:

$$\frac{kT}{Z} \frac{\partial Z}{\partial \mu} = \frac{kT}{Z} \sum_s \frac{\partial}{\partial \mu} e^{-[E(s) - \mu N(s)]/kT}$$

$$= \frac{kT}{Z} \sum_s \frac{N(s)}{kT} e^{-[E(s) - \mu N(s)]/kT}$$

$$= \sum_s N(s) \frac{1}{Z} e^{-[E(s) - \mu N(s)]/kT}$$

$$= \sum_s N(s) \mathcal{P}(s) = \overline{N}.$$

Similarly, making use of the third line above,

$$\frac{(kT)^2}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} = \frac{kT}{\mathcal{Z}}\frac{\partial}{\partial \mu}\sum_s N(s)e^{-[E(s)-\mu N(s)]/kT}$$

$$= \frac{1}{\mathcal{Z}}\sum_s [N(s)]^2 e^{-[E(s)-\mu N(s)]/kT}$$

$$= \sum_s [N(s)]^2 \mathcal{P}(s) = \overline{N^2}.$$

Notice that these two results can be combined to obtain a formula for $\overline{N^2}$ in terms of $\overline{N}$:

$$\overline{N^2} = \frac{(kT)^2}{\mathcal{Z}}\frac{\partial}{\partial \mu}\left(\frac{\overline{N}\mathcal{Z}}{kT}\right) = \frac{kT}{\mathcal{Z}}\left(\frac{\partial \overline{N}}{\partial \mu}\mathcal{Z} + \overline{N}\frac{\partial \mathcal{Z}}{\partial \mu}\right) = kT\frac{\partial \overline{N}}{\partial \mu} + (\overline{N})^2.$$

The standard deviation of a quantity can be calculated as the square root of the average of the squares minus the square of the average:

$$\sigma_N = \sqrt{\overline{N^2} - (\overline{N})^2} = \sqrt{kT(d\overline{N}/\partial\mu)}.$$

For an ideal gas, $\mu = -kT\ln(VZ_{\text{int}}/Nv_Q)$, where v_Q and Z_{int} are functions of temperature only and the N could just as well be $\overline{N}$ if the number of particles in the gas fluctuates. Therefore $\partial\mu/\partial N = kT/N$ or $\partial\overline{N}/\partial\mu = \overline{N}/kT$, and the standard deviation is simply

$$\sigma_N = \sqrt{kT(\overline{N}/kT)} = \sqrt{\overline{N}}.$$

The appearance of the square root is ubiquitous in formulas for fluctuations, so we could have guessed this result (up to a numerical factor) by dimensional analysis. For a gas of about 10^{23} molecules, the number will typically fluctuate by less than 10^{12}, or about one part in a hundred billion of the total.

Problem 7.7. Recall from Problem 5.23 the partial-derivative relation

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

We can think of N as a function of μ, T, and V; then this equation is a first-order differential equation for Φ as a function of μ, with T and V held fixed. Now define $\widetilde{\Phi} \equiv -kT\ln \mathcal{Z}$, and differentiate with respect to μ:

$$\left(\frac{\partial \widetilde{\Phi}}{\partial \mu}\right)_{T,V} = -kT\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu} = -\overline{N},$$

according to the first result of Problem 7.6. In other words, $\widetilde{\Phi}$ obeys exactly the same differential equation as Φ. All that remains is to show that $\widetilde{\Phi} = \Phi$ at one particular value of μ. Consider both quantities at $\mu = 0$. Under this condition the Gibbs factor reduces to a simple Boltzmann factor, so the grand partition function reduces to the ordinary partition function (though still summed over states with all possible N) and therefore $\widetilde{\Phi} = -kT\ln \mathcal{Z} = -kT\ln Z = F$, as shown in Section 6.5. On the other hand, the original Φ is simply $U - TS - \mu N = U - TS = F$, when $\mu = 0$. Since $\widetilde{\Phi}$ and Φ obey the same differential equation with the same "initial" condition at $\mu = 0$, they must be the same function.

Problem 7.10. (A five-particle system with evenly spaced energy levels.)

(a) If the particles are distinguishable, then all five will settle into the lowest energy level. The same will happen if they are indistinguishable bosons. If they are indistinguishable fermions, however, then only one may occupy each level so each of the five lowest levels will contain one particle. The occupancies of the five lowest levels are therefore:

Distinguishable or Bosons	Fermions
5 0 0 0 0	1 1 1 1 1

(b) If the particles are distinguishable or bosons, then the system's first excited state has one of the five particles promoted to the second-lowest level. For distinguishable particles, there are *five* different ways to do this (choose any one of the five particles to promote), while for identical bosons there is only *one* way (it's meaningless to ask which particle has been promoted). For the system of fermions, the first excited state has the highest-energy particle promoted from the fifth state to the sixth (again adding just one unit of energy), and again there is only one way to do this. Graphically,

Distinguishable or Bosons	Fermions
4 1 0 0 0 0	1 1 1 1 0 1

(c) To add another unit of energy to the systems of bosons or distinguishable particles, we can either promote a second particle to the second-lowest level (leaving three in the lowest level) or leave four in the lowest level and promote the fifth up two levels. For bosons, there is only one way to do either of these things, but for distinguishable particles there are ten ways (5 choose 2) of doing the first and five of doing the second, for a total degeneracy of 15. Meanwhile, for the fermionic system there are two ways of putting in two units of energy, as illustrated below:

Distinguishable or Bosons	Fermions
3 2 0 0 0 0 0	1 1 1 0 1 1 0
4 0 1 0 0 0 0	1 1 1 1 0 0 1

To add yet another unit of energy there are basically three choices for each system, which I'll simply illustrate:

Distinguishable or Bosons	Fermions
2 3 0 0 0 0 0 0	1 1 0 1 1 1 0 0
3 1 1 0 0 0 0 0	1 1 1 0 1 0 1 0
4 0 0 1 0 0 0 0	1 1 1 1 0 0 0 1

Again there is a large degeneracy for the system of distinguishable particles: 10 for the first arrangement (5 choose 3), 20 for the second (5 choices for the highest-energy particle and 4 for the next-highest), and 5 for the third for a total of 35.

(d) The probability for the system to be in any particular state is proportional to the Boltzmann factor for that state, $e^{-E/kT}$ (where E is the total energy of all the particles). For any given E value, this quantity is the same for either system (and furthermore the allowed E values are the same). But the probability, say, of finding the system

with three units of energy is also proportional to the degeneracy, which is 3 for the bosonic system but 35 for the system of distinguishable particles. This means that at low temperatures we are much more likely to find a few units of energy in the system of distinguishable particles than in the system of bosons. Put another way, the ground state of the bosonic system is much more probable (relative to collection of all the low-energy excited states) than we might otherwise guess.

Problem 7.11. The probability of a state being occupied is given by the Fermi-Dirac distribution function, $\dfrac{1}{e^{(\epsilon-\mu)/kT}+1}$. At room temperature, $kT = .026$ eV, so the probabilities are:

(a) For $\epsilon - \mu = -1$ eV, probability $= \dfrac{1}{e^{-1/.026}+1} = (1 + 2\times10^{-17})^{-1} = 1 - 2\times10^{-17} \approx 1.$

(b) For $\epsilon - \mu = -.01$ eV, probability $= \dfrac{1}{e^{-.01/.026}+1} = \dfrac{1}{1.68} = .59.$

(c) For $\epsilon - \mu = 0$, probability $= \dfrac{1}{e^0+1} = \dfrac{1}{2} = .50.$

(d) For $\epsilon - \mu = +.01$ eV, probability $= \dfrac{1}{e^{+.01/.026}+1} = \dfrac{1}{2.47} = .41.$

(e) For $\epsilon - \mu = +1$ eV, probability $= \dfrac{1}{e^{+1/.026}+1} = \dfrac{1}{5\times10^{16}} = 2\times10^{-17}.$

Problem 7.12. According to the Fermi-Dirac distribution, the probability of state B being occupied is

$$\mathcal{P}(B \text{ occupied}) = \frac{1}{e^{(\epsilon_B-\mu)/kT}+1} = \frac{1}{e^{x/kT}+1},$$

since $\epsilon_B = \mu + x$. The probability of state A being *unoccupied* is

$$\mathcal{P}(A \text{ unoccupied}) = 1 - \frac{1}{e^{(\epsilon_A-\mu)/kT}+1} = 1 - \frac{1}{e^{-x/kT}+1} = \frac{e^{-x/kT}+1-1}{e^{-x/kT}+1}$$

$$= \frac{e^{-x/kT}}{e^{-x/kT}+1} = \frac{1}{1+e^{x/kT}},$$

where I've used the fact that $\epsilon_A = \mu - x$. This is exactly the same formula, so the two probabilities are equal as expected.

Problem 7.13. The average occupancy of a state is given by the Bose-Einstein distribution function,

$$\bar{n} = \frac{1}{e^x-1} = \frac{e^{-x}}{1-e^{-x}}, \qquad \text{where } x = (\epsilon-\mu)/kT.$$

The probability of a state being occupied by exactly n particles is

$$\mathcal{P}(n) = \frac{e^{-nx}}{\mathcal{Z}} = (e^{-x})^n(1-e^{-x}).$$

Thus we can compute everything we need from the quantity $e^{-x} = e^{-(\epsilon-\mu)/kT}$, where in this case $kT = .026$ eV.

is equal to $\ln(VZ_{int}/Nv_Q)$. The inequality above is therefore satisfied for all energy levels provided that

$$\frac{VZ_{int}}{Nv_Q} > 200 \quad \text{or} \quad \frac{kTZ_{int}}{Pv_Q} > 200.$$

For nitrogen at room temperature and atmospheric pressure, the left-hand side of this inequality is

$$\frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})(50)}{10^5 \text{ Pa}} \left(\frac{2\pi(28)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{(6.63 \times 10^{-34} \text{ J·s})^2} \right)^{3/2}$$
$$= 3.0 \times 10^8,$$

so the inequality is easily satisfied. At 200 K, colder than anywhere on earth, this expression would be less by a factor of only $(3/2)^{7/2} = 4.1$, so the inequality would still be easily met. Even for a gas like hydrogen or helium, with $Z_{int} \approx 1$ and a mass that is less by an order of magnitude, this expression would evaluate to more than 200. So for ordinary gases under atmospheric conditions, the three distribution functions are always essentially indistinguishable.

Problem 7.15. For a system of particles obeying the Boltzmann distribution, the total number of particles should be

$$N = \sum_{\text{all } s} \overline{n}_{\text{Boltzmann}} = \sum_s e^{-(\epsilon_s - \mu)/kT} = e^{\mu/kT} \sum_s e^{-\epsilon_s/kT}.$$

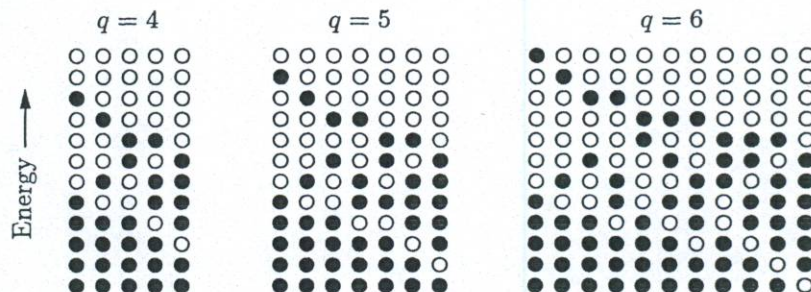But the sum in the last expression is just the single-particle partition function, Z_1, and therefore,

$$\frac{N}{Z_1} = e^{\mu/kT} \quad \text{or} \quad \mu = kT \ln \frac{N}{Z_1} = -kT \ln \frac{Z_1}{N}.$$

(I prefer to write $-\ln(Z_1/N)$ rather than $\ln(N/Z_1)$, since $Z_1 \gg N$ whenever the Boltzmann distribution applies.)

Problem 7.16. (Fermionic system with evenly-spaced levels.)

(a) Here are the diagrams for $q = 4$, 5, and 6:

(b) For $q = 6$ there are 11 states in total. Counting black dots in each row from bottom to top, I therefore find that the probabilities of the levels being occupied are

$$\frac{10}{11}, \frac{10}{11}, \frac{9}{11}, \frac{8}{11}, \frac{7}{11}, \frac{6}{11}, \frac{5}{11}, \frac{4}{11}, \frac{3}{11}, \frac{2}{11}, \frac{1}{11}, \frac{1}{11}.$$