Problem 6.1. To make the table and graphs I modified the spreadsheet from Problem 2.10. I changed \( N_A \) to 1 and \( q_{\text{total}} \) to 500, then deleted all but the first 21 rows of the table (up to \( q_A = 20 \)) and added a column for the logarithm of the total multiplicity. Here are the first few rows of the spreadsheet:

<table>
<thead>
<tr>
<th>( N_A = 1 )</th>
<th>( N_B = 100 )</th>
<th>( q_{\text{total}} = 500 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_A )</td>
<td>( \Omega_A )</td>
<td>( q_B )</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>500</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>499</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>498</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>497</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>496</td>
</tr>
</tbody>
</table>

Here are graphs of the total multiplicity and its logarithm vs. \( q_A \):

![Graphs of multiplicity and logarithm](image)

Notice that the shape of the first graph closely resembles a decaying exponential function, and the linearity of the second graph verifies that the shape is exponential to a good approximation. This is exactly what we should expect, because this system consists of a small system \((A)\) in thermal contact with a much larger reservoir \((B)\). In the approximation where the reservoir is infinitely larger than the small system, the Boltzmann distribution should apply so the probability of the small system containing \( q_A \) units of energy should be proportional to an exponential function of \(-q_A\). The multiplicity of the combined system is proportional to the probability of the small system having \( q_A \) units of energy, so the multiplicity graph should also be a decaying exponential. According to the Boltzmann distribution, the slope of the graph of \( \ln(\Omega) \) should be \(-\epsilon/kT\), where \( \epsilon \) is the size of an energy unit and \( T \) is the temperature of the reservoir. But according to our definition of temperature, the reservoir temperature is given by

\[
\frac{1}{T_B} = \frac{\partial S_B}{\partial U_B} = -\frac{\partial S_B}{\partial U_A} = -\frac{k}{\epsilon} \frac{\partial (\ln \Omega_B)}{\partial q_A}.
\]

The final partial derivative is the slope of the second graph above, so indeed, that slope is \(-\epsilon/kT\), in accord with the Boltzmann distribution.
Problem 6.3. For this two-state system,

\[ Z = e^{0} + e^{-\epsilon/kT} = 1 + e^{-\epsilon/kT}, \]

where \( \epsilon = 2 \text{ eV} \) is the energy of the excited state. Thus \( Z \) varies between 1 (in the limit \( T \to 0 \)) and 2 (in the limit \( T \to \infty \)). To plot the partition function vs. temperature it's convenient to define the dimensionless variable \( t = kT/\epsilon \), so \( Z = 1 + e^{-1/t} \). The value of \( t \) at \( T = 300 \text{ K} \) is about 1/80 = .013, while the value of \( t \) at \( T = 300,000 \text{ K} \) is about 13. (Recall that at 300 K, \( kT = .026 \text{ eV} \approx 1/40 \text{ eV} \).) Here, then, is a plot of \( Z \) vs. \( t \) for values of \( t \) up to 13:

![Plot of Z vs. t](image)

Plugging in the particular temperatures given yields the following values:

\[
\begin{align*}
T &= 300 \text{ K} : & Z &= 1 + e^{-1/0.013} = 1 + 2.2 \times 10^{-34} \\
T &= 3000 \text{ K} : & Z &= 1 + e^{-1/13} = 1.00043 \\
T &= 30,000 \text{ K} : & Z &= 1 + e^{-1/1.3} = 1.46 \\
T &= 300,000 \text{ K} : & Z &= 1 + e^{-1/13} = 1.93
\end{align*}
\]

Notice that the approach to 1 at low temperature is much more dramatic than the approach to 2 at high temperature.

Problem 6.12. If the molecules are in equilibrium with a reservoir of temperature \( T \), then the probability of a molecule being in any one of the excited states, relative to the ground state, should be

\[ \frac{e^{-E_1/kT}}{e^{-E_0/kT}} = e^{-(E_1 - E_0)/kT}. \]

We are given that this relative probability is approximately 1/10. Therefore,

\[ \frac{E_1 - E_0}{kT} = \ln \frac{1}{10} = -2.303, \]

or

\[ T = \frac{4.7 \times 10^{-4} \text{ eV}}{(2.303)(8.62 \times 10^{-5} \text{ eV/K})} = 2.4 \text{ K}. \]

The uncertainty in the data, however, is somewhat large. We now know that the temperature is closer to 2.7 K, and that the "reservoir" is the cosmic background radiation, a gas of photons that fills the entire observable universe (see Section 7.4).
Problem 6.5. (A three-state toy model.)
(a) At 300 K, \( kT = 0.026 \, \text{eV} \), as computed on page 13. Therefore the partition function for this system is
\[
Z = e^{-(-0.05/0.026)} + e^{0} + e^{-(0.05/0.026)} = 6.84 + 1 + 0.15 = 7.99.
\]
(b) Numbering the states 1, 2, and 3 in the order listed, the probabilities are
\[
P_1 = \frac{6.84}{7.99} = 0.86; \quad P_2 = \frac{1}{7.99} = 0.13; \quad P_3 = \frac{0.15}{7.99} = 0.02.
\]
(c) Measuring the energies now relative to the ground state, we have
\[
Z = e^{0} + e^{-(0.05/0.026)} + e^{-(0.10/0.026)} = 1 + 0.15 + 0.02 = 1.17.
\]
And the probabilities are
\[
P_1 = \frac{1}{1.17} = 0.86; \quad P_2 = \frac{0.15}{1.17} = 0.13; \quad P_3 = \frac{0.02}{1.17} = 0.02.
\]
So even though the partition function changes, the probabilities are unchanged, as they must be because nature can’t possibly care what we use as our zero-point for measuring energy.

Problem 6.6. Let \( E_1 \) be the ground-state energy and \( E_2 \) the energy of the first excited \((n = 2)\) level. The probability of being in any one of the first excited states is
\[
P(E_2) = \frac{e^{-E_2/kT}}{Z} \approx \frac{e^{-E_2/kT}}{e^{-E_1/kT}}.
\]
In the last expression I've included only the first term in \( Z \), since it's so much larger than all the other terms, even at 10,000 K. Since there are four such states, the total probability of having energy \( E_2 \) is four times as large:
\[
P(E_2) = 4e^{-(E_2 - E_1)/kT} = 4e^{-(10.2 \, \text{eV})/kT}.
\]
At \( T = 300 \, \text{K} \) we have \( kT = 0.026 \, \text{eV} \), so
\[
P(E_2) = 4e^{-10.2/0.026} = 4e^{-395} = 10^{\log_{10}(4e^{-395})} = 10^{(\log_{10}4) - 395(\log_{10}e)} = 10^{-171}.
\]
In other words, you'll never find a hydrogen atom in its first excited level when it's in equilibrium with a reservoir at room temperature. At 9500 K, on the other hand, \( kT = 0.819 \, \text{eV} \), so
\[
P(E_2) = 4e^{-10.2/0.819} = 4e^{-12.5} = 1.6 \times 10^{-5}.
\]
At this temperature, about one atom in 64,000 is in its first excited level.
Problem 6.10. (Vibrational excitations of H$_2$O.)

(a) The partition function for this vibrating atom is

\[ Z = e^{-\frac{hf}{2kT}} + e^{-3hf/2kT} + e^{-5hf/2kT} + \ldots. \]

At 300 K,

\[ \frac{hf}{kT} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(4.8 \times 10^{13} \text{ s}^{-1})}{(8.617 \times 10^{-5} \text{ eV/K})(300 \text{ K})} = 7.68, \]

so the partition function is approximately

\[ Z = e^{-3.84} + e^{-11.52} + e^{-19.20} + \ldots \]

\[ = 0.0215 + (9.9 \times 10^{-6}) + (4.6 \times 10^{-9}) + \ldots \]

\[ = 0.0215. \]

The probabilities of the lowest two excited states are therefore

\[ P_1 = \frac{9.9 \times 10^{-6}}{0.0215} = 0.0046, \quad P_2 = \frac{4.6 \times 10^{-9}}{0.0215} = 2.1 \times 10^{-7}. \]

The probability of the ground state is very nearly 1; more precisely,

\[ P_0 = 1 - 0.0046 = 0.9954. \]

(b) At 700 K, the ratio \( hf/kT \) is smaller by a factor of 3/7, so \( hf/kT = 3.25 \) and the partition function is

\[ Z = e^{-1.624} + e^{-4.873} + e^{-8.121} + e^{-11.37} + \ldots \]

\[ = 0.1971 + 0.0077 + 0.0003 + 0.00001 + \ldots \]

\[ = 0.2051. \]

The probabilities are therefore

\[ P_0 = \frac{0.1971}{0.2051} = 0.961, \quad P_1 = \frac{0.0077}{0.2051} = 0.038, \quad P_2 = \frac{0.0003}{0.2051} = 0.001. \]

Problem 6.13. The ratio of probabilities under these conditions should be

\[ \frac{P(n)}{P(p)} = \frac{e^{-m_n\sigma^2/kT}}{e^{-m_p\sigma^2/kT}} = e^{-(\Delta m)\sigma^2/kT} = \exp \left( - \frac{(2.3 \times 10^{-30} \text{ kg})(3 \times 10^8 \text{ m/s})^2}{(1.38 \times 10^{-23} \text{ J/K})(10^{11} \text{ K})} \right) = 0.86. \]

In other words, there should be 86 neutrons for every 100 protons. That makes 186 particles total, so the fraction of protons should be \( 100/186 = 0.54 \), and the fraction of neutrons should be \( 86/186 = 0.46 \).
Problem 6.15. (Weberium.)

(a) 
\[ \bar{E} = \frac{4(0 \text{ eV}) + 3(1 \text{ eV}) + 2(4 \text{ eV}) + 1(6 \text{ eV})}{10} = \frac{3 \text{ eV} + 8 \text{ eV} + 6 \text{ eV}}{10} = 1.7 \text{ eV}. \]

(b) Each probability is just the number of atoms with that energy, divided by the total number of atoms:
\[ \mathcal{P}(0 \text{ eV}) = \frac{4}{10}, \quad \mathcal{P}(1 \text{ eV}) = \frac{3}{10}, \quad \mathcal{P}(4 \text{ eV}) = \frac{2}{10}, \quad \mathcal{P}(6 \text{ eV}) = \frac{1}{10}. \]

(c) 
\[ \bar{E} = \sum\limits_{s} E(s) \mathcal{P}(s) = (0 \text{ eV}) \cdot \frac{4}{10} + (1 \text{ eV}) \cdot \frac{3}{10} + (4 \text{ eV}) \cdot \frac{2}{10} + (6 \text{ eV}) \cdot \frac{1}{10} \]
\[ = 0 + \frac{3}{10} \text{ eV} + \frac{8}{10} \text{ eV} + \frac{6}{10} \text{ eV} = 1.7 \text{ eV}. \]

Problem 6.39. (Escape of molecules from the upper atmosphere.)

(a) For a nitrogen molecule at 1000 K, the most probable speed is
\[ v_{\text{max}} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.315 \text{ J/K})(1000 \text{ K})}{0.028 \text{ kg}}} = 771 \text{ m/s}. \]

(Here \( M \) is the mass of a mole of nitrogen molecules.) The escape speed, 11,000 m/s, exceeds \( v_{\text{max}} \) by a factor of \( 11,000/771 = 14.3 \). Following the example in the text on pages 245–246, we can simply plug in this number for \( x_{\text{min}} \) in the integral
\[ \frac{4}{\sqrt{\pi}} \int_{x_{\text{min}}}^{\infty} x^2 e^{-x^2} \, dx \]

to obtain the probability of a molecule moving faster than escape speed. I used Mathematica to do the integral numerically and got the answer \( 2.5 \times 10^{-88} \). (Alternatively, you could use the asymptotic expansion derived in Problem B.5.) The age of the earth is of order \( 10^{17} \) seconds, so even if a molecule has a trillion (\( 10^{12} \)) chances to escape per second over the lifetime of the earth, its chance of escaping by now would be less than one in \( 10^{58} \).

(b) For a hydrogen molecule, \( M \) is only 0.002 kg, so \( v_{\text{max}} \) is larger by a factor of \( \sqrt{14} = 3.7 \), that is, \( v_{\text{max}} = 2880 \text{ m/s} \). Escape speed exceeds this number by a factor of \( 11,000/2880 = 3.81 = x_{\text{min}} \). Evaluating the integral numerically once again, I find that the probability of a hydrogen molecule moving faster than escape speed is \( 2.2 \times 10^{-6} \). This is small but not at all negligible. Over the lifetime of the earth we would expect almost every hydrogen molecule to reach the uppermost atmosphere, achieve this speed, and hence escape. For helium, the mass is twice as great as for hydrogen so \( v_{\text{max}} = 2030 \text{ m/s}, x_{\text{min}} = 5.39 \), and the probability evaluates to \( 1.5 \times 10^{-12} \). Again, this is large enough that every atom should have had plenty of chances to escape by now.

(c) Consider a nitrogen molecule in the moon's (former) atmosphere. Assuming a temperature of 1000 K as in earth's upper atmosphere, the most probable speed is again 771 m/s, but the escape speed of 2400 m/s exceeds this by a factor of only 3.1, and therefore our integral for the probability evaluates to \( 2.3 \times 10^{-4} \). Nitrogen on the moon should therefore escape even faster than hydrogen on earth. Presumably this happened long long ago, leaving the moon with no atmosphere today.
**Problem 6.23.** For the numbers given,

\[
\frac{kT}{\varepsilon} = \frac{(8.62 \times 10^{-5} \, \text{eV/K})(300 \, \text{K})}{0.0024 \, \text{eV}} = 107.8.
\]

This is the approximate value of \(Z_{\text{rot}}\) according to equation 6.31. To compute the "exact" partition function you need to include terms in the sum up to about \(j = 30\). The *Mathematica* instruction \[\text{Sum[(2j+1)Exp[-j (j+1)/(107.8)],\{j,0,30\}]\] returns 108.1, and increasing the upper limit affects only the second decimal place, so it seems that the approximate formula is too low by about 0.3. (You can also carry out the sum with a calculator or a computer spreadsheet program.)

**Problem 6.33.** The mass of an oxygen molecule is 32 u, so for oxygen at 300 K,

\[
\sqrt{\frac{kT}{m}} = \sqrt{\frac{(1.38 \times 10^{-23} \, \text{J/K})(300 \, \text{K})}{32(1.66 \times 10^{-27} \, \text{kg})}} = 279 \, \text{m/s}.
\]

The most likely speed, \(v_{\text{max}}\), is just this times \(\sqrt{2}\), or 395 m/s. To get the rms speed, we instead multiply by \(\sqrt{3}\) to get 484 m/s. And to get the average speed, we multiply by \(\sqrt{8/\pi}\) to get 446 m/s.

**Problem 6.34.** Let me define the constant \(v_0 \equiv \sqrt{2kT/m}\) for \(T = 300\) K. The mass of a nitrogen molecule is 28 u, so

\[
v_0 = \sqrt{\frac{2k(300 \, \text{K})}{m}} = \sqrt{\frac{2(1.38 \times 10^{-23} \, \text{J/K})(300 \, \text{K})}{28(1.66 \times 10^{-27} \, \text{kg})}} = 422 \, \text{m/s}.
\]

The Maxwell speed distribution can then be written

\[
D(v) = \frac{4}{\sqrt{\pi} v_0^2} t^{-3/2} e^{-v^2/v_0^2},
\]

where \(t\) is the temperature in units of 300 K. To plot this function for \(t = 1\) and \(t = 2\), I gave *Mathematica* the following instructions:

```mathematica
v0 = 422;
maxwell[t_, v_] := 2.257*(v^2/v0^3)*t^-3/2*Exp[-v^2/(v0^2*t)]
Plot[{maxwell[1, v], maxwell[2, v]}, {v, 0, 1700}]
```

Here's the plot:

![Maxwell speed distribution plot](image)

Notice that the area under each curve is equal to 1. Therefore, as the location of the peak moves to the right (in proportion to \(\sqrt{T}\)), its height must decrease.