Generally useful constants (MKS):

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>amu</td>
<td>(1.6605 \times 10^{-27}) kg</td>
</tr>
<tr>
<td>NA</td>
<td>(6.0221 \times 10^{23}) / mole</td>
</tr>
<tr>
<td>(k)</td>
<td>(1.38066 \times 10^{-23}) J/K</td>
</tr>
<tr>
<td>me</td>
<td>(9.1094 \times 10^{-31}) kg</td>
</tr>
<tr>
<td>h</td>
<td>(6.62608 \times 10^{-34}) J s</td>
</tr>
<tr>
<td>q</td>
<td>(1.6022 \times 10^{-19}) C</td>
</tr>
<tr>
<td>c</td>
<td>(2.9979 \times 10^{8}) m/s</td>
</tr>
</tbody>
</table>

Problem 2.1 (Engel)

Assume that a system has a very large number of energy levels given by the formula \(e = e_0 l^2\) with \(e_0 = 2.34 \times 10^{-22}\) J, where \(l\) takes on the integer values 1, 2, 3, ... . Assume also that the degeneracy of a level is given by \(g_l = 2l\). Calculate the population ratios \(n_1/n_1\) and \(n_{10}/n_1\) for \(T = 100\) K and 650 K, respectively.

Solution

**Strategy.** Population ratios are obtained by assuming a Boltzmann distribution (which holds only if the system is at thermal equilibrium).

\[
\frac{n_l}{n_1} = \frac{g_l}{g_1} e^{-(e_l - e_1)/kT}
\]
Prediction. Populations should fall as state energy increases. In other words, \( n_1 > n_5 > n_{10} \) should hold at both temperatures. However, the populations should fall less at higher temperature.

Execution. First, calculate \( \epsilon_i - \epsilon_1 \)

\[
\begin{align*}
e_0 &= 2.34 \times 10^{-22} \text{J} \\
e_{51} &= e_0 \times (5^2 - 1^2) \\
e_{101} &= e_0 \times (10^2 - 1^2) \\
2.34 \times 10^{-22} \text{J} \\
5.616 \times 10^{-21} \text{J} \\
2.3166 \times 10^{-20} \text{J}
\end{align*}
\]

Next, calculate \( kT \)

\[
\begin{align*}
T &= \{100 \text{ K}, 650 \text{ K}\} \\
kT &= kT \\
{100 \text{ K}, 650 \text{ K}}
\end{align*}
\]

\[
\{1.38066 \times 10^{-21} \text{J}, 8.97429 \times 10^{-21} \text{J}\}
\]

Next, calculate the ratio of state degeneracies, \( g_i / g_1 \)

\[
\begin{align*}
g_{51} &= (2 \times 5) / (2 \times 1) \\
g_{101} &= (2 \times 10) / (2 \times 1) \\
5 \\
10
\end{align*}
\]

- General::spell1: Possible spelling error: new symbol \( g_{101} \) is similar to existing symbol \( e_{101} \). More...

Ignore warning about similarity in variable names. Calculate \( n_5 / n_1 \) at both temperatures
Calculate $n_{10}/n_1$ at both temperatures

\[
g_{10} e^{-e_{10}/kT} \\
(5.16419 \times 10^{-7}, 0.7567)
\]

Comment

Part of my prediction was flawed. It is possible for excited states to have higher populations than lower energy states, but only if the excited states have higher degeneracies. Thus, at 650 K, $n_5 > n_1$.

The other parts of my prediction worked out as expected.