Chemistry 4000/5000/7001, Fall 2012, Assignment 3 Solutions

1. (a)

$$hc\tilde{\nu}_0 = \hbar\omega_0 = \frac{h}{2\pi}\omega_0$$
$$\therefore \omega_0 = 2\pi c\tilde{\nu}_0$$

(b)

$$\begin{aligned}\omega_0 &= 2\pi(2.997\,924\,58 \times 10^8\,\mathrm{m/s})(100\,\mathrm{cm\,m^{-1}})(2990.95\,\mathrm{cm^{-1}})\\ &= 5.633\,91 \times 10^{14}\,\mathrm{s^{-1}}\end{aligned}$$

(c)

$$\begin{aligned}Q &= \left[1 - \exp\left(-\frac{\hbar\omega_0}{k_BT}\right)\right]^{-1}\\ &= \left[1 - \exp\left(-\frac{(1.054\,571\,73 \times 10^{-34}\,\mathrm{J\,s})(5.633\,91 \times 10^{14}\,\mathrm{s^{-1}})}{(1.380\,6488 \times 10^{-23}\,\mathrm{J\,K^{-1}})(293.15\,\mathrm{K})}\right)\right]^{-1}\\ &= 1.000\,000\,4\end{aligned}$$

(I don't know how many significant figures this number really has, but I just wanted to show that it was just a bit bigger than 1.)

$$\begin{aligned}P(v=0) &= \frac{1}{Q}\exp\left(-\frac{\hbar\omega_0 v}{k_BT}\right)\\ &= \frac{e^0}{1.000\,000\,4} = 0.999\,999\,6.\end{aligned}$$

(Again, it's too many significant figures, but the point is to illustrate that the probability that the ground state is occupied is extremely close to 1 at room temperature.)

(d) See figure 1 for my graph. At low temperatures, $Q \approx 1$, meaning that the ground state is the only one with a significant population. Values of $Q > 1$ indicate that excited states are also populated. The temperature where we think this effect is "significant" is somewhat arbitrary. Any temperature between 1000 and 2000 K would be a sensible answer.

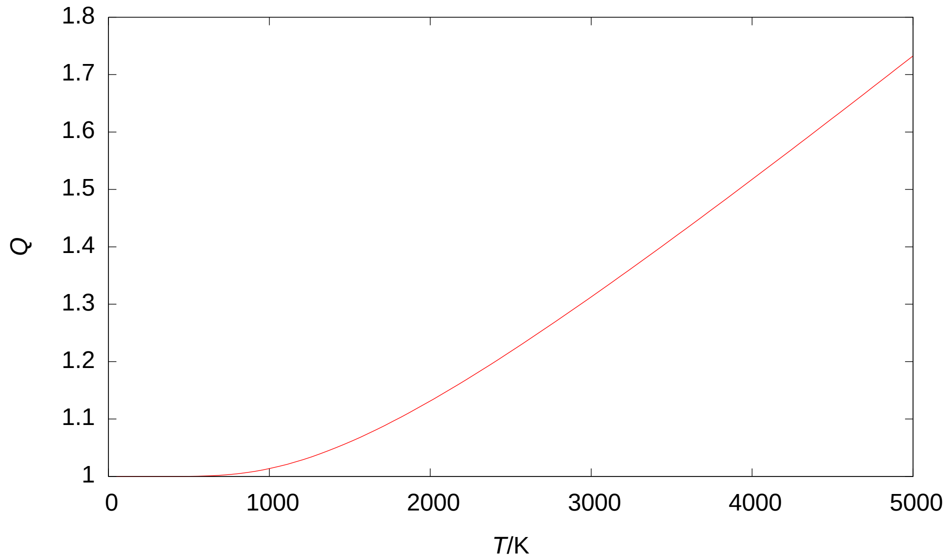

Figure 1: $Q(T)$ for the vibrational degree of freedom of HCl

2. We have the equation

$$p(\epsilon) = \frac{1}{Q} g(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

for the probability density $p(\epsilon)$. This density must integrate out to 1 over the allowed energy region ($\mathcal{A}$), i.e.

$$\int_{\mathcal{A}} \frac{1}{Q} g(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon = 1.$$

Note that the partition function depends only on T, so we can pull it out of the integral:

$$\frac{1}{Q} \int_{\mathcal{A}} g(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon = 1.$$

$$\therefore Q = \int_{\mathcal{A}} g(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon.$$

3. The value of the translational partition function answers this question. The only catch is that we have to do a whole bunch of unit conversions

in order to get our answer.

$$\begin{aligned}
m &= 2(1.007\,825\,032\,07\,\mathrm{u}) = 2.015\,650\,064\,14\,\mathrm{u} \\
&\equiv \frac{2.015\,650\,064\,14\,\mathrm{g\,mol^{-1}}}{(1000\,\mathrm{g\,kg^{-1}})(6.022\,141\,29 \times 10^{23}\,\mathrm{mol^{-1}})} \\
&= 3.347\,065\,38 \times 10^{-27}\,\mathrm{kg}
\end{aligned}$$

(This is one of those rare cases where the number of significant digits in the answer is limited by the number of significant digits in a fundamental constant, due in this case to the exquisite accuracy with which we are able to weigh atoms.)

$$\begin{aligned}
V &= \frac{1.050\,\mathrm{L}}{1000\,\mathrm{L\,m^{-3}}} = 1.050 \times 10^{-3}\,\mathrm{m^3}. \\
Q_{\mathrm{tr}} &= \frac{V}{h^3}(2\pi m k_B T)^{3/2} \\
&= (1.050 \times 10^{-3}\,\mathrm{m^3})(6.626\,069\,57 \times 10^{-34}\,\mathrm{J\,s})^{-3} \\
&\quad \times \left[2\pi(3.347\,065\,38 \times 10^{-27}\,\mathrm{kg})(1.380\,6488 \times 10^{-23}\,\mathrm{J\,K^{-1}})(293.15\,\mathrm{K})\right]^{3/2} \\
&= 2.834 \times 10^{27}.
\end{aligned}$$

Needless to say, this is a truly colossal number.

4. The mass of a deuterium molecule is approximately 4 u, about twice as much as the mass of an ordinary hydrogen molecule. Since Q_{tr} depends on $m^{3/2}$, the number of translational levels accessible should increase by a factor of $2^{3/2} \approx 2.828$, so the number of translational states should be approximately $(2.828)(2.834 \times 10^{27}) = 8.017 \times 10^{27}$. This happens because the particle-in-a-box energy levels depend inversely on m, i.e. the levels shift to lower energies for larger values of m.