Statistical Mechanics Assignment 3 Solutions

1. (a) 3 rotational modes, $3(5) - 6 = 9$ vibrational modes, $\sigma = 12$

   (b) 2 rotational modes, $3(6) - 5 = 13$ vibrational modes, $\sigma = 2$

   (c) 3 rotational modes, $3(4) - 6 = 6$ vibrational modes, $\sigma = 6$

2.

$$Q = \frac{q_T^N}{N!}.$$
$$\therefore \ln Q = N \ln q_T - \ln N!.$$

To evaluate $\ln N!$, we use Stirling's approximation:

$$\ln N! = N \ln N - N.$$
$$\therefore \ln Q = N \ln q_T - (N \ln N - N)$$
$$= N \left[\ln \left(\frac{q_T}{N} \right) + 1 \right].$$

In this case, we have $N = 6.022\,136\,7 \times 10^{23}$. We calculate q_T as follows:

$$m = \frac{20.180\,\text{g/mol}}{(6.022\,136\,7 \times 10^{23}\,\text{mol}^{-1})(1000\,\text{g/kg})} = 3.3510 \times 10^{-26}\,\text{kg}.$$

$$q_T = (2\pi m k T)^{3/2} \frac{V}{h^3}$$
$$= \left[2\pi (3.3510 \times 10^{-26}\,\text{kg})(1.380\,658 \times 10^{-23}\,\text{J/K})(200\,\text{K}) \right]^{3/2}$$
$$\times \frac{10\,\text{L}}{(1000\,\text{L/m}^3)(6.6260755 \times 10^{-34}\,\text{J/Hz})^3}$$
$$= 4.82 \times 10^{29}.$$

$$\therefore \ln Q = (6.022\,136\,7 \times 10^{23}) \left[\ln \left(\frac{4.82 \times 10^{29}}{6.022\,136\,7 \times 10^{23}} \right) + 1 \right]$$
$$= 8.79 \times 10^{24}.$$

Bonus: The partition function for a system made up of a number of independent units is the product of the partition functions for the individual units. If some of the units are indistinguishable, we have to divide this product by the number of permutations of these units. Thus we have

$$Q = \frac{q_{20}^{N_{20}}\, q_{21}^{N_{21}}\, q_{22}^{N_{22}}}{N_{20}!\, N_{21}!\, N_{22}!},$$

where q_i and N_i are, respectively, the partition function and number of atoms of isotope i. If we take the logarithm of this expression, we get, after some algebra,

$$\ln Q = N_{20} \left[\ln \left(\frac{q_{20}}{N_{20}} \right) + 1 \right] + N_{21} \left[\ln \left(\frac{q_{21}}{N_{21}} \right) + 1 \right] + N_{22} \left[\ln \left(\frac{q_{22}}{N_{22}} \right) + 1 \right].$$

The numbers of each isotope are easily calculated from the total quantity (1 mol) and percentages. The following table summarizes the calculations:

Isotope	N_i	m_i/kg	q_i
^{20}Ne	5.449×10^{23}	$3.193\,125\,817\,93 \times 10^{-26}$	4.75×10^{29}
^{21}Ne	1.6×10^{21}	$3.486\,112\,618 \times 10^{-26}$	5.11×10^{29}
^{22}Ne	5.57×10^{22}	$3.651\,757\,940 \times 10^{-26}$	5.48×10^{29}

Finally, we get
$$\ln Q = 8.98 \times 10^{24}.$$

This is a little larger than the partition function treating all atoms as equivalent.

3. (a) The combined vibrational-rotational energy is

$$\epsilon_{v,J} = hc\tilde{\nu}\left(v + \frac{1}{2}\right) + hcBJ(J+1).$$

For the transition specified, we have

$$\Delta\epsilon = \epsilon_{1,1} - \epsilon_{0,0} = hc\tilde{\nu} + 2hcB.$$

Putting in the numbers for $^{12}\text{C}^{16}\text{O}$, we get

$$
\begin{aligned}
\frac{\Delta\epsilon}{hc} &= \tilde{\nu} + 2B \\
&= 2170.21 + 2(1.9313)\,\text{cm}^{-1} = 2174.07\,\text{cm}^{-1}. \\
\therefore \lambda &= \frac{hc}{\Delta\epsilon} \\
&= \frac{1}{2174.07\,\text{cm}^{-1}} = 4.5997 \times 10^{-4}\,\text{cm} \\
&\equiv \frac{4.5997 \times 10^{-4}\,\text{cm}}{100\,\text{cm/m}} = 4.5997 \times 10^{-6}\,\text{m}.
\end{aligned}
$$

If we look up this wavelength in a spectral chart, we find that it is in the infrared part of the spectrum.

(b) The rotational temperature is

$$\Theta_R = \frac{B}{k} = \frac{1.9313\,\text{cm}^{-1}}{0.695\,038\,\text{cm}^{-1}\text{K}^{-1}} = 2.7787\,\text{K}.$$

$\Theta_R \ll T$ in the range of interest, so we can use the integrated form of the partition function.

(c) In general,

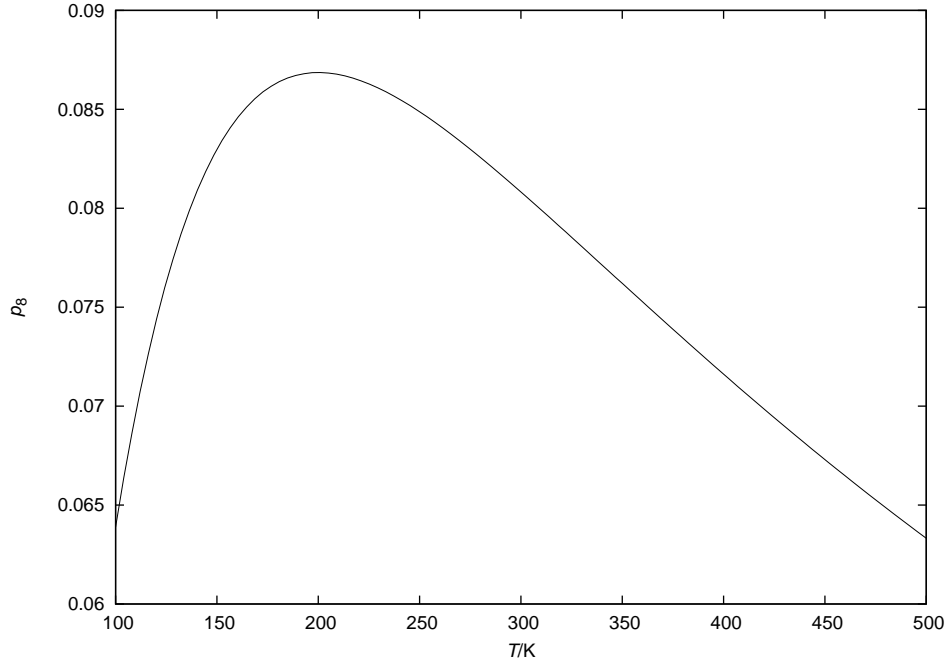$$p_J = \frac{(2J+1)e^{-\Theta_R J(J+1)/T}}{q_R(T)},$$

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Figure 1: Probability that a CO molecule is in the $J = 8$ rotational state as a function of temperature.

where $q_R(T) = T/(\sigma\Theta_R)$. In this case, $\sigma = 1$. For $J = 8$, we therefore have

$$p_8 = \frac{17}{T}\Theta_R e^{-72\Theta_R/T}.$$

Figure 1 shows the probability as a function of temperature. We see that there is a maximum in the probability near $T = 200\,\text{K}$. At this temperature, $kT = 139\,\text{cm}^{-1}$, while $\epsilon_8 = BJ(J+1) = 139\,\text{cm}^{-1}$. We see that the probability is a maximum when the energy of the rotational state is about the same as kT.