**Problem Set 7**

**Q31.4** For which energetic degrees of freedom are the spacings between energy levels small relative to $k_B T$ at room temperature?

Spacings between translational energy levels are very small compared to $k_B T$ at room temperature. Spacings between rotational energy levels are often small compared to $k_B T$ at room temperature, but for molecules made up of light atoms, such as $\text{H}_2$, the spacings may be comparable to $k_B T$ at room temperature. Vibrational and electronic energy level spacings are usually larger than $k_B T$ at room temperature.

**Q31.15** Why is the electronic partition function generally equal to the degeneracy of the ground electronic state?

The spacing between the electronic ground state and first excited state is usually much larger than $k_B T$ at room temperature. Therefore only the first term contributes to the partition function. If we take the ground state energy to be zero, then the first term is just the degeneracy of the ground state.

**P31.1** Evaluate the translational partition function for $\text{H}_2$ confined to a volume of 100 cm$^3$ at 298 K. Perform the same calculate for $\text{N}_2$ under identical conditions.

$q_T = \left(2\pi m k_B T\right)^{3/2} V/\hbar^3$.

For $\text{H}_2$, $m = 2.02 \text{ amu} \times \left(1.661 \times 10^{-26} \text{ kg/amu}\right) = 3.35 \times 10^{-27} \text{ kg}$

$V = 100 \text{ cm}^3 = 1.00 \times 10^{-4} \text{ m}^3$

$q_T = 2.77 \times 10^{26}$

Mass of $\text{N}_2$ is 14.0 times the mass of $\text{H}_2$. Therefore $q_T$ for $\text{N}_2$ is $(14.0)^{3/2}$ times as large as $q_T$ for $\text{H}_2$.

For $\text{N}_2$, $q_T = (14.0)^{3/2} \times 2.77 \times 10^{26} = 1.45 \times 10^{28}$

**P31.14** Calculate the rotational partition function for $^{35}\text{Cl}_2$ ($B = 0.244 \text{ cm}^{-1}$) at 298 K.

$q_R = \frac{k_B T}{\sigma h c B} = \frac{(1.38 \times 10^{-23} \text{ J} / \text{K})(298\text{K})}{(2)(6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^{10} \text{ cm/s})(0.244 \text{ cm}^{-1})} = 424$. 
P31.26 Calculate the vibrational partition function for H35Cl at 300 K and 3000 K. What fraction of molecules will be in the ground vibrational states at these temperatures? The vibrational frequency of H35Cl is 2990 cm⁻¹.

At 300 K:

\[ q_v = \frac{1}{1 - e^{-\beta \nu}} = \frac{1}{1 - e^{-\frac{h \nu}{kT}}} = \frac{1}{1 - e^{-\left(6.626 \times 10^{-34} \text{ J}\cdot\text{m}\cdot\text{s}^{-1}\right)(2990 \text{ cm}^{-1})(3.00 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})/(1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(300 \text{ K})}} = 1.00 \]

This means that there is essentially only one vibrational state of H35Cl that is thermally populated at 300 K (the ground state).

The probability to be in state \( n \), \[ p_n = \frac{e^{-nh\nu/kT}}{q_v}. \]

For the ground state (\( n = 0 \)) at 300 K, \[ p_0 = \frac{1}{q_v} = 1. \]

At 3000 K:

\[ q_v = \frac{1}{1 - e^{-\beta \nu}} = \frac{1}{1 - e^{-\frac{h \nu}{kT}}} = \frac{1}{1 - e^{-\left(6.626 \times 10^{-34} \text{ J}\cdot\text{m}\cdot\text{s}^{-1}\right)(2990 \text{ cm}^{-1})(3.00 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})/(1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(3000 \text{ K})}} = 1.31 \]

The probability to be in the ground state (\( n = 0 \)) at 3000 K, \[ p_0 = \frac{1}{q_v} = 0.762 \]

P30.45 The absorption spectrum of rhodopsin is centered at roughly 500 nm. Using this information, determine the value of \( q_E \) for retinal. Do you expect thermal excitation to result in significant excited-state population of retinal?

The excited state energy is \( \epsilon_{\text{excited}} = h \nu = \frac{hc}{\lambda} = 3.97 \times 10^{-19} \text{ J} \)

when \( \lambda = 500 \text{ nm} \).

The partition function contains only two terms: the ground state (0 J) and the first excited state (\( 3.97 \times 10^{-19} \text{ J} \)).

\[ q = \sum_{n=0}^{1} e^{-\beta \epsilon_n} = e^{-0} + e^{-\left(3.97 \times 10^{-19} \text{ J}\right)/(1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(298 \text{ K})} = 1. \]

The contribution of the excited state of rhodopsin to \( q_E \) is essentially 0 at 298 K. To get to the excited state rhodopsin absorbs a 500 nm photon.