CH 12.III: THE BOLTZMANN DISTRIBUTION AND POPULATIONS OF QUANTUM STATES

1. Explain why evaporation is a cooling process. Hint: Assume that the Maxwell-Boltzmann speed distribution applies to liquids as well as to gasses. Also note that it takes a certain minimum energy for a molecule in a liquid to escape the surface tension of the liquid, which is what results in evaporation.

2. After analyzing the emission spectrum of sodium-chloride molecules, it is determined that the wavelength emitted in the transitions from the second excited state to the first excited state for vibrational quantum energy levels is 26.4 \( \mu \text{m} \), while the emitted wavelength for the same transition in rotational quantum energy levels 1.32 \( \text{cm} \). The mass of a sodium atom is \( 3.818 \times 10^{-26} \) kg, while the mass of a chlorine atom is \( 5.887 \times 10^{-26} \) kg.

(a) What is the reduced mass of an NaCl molecule?
(b) What is the moment of inertia of the NaCl molecule about its center-of-mass?
(c) What is the equilibrium distance between the sodium and the chlorine nuclei in the NaCl molecule?
(d) What is the natural frequency of vibration of the atoms in the NaCl molecule, \( v_0 \)?
(e) What is the chemical bond strength between the two atoms in the NaCl molecule as represented by the effective spring constant between them?
(f) What is the approximate ratio of the number of NaCl molecules in the second excited state to the first excited state for vibration in a gas of molecules at room temperature?
(g) What is the approximate ratio of the number of NaCl molecules in the second excited state to the first excited state for rotation in a gas of molecules at room temperature?
From the Maxwell-Boltzmann speed distribution, we showed in class that the rms speed of molecules is given by
\[ v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{v}{m}}. \]
Since the average kinetic energy of a molecule in the liquid is
\[ \bar{K} = \frac{1}{2} m v^2 = \frac{1}{2} m v_{\text{rms}}^2 = \frac{1}{2} m \frac{3 k_B T}{m}, \]
we see that the (macroscopic) temperature can be thought of as being proportional to the (microscopic) average kinetic energy of the molecules in the liquid.

The Maxwell-Boltzmann speed distribution looks like:

As only the most energetic molecules can escape the surface tension in the liquid, it follows that, as the liquid evaporates, the average speed of molecules in the liquid must decrease, which means that \( v_{\text{rms}} \) must decrease, which means that the temperature of the liquid must decrease. Hence, anything in contact with the liquid will feel the temperature go down. Thus, evaporation is a cooling process. (This is why our body sweats in hot conditions— the sweat will evaporate and cool our body!)
(2) NOCL spectrum:

Vibrational: \( E_n = E_0 + n \hbar \omega \) for \( n = 0, 1, 2, 3, \ldots \)

Thus, \( \Delta E_v (2 \rightarrow 1) = (E_0 + 2 \hbar \omega) - (E_0 + 1 \hbar \omega) = \hbar \omega \)

\[ \frac{\hbar c}{\lambda_v (2 \rightarrow 1)} \]

Rotational: \( E_{rot} = \frac{l(l+1) \hbar^2}{2I} \) for \( l = 0, 1, 2, 3, \ldots \)

Thus, \( E_{rot} = \frac{2(2+1) \hbar^2}{2I} = \frac{3 \hbar^2}{I} \) and \( E_{rot} = \frac{1(1+1) \hbar^2}{2I} = \frac{\hbar^2}{I} \)

So that \( \Delta E_{rot} (2 \rightarrow 1) = \frac{3 \hbar^2}{I} - \frac{\hbar^2}{I} = 2 \frac{\hbar^2}{I} = \frac{hc}{\lambda_{rot} (2 \rightarrow 1)} \)

Given:
\( \lambda_v (2 \rightarrow 1) = 26.4 \mu m = 26.4 \times 10^{-6} m \), and
\( \lambda_{rot} (2 \rightarrow 1) = 1.32 \text{ cm} = 0.0132 \text{ m} \)
\( M_{Na} = 3.818 \times 10^{-26} \text{ kg} \), \( M_{Cl} = 5.887 \times 10^{-26} \text{ kg} \)

(d) \[ \mu = \frac{M_{Na} \cdot M_{Cl}}{M_{Na} \cdot M_{Cl} + M_{Cl}} = \frac{2.32 \times 10^{-26} \text{ kg}}{2.32 \times 10^{-26} \text{ kg}} \]

(b) Find \( I \). From (B) above,
\[ \frac{2 \hbar^2}{I} = \frac{hc}{\lambda_{rot} (2 \rightarrow 1)} \Rightarrow \frac{2 \hbar^2 \lambda_{rot} (2 \rightarrow 1)}{2 \pi \hbar c} = \frac{\hbar \lambda_{rot} (2 \rightarrow 1)}{\pi c} \]

or \[ I = 1.47 \times 10^{-45} \text{ kg} \cdot \text{m}^2 \]

(c) Find \( R \). Recall: \( I = \mu R^2 \)
\[ R = \sqrt{\frac{I}{\mu}} = 2.52 \times 10^{-10} \text{ m} = 2.52 \text{ Å} \]

(d) Find \( \omega \). From (A), \( \omega_0 = \frac{2 \pi \hbar c}{\hbar \lambda_v (2 \rightarrow 1)} = \frac{2 \pi c}{\lambda_v (2 \rightarrow 1)} \)

or \( \omega_0 = 7.14 \times 10^{13} \text{ rad} \cdot \text{s}^{-1} \)

But \( \omega_0 = 2 \pi \nu_0 \), so that \( \nu_0 = \frac{c}{\lambda_v (2 \rightarrow 1)} = \frac{1.14 \times 10^{13} \text{ Hz}}{2 \pi} \)
(e) Find $K_{eff}$. Recall: $\omega_0 = \sqrt{\frac{K_{eff}}{m}}$

$\Rightarrow K_{eff} = m\omega_0^2 = \boxed{118 \frac{N}{m}}$

(f.) Find $\frac{N(n=2)}{N(n=1)}$ for vibration at $T = 300 \text{ K}$.

Note: $k_B = 1.38 \times 10^{-23} \frac{J}{K}$

$\Rightarrow k_B T = 4.14 \times 10^{-21} J \left( \frac{1 \text{ eV}}{1.6 \times 10^{-19} J} \right) = 0.0259 \text{ eV} \approx 0.03 \text{ eV}$.

Let $N$ be the total number of NOCl molecules in the gas. Also, since the multiplicity for vibration is $\Omega(E_1) = 1$,
we get that

$$\frac{N(n=2)}{N(n=1)} = \frac{N A \Omega(E_2) e^{-E_2/k_B T}}{N A \Omega(E_1) e^{-E_1/k_B T}} = e^{-\frac{(E_2-E_1)}{k_B T}} = e^{-\Delta E_{v(2\rightarrow1)}}$$

From (A): $\Delta E_{v(2\rightarrow1)} = \frac{hc}{\lambda_{v_{(2\rightarrow1)}}} = 7.53 \times 10^{-21} J = 0.047 \text{ eV}$.

Thus, $\frac{N(n=2)}{N(n=1)} = e^{-\frac{\Delta E_{v(2\rightarrow1)}}{k_B T}} = \boxed{0.208}$

(g.) Find $\frac{N(l=2)}{N(l=1)}$ for rotation at $T = 300 \text{ K}$.

From (B), $\Delta E_{rot(l=2\rightarrow1)} = \frac{hc}{\lambda_{rot(l=2\rightarrow1)}} = 1.51 \times 10^{-23} J = 9.41 \times 10^{-5} \text{ eV}$.

Note: $\Omega(E_2) = \Omega(E_1) = 1$;

$$\frac{N(l=2)}{N(l=1)} = \frac{N A \Omega(E_2) e^{-E_2/k_B T}}{N A \Omega(E_1) e^{-E_1/k_B T}} = e^{-\frac{(E_2-E_1)}{k_B T}} = e^{-\Delta E_{rot(2\rightarrow1)}} = \boxed{0.997}$$

Note that means that these two populations are nearly equal.

From our results in class, we expect these two populations to be nearly equal and very, very small!