1. Hydrogen gas has the following characteristic temperatures:
   - Rotational temperature: $\Theta_{\text{rot}} = 87.5$ K
   - Vibrational temperature: $\Theta_{\text{vib}} = 6215$ K

   (a) What temperature is required for 50% of the molecules to be rotationally excited?

   Using $P_{\text{rot,excited}} = 1 - \Theta_{\text{rot}}/T$:

$$0.50 = 1 - \frac{87.5}{T}$$
$$T = 175 \text{ K}$$

   (b) What temperature is required for 50% of the molecules to be vibrationally excited?

   Using $P_{\text{vib,excited}} = e^{-\Theta_{\text{vib}}/T}$:

$$0.50 = e^{-6215/T}$$
$$T = \frac{6215}{\ln 2} \approx 9.0 \times 10^3 \text{ K}$$

   (c) For the temperature found in part (a), what percentage of molecules are vibrationally excited? What does this tell you about the relative accessibility of rotational versus vibrational energy levels?

   At $T = 175$ K:

$$P_{\text{vib}} = e^{-6215/175} \approx 4 \times 10^{-16}$$

   Basically 0% are vibrationally excited. Rotational levels are more accessible than vibrational levels.

(d) If we replaced hydrogen gas with a heavier gas like helium, would the characteristic temperatures increase, decrease, or do something else?

Helium is monatomic, so it has no rotational or vibrational modes and thus has no characteristic temperatures

2. Derive the expression for the molar energy $\overline{U}$ of a diatomic ideal gas, excluding the electronic contribution, starting from the molecular partition function:

$$q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{\text{rot}}} \cdot \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}}$$

$$\overline{U} = \frac{5}{2}RT + R\frac{\Theta_{\text{vib}}}{2} + R\frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}$$

Recall the relation:

$$U = k_B T^2 \frac{\partial \ln Q}{\partial T} = N k_B T^2 \frac{\partial \ln q}{\partial T}$$

Taking the natural logarithm of q:

$$\begin{aligned}\ln q = \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) + \ln V + \ln T - \ln(\sigma\Theta_{\text{rot}}) \\ - \frac{\Theta_{\text{vib}}}{2T} - \ln(1 - e^{-\Theta_{\text{vib}}/T})\end{aligned}$$

Computing the partial derivative with respect to T:

$$\frac{\partial \ln q}{\partial T} = \frac{3}{2}\cdot\frac{1}{T} + \frac{1}{T} + \frac{\Theta_{\text{vib}}}{2T^2} - \frac{\partial}{\partial T}\ln(1 - e^{-\Theta_{\text{vib}}/T})$$

For the vibrational logarithmic term:

$$\begin{aligned}\frac{\partial}{\partial T}\ln(1 - e^{-\Theta_{\text{vib}}/T}) &= \frac{\Theta_{\text{vib}}}{T^2}\frac{-e^{-\Theta_{\text{vib}}/T}}{1 - e^{-\Theta_{\text{vib}}/T}} = -\frac{\Theta_{\text{vib}}}{T^2}\frac{1}{e^{\Theta_{\text{vib}}/T} - 1} \\ \frac{\partial \ln q}{\partial T} &= \frac{3}{2T} + \frac{1}{T} + \frac{\Theta_{\text{vib}}}{2T^2} + \frac{\Theta_{\text{vib}}}{T^2}\frac{1}{e^{\Theta_{\text{vib}}/T} - 1}\end{aligned}$$

Using $U = N k_B T^2 \frac{\partial \ln q}{\partial T}$:

$$\begin{aligned}U &= N k_B T^2 \left[\frac{3}{2T} + \frac{1}{T} + \frac{\Theta_{\text{vib}}}{2T^2} + \frac{\Theta_{\text{vib}}}{T^2}\frac{1}{e^{\Theta_{\text{vib}}/T} - 1}\right] \\ &= N k_B \left[\frac{3T}{2} + T + \frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}\right]\end{aligned}$$

Molar internal energy is $\overline{U} = U/n$:

$$\overline{U} = \frac{U}{n} = \frac{N k_B}{n}\left[\frac{3T}{2} + T + \frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}\right]$$

Using $N = nN_A$:

$$\overline{U} = N_A k_B \left[\frac{3T}{2} + T + \frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}\right]$$

and $R = N_A k_B$:

$$\overline{U} = R\left[\frac{3T}{2} + T + \frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}\right]$$

Homework Problem 8

1. Derive an expression for $J_{\max}$, the rotational quantum number that has the highest population at a given temperature T, and verify for NO($\Theta_{\text{rot}} = 2.39$) that $J_{\max} = 7$ at $300K$. Remember quantum numbers must be integers. The probability distribution is given by:

$$P_J = \frac{\Theta_{\text{rot}}}{T}(2J+1)e^{-\frac{\Theta_{\text{rot}} J(J+1)}{T}}$$