1. What are the molar heat capacities for each of the following from the Equipartition Theorem:
   (a) Ar

   (b) NH_3

   (c) Cl_2

   (d) H_2

   (e) SO_2

2. The vibrational normal modes of water molecules have the following vibrational temperatures, Θ_{vib}: 2290 K, 5160 K, and 5360 K. At room temperature, which of these modes contributes most to the molar heat capacity?

3. The equipartition theorem only applies at the high temperature limit. Let us look at the experimental vs theoretical heat capacities per unit mass at low temperatures.

Molecule	Exp C_V/m (J/kg·K)	Calc C_V/m (J/kg·K)
Ar	320	310
NH_3	1600	1400
Cl_2	360	290
H_2	1020	1030
SO_2	492	390

From the data, we see that the equipartition theorem underestimates the heat capacity because one of the modes (translation, rotational, vibrational) is "frozen out" due to its quantum mechanical nature.

(a) Make an argument for which mode this is based on energy level spacings, and tie it to the molar energy expression below.

$$\overline{U} = \frac{5}{2}RT + R\frac{\Theta_{\text{vib}}}{2} + R\frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1} = \frac{3}{2}RT + RT + \frac{N_{\text{A}}h\nu}{2} + \frac{N_{\text{A}}h\nu}{e^{\beta h\nu} - 1}$$

(b) Using a Taylor series expansion ($e^x \approx 1 + x$ for small x), evaluate the high-temperature and low-temperature limits and connect your result to the equipartition theorem

Homework Problem 9

1. Order the following molecules by their molar heat capacity smallest to largest:

$$CO_2 \qquad NH_3 \qquad H_2O \qquad N_2$$