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

   (a) Ar

   Monatomic (no rotation or vibration)

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} = \boxed{\tfrac{3}{2}R}$$

   (b) NH_3

   Nonlinear molecule (3 translational, 3 rotational, $3N-6=6$ vibrational)

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} + \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{rotational}} + \underbrace{6(R)}_{\text{vibrational}} = 3R + 6R = \boxed{9R}$$

   (c) Cl_2

   Linear molecule (3 translational, 2 rotational, $3N-5=1$ vibrational)

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} + \underbrace{2\left(\tfrac{1}{2}R\right)}_{\text{rotational}} + \underbrace{1(R)}_{\text{vibrational}} = \tfrac{5}{2}R + R = \boxed{\tfrac{7}{2}R}$$

   (d) H_2

   Linear molecule (3 translational, 2 rotational, $3N-5=1$ vibrational)

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} + \underbrace{2\left(\tfrac{1}{2}R\right)}_{\text{rotational}} + \underbrace{1(R)}_{\text{vibrational}} = \tfrac{5}{2}R + R = \boxed{\tfrac{7}{2}R}$$

   (e) SO_2

   Nonlinear molecule (3 translational, 3 rotational, $3N-6=3$ vibrational)

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} + \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{rotational}} + \underbrace{3(R)}_{\text{vibrational}} = 3R + 3R = \boxed{6R}$$

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?

   Lowest temperature is the state with highest occupancy, so greatest contribution to molar heat capacity. $\boxed{2290\text{ K}}$

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.

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

Vibrational. Vibrational has the greatest energy level spacing, so at low T there is not enough thermal energy have large population.

(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

High-T: recovers equipartition

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

Using Taylor series:

$$e^{\Theta_{\text{vib}}/T} - 1 \approx 1 + \Theta_{\text{vib}}/T - 1 = \frac{\Theta_{\text{vib}}}{T}$$
$$\frac{R\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1} = \frac{R\Theta_{\text{vib}}}{\Theta_{\text{vib}}/T} = RT$$
$$\overline{U} = \frac{5}{2}RT + \frac{1}{2}R\Theta_{\text{vib}} + RT$$
$$= \frac{7}{2}RT + \frac{1}{2}R\Theta_{\text{vib}}$$
$$\overline{C_V} = \frac{7}{2}R$$

Low-T: vibrational mode frozen

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

Considering the limit:

$$\frac{R\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1} = \frac{R\Theta_{\text{vib}}}{\infty} \to 0$$
$$\overline{U} = \frac{5}{2}RT + \frac{1}{2}R\Theta_{\text{vib}}$$
$$\overline{C_V} = \frac{5}{2}R$$

Homework Problem 9

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

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