1. 40 points.

(a) Write an expression (in terms of $B$ and $T$) for the probability of finding a diatomic molecule in the $J = 1$ rotational state at temperature $T$. Solution:

$$\mathcal{P}(J = 1) = \frac{g(J) e^{-\epsilon_{\text{rot}}/(k_B T)}}{q_{\text{rot}}(T)} = \frac{(2J + 1) e^{-BJ/(k_B T)}}{k_B T} = \frac{3B e^{-2B/(k_B T)}}{k_B T}. $$

(b) If the interaction energy for two rotating dipoles is initially 4.0 kJ mol$^{-1}$, what is the new interaction energy for the following changes:

i. If $T$ (in K) doubles? Solution: $u$ decreases by factor of 2, so $2.0$ kJ mol$^{-1}$.

ii. If $R$ doubles? Solution: $u$ decreases by factor of $2^6 = 64$, so $0.0625$ kJ mol$^{-1}$.

(c) What volume in L is occupied by 2.00 mol of an ideal gas at 1.50 bar and 350.0 K? Solution:

$$V = \frac{nRT}{P} = \frac{(2.00 \text{ mol})(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})}{(350.0 \text{ K})(1.50 \text{ bar})} = 38.8 \text{ L.}$$

(d) Identify each of the following particles as a boson (B) or a fermion (F):

i. electron Solution: Each electron, proton, and neutron has a spin of $1/2$. Any combination of an even total number of these particles is a boson, any odd number is a fermion. F.

ii. $^2\text{H}^+$ Solution: $1p+1n$ B.

iii. $^{13}\text{C}$ Solution: $6p+7n+6e$ F.

iv. $^{14}\text{N}$ Solution: $7p+7n+7e$ F.

2. Evaluate the following limiting values. If a numerical answer is not possible, give the simplest algebraic expression.

(a) $\lim_{T \to 0} q_{\text{rot}}(T) = \lim_{T \to 0} \sum_{J=0}^{\infty} n f_{J}(2J + 1) e^{-BJ/(k_B T)} = 1 + 0 + 0 + \ldots = 1.$

(b) $\lim_{T \to \infty} q_{\text{rot}}(T) = \lim_{T \to \infty} \frac{k_B T}{B} = \infty.$ 

(c) $\lim_{\omega_e \to \infty} q_{\text{vib}}(T) = \lim_{\omega_e \to \infty} (1 - e^{-\omega_e/(k_B T)})^{-1} = (1 - 0)^{-1} = 1.$

(d) $\lim_{u(R) \to 0} Q'_U(T, V) = \frac{V^N}{(\text{assume} \ N \ \text{particles})}.$

(e) $\lim_{v \to 0} \mathcal{P}_v(v) = \lim_{v \to 0} v^2 e^{-mv^2/(2k_B T)} = (0)(1) = 0.$

(f) $\lim_{v \to \infty} \mathcal{P}_v(v) = \lim_{v \to \infty} v^2 e^{-mv^2/(2k_B T)} = \lim_{v \to 0} v^2(0) = 0.$

(g) $\lim_{R \to 0} G(R) = \lim_{R \to 0} e^{-u(R)/(k_B T)} = 0,$ because $\lim_{R \to 0} u(R) = \infty.$

(h) $\lim_{T \to \infty} B_2(T) = \lim_{T \to \infty} (b - \frac{7}{RT}) = b.$

3. We open a small hole in one side of a container of water vapor at 373 K and connect it to a chilled tube. Only molecules with $v \approx v_Z$ leave the container through the tube.
(a) What is the average speed of the molecules in the container? Solution:
\[ \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} = \left[ \frac{8(1.381 \cdot 10^{-23} \text{ J K}^{-1})(373 \text{ K})}{\pi(18.0 \text{ amu})(1.661 \cdot 10^{-27} \text{ kg amu}^{-1})} \right]^{1/2} = 662 \text{ m s}^{-1}. \]

(b) What is the average speed of the molecules exiting the tube? Solution: The molecules leaving are still characterized by a Maxwell-Boltzmann distribution, because the canonical distribution predicts the probability of being at a particular value of \( v_Z \) will be proportional to \( v_Z^2 e^{-mv_Z^2/(2k_B T)} \). However, the distribution of values of \( v_Z \) in the container is different from the distribution of speeds \( v \), because
\[ \langle v \rangle = \left( \sqrt{\frac{v_X^2 + v_Y^2 + v_Z^2}{3}} \right) = \ left( \sqrt{3} v_Z \right) = \sqrt{3} \langle v_Z \rangle. \]
Recall that we can set \( \langle v_X^2 \rangle = \langle v_Y^2 \rangle = \langle v_Z^2 \rangle \) because motion along each of the three axes is equivalent. Therefore,
\[ \langle v_{\text{exit}} \rangle = \langle v_Z \rangle = \frac{1}{\sqrt{3}} \langle v \rangle = 382 \text{ m s}^{-1}. \]

(c) If we use the speeds to determine the temperature, what is the temperature of the vapor exiting the tube? Solution: The speed is proportional to \( \sqrt{T} \), so temperature is proportional to \( v^2 \). Therefore, if the speed decreases by a factor of \( \sqrt{3} \), the apparent temperature is lower by a factor of 3:
\[ T_{\text{eff}} = \frac{373 \text{ K}}{3} = 124 \text{ K}. \]

4. For three interacting particles, briefly show the steps and approximations used to rewrite
\[ Q_U' = \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} e^{-U(X_1 \ldots Z_3)/(k_B T)} dX_1 \ldots dZ_3 \]
in terms of an integral over the single variable \( R \). Solution: Begin with the approximation that the overall potential energy \( U \) is the sum of all pair potential energies \( u \):
\[ U(X_1 \ldots Z_3) \approx \sum_{\text{pairs } ij} u(R_{ij}) = u(R_{12}) + u(R_{23}) + u(R_{13}) \]
\[ Q_U' = \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} e^{-U(X_1 \ldots Z_3)/(k_B T)} dX_1 \ldots dZ_3 \approx \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} e^{-|u(R_{12}) + u(R_{23}) + u(R_{13})|/(2k_B T)} dX_1 \ldots dZ_3. \]
Each \( dX \) \( dY \) \( dZ \) is equivalent to \( 4\pi R^2 dR \), where we integrate \( R \) from 0 to \( \infty \):
\[ Q_U' \approx (4\pi)^3 \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} e^{-u(R_{12})/(k_B T)} R_{12}^2 dR_{12} R_{23}^2 dR_{23} R_{13}^2 dR_{13} \]
\[ = (4\pi)^3 \int_{0}^{\infty} e^{-u(R_{12})/(k_B T)} R_{12}^2 dR_{12} \int_{0}^{\infty} e^{-u(R_{23})/(k_B T)} R_{23}^2 dR_{23} \int_{0}^{\infty} e^{-u(R_{13})/(k_B T)} R_{13}^2 dR_{13} \]
and these three integrals are all equal, so we can just set \( R_{ij} = R \):
\[ = \left[ (4\pi) \int_{0}^{\infty} e^{-u(R)/(k_B T)} R^2 dR \right]^3. \]