1. (a) Find the value of $z = PV_m/(RT)$ for the ideal gas. **Solution:** For the ideal gas, $PV = nRT$, $V_m = V/n = RT/P$, so

$$z = \frac{PV_m}{RT} = \frac{P(RT/P)}{RT} = 1.$$ 

(b) Put an X next to the name of the molecule that will have the greatest value of $z$ at a pressure of 1.00 bar and 298 K. **Solution:** We want the molecule which, at given observed pressure and temperature, has the highest molar volume. Solving the van der Waals equation for $V_m$, we find

$$V_m = \frac{RT}{P + \frac{a}{RT} + b}.$$ 

Therefore, we want the molecule with the smallest value of $a$ and largest value of $b$, which is [HCN].

2. Assuming the integral approximation is valid for the rotational partition function, and that the harmonic approximation is valid for vibrations, write an expression for the fraction of the sample of a gas-phase, diatomic molecule that will be in the rotational and vibrational ground state ($J = 0$, $v = 0$), in terms of the temperature $T$ and the constants $B$ and $\omega_e$. **Solution:** We know that the numerator will be 1, because we measure the energy from the ground state (so $E = 0$ for the ground state) and the degeneracy of the ground state is 1. Then we use the approximate forms of the partition functions:

$$P(v, J) = P(J = 0)P(v = 0) = \frac{g(J)e^{E_{rot}/(k_BT)}g(J)e^{E_{vib}/(k_BT)}}{(k_BT/B)(1 - e^{-\omega_e/(k_BT)})^{-1}} = \frac{q_{rot}g_{vib}}{B(1 - e^{-\omega_e/(k_BT)})} \frac{k_BT}{B}.$$ 

3. An isotopically enhanced sample has $n_{\text{DI}}$ moles of deuterated hydrogen iodide and $n_{\text{HI}}$ moles of common HI at 398 K. Comparison of the infrared intensities of the $v = 1 \rightarrow 2$ transition finds a ratio of 0.100 for DI molecules ($\omega_e = 1640 \text{ cm}^{-1}$) in the $v = 1$ state to HI molecules ($\omega_e = 2310 \text{ cm}^{-1}$) in the $v = 1$ state. What is the ratio $n_{\text{DI}}/n_{\text{HI}}$ in the entire sample? **Solution:** The number of molecules in each state is the total number of molecules times the probability for that state. Converting the vibrational constants to temperature units gives $\omega_e/KB = 2360 \text{ cm}^{-1}$ and $\omega_e/KB = 3324 \text{ cm}^{-1}$.

$$0.100 = \frac{N_{\text{DI}}e^{-\omega_e/(k_BT)}(1 - e^{-\omega_e/(k_BT)})}{N_{\text{HI}}e^{-\omega_e/(k_BT)}(1 - e^{-\omega_e/(k_BT)})} = \left( \frac{N_{\text{DI}}}{N_{\text{HI}}} \right) e^{-2360/398(1 - e^{-2360/398})} = \left( \frac{N_{\text{DI}}}{N_{\text{HI}}} \right) (11.24).$$
\[
\frac{n_{\text{DI}}}{n_{\text{HI}}} = \frac{0.100}{11.24} = 0.0089
\]

By the way, you could also just assume \( q_{\text{vib}} \approx 1 \), after seeing that \( \omega_e \gg k_B T \) for both molecules.

4. The possible spin states for one \(^{14}\text{N}\) nucleus, which has spin \( I = 1 \), are \( m_I = 1 \) (\( \alpha \)), \( m_I = 0 \) (\( \beta \)), and \( m_I = -1 \) (\( \gamma \)).

(a) List all the distinct \( \text{two-particle} \) nuclear spin states for \(^{14}\text{N}_2\).

(b) Put an “\( e \)” next to each of these nuclear spin states that will be associated with even \( J \) rotational levels of the \( \text{N}_2 \) molecule. \textbf{Solution:} There should be nine states altogether, since there are three possible \( m_I \) values for each nucleus. Because the \(^{14}\text{N}\) nucleus has integer spin, it is a boson, and the even \( J \) values (symmetric rotational wavefunction) must have a symmetric nuclear wavefunction:

\[
\begin{align*}
(\alpha\alpha)e & \quad (\beta\beta)e & \quad (\gamma\gamma)e \\
(\alpha\beta + \beta\alpha)e & \quad (\alpha\gamma + \gamma\alpha)e & \quad (\beta\gamma + \gamma\beta)e \\
(\alpha\beta - \beta\alpha) & \quad (\alpha\gamma - \gamma\alpha) & \quad (\beta\gamma - \gamma\beta)
\end{align*}
\]

Whereas a diatomic with \( I = 0 \) indistinguishable nuclei has no odd \( J \) states, and with \( I = 1/2 \) has a weight of 1:3 for even \( J \) to odd \( J \), here the weight is 6:3 for even \( J \) spin weights approaches 1.

5. The derivation of \( C_{Vm} \) for a fluid arrives at

\[
C_{Vm} = \frac{3R}{2} + 2\pi N_A^2 \left( \frac{\rho_m}{M} \right) \int_0^\infty u(R) e^{-u(R)/(k_B T)} \left( \frac{u(R)}{k_B T^2} \right) R^2 dR
\]

Assume instead a potential \( u(R) = -\epsilon \) if \( R_{1,2} < R < 2R_{1,2} \) and \( u(R) = \infty \) everywhere else. \textbf{Solution:} The \( e^{-u(R)/(k_B T)} \) term makes the integrand vanish outside the range \( R_{1,2} < R < 2R_{1,2} \), so we just plug in and integrate over this region:

\[
C_{Vm} = \frac{3R}{2} + 2\pi N_A^2 \left( \frac{\rho_m}{M} \right) \int_{R_{1,2}}^{2R_{1,2}} u(R) e^{-u(R)/(k_B T)} \left( \frac{u(R)}{k_B T^2} \right) R^2 dR
\]

\[
= \frac{3R}{2} + 2\pi N_A^2 \left( \frac{\rho_m}{M} \right) \left( \frac{\epsilon^2}{k_B T^2} \right) e^{-\epsilon/(k_B T)} \frac{R^3}{3} \Bigg|_{R_{1,2}}^{2R_{1,2}}
\]

\[
= \frac{3R}{2} + 2\pi N_A^2 \left( \frac{\rho_m}{M} \right) \left( \frac{\epsilon^2}{k_B T^2} \right) e^{-\epsilon/(k_B T)} \left( \frac{7R_{1,2}^3}{3} \right)
\]

This will generally be smaller than the liquid value, in agreement with observation.