1. Estimate the degeneracy of two argon atoms in a container of volume $1.00 \cdot 10^{-9} \text{ m}^3$ with a total energy of $2.00 \cdot 10^{-20} \text{ J}$. **Solution:** This is applying our approximation that the 2-particle degeneracy $g_2$ is roughly $g_1^2$. We start from the one-particle degeneracy in the three-dimensional box, but use $\varepsilon$ equal to one half the total energy:

$$g_1(\varepsilon) = \frac{32\pi V(2m^3\varepsilon)^{1/2}}{h^3}$$

$$\approx \frac{32\pi (1.00 \cdot 10^{-9} \text{ m}^3)(2(39.9 \text{ amu})(1.661 \cdot 10^{-27} \text{ kg amu}^{-1})^3(1.00 \cdot 10^{-20} \text{ J})^{1/2}(2.5 \cdot 10^{-26} \text{ J})}{(6.626 \cdot 10^{-34} \text{ J s})^3}$$

$$= 2.08 \cdot 10^{19}$$

$$g_2 \approx g_1^2 = 4.35 \cdot 10^{38}$$

2. A sample and reservoir are in contact with each other. The degeneracy of the sample obeys the equation $g = AE^2$, while for the reservoir, $g_r = A_rE_r^{20}$. If the sample has an energy of 1.00 J, what is the energy of the reservoir $E_r$ when the sample and reservoir are at the same temperature? **Solution:** Our rigorous definition for temperature relates the derivatives of the $E$ and $\ln g$, so if we know $g$ in terms of $E$, we can obtain an analytical expression for $T$:

$$\ln g = \ln A + 2 \ln E$$

$$\left( \frac{\partial \ln g}{\partial E} \right)_{V,N} = \frac{2}{E} = \frac{1}{k_B T}$$

$$\ln g_r = \ln A_r + 20 \ln E_r$$

$$\left( \frac{\partial \ln g_r}{\partial E_r} \right)_{V,N} = \frac{20}{E_r} = \frac{1}{k_B T}$$

The temperature is the same for both reservoir and sample:

$$\frac{2}{E} = \frac{20}{E_r} \quad E_r = 10E = \boxed{10.0 \text{ J}}$$

3. Our sample consists of $N$ gas-phase ions of mass $m$ at temperature $T$, confined in a chamber that measures from $-a/2$ to $+a/2$ along each of the $X$, $Y$, and $Z$ axes. The potential energy seen by each ion is $u_i = E_0 Z_i^2$. Neglect interactions between the ions.

(a) Write an expression for the total potential energy.

$$U(X_1, \ldots, Z_N) = \sum_{i=1}^{N} u_i = \sum_{i=1}^{N} E_0 Z_i^2$$
(b) Find the total translational partition function.

\[
Q_{\text{trans}}(\beta, V) = \frac{1}{N!} \left( \frac{8\pi m}{h^2} \right)^{3N/2} Q_U(\beta, V) = \frac{1}{N!} \left( \frac{8\pi m}{h^2} \right)^{3N/2} \int_{-a/2}^{a/2} \ldots \int_{-a/2}^{a/2} e^{-U(x_1, \ldots, z_N)/(k_B T)} dX_1 \ldots dZ_N
\]

\[
= \frac{1}{N!} \left( \frac{8\pi m k_B T}{h^2} \right)^{3N/2} \int_{-a/2}^{a/2} \ldots \int_{-a/2}^{a/2} e^{-\sum_i \epsilon_0 Z_i^2} dX_1 \ldots dZ_N
\]

\[
= \frac{1}{N!} \left( \frac{8\pi m k_B T}{h^2} \right)^{3N/2} \left[ \int_{-a/2}^{a/2} dX_1 \right] \left[ \int_{-a/2}^{a/2} dY_1 \right] \ldots \left[ \int_{-a/2}^{a/2} dY_N \right]
\]

\[
\times \left[ \int_{-a/2}^{a/2} e^{-\epsilon_0 Z_1^2} dZ_1 \right] \ldots \left[ \int_{-a/2}^{a/2} e^{-\epsilon_0 Z_N^2} dZ_N \right]
\]

\[
= \frac{1}{N!} \left( \frac{8\pi m k_B T}{h^2} \right)^{3N/2} a^{2N} \left[ Z_1 - \frac{1}{3} \epsilon_0 Z_1^3 \right]_{-a/2}^{a/2} \ldots \left[ Z_N - \frac{1}{3} \epsilon_0 Z_N^3 \right]_{-a/2}^{a/2}
\]

\[
= \frac{1}{N!} \left( \frac{8\pi m k_B T}{h^2} \right)^{3N/2} a^{2N} \left[ a - \frac{1}{12} \epsilon_0 a^3 \right]^N
\]

4. If the vibrational partition function of an O₂ sample is 1.045, what percentage of the molecules is in the state \( v = 0 \)? Solution: This is asking for the probability function \( P(v = 0) \), which we can calculate in one step if we already know \( q_{vib} \), because the energy of the \( v = 0 \) ground state we have set to zero:

\[
P(v = 0) = \frac{e^{E(v=0)/(k_B T)}}{q_{vib}} = \frac{1}{1.045} = 0.957.
\]

The percentage in the \( v = 0 \) state is therefore \( 95.7\% \).

5. Begin with a sample of 1.00 mol N₂ gas at 300 K. Indicate the factor by which the energy \( E_0 \) of the original sample changes. Solution: We’re working from \( E = \frac{1}{2} N_{ep} N k_B T \). The change is proportional to the number of moles \( n \) and the temperature \( T \), and to the number of equipartition degrees of freedom \( N_{ep} \). For N₂ and CO₂ at low \( T \), \( N_{ep} = 5 \), because we count only the three translational and two rotational degrees of freedom. At high \( T \), we add 2 to get 7 for N₂ (for the kinetic and potential terms in the stretch) and 8 to get 13 for CO₂ (which has four vibrational modes).

<table>
<thead>
<tr>
<th>changing original sample by</th>
<th>multiplies ( E_0 ) by factor of</th>
</tr>
</thead>
<tbody>
<tr>
<td>raising temperature by 300 K</td>
<td>( T/T_0 = 2 )</td>
</tr>
<tr>
<td>raising temperature by 900 K</td>
<td>( (T/T_0)(N_{ep}/N_{ep,0}) = 4(7/5) = 28/5 )</td>
</tr>
<tr>
<td>removing 0.50 mol N₂ at 300 K</td>
<td>( N/N_0 = 1/2 )</td>
</tr>
<tr>
<td>adding 3.00 mol CO₂ at 300 K</td>
<td>( N/N_0 = 4 )</td>
</tr>
<tr>
<td>adding 3.00 mol CO₂ and raising temperature by 900 K</td>
<td>( T(N_{N_2 N_{ep,N_2}} + N_{CO_2 N_{ep,CO_2}})/(T_0 N_0 N_{ep,0}) = 184/5 )</td>
</tr>
</tbody>
</table>