1. 40 points.

(a) Identify the following parameters as intensive (I) or extensive (E):

i. temperature [I]

ii. entropy [E]

iii. mass [E]

(b) What is $P(J = 0)$ for HF at 298 K if $q_{\text{rot}} = 9.88$? Solution:

$$P(J = 0) = \frac{(2J + 1)e^{-B(J+1)/(k_B T)}}{q_{\text{rot}}} = \frac{1}{9.88} = 0.101.$$ 

(c) Calculate the partition function of carbon dioxide at 400 K, based on the energies and degeneracies given in the table. Solution: Use $k_B = 0.6950 \text{ cm}^{-1} \text{ K}^{-1}$ to calculate $g \exp \left[-\frac{\epsilon_{\text{vib}}}{(k_B T)}\right]$, and then add all the values up:

<table>
<thead>
<tr>
<th>state</th>
<th>$g$</th>
<th>$\epsilon_{\text{vib}}$ (cm$^{-1}$)</th>
<th>$g \exp \left[-\frac{\epsilon_{\text{vib}}}{(k_B T)}\right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(0,1,0)</td>
<td>2</td>
<td>667</td>
<td>0.182</td>
</tr>
<tr>
<td>(0,2,0)</td>
<td>3</td>
<td>1334</td>
<td>0.025</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>2</td>
<td>2000</td>
<td>0.002</td>
</tr>
<tr>
<td>total</td>
<td>$g = 1.21$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(d) What is the number of equipartition degrees of freedom in sulfur hexafluoride (SF$_6$)

i. when vibrations are not included? Solution: SF$_6$ is non-linear, so there are 3 translations and 3 rotations, so $N_{\text{ep}} = 3 + 3 = 6$.

ii. when vibrations are included? Solution: Now add $2 \times (3 \cdot 7 - 6) = 30$ vibrational contributions, so $N_{\text{ep}} = 3 + 3 + 30 = 36$.

2. A system consists of $N$ distinguishable particles is energized by $M$ photons, each with energy $\epsilon_0$. Each particle may absorb any number of photons, and many particles may absorb the same number of photons. (However, the photons are not distinguishable.)

(a) Write an expression for the ensemble size $\Omega$ in terms of the total energy $E = M\epsilon_0$. Solution:

The number of ways of putting $M$ photons into $N$ particles is $N^M$, but then we divide by $M!$ because we don’t care about the order in which the photons enter the system:

$$\Omega = \frac{N^M}{M!} = \frac{N^{E/\epsilon_0}}{(\frac{E}{\epsilon_0})^!}.$$ 

(b) Find a usable expression for $S$ assuming $N$ and $M$ are large. Solution: The warning to make the equation usable for large values is to remind us to use Stirling’s approximation to make $\ln M!$ tractable:

$$S = k_B \ln \Omega = k_B \ln \frac{N^M}{M!} = k_B \left[ M \ln N - M \ln M + M \right]$$

$$= Mk_B \left[ \ln N - \ln M + 1 \right] = Mk_B \left[ \ln \left( \frac{N}{M} \right) + 1 \right]$$
3. Based on the values shown in the plot below, estimate (a) the Gibbs entropy of the system in SI units and (b) the partition function at this temperature.

![Plot](image_url)

**Solution:** There are ten particles, so the probabilities \( P(J) \) are approximately the number of particles in state \( J \) divided by 10, so \( J = 3 \) appears to have a probability of roughly \( 2/10 \), \( J = 6 \) has a probability about \( 3/10 \), and 5 states have probability of about \( 1/10 \). We then use these values to estimate the Gibbs entropy:

\[
S = -Nk_B \sum_{J=0}^{\infty} P(J) \ln P(J)
\]

\[
= -10(1.381 \cdot 10^{-23} J K^{-1}) \left[ (5) \frac{1}{10} \ln \left( \frac{1}{10} \right) + 2 \frac{1}{10} \ln \left( \frac{2}{10} \right) + 3 \frac{1}{10} \ln \left( \frac{3}{10} \right) \right] = 2.53 \cdot 10^{-22} J K^{-1}
\]

(b) The partition function is roughly the number of occupied states at this temperature, Almost all of the particles in this plot are in states \( J \leq 7 \). Taking the \( 2J + 1 \) degeneracy into account for \( J \) from 0 to 7, \( q \) is probably less than \( 1 + 3 + 5 + 7 + 9 + 11 + 13 + 15 = 64 \).

We could also use the \( J = 0 \) population, which is \( 1/10 \) of the total population, to estimate \( q \):

\[
P(J = 0) = \frac{(2J + 1)e^{-BJ(J+1)/(kB T)}}{q} = \frac{1}{q} \approx \frac{1}{10} \quad q \approx 10
\]

Because this result is based on only one particle, it is not very accurate, and almost certainly too low. A value of \( q = 10 \) would suggest that it is unlikely many of the particles would be found at \( J > 4 \) (because there are more than 10 states in \( J \leq 4 \)), but most of the particles are at \( J > 4 \). Answers in this range would be accepted. The actual \( q \) in this simulation was equal to 30.

4. Consider neutrons bouncing on a surface in Earth’s gravitational field. The potential energy is \( mgz \), where \( m = 1.675 \cdot 10^{-27} \text{kg} \), \( g = 9.81 \text{m/s}^2 \), and \( z \) is the height. Find an approximate equation for the average total energy per neutron as a function of the temperature. **Solution:**

\[
\langle \epsilon \rangle = \frac{m}{2} \langle v_z^2 \rangle + mg \langle z \rangle
\]

\[
\frac{m}{2} \langle v_z^2 \rangle = \frac{1}{2} k_B T
\]

\[
mg \langle z \rangle = mg \left[ \frac{\int_0^\infty e^{-mgz/(k_B T)} dz}{\int_0^\infty e^{-mgz/(k_B T)} dz} \right]
\]

\[
mg \langle z \rangle = mg \left[ (1)/(mg/(k_BT))^2 \right] = mg \left( \frac{k_BT}{mg} \right) = k_BT \quad \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}
\]

\[
\langle \epsilon \rangle = \frac{1}{2} k_B T + k_B T = \frac{3}{2} k_B T.
\]