Some useful constants and conversions:

Avogadro’s Constant ($N_A$) = $6.02214 \times 10^{23}$ mol$^{-1}$

Gas Constant ($R$) = $8.3145$ J·K$^{-1}$·mol$^{-1}$ = $0.08206$ L·atm·K$^{-1}$·mol$^{-1}$ = $0.083145$ L·bar·K$^{-1}$·mol$^{-1}$

Boltzmann Constant ($k_B$) = $1.38066 \times 10^{-23}$ J·K$^{-1}$ = $0.695$ cm$^{-1}$·K$^{-1}$ (Note: $nR = N_A k$)

Plank’s Constant ($h$) = $6.62608 \times 10^{-34}$ J·s

Speed of Light ($c$) = $2.9979 \times 10^8$ m/s

1 Atomic Mass Unit (amu) = $1.6606 \times 10^{-27}$ kg

1 atmosphere (atm) = 760 torr = $1.01325 \times 10^5$ Pa = 1.01325 bar

$$\varepsilon_{\text{vibrations}} = \frac{\varepsilon_{\text{vibrations}}}{hc} \quad c = \frac{\lambda}{\nu} \quad \varepsilon_{\text{photon}} = \frac{h \nu}{\text{photon}} \quad T = \frac{1}{\nu}$$

Some useful equations:

Ideal gas equation \[ PV = nRT \] \[ P\overline{V} = RT \]

Van der Waals equation \[ \left( P + \frac{a}{V^2} \right)(\overline{V} - b) = RT \]

Boltzmann population distribution \[ P_j = \sum e^{-BE_j} \]

Partition function definition \[ Q(N, V, \beta) = \sum e^{-\beta E_i} \]

Average energy \[ \langle E \rangle = U = -\frac{\partial \ln Q}{\partial \beta} = k_B T^2 \frac{\partial \ln Q}{\partial T} \]

Heat capacity \[ C_v = \frac{\partial \langle E \rangle}{\partial T} \]

Pressure-volume work \[ w = -\int P_{\text{ext}} dV \]

Internal energy and Enthalpy \[ \Delta U = \int C_v dT \quad \Delta H = \Delta U + \Delta(PV) \]

Adiabatic, reversible process \[ \left( \frac{T_2}{T_1} \right)^{\frac{C_p}{C_v}} = \frac{V_1}{V_2} \]

and \[ P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \] where \[ \gamma = \frac{C_p}{C_v} \quad \text{and} \quad C_p - C_v = R \] for ideal gas
1. You hold in your hands a container that holds a large number of oxygen molecules – O₂. With your incredible powers of observation, you are able to discern the population in each vibrational state of each molecule in the container. After careful study you find the following relative populations:

<table>
<thead>
<tr>
<th>ν</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(ν)</td>
<td>1.000</td>
<td>0.4084</td>
<td>0.1668</td>
<td>0.0681</td>
<td></td>
</tr>
<tr>
<td>p₀</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. (5 pts) What is the vibrational temperature given by the relative populations of states ν = 0 and ν = 1?
b. (5 pts) Using this temperature, what is the population of state \( v = 4 \) relative to state \( v = 0 \).

c. (10 pts) Are all of the four vibrational states given in the table \( v = 0-3 \) in thermal equilibrium with each other?
2. You and your sidekick have been captured by your arch nemesis – Capa Girl. Capa Girl has locked you in one of those fancy rooms where the walls close in on each other to crush you. Being an evil supervillan, Capa Girl has left a keypad on the inside of the room with which you can open the door. You happen to know that Capa Girl’s door code has to do with the partition function values of her favorite gas, $D^{35}Cl$. You now decide to take advantage of your sidekick – Partition Function Boy. You happen to have a container of pure $H^{35}Cl$, from which Partition Function Boy tells you that the values of the individual molecular partition functions are:

\[
\begin{align*}
q_{\text{trans}} &= 2.11 \times 10^{27} \\
q_{\text{rot}} &= 19.5 \\
q_{\text{vib}} &= 1.00000098 \\
q_{\text{elec}} &= 1
\end{align*}
\]

(Note that Partition Function Boy uses the zero-point-corrected form of the vibrational partition function: $q_{\text{vib}} = \frac{1}{1 - e^{-hv/kT}}$.)

Fortunately, you also have a list of old Capa Girl PINs from which to choose. So, select the best choice below for the partition function values of $D^{35}Cl$. (Assume that the $D^{35}Cl$ and $H^{35}Cl$ are at the same temperature.) You do NOT need to do any tough calculations for this problem, but you do need to explain how you made your selection.

IN OTHER WORDS, I have given you $q$ values for HCl and I’m asking you to pick out $q$ values for DCI below and to explain the reasoning behind your choice.

a. (6 pts) $D^{35}Cl$ $q_{\text{trans}}$
   \[
   \begin{array}{cccc}
   2.02 \times 10^{27} & 2.11 \times 10^{27} & 2.20 \times 10^{27} & 5.97 \times 10^{27}
   \end{array}
   \]

b. (6 pts) $D^{35}Cl$ $q_{\text{rot}}$
   \[
   \begin{array}{cccc}
   10.0 & 19.5 & 20.4 & 38.0
   \end{array}
   \]
c. (6 pts) $D^{35}\text{Cl} \ q_{\text{vib}}$

\[
\begin{array}{l}
\text{1} \quad 1.00000098 \quad 1.000048 \quad 1.95 \\
\end{array}
\]

d. (6 pts) $D^{35}\text{Cl} \ q_{\text{elec}}$

\[
\begin{array}{l}
\text{1} \quad 1.004 \quad 1.41 \quad 1.95 \\
\end{array}
\]

3. Below is a plot of the Gibbs free energy vs. temperature for the solid, liquid, and gas phases of a typical substance at a pressure of 10 atm.
a. (8 pts) Below is a copy of the same plot. On it, sketch the corresponding plots for the substance at a pressure of 8 atm. Assume that all three phases of the substance can still exist at this pressure. Be sure to indicate approximate temperatures for the two transition temperatures. (There is no need to do any calculation. The key things are the appearance of the solid, liquid, and gas lines and the transition temperatures relative to the 10 atm plot.)

\[
\begin{array}{c}
G \\
\end{array}
\]

\[
\begin{array}{c}
T \text{ (K)} \\
250 & 450 \\
\end{array}
\]

b. (8 pts) Now sketch a similar plot for the three phases of the substance at a pressure of 1 atm. At this pressure the substance now exhibits sublimation at a temperature of 100 K.

\[
\begin{array}{c}
G \\
\end{array}
\]

\[
\begin{array}{c}
T \text{ (K)} \\
\end{array}
\]
c. (10 pts) Finally, sketch the phase diagram of the substance. Be quantitatively consistent with the previous plots. Be sure to label points where $p$ and $T$ are known (from parts a and b). Also label the locations of the three phases and any other important points in the phase diagram.

4. After Partition Function Boy ran off with Capa Girl, you were left sidekickless and in a terrible depression. Fortunately, Equilibrium Constant Man/Woman came to your rescue. He/She began by measuring the equilibrium constant of a certain reaction (the reaction of love) at two temperatures:

$$K = 1.95 \quad \text{at 280 K}$$
$$K = 1.68 \quad \text{at 320 K}$$

a. (18 pts) Calculate $\Delta H$, $\Delta G$, and $\Delta S$ for this reaction at 300 K. When calculating $\Delta H$, state any assumptions or approximations that must be made.
b. (3 pts) Are products or reactants favored at 300 K for this reaction? Explain.

c. (3 pts) Is this reaction enthalpy-driven or entropy-driven at 300 K? Explain.

5. (6 pts) Sketch a plot, derive or explain an equation, or otherwise prove knowledge in an area that was not tested by any of the previous problems. Be sure to earn your 6 points.