The Partition Function

- Partition functions play a central role in statistical mechanics. They are the key to calculating thermodynamic functions.

- **Mathematical definition:**

\[ q = \sum g_i e^{-\varepsilon_i/kT} \]

where \( g_i \) = the degeneracy of energy level \( \varepsilon_i \).

- Molecules will distribute themselves over the available energy levels according to the Boltzmann distribution.

- **Physical interpretation:** \( q \) is a measure of the number of thermally accessible energy states. Note that it is a function of the pattern of energy levels \( (\varepsilon_i) \) and the temperature \( (T) \).

- For a set of discrete levels:

\[ q = g_0 e^{-0/kT} + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \ldots \]

\[ = g_0(1) + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \ldots \]
The Total Partition Function

- To a good approximation the different forms of molecular energy are independent, so that we can write

\[ \varepsilon_{\text{total}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{el}} \]

- Since \( q = \sum e^{-\varepsilon/kT} \), the sum in the exponents becomes a product

\[ q_{\text{total}} = (\sum e^{-\varepsilon/kT})_{\text{trans}}(\sum e^{-\varepsilon/kT})_{\text{rot}}(\sum e^{-\varepsilon/kT})_{\text{vib}}(\sum e^{-\varepsilon/kT})_{\text{el}} \]

or \[ q_{\text{total}} = q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{el}} \]

- Thus we can calculate each of these partition functions separately and multiply them.
Partition Functions Depend on Energy Level Spacing and Temperature

- Consider some simple two-level systems:


\[
\begin{array}{c|c|c|c}
0 & 5 \text{ kT} & 1 \text{ kT} & 0.1 \text{ kT} \\
\hline
\exp^{-100} \approx 0 & \exp^{-5} = 0.007 & \exp^{-1} = 0.368 & \exp^{-0.1} = 0.904 \\
q \approx 1 & q = 1.007 & q = 1.368 & q = 1.904 \\
\end{array}
\]

- Note that if the temperature increases the partition function increases. Molecules can more easily reach the higher levels.
Partition Function for the Oxygen Atom

- The oxygen atom has three low-lying energy levels:

\[ ^3P_0 \quad \varepsilon = 226.1 \text{ cm}^{-1} \]

\[ ^3P_1 \quad \varepsilon = 157.4 \text{ cm}^{-1} \]

\[ ^3P_2 \quad \varepsilon = 0 \text{ cm}^{-1} \]

- Recall that \( q = \sum g_i e^{-\varepsilon_i/kT} \).

- The degeneracies of these levels are given by \( g_J = (2J + 1) \), where \( J \) is the subscript in the term symbol.

- At \( T = 25^\circ C \), \( kT = 207.2 \text{ cm}^{-1} \). Thus the partition function \( q \) is

\[
q = (5)e^{-0/207.2} + (3)e^{-157.4/207.2} + (1)e^{-226.1/207.2}
= 5(1) + (3)(0.468) + (1)(0.336) = 6.739
\]
System Partition Functions

• So far we have discussed the molecular partition function $q$.

• We can also discuss the partition function $Q$ for an assembly of $N$ identical molecules. We call $Q$ the system partition function.

• We must determine whether the particles in the assembly are distinguishable or indistinguishable:

  **Crystal**--the molecules can be distinguished by their positions, $Q = q^N$.

  **Gas**--the molecules cannot be distinguished, $Q = q^N/N!$ [The $N!$ accounts for the permutations of the $N$ molecules.]

• We shall be mainly concerned with gases, and thus with indistinguishable molecules.