Statistical Molecular Thermodynamics

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Video 4.7

Ideal Polyatomic Gases: Part 1
Energy of an Ideal Polyatomic Gas

In addition to translational and electronic degrees of freedom, a polyatomic also can rotate and has *multiple* vibrations.

The Energy:

\[ \varepsilon_{\text{polyatomic}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} \quad \text{(sum)} \]

As for monatomic and diatomic gases, *translational* energy comes from the particle in a box approximation and depends only on the mass of the particle and a chosen volume.

As for a diatomic gas, we assume a ground *electronic* state but instead of a single \( D_e \) we sum over the dissociation energies of *all* of the bonds.
Polyatomic Rotations

Linear polyatomics: Result the same as that for the diatomic rigid rotator.

\[ q_{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}} \]
\[ \sigma = 1 \text{ for } \text{COS} \]
\[ \sigma = 2 \text{ for } \text{CO}_2 \]

Nonlinear polyatomics: For each of the 3 degrees of rotational freedom, (labeled A, B, C) we have a separate moment of inertia and a separate rotational temperature,

Three possible cases:

\[ I_A = I_B = I_C, \quad \Theta_{\text{rot},A} = \Theta_{\text{rot},B} = \Theta_{\text{rot},C} \]
spherical top

\[ I_A = I_B \neq I_C, \quad \Theta_{\text{rot},A} = \Theta_{\text{rot},B} \neq \Theta_{\text{rot},C} \]
symmetric top

\[ I_A \neq I_B \neq I_C, \quad \Theta_{\text{rot},A} \neq \Theta_{\text{rot},B} \neq \Theta_{\text{rot},C} \]
asymmetric top
Quantum mechanics provides *energy levels*, for example, for the spherical top:

\[ \epsilon_J = \frac{J(J+1)\hbar^2}{2I} \]

\[ g_J = (2J+1)^2 \quad J = 0, 1, 2, \ldots \]

In *all* cases, as long as each \( \Theta_{\text{rot}} \ll T \), one can approximate the sum as an integral,

\[ q_{\text{rot}}(T) = \int_0^\infty dJ \ g_J \ e^{-\beta \epsilon_J} \]

Which provides solutions:

### Spherical Top

\[
q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{\text{rot}}} \right)^{3/2}
\]

### Symmetric Top

\[
q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{\text{rot,A}}} \right)^{1/2} \left( \frac{T}{\Theta_{\text{rot,C}}} \right)^{1/2}
\]

### Asymmetric Top

\[
q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2}
\]
Nonlinear Rotational $\overline{U}$ and $\overline{C}_V$

\[ Q(N,V,T) = \frac{q(V,T)^N}{N!} \]

**spherical top**

\[ q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{rot}} \right)^{3/2} \]

**symmetric top**

\[ q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_{rot,A}} \right)^{1/2} \]

**asymmetric top**

\[ q_{rot}(T) = \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_{rot,A} \Theta_{rot,B} \Theta_{rot,C}} \right)^{1/2} \]

**Note that all $q_{rot}$ have 3/2 power temperature dependence**

- **Energy**
  \[ \overline{U}_{rot} = RT^2 \frac{\partial \ln T^{3/2}}{\partial T} = \frac{3}{2} RT \]

- **Heat Capacity**
  \[ \overline{C}_V = \left( \frac{\partial \overline{U}}{\partial T} \right)_V = \frac{3}{2} R \]