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:

$$\varepsilon_{\text{polyatomic}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} \qquad \text{(sum)}$$

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.

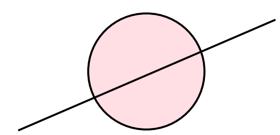
$$q_{\text{rot}} = \frac{T}{\sigma\,\Theta_{\text{rot}}}$$

σ = 1 for COS
σ = 2 for CO_2

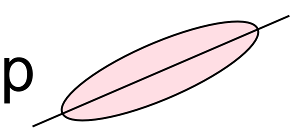
Nonlinear polyatomics: For each of the 3 degrees of rotational freedom, (labeled A, B, C) we have a *separate moment of inertia* and a *separate rotational temperature*,

<u>Three possible cases:</u>

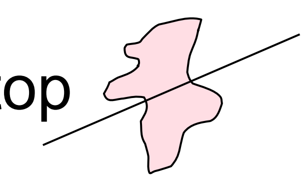
$I_A = I_B = I_C$, $\Theta_{\text{rot,A}} = \Theta_{\text{rot,B}} = \Theta_{\text{rot,C}}$ spherical top



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



$I_A \neq I_B \neq I_C$, $\Theta_{\text{rot,A}} \neq \Theta_{\text{rot,B}} \neq \Theta_{\text{rot,C}}$ asymmetric top



Nonlinear Rotational Partition Functions

Quantum mechanics provides *energy levels*, for example,

for the spherical top: $\varepsilon_J = \dfrac{J(J+1)\hbar^2}{2I} \quad g_J = (2J+1)^2 \quad J = 0,1,2,\ldots$

In *all* cases,

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} g_J\, e^{-\beta\varepsilon_J}$$

As long as each $\Theta_{\text{rot}} \ll T$, one can *approximate the sum as an integral*, $q_{\text{rot}} = \int_0^{\infty} dJ\; g_J\, e^{-\beta\varepsilon_J}$

Which provides solutions:

spherical top $\quad q_{\text{rot}}(T) = \dfrac{\pi^{1/2}}{\sigma}\left(\dfrac{T}{\Theta_{\text{rot}}}\right)^{3/2}$

symmetric top

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

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

symmetric top

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

asymmetric top

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

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

- **Energy** $\overline{U}_{\text{rot}} = RT^2 \frac{\partial \ln T^{3/2}}{\partial T} = \frac{3}{2}RT$
- **Heat Capacity** $\overline{C}_V = \left(\frac{\partial \overline{U}}{\partial T}\right)_V = \frac{3}{2}R$