Statistical Molecular Thermodynamics

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Video 4.8

Ideal Polyatomic Gases: Part 2

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:

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

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

Rotation depends on up to 3 distinct moments of inertia

Polyatomic Vibrations

We divide intramolecular motions into normal modes and express each as an *independent* harmonic oscillator

- Energy from a sum over modes *j*,

$$\varepsilon_{\text{vib}} = \sum_{j=1}^{\alpha} h\nu_j\left(n_j + \frac{1}{2}\right) \quad n_j = 0,1,2,\ldots$$

Recall $\alpha = 3N-5$ (linear molecule) or $\alpha = 3N-6$ (nonlinear molecule)

- Partition function is the product,

$$q_{\text{vib}}(T) = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{\text{vib},j}/2T}}{\left(1 - e^{-\Theta_{\text{vib},j}/T}\right)}$$

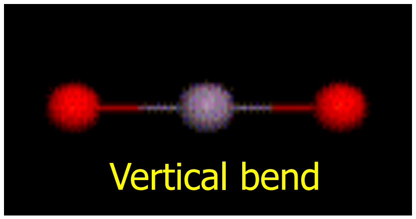
$$E_{\text{vib}} = Nk_{\text{B}} \sum_{j=1}^{\alpha}\left(\frac{\Theta_{\text{vib},j}}{2} + \frac{\Theta_{\text{vib},j}}{e^{\Theta_{\text{vib},j}/T} - 1}\right)$$

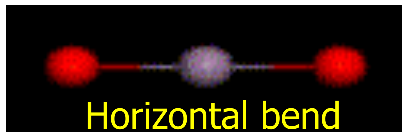
$$C_{V,\text{vib}} = Nk_{\text{B}} \sum_{j=1}^{\alpha}\left[\left(\frac{\Theta_{\text{vib},j}}{\text{T}}\right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{\left(1 - e^{-\Theta_{\text{vib},j}/T}\right)^2}\right]$$

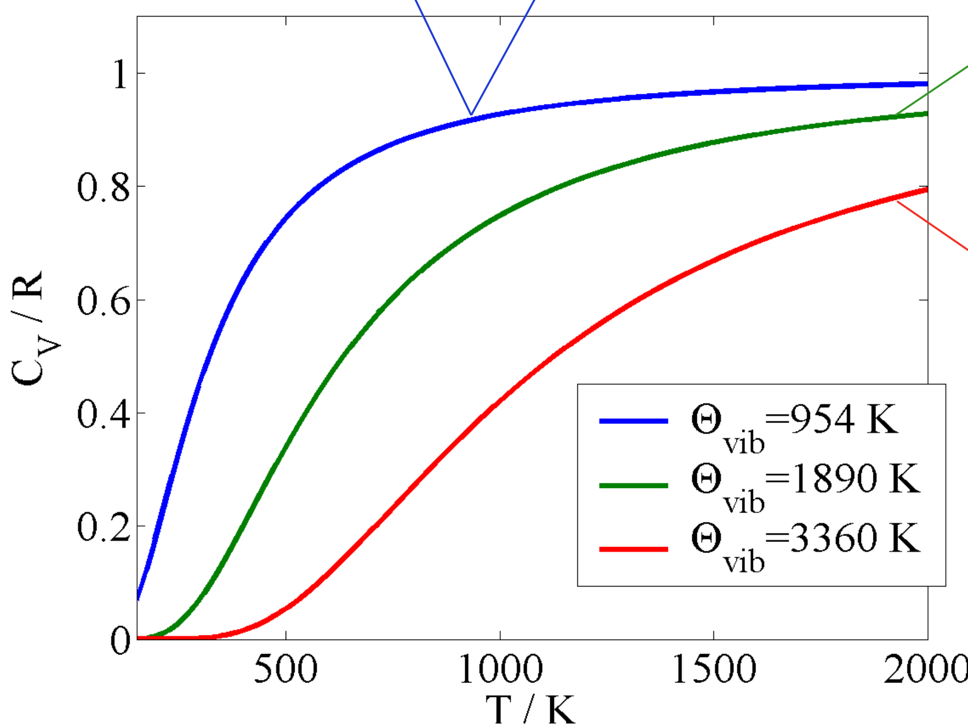
Vibrational Heat Capacity: CO_2

$$\bar{C}_{V,\mathrm{vib}} = R\sum_{j=1}^{4}\left[\left(\frac{\Theta_{\mathrm{vib},j}}{\mathrm{T}}\right)^2 \frac{e^{-\Theta_{\mathrm{vib},j}/T}}{\left(1-e^{-\Theta_{\mathrm{vib},j}/T}\right)^2}\right]$$

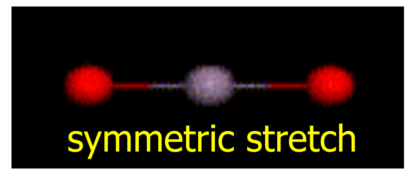
degenerate, Θ_{vib}= 954 K



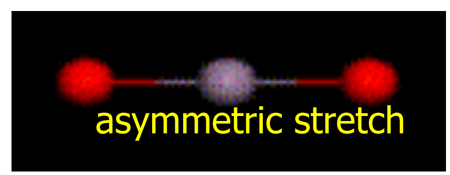




Θ_{vib}= 1890 K



Θ_{vib}= 3360 K



Full Polyatomic Ideal Gas Q

Linear: $q(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{\text{rot}}} \cdot \left(\prod_{j=1}^{3n-5} \frac{e^{-\Theta_{\text{vib,j}}/2T}}{1 - e^{-\Theta_{\text{vib,j}}/T}} \right) \cdot g_1 e^{D_e/k_B T}$

$$\overline{U} = \frac{5}{2} RT + R \sum_{j=1}^{3n-5} \left(\frac{\Theta_{\text{vib,j}}}{2} + \frac{\Theta_{\text{vib,j}}}{e^{\Theta_{\text{vib,j}}/T} - 1} \right) - N_A D_e$$

$$\overline{C}_V = \frac{5}{2} R + R \sum_{j=1}^{3n-5} \left(\frac{\Theta_{\text{vib},j}}{\text{T}} \right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{\left(1 - e^{-\Theta_{\text{vib},j}/T}\right)^2}$$

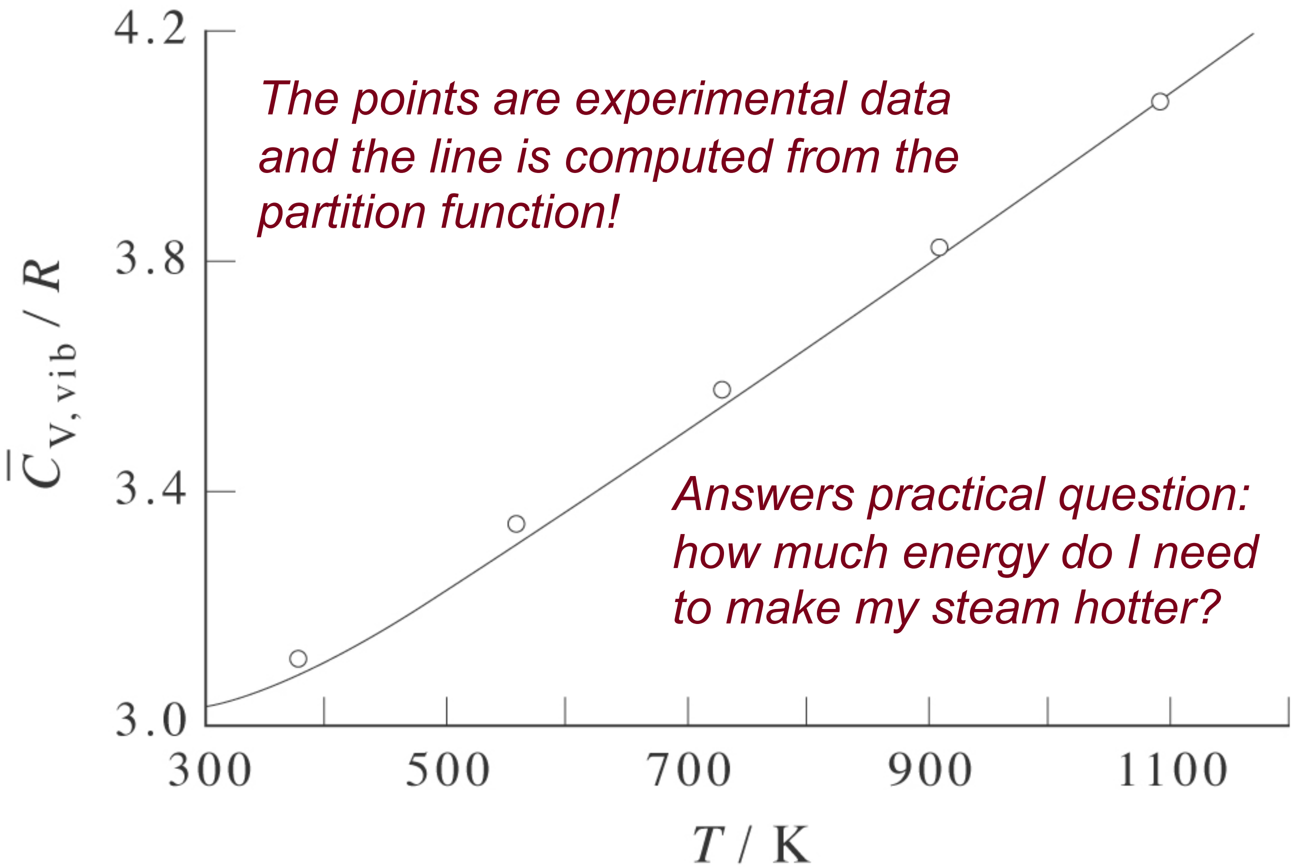
Nonlinear:

$$q(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \cdot \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \cdot \left(\prod_{j=1}^{3n-6} \frac{e^{-\Theta_{\text{vib,j}}/2T}}{1 - e^{-\Theta_{\text{vib,j}}/T}} \right) \cdot g_1 e^{D_e/k_B T}$$

$$\overline{U} = 3RT + R \sum_{j=1}^{3n-6} \left(\frac{\Theta_{\text{vib,j}}}{2} + \frac{\Theta_{\text{vib,j}}}{e^{\Theta_{\text{vib,j}}/T} - 1} \right) - N_A D_e$$

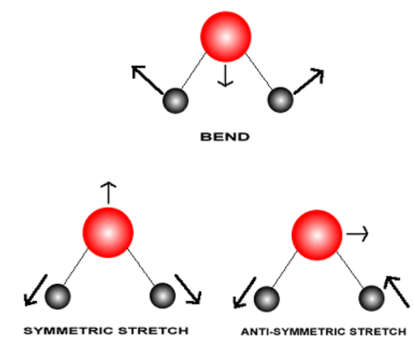
$$\overline{C}_V = 3R + R \sum_{j=1}^{3n-6} \left(\frac{\Theta_{\text{vib},j}}{\text{T}} \right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{\left(1 - e^{-\Theta_{\text{vib},j}/T}\right)^2}$$

Does This All Work? Water Example



The points are experimental data and the line is computed from the partition function!

Answers practical question: how much energy do I need to make my steam hotter?



$3N$-6=3
vibrational modes

$\Theta_{\text{vib},1}$ = 2290 K
$\Theta_{\text{vib},2}$ = 5160 K
$\Theta_{\text{vib},3}$ = 5360 K

$$\overline{C}_V = 3R + R\sum_{j=1}^{3}\left(\frac{\Theta_{\text{vib},j}}{\text{T}}\right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{\left(1-e^{-\Theta_{\text{vib},j}/T}\right)^2}$$