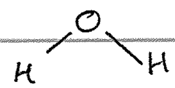
Polyatomic molecules

$O=C=O$ ← 3 atoms = 9 degrees of freedom
$- 2$ rotations
$- 3$ translations
4 vibrational modes


← 3 atoms = 9 degrees of freedom
-3 rotations
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3 vibrational modes

The polyatomic partition function is pretty similar to the diatomic:

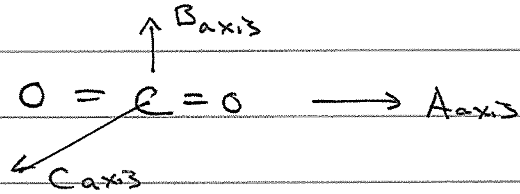
$$q = q_{trans} * q_{elect} * q_{vib} * q_{rot}$$

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V * \left(g_1 e^{+\beta D_e} + g_2 e^{-\beta \varepsilon_2} + \dots\right)\left(\prod_{j=1}^{N_{vib}} q_{vib}^{j}(T)\right)\left(\ ?\ \right)$$

product of N_{vib} partition functions, one for each Normal Mode

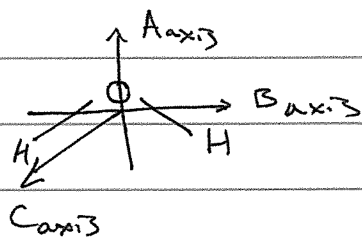
Rotation needs a bit more explanation

All rigid objects have 3 principal axes of rotation, each with its own moment of inertia. They can sometimes be hard to identify or degenerate with each other, but they are there!



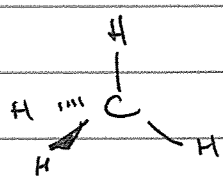
$$\left.\begin{array}{l} I_A = 0 \\ I_B = I_C \end{array}\right\}$$ this is a linear rotor, so one I value is zero.

- All diatomics are linear rotors.



$I_A \neq I_B \neq I_C$

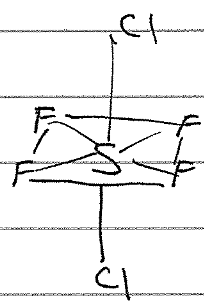
this is called an asymmetric top



$I_A = I_B = I_C$

this is called a spherical top

CH_4, SF_6 ← all spherical tops



$I_A \neq I_B = I_C$

symmetric rotor

NH_3, C_6H_6 (an "oblate"), CH_2Cl_2

Spherical tops : $q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{T}{\Theta_{rot}}\right)^{3/2}$

Symmetric tops : $q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\left(\frac{T}{\Theta_{rot}^{A}}\right)\left(\frac{T}{\Theta_{rot}^{B}}\right)\right)^{1/2}$

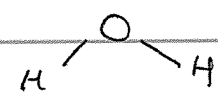
Asymmetric tops : $q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{T^3}{\Theta_{rot}^{A}\,\Theta_{rot}^{B}\,\Theta_{rot}^{C}}\right)^{1/2}$

Linear rotors : $q_{rot} = \frac{T}{\sigma\,\Theta_{rot}}$

To get these partition functions, we need moments of inertia: $\Theta_{rot}^{A} = \frac{h^2}{8\pi^2 I_A k_B}$

I_A, I_B, I_C come from the geometry of the molecule and the atomic masses.

Multiple vibrational modes



$$\varepsilon_{tot}^{vib} = \varepsilon_{\substack{symmetric\\stretch}} + \varepsilon_{\substack{asymmetric\\stretch}} + \varepsilon_{bend}$$

$$\varepsilon = \left(v_{ss}+\tfrac{1}{2}\right)h\nu_{ss} + \left(v_{as}+\tfrac{1}{2}\right)h\nu_{as} + \left(v_b+\tfrac{1}{2}\right)h\nu_b$$

v = quantum number for that mode

ν = frequency for that mode

$$q_{vib} = \sum_{v_{ss}=0}^{\infty}\sum_{v_{as}=0}^{\infty}\sum_{v_b=0}^{\infty} e^{-\beta h\nu_{ss}(v_{ss}+\frac{1}{2})-\beta h\nu_{as}(v_{as}+\frac{1}{2})-\beta h\nu_b(v_b+\frac{1}{2})}$$

$$= q_{vib}^{ss} * q_{vib}^{as} * q_{vib}^{bend}$$

$$q_{vib}(T) = \prod_{j=1}^{N_{vib}} \frac{e^{-\Theta^j_{vib}/2T}}{1-e^{-\Theta^j_{vib}/T}} \qquad \Theta^j_{vib} = \frac{h\nu_j}{k_B}$$

q is a product of modes