STATISTICAL MOLECULAR THERMODYNAMICS

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Video 4.5

Ideal Diatomic Gas: Part 2

ENERGY OF AN IDEAL DIATOMIC GAS

In addition to translational and electronic degrees of freedom, a diatomic also can rotate and vibrate. These motions can be treated within the *rigid rotator* and *harmonic oscillator* approximations, respectively (*exactly solvable QM problems*)

The Energy:

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

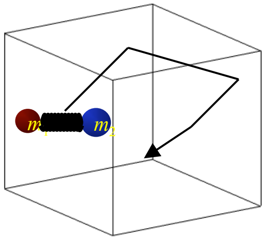
total energy

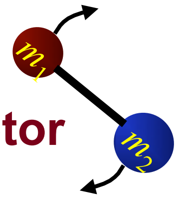
translational energy

rotational energy

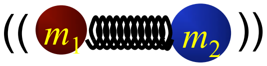
vibrational energy

electronic energy



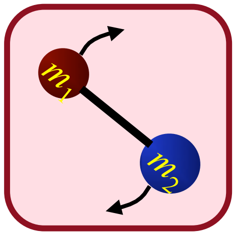


rigid rotor



harmonic oscillator

DIATOMIC ROTATIONS



Within the rigid-rotator approximation,

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0,1,2,\ldots$$

degeneracy of the J^{th} level,

$$g_J = 2J + 1$$

$$q_{\text{rot}}(T) = \sum_{\text{levels}, J} g_J \, e^{-\beta\varepsilon_{\text{rot}}} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta\hbar^2 J(J+1)/2I}$$

Define a *rotational temperature*: $\Theta_{\text{rot}} = \dfrac{\hbar^2}{2Ik_{\text{B}}}$

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\Theta_{\text{rot}} J(J+1)/T}$$

EVALUATION OF q_{rot}

$$q_{\mathrm{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)\, e^{-\Theta_{\mathrm{rot}} J(J+1)/T}$$

No closed form solution for this series

As was true for the translational partition function, *if the energy levels are sufficiently closely spaced*, we can replace the sum by an integral

$$q_{\mathrm{rot}}(T) = \int_{0}^{\infty} dJ\, (2J+1)\, e^{-\Theta_{\mathrm{rot}} J(J+1)/T}$$

Close spacing of energy levels occurs for $\Theta_{\mathrm{rot}} << T$

SOME ROTATIONAL TEMPERATURES

Gas	Θ_{rot}, K
H_2	85.3
CO	2.8
N_2	2.9
NO	2.4
O_2	2.1
HCl	15.0
HBr	12.0
HI	9.2
Cl_2	0.4
Br_2	0.1

$$q_{\text{rot}}(T) = \int_0^\infty dJ\,(2J+1)\,e^{-\Theta_{\text{rot}} J(J+1)/T}$$

Valid for $\Theta_{\text{rot}} \ll T$

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_{\text{B}}}$$

Easily satisfied for all but the lightest of gases at the lowest of temperatures

A VERY FRIENDLY INTEGRAL

$$q_{\mathrm{rot}}(T) = \int_0^\infty dJ\,(2J+1)\,e^{-\Theta_{\mathrm{rot}} J(J+1)/T}$$

Making substitutions $x = J(J+1), \quad dx = (2J+1)\,dJ, \quad a = \Theta_{\mathrm{rot}}/T$

$$q_{\mathrm{rot}}(T) = \int_0^\infty dx\, e^{-ax} = -\frac{1}{a} e^{-ax}\Big|_0^\infty = 0 + \frac{1}{a} = \frac{T}{\Theta_{\mathrm{rot}}}$$

$$q_{\mathrm{rot}}(T) = \frac{T}{\Theta_{\mathrm{rot}}} = \frac{2Ik_{\mathrm{B}}T}{\hbar^2} = \frac{8\pi^2 Ik_{\mathrm{B}}T}{h^2}, \qquad \Theta_{\mathrm{rot}} << T$$

DIATOMIC IDEAL GAS ROTATIONAL <*E*> AND C_V

Rotational energy:

$$\langle E_{\text{rot}} \rangle = Nk_{\text{B}}T^2 \frac{\partial \ln q_{\text{rot}}}{\partial T} = Nk_{\text{B}}T^2 \frac{\partial \ln\left(\dfrac{8\pi^2 I k_{\text{B}} T}{h^2}\right)}{\partial T} = Nk_{\text{B}}T^2 \frac{1}{T}$$

$$= Nk_{\text{B}}T$$

Molar heat capacity: $$\overline{C}_{\text{V,rot}} = \frac{d\langle \overline{E}_{\text{rot}} \rangle}{dT} = \frac{d(RT)}{dT} = R$$

A diatomic has 2 degrees of rotational freedom, each contributes $R/2$ to $\overline{C}_V$.

ROTATIONAL STATE OCCUPATIONS

Fraction of molecules

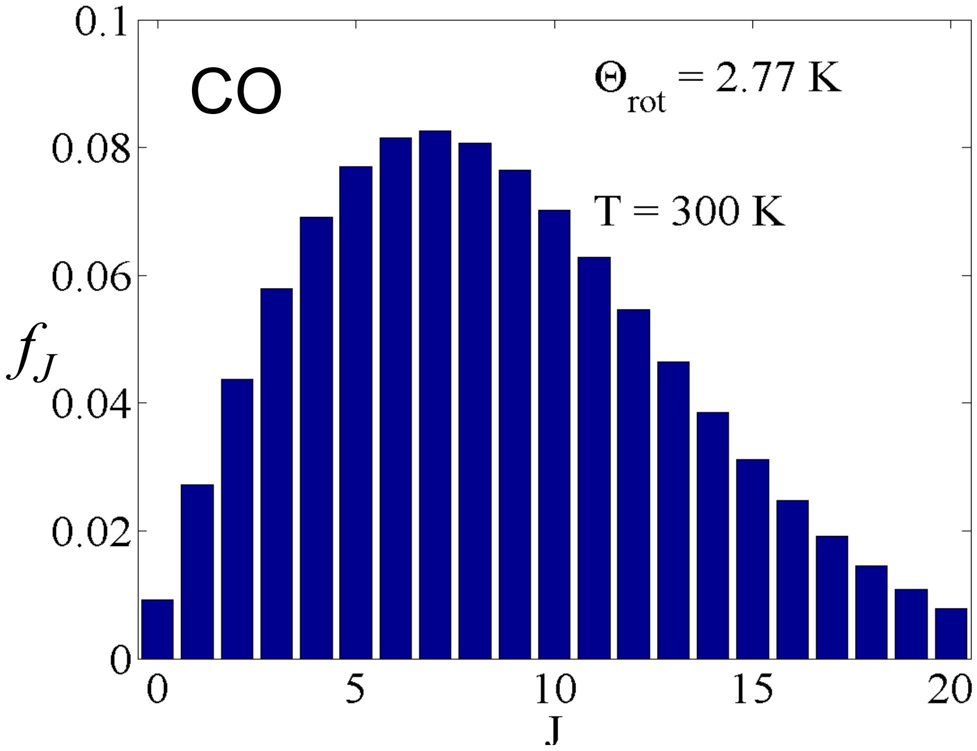
in rotational level *J*

$$f_J = \frac{g_J e^{-\beta\varepsilon_J}}{q_{\text{rot}}} = \frac{(2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T}}{q_{\text{rot}}}$$

$$= \left(\frac{\Theta_{\text{rot}}}{T}\right)(2J+1)e^{-\Theta_{\text{rot}}J(J+1)/T}$$

Increases with increasing J (linearly)

Decreases with increasing J (exponentially)



Many accessible levels into which to flow energy