Diatomic Molecules

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

$$\varepsilon = \varepsilon_{tras} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec}$$

$$q(V,T) = q_{trans} q_{rot} q_{vib} q_{elec}$$

Translational: q_{trans}

Like the monatomic molecule

$$q_{trans} = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \quad \text{now } M = m_1 + m_2$$

Zero of energy

Rotational Energy zero is when $J = 0$

The zero of the vibrational energy – where do we choose? Bottom of the well. So the G.S. vibrational energy is $h\nu/2$

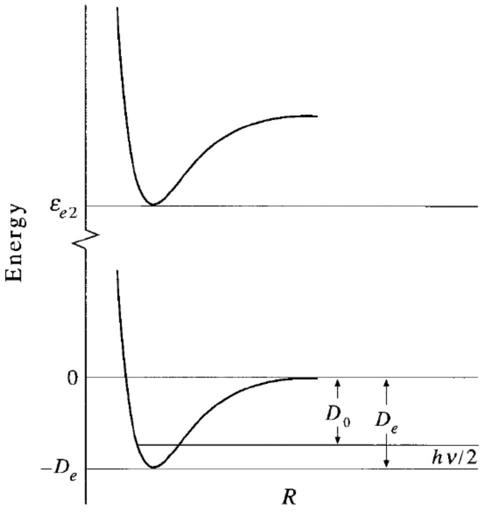
Electronic: q_{elec} [MOST MOLECULES IN G.S.]

Electronic also remains the same. Can take the zero as the energy when the two atoms are separated.

$$q_{elec} = g_{e1} e^{D_e/k_B T} + g_{e2} e^{-\varepsilon_2/k_B T}$$

The difference is huge (on the order of eV's) so everything is in the ground state that has degeneracy g_{e1}

$\boxed{D_e \sim \text{few 100 kJ mol}^{-1}}$ $\boxed{\frac{1}{2}h\nu \sim \text{few 10 kJ mol}^{-1}}$



Vibrational: q_{vib} [MOST MOLECULES IN G.S.]

Harmonic oscillator approximation

$$\varepsilon_{vib} = \left(v + \frac{1}{2}\right) h\nu \qquad v = 0,1,2 \ldots$$

$$q_{vib}(T) = \sum_{v=0}^{\infty} e^{-\beta\varepsilon_v} = \sum_{v=0}^{\infty} e^{-\beta\left(v+\frac{1}{2}\right)h\nu} = e^{-\beta h\nu/2} \sum_{v=0}^{\infty} e^{-\beta h\nu v}$$

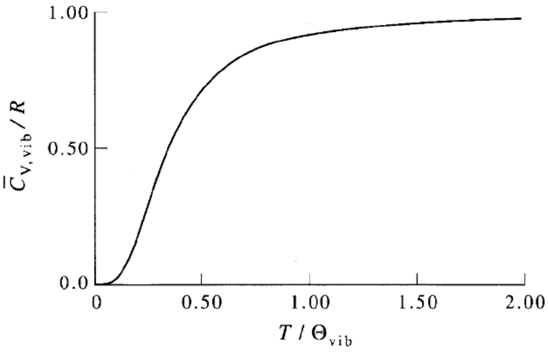
This is a geometric series $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$

$$\therefore q_{vib}(T) = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} = \frac{e^{-\Theta_{\mathrm{vib}}/2T}}{1-e^{-\Theta_{\mathrm{vib}}/T}}$$

Vibrational temperature $\Theta_{vib} = h\nu/k_B$

$$\langle E_{vib}\rangle = Nk_BT^2\frac{d}{dT}\ln q_{vib}$$

$$= Nk_B\left(\frac{\Theta_{vib}}{2}+\frac{\Theta_{vib}}{e^{\Theta/T}-1}\right)$$



Vibrational contribution to molar heat capacity for diatomics

$$\bar{C}_{V,vib} = \frac{d\langle\bar{E}_{vib}\rangle}{dT} = R\left(\frac{\Theta_{vib}}{T}\right)^2\frac{e^{-\Theta_{vib}/T}}{(1-e^{-\Theta_{vib}/T})^2}$$

Fraction in v^{th} state

$$f_v = \frac{e^{-\beta h\nu(v+1/2)}}{q_{vib}}$$

$$f_v = \left(1-e^{-\beta h\nu}\right)e^{-\beta h\nu v} = \left(1-e^{-\Theta_{\mathrm{vib}}/T}\right)e^{v\Theta_{vib}/T}$$

$$f_{v>0} = \sum_{v=1}^{\infty} f_v = 1-f_0 = 1-\left(1-e^{-\Theta_{\mathrm{vib}}/T}\right) = e^{-\Theta_{\mathrm{vib}}/T} = e^{-\beta h\nu} = e^{-h\nu/k_BT} = e^{-\Delta E/k_BT}$$

Gas	Θ_{vib}/K	$f_{v>0}$ $(T = 300\ K)$	$f_{v>0}$ $(T = 1000\ K)$
H_2	6332	1.01×10^{-9}	2.00×10^{-3}
HCl	4227	7.59×10^{-7}	1.46×10^{-2}
N_2	3374	1.30×10^{-5}	3.42×10^{-2}
CO	3103	3.22×10^{-5}	4.49×10^{-2}
Cl_2	805	6.82×10^{-2}	4.47×10^{-1}
I_2	308	3.58×10^{-1}	7.35×10^{-1}

Rotational: q_{rot} [MOST MOLECULES IN EXCITED STATES AT R.T.]

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

$$g_J = 2J+1$$

$$q_{rot}(T) = \sum_{J=0}^{\infty}(2J+1)e^{-\beta\hbar^2 J(J+1)/2I} \quad \text{remember } 2J+1 \text{ is the degeneracy}$$

$$\Theta_{rot} = \frac{\hbar^2}{2Ik_B} = \frac{hB}{k_B} \ll \text{room temperature energy (usually)}$$

($B = h^2/8\pi^2 I$ is the rotational constant)

If the rotational temperature is small compared to r.t. $\Theta_{rot} \ll T$, we can write the summation as an integral

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

$$Let \quad x = J(J+1), \qquad dx = (2J+1)dJ$$

$$q_{rot}(T) = \int_{0}^{\infty} e^{-\Theta_{\text{rot}}\, x/T} dx = \frac{T}{\Theta_{rot}} = \frac{8\pi^2 I k_B T}{h^2} = \frac{2 I k_B T}{\hbar^2}$$

$$\langle E_{rot} \rangle = N k_B T^2 \left(\frac{d}{dT} \ln q_{rot} \right) = N k_B T$$

$$\bar{C}_{V,rot} = R$$

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

Most molecules are in the excited state

The most probable state in terms of occupancy is given by

$$J_{m.p.} \cong \left(\frac{T}{2\Theta_{rot}}\right)^{1/2} - \frac{1}{2}$$

Use $\frac{df_J}{dJ} = 0$ assuming J to be continuous.

High rotational energy case:

In case Θ_{rot} is not so small in comparison to the temperature (e.g. for H_2(g) $\Theta_{rot} = 85.3\ \text{K}$). Then just use the sum. The first few terms are enough. For this course, we will use only the high T limit.

For this course, we will also not worry about the symmetry numbers in homonuclear diatomic molecules for the rotational partition function.

Diatomic Ideal Gas

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!} \quad \text{where} \quad q(V,\beta) = \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V \left(\frac{8\pi^2 I}{h^2 \beta}\right) \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

$$\bar{U} = \frac{3}{2}RT + RT + \frac{N_A h\nu}{2} + \frac{N_A h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

$$\overline{C_V} = \frac{5}{2}R + R\left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{-h\nu/k_B T}}{(1 - e^{-h\nu/k_B T})^2}$$