STATISTICAL MOLECULAR THERMODYNAMICS

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Video 4.4

Ideal Diatomic Gas: Part 1

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:

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

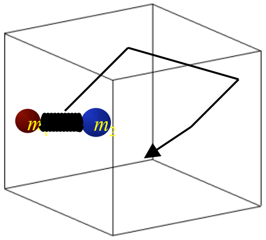
total energy

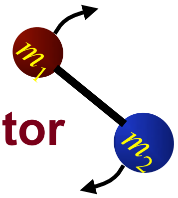
translational energy

rotational energy

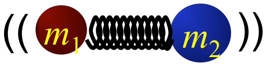
vibrational energy

electronic energy





rigid rotor



harmonic oscillator

Diatomic Ideal Gas Components of Q

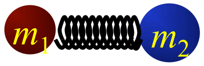
Start from the general expression: $Q(N,V,T) = \dfrac{q(V,T)^N}{N!}$

Now with the diatomic molecular partition function:

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \longrightarrow Q(N,V,T) = \frac{\left(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}\right)^N}{N!}$$

Consider each degree of freedom:

The translational partition function: q_{trans} is the same as in the monatomic case but the mass is now equal to $m_1 + m_2$



$$\boxed{q_{\text{trans}}(V,T) = \left(\frac{2\pi(m_1 + m_2)k_{\text{B}}T}{h^2}\right)^{3/2} V}$$

DIATOMIC IDEAL GAS COMPONENTS OF Q

- For *rotations* set ε_J=0 at J=0:

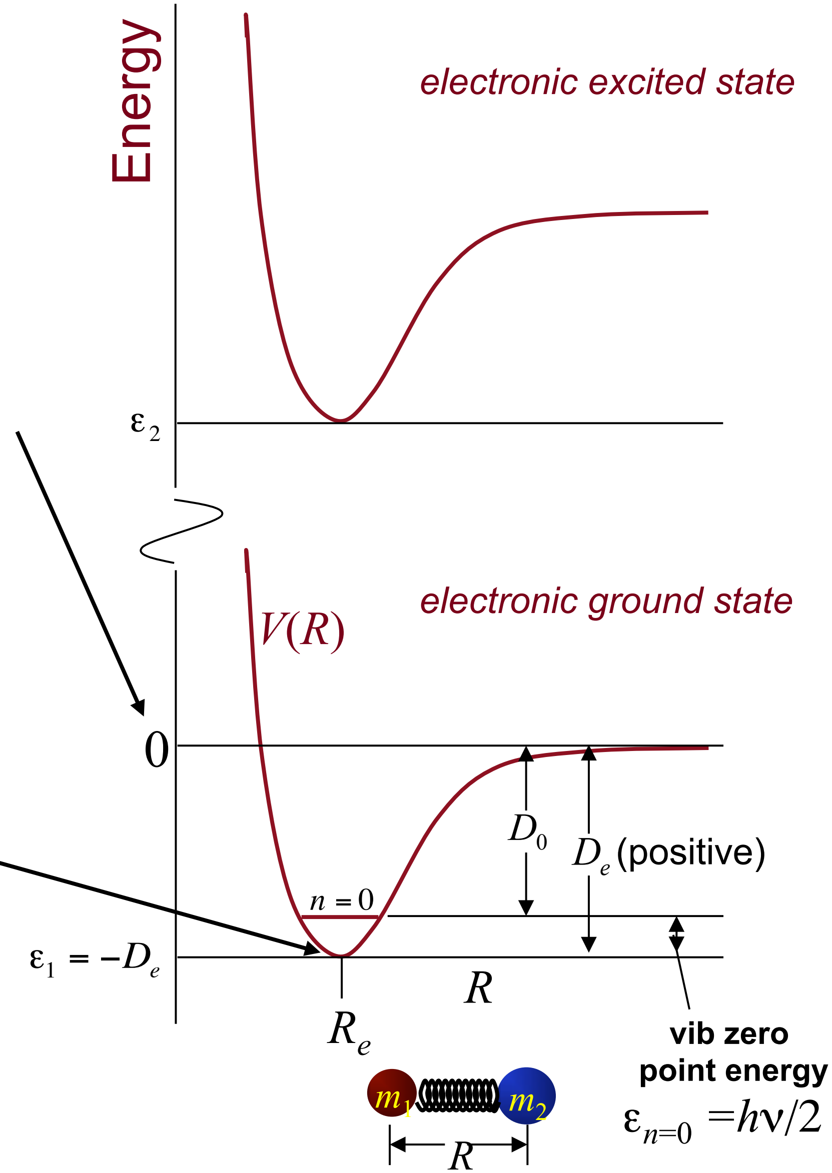
$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0,1,2,\ldots$$

- For *electronic*, we take the zero of energy to be the infinitely separated atoms in their ground electronic states. Thus, $\varepsilon_1 = -D_e$ and:

$$q_{\text{elec}}(T) \approx g_1 e^{D_e/k_{\text{B}}T}\left(+g_2 e^{-\varepsilon_2/k_{\text{B}}T} + \cdots\right)$$

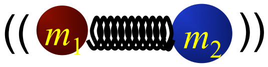
- For *vibrations*, we take the zero of energy *at the bottom of the inter-nuclear well*, so $\varepsilon_{n=0}=h\nu/2$.

$$\varepsilon_n = h\nu\left(n + \frac{1}{2}\right) \quad n = 0,1,2,\ldots$$



DIATOMIC IDEAL GAS q_{vib}

Within the harmonic oscillator approximation:



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

Quantum number, n (enn)

Vibrational frequency, ν (nu)

all levels are non-degenerate

(g_n=1 for all n)

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

We use $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ with $x = e^{-\beta h\nu} < 1$

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

THE VIBRATIONAL TEMPERATURE Θ_{vib}

It is common to define a *vibrational temperature*,

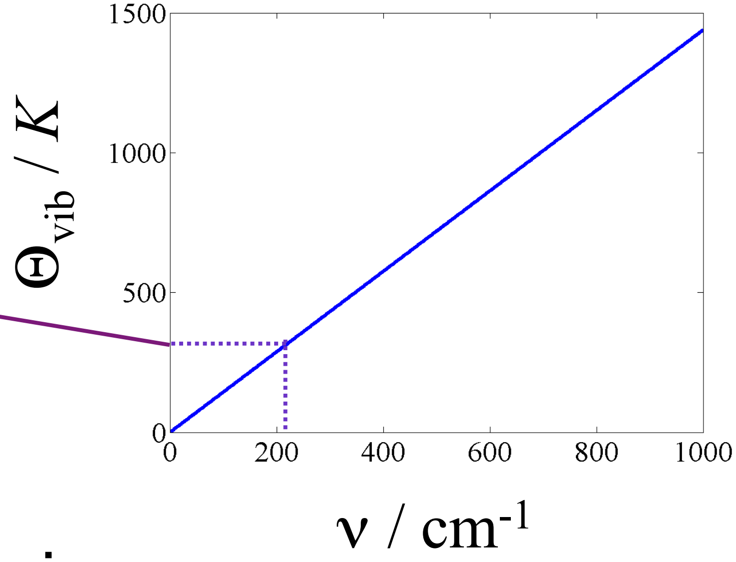
$$\Theta_{\text{vib}} = \frac{h\nu}{k_{\text{B}}}$$

note units: $\frac{(\text{J}\cdot\text{s})(\text{s}^{-1})}{(\text{J}\cdot\text{K}^{-1})} = \text{K}$

For example:

At 298 K, $k_{\text{B}}T \approx 200\ \text{cm}^{-1}$

$\nu = 210\ \text{cm}^{-1}$, $\Theta_{\text{vib}} = 302\ K$



One can write q_{vib} in terms of Θ_{vib}:

$$q_{\text{vib}}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \xrightarrow{\Theta_{\text{vib}} = h\nu/k_{\text{B}}} q_{\text{vib}}(T) = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}}$$

DIATOMIC IDEAL GAS VIBRATIONAL <*E*> AND C_V

From the partition function, we can calculate the vibrational contribution to the average energy,

$$\langle E_{\mathrm{vib}} \rangle = Nk_{\mathrm{B}}T^2 \frac{\partial \ln q_{\mathrm{vib}}}{\partial T} = Nk_{\mathrm{B}}T^2 \frac{\partial}{\partial T} \ln\left(\frac{e^{-\Theta_{\mathrm{vib}}/2T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}} \right)$$

$$\langle E_{\mathrm{vib}} \rangle = Nk_{\mathrm{B}} \left(\frac{\Theta_{\mathrm{vib}}}{2} + \frac{\Theta_{\mathrm{vib}}}{e^{\Theta_{\mathrm{vib}}/T} - 1} \right)$$

and to the molar heat capacity,

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

DIATOMIC VIBRATIONAL HEAT CAPACITY

$$\frac{\overline{C}_{V,\mathrm{vib}}}{R} = \left(\frac{\Theta_{\mathrm{vib}}}{\mathrm{T}}\right)^2 \frac{e^{-\Theta_{\mathrm{vib}}/T}}{\left(1-e^{-\Theta_{\mathrm{vib}}/T}\right)^2}$$

Classical limit, $C_{V,\mathrm{vib}} = R$ (a good approximation for $T >> \Theta_{\mathrm{vib}}$)