The vibrational energy levels of a diatomic are given by
\[E_v = (v + 1/2) \hbar \nu\]
where \(\hbar\) is the vibrational frequency and \(v\) is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below
\[
q_{vib} = \sum_{v=0}^{\infty} e^{-( v + 1/2) \hbar \nu / k T}
\]
\[
= e^{-\hbar \nu / 2k_BT} \left( 1 + e^{-(h \nu / 2k_BT)} + e^{-2 h \nu / 2k_BT} + ... \right)
\]
or rewritten as
\[
q_{vib} = e^{-h \nu / 2k_BT} \left( 1 +x + x^2 +x^3 + ... \right) \tag{eq0}
\]
where \(x = e^{-h \nu / k_BT}\).

Given the following power series expansion
\[
\frac{1}{1 - x} = 1 + x + x^2 + x^3 + x^4 + ....
\]
Equation \(\text{(refeq0)}\) can be rewritten as
\[
q_{vib} = e^{-h \nu / 2k_BT} \left( \frac{1}{1-x} \right) \tag{eq1}
\]
or
\[
q_{vib} = \frac{e^{-h \nu / 2k_BT}}{1 - e^{-h \nu / k_BT}} \tag{VIBQ}
\]
If the zero of energy scale is at \(\hbar \nu / 2k_BT\), then Equation \(\text{(refeq1)}\) can be rewritten as
\[
q_{vib} \approx \frac{1}{1 - e^{-h \nu / k_BT}} \tag{VIBQ}
\]
A vibrational temperature \(\Theta_{vib}\) may be defined as
\[
\Theta_{vib} = \frac{hc \tilde{\nu}}{k}\]
where \(\tilde{\nu}\) is the vibrational frequency in cm\(^{-1}\).

\(\Theta_{vib}\) is a good way to express the stiffness of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond you are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.
### Table \(\PageIndex{1}\): Representative molecular data for a few diatomics

<table>
<thead>
<tr>
<th>Molecule</th>
<th>g</th>
<th>Bond Length (pm)</th>
<th>(\langle \omega \rangle) (cm(^{-1}))</th>
<th>(\Theta_{\text{vib}}) (K)</th>
<th>(\tilde{B}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2)</td>
<td>1</td>
<td>0.7474</td>
<td>4400</td>
<td>6332</td>
<td>60.9</td>
</tr>
<tr>
<td>(D_2)</td>
<td>1</td>
<td>0.7415</td>
<td>3118</td>
<td>4487</td>
<td>30.45</td>
</tr>
<tr>
<td>(N_2)</td>
<td>1</td>
<td>1.097</td>
<td>2358</td>
<td>3393</td>
<td>2.001</td>
</tr>
<tr>
<td>(O_2)</td>
<td>3</td>
<td>1.207</td>
<td>1580</td>
<td>2274</td>
<td>1.446</td>
</tr>
<tr>
<td>(Cl_2)</td>
<td>1</td>
<td>1.987</td>
<td>560</td>
<td>805</td>
<td>0.244</td>
</tr>
<tr>
<td>(CO)</td>
<td>1</td>
<td>1.128</td>
<td>2170</td>
<td>3122</td>
<td>1.931</td>
</tr>
<tr>
<td>(NO)</td>
<td>2</td>
<td>1.15</td>
<td>190</td>
<td>2719</td>
<td>1.695</td>
</tr>
<tr>
<td>(HCl)</td>
<td>1</td>
<td>1.275</td>
<td>2938</td>
<td>4227</td>
<td>10.44</td>
</tr>
<tr>
<td>(HI)</td>
<td>1</td>
<td>1.609</td>
<td>2270</td>
<td>3266</td>
<td>6.46</td>
</tr>
<tr>
<td>(Na_2)</td>
<td>1</td>
<td>3.096</td>
<td>159</td>
<td>229</td>
<td>0.154</td>
</tr>
<tr>
<td>(K_2)</td>
<td>1</td>
<td>3.979</td>
<td>92.3</td>
<td>133</td>
<td>0.0561</td>
</tr>
</tbody>
</table>

#### Example \(\PageIndex{1}\)

The vibrational frequency of \(I_2\) is \(214.57\; \text{cm}^{-1}\). Calculate the vibrational partition function of \(I_2\) at 300 K.

**Solution:**

\[
\frac{h\nu}{k_BT} = \frac{214.57}{209.7} = 1.0232
\]

so

\[
e^{-\frac{h\nu}{kT}} = 0.3595
\]

and

\[
q_{\text{vib}} = \frac{1}{1-0.3595} = 1.561
\]
This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

---

**Vibrational Heat Capacity**

The vibrational energy is given by the above expression and the molar heat capacity at constant volume, \(\bar{C}_V\) is given by

\[
\bar{C}_V = \left(\frac{\partial E}{\partial T}\right)_V
\]

We have,

\[
\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} = \frac{-1}{kT^2} \frac{\partial}{\partial \beta}
\]

Therefore,

\[
\bar{C}_V = (-k \beta^2) \left(\frac{\partial \varepsilon_{vib}}{\partial \beta}\right)
\]

and when the vibrational partition function (Equation \(\ref{VIBQ}\)) is introduced

\[
\bar{C}_V = k_B \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1 - e^{-\Theta_{\text{vib}}/T}\right)^2}
\]

For large \(T\), the \(\bar{C}_V\) becomes

\[
N_A k = R
\]

and for small \(T\), \(\bar{C}_V\) goes to zero as demonstrated in Figure \(\PageIndex{1}\).

![Vibrational Heat Capacity](image)

Figure \(\PageIndex{1}\): Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature \(T/\Theta\) to get a general picture valid for all diatomic gases. Compare the parameters on Table \(\PageIndex{1}\) to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity depends on temperature. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of \(\Theta_{\text{vib}}\) is determined mostly by
1. the strength of a bond (the stronger the higher $\Theta_{\text{vib}}$) 
2. the (effective) mass of the molecule (the lighter the higher $\Theta_{\text{vib}}$) 

Molecules with low $\Theta_{\text{vib}}$ often dissociate at higher temperatures, although the harmonic oscillator model is not sufficient to describe that phenomenon.

Contributors