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:

\[ \varepsilon_{\text{diatomic}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} \]  

(total)

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).
Within the rigid-rotator approximation,

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

Degeneracy of the \( J^{\text{th}} \) level,

\[ g_J = 2J + 1 \]

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

Define a rotational temperature: \[ \Theta_{\text{rot}} = \frac{\hbar^2}{2IK_B} \]

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

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

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

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

Close spacing of energy levels occurs for $\Theta_{rot} \ll T$
**Some Rotational Temperatures**

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

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

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2 I k_B}$$

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\Theta_{\text{rot}},$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>85.3</td>
</tr>
<tr>
<td>CO</td>
<td>2.8</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.9</td>
</tr>
<tr>
<td>NO</td>
<td>2.4</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2.1</td>
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<tr>
<td>HCl</td>
<td>15.0</td>
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<tr>
<td>HBr</td>
<td>12.0</td>
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<tr>
<td>HI</td>
<td>9.2</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>0.4</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>0.1</td>
</tr>
</tbody>
</table>
A Very Friendly Integral

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

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

\[ q_{\text{rot}}(T) = \int_{0}^{\infty} dx \ e^{-ax} = -\frac{1}{a} e^{-ax} \bigg|_{0}^{\infty} = 0 + \frac{1}{a} = \frac{T}{\Theta_{\text{rot}}} \]

\[ q_{\text{rot}}(T) = \frac{T}{\Theta_{\text{rot}}} = \frac{2Ik_{B}T}{\hbar^2} = \frac{8\pi^2 Ik_{B}T}{\hbar^2} , \quad \Theta_{\text{rot}} \ll T \]
Diatomic Ideal Gas Rotational $\langle E \rangle$ and $C_v$

Rotational energy:

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

$$= Nk_B T$$

Molar heat capacity:

$$\overline{C}_{V,\text{rot}} = \frac{d\langle E_{\text{rot}} \rangle}{dT} = \frac{d(RT)}{dT} = R$$

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 $J$

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

$$q_{\text{rot}} = \frac{\Theta_{\text{rot}}}{T}$$

Increases with increasing $J$ (linearly)

Decreases with increasing $J$ (exponentially)

Many accessible levels into which to flow energy