5.62 Physical Chemistry II
Spring 2008

For information about citing these materials or our Terms of Use, visit: http://ocw.mit.edu/terms.
DEGREES OF FREEDOM

A molecule with \( n \) atoms has \( 3n \) "degrees of freedom" or \( 3n \) coordinates to describe its position and therefore has \( 3n \) ways of incorporating energy due to nuclear motion where \( n \) is the number of atoms in the molecule.

For a diatomic or a linear polyatomic molecule:

<table>
<thead>
<tr>
<th>Degrees of Freedom</th>
<th>( \text{translational} )</th>
<th>( \text{rotational} )</th>
<th>( \text{vibrational} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3n )</td>
<td>( 3n-5 )</td>
<td>( 3n )</td>
<td></td>
</tr>
</tbody>
</table>

For a diatomic molecule \( 3n - 5 = 1 \) vibrational degree of freedom

MOLECULAR ROTATIONAL PARTITION FUNCTION — \( q_{\text{rot}} \) — DIATOMIC

\[
\varepsilon_{\text{rot}}(J) = J(J + 1) \hbar c B_e \quad \text{for } J = 0, 1, 2, \ldots \quad g_J = 2J + 1
\]

\[
q_{\text{rot}} = \sum g(\varepsilon) e^{-\varepsilon/kT} = \sum_{J=0}^{\infty} (2J + 1) \exp[-\hbar c B_e J(J+1)/kT]
\]

allowed rotational energies

Question: How do you do the summation? Two cases … (Low-T limit case [next Lecture])

Case 1: \( \varepsilon_{\text{rot}}/kT \ll 1 \) or \( \hbar c B_e (J + 1)/kT \ll 1 \)
[More precisely, we want \( (E(J + 1) - E(J)) \ll kT \) at \( E(J) \approx kT \).]

rotational states are closely spaced in energy compared to \( kT \) — since energy spacings are so close together, can consider
\( \varepsilon_{\text{rot}} \) as continuous and use Euler-MacLaurin Summation Formula (draw a picture!)

this case is the classical or high-temperature limit.

\[
\sum_{J=m}^{n} f(J) = \int_{m}^{n} f(J)dJ + \frac{1}{2} [f(m) + f(n)] + \text{residue} \ldots
\]

so:

\[
q_{\text{rot}} = \int_{0}^{\infty} (2J+1) \exp[-hcB_{e} J(J+1)/kT] dJ + \frac{1}{2} [1 + 0] + \ldots
\]

substitute \( \omega = J(J+1) \) thus \( d\omega = (2J+1)dJ \)

\[
q_{\text{rot}} = \int_{0}^{\infty} \exp[-hcB_{e} \omega / kT] d\omega + \frac{1}{2} + \ldots
\]

\[
= -\frac{kT}{hcB_{e}} e^{-hcB_{e}\omega/kT} \int_{0}^{\infty} + \frac{1}{2} + \ldots
\]

\[
= 0 - \left( \frac{-kT}{hcB_{e}} \right) + \frac{1}{2} + \ldots
\]

\[
q_{\text{rot}} = \frac{kT}{hcB_{e}} + \frac{1}{2} \approx \frac{kT}{hcB_{e}} \quad \text{usually can ignore the } \frac{1}{2}
\]

What happens for a \( ^1\Delta \) state where \( J_{\text{min}} = 2 \) rather than 0?

Hold on — One correction needed to \( q_{\text{rot}} \) ...

SYMMETRY NUMBER \( \equiv \sigma \equiv \# \) of equivalent orientations in space which leave appearance of molecule unchanged — \# of indistinguishable orientations in which molecules can be found as a result of rotation. We divide by \( \sigma \) because otherwise we would be overcounting by counting indistinguishable orientations.

A homonuclear molecule, \( O_2 \), has \( \sigma = 2 \) because an end over end (half) rotation by \( \pi \) does not alter the appearance of \( O_2 \).

The symmetry number is rigorously based on the nuclear spins. We’ll see the details later.

So

\[
q_{\text{rot}} = \frac{kT}{\sigma hcB_{e}}
\]

for \( hcB_{e} \ll kT \)

or \( \varepsilon_{\text{rot}} \ll kT \)
where $\sigma \equiv$ symmetry # = 1 for heteronuclear diatomics
= 2 for homonuclear diatomics

Really this is $q_{\text{rot-nuc}}$ but we’ll refer to it as $q_{\text{rot}}$.

Define $\theta_{\text{rot}} = \frac{\hbar B_e}{k}$ “rotational temperature”, $\theta_{\text{rot}}$ (has units of K)

So

$$q_{\text{rot}} = \frac{kT}{\sigma \hbar B_e} = \frac{T}{\sigma \theta_{\text{rot}}}$$

for $\theta_{\text{rot}} \ll T$

Molecular Rotational Partition Function for Diatomics

also written as …

$$q_{\text{rot}} = \frac{8\pi^2 I}{\sigma \hbar^2} \frac{kT}{c^2}$$

because $B_e = \frac{\hbar}{8\pi^2 I}$

$I = \mu R e^2$

Let’s go back and check whether dropping extra terms in Euler-MacLaurin series was a good approximation …

$$q_{\text{rot}} = \frac{kT}{\sigma \hbar B_e} + \frac{1}{2} + \ldots$$

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>$B_e$ (cm$^{-1}$)</th>
<th>$\sigma$</th>
<th>$\theta_{\text{rot}}$ (K)</th>
<th>$q_{\text{rot}} = T/\sigma \theta_{\text{rot}} + 1/2$</th>
<th>% error (neglect of 1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>10.59</td>
<td>1</td>
<td>15.24</td>
<td>19.688 + 0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>CO</td>
<td>1.93</td>
<td>1</td>
<td>2.77</td>
<td>108.30 + 0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>I$_2$</td>
<td>0.037</td>
<td>2</td>
<td>0.1065</td>
<td>1408.5 + 0.5</td>
<td>0.04</td>
</tr>
</tbody>
</table>

As $B_e$ becomes smaller or equivalently as $\theta_{\text{rot}}$ becomes smaller compared to $T$,
dropping extra terms becomes better approximation;
also, discrete to continuous approximation becomes better.
Contributions of Rotation to Thermodynamic Functions for $\varepsilon_{rot} \ll kT$

$$q_{rot} = \frac{kT}{\sigma hcB_e} \rightarrow Q_{rot} = \left( q_{rot} \right)^N = \left( \frac{kT}{\sigma hcB_e} \right)^N$$

$$A_{rot} = -kT \ln Q_{rot} = -NkT \ln q_{rot} = -NkT \ln \left( \frac{kT}{\sigma hcB_e} \right)$$

$$p_{rot} = -\left( \frac{\partial A}{\partial V} \right)_{N,T} = \frac{\partial}{\partial V} \left( NkT \ln \left( \frac{kT}{\sigma hcB_e} \right) \right)_{N,T} = 0$$

because $\varepsilon_{rot}$ does not depend on $V$

$$E_{rot} = kT^2 \left( \frac{\partial \ln Q_{rot}}{\partial T} \right)_{N,V} = NkT^2 \frac{\partial \ln q_{rot}}{\partial T}$$

$$= NkT^2 \frac{\partial \ln T}{\partial T} + nkT^2 \frac{\partial \ln (k/\sigma hcB_e)}{\partial T} = NkT^2 \left( \frac{1}{T} \right) + 0$$

average rotational energy of a diatomic molecule

$$E_{rot} = NkT$$

for $\theta_{rot} \ll T$ or $\varepsilon_{rot} \ll kT$ (not $\frac{1}{2} NkT$; why?)

a "quantum" result (but based on the approximation of replacing a sum by an integral)

**CLASSICAL EQUIPARTITION RESULT FOR ROTATIONAL ENERGY**

$$2 \left( \frac{1}{2} NkT \right) = NkT$$

Each degree of translational and rotational energy contributes $(1/2)kT$ to total energy. For a diatomic molecule, there are 2 rotational degrees of freedom [Why 2?]. Therefore, $2(1/2 NkT) = NkT$. This is why $\bar{C}_V$ for monatomic gases is $\sim (3/2)R$ and for most diatomic gases at moderate $T$ is $\sim (5/2)R$!

Quantum and classical approach lead to same result for rotation at 300 K. Why? Because rotational energy levels are very closely spaced compared to $kT$. We calculated...
q_{rot} by approximating a sum over energy levels as an integral over energy levels. Rotational energy levels are so closely spaced that they "look" continuous compared to kT at room temperature for most molecules. E_{rot} does not depend on the properties of the molecule in the classical limit!

“Quantum” result for C_V

\[
C_V^{\text{rot}} = \left( \frac{\partial E}{\partial T} \right)_{N,V} = Nk \left( \frac{\partial T}{\partial T} \right) = Nk = R \text{ if } N = N_a \text{ (or } C_V^{\text{rot}} = nR) \\
\text{for } \epsilon_{\text{rot}} \ll kT \text{ or } \theta_{\text{rot}} \ll T \text{ (} \epsilon_{\text{rot}} \text{ needs to be better defined, see below)}
\]

1. More about high temperature limit, which is the requirement that permits the sum,

\[
q_{\text{rot}} = \sum_{J_{\text{min}}}^{\infty} g(J) e^{-hcBJ(J+1)/kT},
\]

to be replaced by an integral,

\[
q_{\text{rot}} = \int_{J_{\text{min}}}^{\infty} dJ (2J + 1) e^{-hcBJ(J+1)/kT} + \frac{1}{2}[(2J_{\text{min}} + 1) + 0].
\]

It is necessary that \( \Delta \epsilon_{\text{rot}} \ll kT \) at \( \epsilon_{\text{rot}} \approx kT \). The rotational energy level spacing must be small relative to \( kT \).

\[
\Delta \epsilon_{\text{rot}} (J) = hcB[(J + 1)(J + 2) - J(J + 1)] = hcB(2J + 1).
\]

This spacing must be small relative to \( kT \) when \( \epsilon_{\text{rot}} = kT \)

\[\epsilon_{\text{rot}} = hcBJ(J+1) = kT\]

Thus \( hcBJ(J+1) \gg hcB(2J + 1) \), which requires that

\[J \gg 2.\]

This means that we want

\[kT \gg \epsilon_{\text{rot}} (J = 2) = 6hcB.\]

\( kT \gg 6hcB \) is the requirement that specifies when it is OK to replace sum by integral.
2. Some useful stuff concerning fractional populations in rotational levels.

A. Fraction of population in J-th level

\[ f_J = \frac{(2J + 1)e^{-\theta_{rot}J(T+1)/T}T}{\sigma \theta_{rot}} \]

\[ \theta_{rot} = \frac{hcB}{k} \]

B. Most populated J

\[ \frac{df_J}{dJ} = 0 = 2e^{-\theta_{rot}J(T+1)/T} - (2J + 1)^2 \left( \theta_{rot}/T \right) e^{-\theta_{rot}J(T+1)/T} q_{rot} \]

Thus

\[ 2 = (2J + 1)^3 \frac{\theta_{rot}}{T} \]

\[ J_{\text{max}} = \frac{\left( \frac{2T}{\theta_{rot}} \right)^{3/2} - 1}{2} \]

For \( T / \theta_{rot} = 100 \)

\[ J_{\text{max}} = 6.5 \]

C. Fractional population in most populated J level

\[ f_{J_{\text{max}}} = \frac{\left[ \frac{2T}{\theta_{rot}} \right]^{3/2} e^{-\theta_{rot} \left[ \left( \frac{2T}{\theta_{rot}} \right)^{3/2} - 1 \right]} \left[ \frac{2T}{\theta_{rot}} \right]^{3/2} \} {T/\theta_{rot}} \approx \left( \frac{2\theta_{rot}}{T} \right)^{3/2} e^{-1/2} = 0.85 \left( \frac{\theta}{T} \right)^{3/2}. \]

For \( T / \theta_{rot} = 100 \)

\[ f_{J_{\text{max}}} = 0.085. \]

D. Fractional population in \( J = \frac{T}{\theta_{rot}} \). This is a simple-minded way of asking about the population of the “last” thermally accessible level.
\[
\frac{f_{J=T/\theta_{rot}}}{T/\theta_{rot}} = \left(2 \frac{T}{\theta_{rot}} + 1\right) e^{-\frac{T}{\theta_{rot}}} = 2e^{-\frac{T}{\theta_{rot}}+1}.
\]

For \(T/\theta_{rot} \approx 100\)
\[
f_{J=T/\theta_{rot}} = 2e^{-101} = 3 \times 10^{-44}.
\]

This is a very small fractional population. It would be more appropriate to ask for the fractional population of the \(J'\) value for which
\[
\sum_{J=J_{\text{min}}}^{J'} (2J+1) = T/\theta_{rot},
\]

because this sets the total number of significantly populated \(J, M_J\) levels equal to \(q_{rot}\). Using
\[
\sum_{J=0}^{J'} (2J+1) = (J'+1)^2
\]

and \(T/\theta_{rot} = 100\), we get \(J' = 9\) and
\[
f_{J'=9} = \frac{19e^{-9(10)/100}}{100} = 0.077.
\]

Low-T limit results for \(\tilde{E}\) and \(\tilde{C}_V\) next time. But what do you know without any equations about \(\tilde{E}\) and \(\tilde{C}_V\) in the limit \(T \to 0K\)?