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5.62 Physical Chemistry II  
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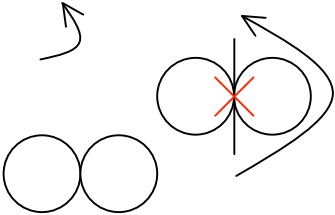
## 5.62 Lecture #12: Rotational Partition Function. Equipartition

Readings: Hill, pp. 153-159;  
Maczek, pp. 47-53  
Metiu, pp. 131-142

### 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:

	3 TRANSLATIONAL	degrees of freedom
	2 ROTATIONAL	degrees of freedom
	$3n-5$ VIBRATIONAL	degrees of freedom
	$3n$ TOTAL	degrees of freedom

For a diatomic molecule  $3n - 5 = 1$  vibrational degree of freedom

### MOLECULAR ROTATIONAL PARTITION FUNCTION — $q_{\text{rot}}$ — DIATOMIC

$$\epsilon_{\text{rot}}(J) = J(J + 1) hcB_e \quad \text{for } J = 0, 1, 2, \dots \quad g_J = 2J + 1$$

$$q_{\text{rot}} = \sum_{\text{allowed rotational energies}} g(\epsilon) e^{-\epsilon/kT} = \sum_{J=0}^{\infty} (2J + 1) \exp[-hcB_e J(J+1)/kT]$$

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

Case 1:  $\epsilon_{\text{rot}}/kT \ll 1$       or       $hcB_e J(J + 1)/kT \ll 1$

[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

$\epsilon_{\text{rot}}$  as continuous and use Euler-MacLaurin Summation Formula (draw a picture!)

this case is the classical or high-temperature limit.

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

so:

$$q_{\text{rot}} = \int_0^{\infty} (2J+1) \exp[-hcB_e J(J+1)/kT] dJ + \frac{1}{2} [1 + 0] + \dots$$

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

$$\begin{aligned} q_{\text{rot}} &= \int_0^{\infty} \exp[-hcB_e \omega / kT] d\omega + \frac{1}{2} + \dots \\ &= \frac{-kT}{hcB_e} e^{-hcB_e \omega / kT} \Big|_0^{\infty} + \frac{1}{2} + \dots \\ &= 0 - \left( \frac{-kT}{hcB_e} \right) + \frac{1}{2} + \dots \\ q_{\text{rot}} &= \frac{kT}{hcB_e} + \frac{1}{2} \approx \frac{kT}{hcB_e} \text{ usually can ignore the } \frac{1}{2} \end{aligned}$$

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  $\epsilon_{\text{rot}} \ll kT$

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  $\theta_{\text{rot}} = \frac{hcB_e}{k}$  "rotational temperature",  $\theta_{\text{rot}}$   
 (has units of K)

$$\text{So } q_{\text{rot}} = \frac{kT}{\sigma hcB_e} = \frac{T}{\sigma \theta_{\text{rot}}} \quad \text{for } \theta_{\text{rot}} \ll T$$

Molecular Rotational Partition Function for Diatomics

also written as ...

$$q_{\text{rot}} = \frac{8\pi^2 I k T}{\sigma h^2} \quad \text{because } B_e = \frac{h}{8\pi^2 I c} \quad I = \mu R_e^2$$

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

$$q_{\text{rot}} = \frac{kT}{\sigma hcB_e} + \frac{1}{2} + \dots$$

MOLECULE	$B_e$ (cm <sup>-1</sup> )	$\sigma$	$\theta_{\text{rot}}$ (K)	at T = 300K $q_{\text{rot}} = T/\sigma\theta_{\text{rot}} + 1/2$	% error (neglect of 1/2)
HCl	10.59	1	15.24	19.688 + 0.5	2.5
CO	1.93	1	2.77	108.30 + 0.5	0.4
I <sub>2</sub>	0.037	2	0.1065	1408.5 + 0.5	0.04

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  $\epsilon_{\text{rot}} \ll kT$ 

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

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

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

because  $\epsilon_{\text{rot}}$  does not depend on  $V$

$$\begin{aligned} E_{\text{rot}} &= kT^2 \left( \frac{\partial \ln Q_{\text{rot}}}{\partial T} \right)_{N,V} = NkT^2 \frac{\partial \ln q_{\text{rot}}}{\partial T} \\ &= NkT^2 \frac{\partial \ln T}{\partial T} + nkT^2 \frac{\partial \ln(k / \sigma hc B_e)}{\partial T} = NkT^2 \left( \frac{1}{T} \right) + 0 \end{aligned}$$

average rotational energy of a diatomic molecule

$$\boxed{E_{\text{rot}} = NkT} \quad \text{for } \theta_{\text{rot}} \ll T \text{ or } \epsilon_{\text{rot}} \ll kT \quad \left( \text{not } \frac{1}{2} NkT; \text{ why?} \right)$$

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

CLASSICAL EQUIPARTITION RESULT FOR ROTATIONAL ENERGY

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

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  $C_V$

$$C_V^{rot} = \left( \frac{\partial E}{\partial T} \right)_{N,V} = Nk \left( \frac{\partial T}{\partial T} \right) = Nk = R \quad \text{if } N = N_A \quad (\text{or } C_V^{rot} = nR)$$

for  $\epsilon_{rot} \ll kT$  or  $\theta_{rot} \ll T$  ( $\epsilon_{rot}$  needs to be better defined, see below)

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

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

to be replaced by an integral,

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

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

$$\begin{aligned} \Delta\epsilon_{rot}(J) &= hcB[(J+1)(J+2) - J(J+1)] \\ &= hcB2(J+1). \end{aligned}$$

This spacing must be small relative to  $kT$  when  $\epsilon_{rot} = kT$

$$\epsilon_{rot} = hcBJ(J+1) = kT$$

Thus  $hcBJ(J+1) \gg hcB2(J+1)$ , which requires that

$$J \gg 2.$$

This means that we want

$$kT \gg \epsilon_{rot}(J=2) = 6hcB.$$

$kT \gg 6hcB$  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

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

$$\theta_{rot} = \frac{hcB}{k}$$

- B. Most populated J

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

Thus

$$2 = (2J+1)^2 \frac{\theta_{rot}}{T}$$

$$J_{\max} = \frac{\left(\frac{2T}{\theta_{rot}}\right)^{1/2} - 1}{2}.$$

For  $T/\theta_{rot} = 100$   
 $J_{\max} = 6.5$

- C. Fractional population in most populated J level

$$f_{J_{\max}} = \frac{\left[\frac{2T}{\theta_{rot}}\right]^{1/2} e^{-\frac{\theta_{rot}}{4T} \left(\left[\frac{2T}{\theta_{rot}}\right]^{1/2} - 1\right) \left(\left[\frac{2T}{\theta_{rot}}\right]^{1/2}\right)}}{T/\theta_{rot}} \approx \left(\frac{2\theta_{rot}}{T}\right)^{1/2} e^{-1/2} = 0.85 \left(\frac{\theta}{T}\right)^{1/2}.$$

For  $T/\theta_{rot} = 100$   $f_J^{\max} = 0.085$ .

- 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.

$$f_{J=T/\theta_{rot}} = \frac{\left(2\frac{T}{\theta_{rot}} + 1\right) e^{-\left(\frac{T}{\theta_{rot}}\right)\left(\frac{T}{\theta_{rot}} + 1\right)\frac{\theta_{rot}}{T}}}{T/\theta_{rot}} = 2e^{-\left(\frac{T}{\theta_{rot}} + 1\right)}.$$

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

$$\sum_{J_{min}}^{J'} (2J + 1) = T/\theta_{rot},$$

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  $\bar{E}$  and  $\bar{C}_V$  next time. But what do you know without any equations about  $\bar{E}$  and  $\bar{C}_V$  in the limit  $T \rightarrow 0K$ ?