CHAPTER 6
IDEAL DIATOMIC GAS

Monatomic gas:
- Has translational and electronic degrees of freedom
- Nuclear partition function can be treated as a constant factor

Diatomic gas:
- Has vibrational and rotational degrees of freedom as well.
- Electronic energy state is similar to that of monatomic gas.
- Nuclear partition function may be combined with the rotational one.

1 PRELIMINARY THOUGHTS

* How to generalize to diatomic molecules *

- The general procedure would be to set up the Schrodinger equation for 2 nuclei and n-electrons, and solve it for the set of eigenvalues of the diatomic molecule. This is again too hard.

- We will thus need a good approximation that allows all degrees of freedom to be written separately, like

$$H = H_{\mathrm{trans}} + H_{\mathrm{rot}} + H_{\mathrm{vib}} + H_{\mathrm{elec}} + H_{\mathrm{nucl}}$$ (6-14)

which implies that

$$\varepsilon = \varepsilon_{\mathrm{trans}} + \varepsilon_{\mathrm{rot}} + \varepsilon_{\mathrm{vib}} + \varepsilon_{\mathrm{elec}} + \varepsilon_{\mathrm{nucl}} \qquad \text{and}$$

$$\boxed{q = q_{\mathrm{trans}}\, q_{\mathrm{rot}}\, q_{\mathrm{vib}}\, q_{\mathrm{elec}}\, q_{\mathrm{nucl}}}$$ (6-14')

Within that approximation, the partition function of the gas itself will be given by

$$\boxed{Q(N,V,T) = \frac{\left(q_{\mathrm{trans}}\, q_{\mathrm{rot}}\, q_{\mathrm{vib}}\, q_{\mathrm{elec}}\, q_{\mathrm{nucl}} \right)^N}{N!}}$$ (6-17)

- But we do not know yet whether (6-14') is possible or not. At least we can write

$$q = q_{\mathrm{trans}}\, q_{\mathrm{int}} \quad \text{where} \quad q_{\mathrm{int}} \quad \text{includes (rot, vib, elec, nucl) degrees of freedom.}$$
and we hopefully get a good approximation for q_{int}.

- THE VIBRATIONAL AND ROTATIONAL MOTION: The *rigid rotor-harmonic oscillator approximation* allows the Hamiltonian of the relative motion of the nuclei to be written as

$H_{\text{rot,vib}} = H_{\text{rot}} + H_{\text{vib}}$ which implies

$\varepsilon_{\text{rot,vib}} = \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}$ and $\boxed{q_{\text{rot,vib}} = q_{\text{rot}}\, q_{\text{vib}}}$

- THE TRANSLATIONAL MOTION:

$m \to m_1 + m_2$ so that $q_{\text{trans}} = \left[\dfrac{2\pi(m_1 + m_2)kT}{h^2} \right]^{3/2} V$

- THE ELECTRONIC PARTITION FUNCTION will be similar to that for a monatomic gas, except the definition of the ground state.

- THE NUCLER PARTITION FUNCTION q_{nucl} may not be separable from q_{rot} because of the symmetry requirement.

2 THE VIBRATIONAL DEGREE OF FREEDOM

2-1 The Born-Oppenheimer approximation

The nuclei are much more massive than the electrons, and thus move slowly relative to the electrons. Therefore the electrons can be considered to move in a field produced by the nuclei fixed at some internuclear separation.

The Schrodlnger equation approximately separates into two simpler equations for: (i) motion of the electrons in the field of the fixed nuclei, and (ii) the motion of the nuclei in the electronic potential $u_j(r)$, that is, the potential set up by the electrons in the electronic state j. Each electronic state of the molecule creates its own characteristic internuclear potential. The calculation of $u_j(r)$ for even the ground state is a difficult n-electron calculation, and so semiempirical approximations such as the Morse potential are often used. See Figure 6-1.
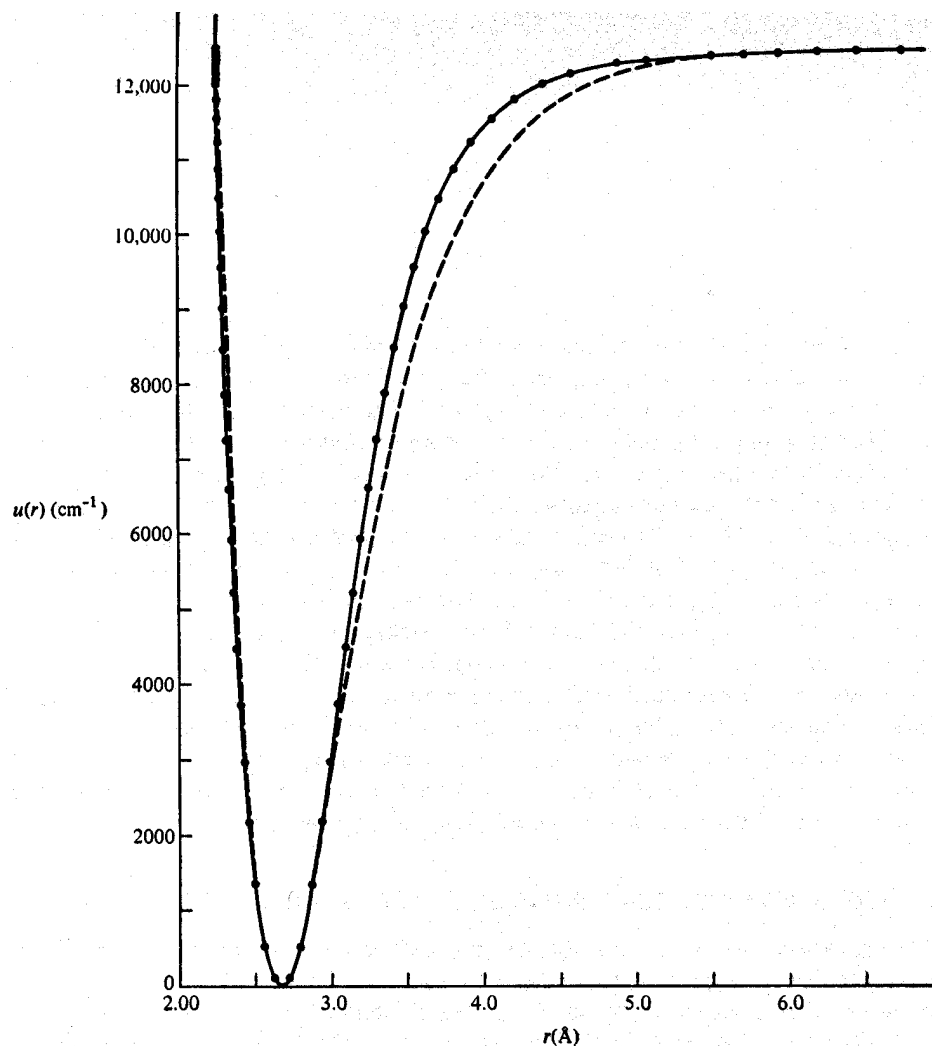
Figure 6–1. **The internuclear potential energy curve for the ground state of I_2 as computed from ultraviolet spectroscopy. The dashed curve is the Morse curve. (From R. D. Verma, *J. Chem. Phys.*, 32, 738, 1960.)**

The relative motion of the two nuclei in the potential $u_j(r)$ consists of rotary motion about the center of mass and relative vibratory motion of the two nuclei. It turns out that the amplitude of the vibratory motion is very small, and so it is a good approximation to consider the angular motion to be that of a rigid dumbbell of fixed internuclear distance r_e. In addition, the internuclear potential $u_j(r)$ can be expanded about r_e:

$$u(r) = u(r_e) + (r - r_e)\left(\frac{du}{dr}\right)_{r=r_e} + \frac{1}{2}(r - r_e)^2 \left(\frac{d^2u}{dr^2}\right)_{r=r_e} + \cdots$$

$$= u(r_e) + \frac{1}{2}k(r - r_e)^2 + \cdots$$

(6-3)

The parameter k is a measure of the curvature of the potential at the minimum and is called the force constant. A large value of k implies a stiff bond; a small value implies a loose bond.

The energy and degeneracy of an harmonic oscillator are [cf Eq. (1-31)]

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$$\varepsilon_{\text{vib}} = h\nu\left(n + \frac{1}{2}\right) \qquad \omega_n = 1 \qquad n = 0,1,2,\ldots \qquad (6\text{-}8)$$

where

$$\text{where} \quad \nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (6\text{-}9)$$

For a molecule to change its vibrational state by absorbing radiation it must (1) change its dipole moment when vibrating and (2) obey the selection rule $\Delta n = \pm 1$. The frequency of absorption is, then, seen to be

$$\nu = \frac{\varepsilon_{n+1} - \varepsilon_n}{h} = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad (6\text{-}13)$$

Equation (6-13) predicts that the vibrational spectrum of a diatomic molecule will consist of just one line. This line occurs in the infrared, typically around 1000 cm^{-1}, giving force constants k of the order of 105 or 106 dynes/cm. (See Problem 6-5.) Table 6-1 gives the force constants of a number of diatomic molecules.

Table* 6–1. Molecular constants for several diatomic molecules

molecule	electronic state	$\bar{\omega}$ (cm^{-1})	Θ_v (°K)	B (cm^{-1})	Θ_r (°K)	$k \times 10^{-5}$ (dynes/cm)	D_0 (kcal/mole)
H$_2$	$^1\Sigma_g^+$	4320	6215	59.3	85.3	5.5	103.2
D$_2$	$^1\Sigma_g^+$	3054	4394	29.9	42.7	5.5	104.6
Cl$_2$	$^1\Sigma_g^+$	561	808	0.244	0.351	3.2	57.1
Br$_2$	$^1\Sigma_g^+$	322	463	0.0809	0.116	2.4	45.4
I$_2$	$^1\Sigma_g^+$	214	308	0.0373	0.0537	1.7	35.6
O$_2$	$^3\Sigma_g^-$	1568	2256	1.437	2.07	11.6	118.0
N$_2$	$^1\Sigma_g^+$	2345	3374	2.001	2.88	22.6	225.1
CO	$^1\Sigma^+$	2157	3103	1.925	2.77	18.7	255.8
NO	$^2\Pi_{1/2}$	1890	2719	1.695	2.45	15.7	150.0
HCl	$^1\Sigma^+$	2938	4227	10.44	15.02	4.9	102.2
HBr	$^1\Sigma^+$	2640	3787	8.36	12.02	3.9	82.4
HI	$^1\Sigma^+$	2270	3266	6.46	9.06	3.0	70.5
Na$_2$	$^1\Sigma_g^+$	159	229	0.154	0.221	0.17	17.3
K$_2$	$^1\Sigma_g^+$	92.3	133	0.0561	0.081	0.10	15.8

* These parameters were obtained from a variety of sources and do not necessarily represent the most accurate values since they are obtained under the rigid rotor–harmonic oscillator approximation.

2-2 The Vibrational Partition Function

Since we are measuring the vibrational energy levels relative to the bottom of the internuclear potential well, we have

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu \qquad n = 0,1,2,\ldots \tag{6-19}$$

The vibrational partition function q_{vib} then, becomes

$$q_{\text{vib}}(T) = \sum_n e^{-\beta \varepsilon_n} = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu n} = e^{-\beta h\nu/2} \frac{1}{1 - e^{-\beta h\nu}} \tag{6-20}$$

where we have recognized the summation above as a geometric series. This is one of the rare cases in which q can be summed directly without having to approximate it by an integral, as we did in the translational case in Chapter 5 and shall do shortly in the rotational case. The quantity $\beta h\nu$ is ordinarily larger than 1, but if the temperature is high enough, $\beta h\nu \ll 1$, and we can replace the sum in (6-20) by an integral to get

$$q_{\text{vib}}(T) = e^{-\beta h\nu/2} \int_0^{\infty} e^{-\beta h\nu n} dn = \frac{kT}{h\nu} \qquad (kT \gg h\nu) \tag{6-21}$$

Although we can calculate $q_{\text{vib}}(T)$ exactly, it is worthwhile to compare this approximation to some others which we shall derive later on.

2-3 Contribution to the Thermodynamic Energy

$$E_v = NkT^2 \frac{d\ln q_v}{dT} = Nk\left(\frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1}\right) \tag{6-22}$$

where $\Theta_v \equiv h\nu/k$ and is called the vibrational temperature. Table 6-1 gives Θ_v for a number of diatomic molecules. The vibrational contribution to the heat capacity is

$$\left(\frac{\partial E_v}{\partial T}\right)_N = Nk\left(\frac{\Theta_v}{T}\right)^2 \frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T} - 1\right)^2} \tag{6-23}$$

Notice that as $T \to \infty$, $E_v \to NkT$ and $C_v \to Nk$, a result given in many physical chemistry courses and one whose significance we shall understand more fully when we discuss equipartition of energy.
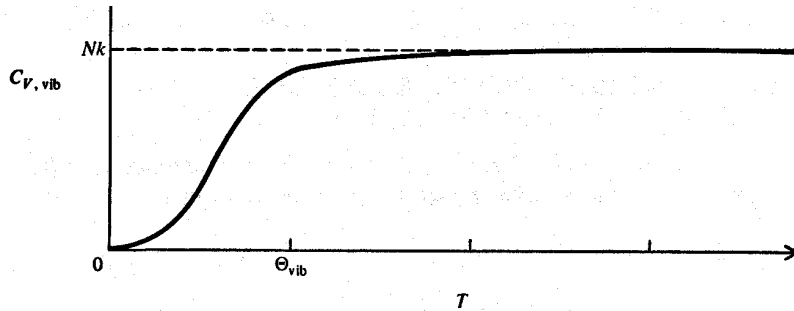
Figure 6–3. The vibrational contribution of an ideal diatomic gas to the molar heat capacity as a function of temperature. Room temperature is typically $O(0.1\Theta_v)$(*Cf.* Table 6–1).

2-4 The Level Population

The fraction of molecules in excited vibrational states designated by *n* is

$$f_n = \frac{e^{-\beta h\nu(n+1/2)}}{q_{\text{vib}}} \tag{6-24}$$

This equation is shown in Fig. 6-4 for Br_2 at 300 K. Notice that most molecules are in the ground vibrational state and that the population of the higher vibrational states decreases exponentially. Bromine has a force constant smaller than most molecules, however (cf Table 6-1), and so the population of excited vibrational levels of Br_2 is greater than most other molecules. Table 6-2 gives the fraction of molecules in all excited states for a number of molecules. This fraction is given by

$$f_{n>0} = \sum_{n=1}^{\infty} \frac{e^{-\beta h\nu(n+1/2)}}{q_{\text{vib}}} = 1 - f_0 = e^{-\beta h\nu} = e^{-\Theta/T} \tag{6-25}$$
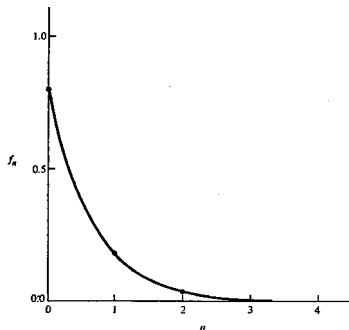

Figure 6–4. The population of the vibrational levels of Br_2 at 300°K.

Table 6–2. The fraction of molecules in excited vibrational states at 300°K and 1000°K

gas	Θ_v, °K	$e^{-\Theta_v/T}$ 300°K	$e^{-\Theta_v/T}$ 1000°K
H_2	6215	1.04×10^{-9}	2.03×10^{-3}
HCl	4227	1.02×10^{-6}	1.59×10^{-2}
N_2	3374	1.51×10^{-5}	3.55×10^{-2}
CO	3100	3.71×10^{-5}	4.65×10^{-2}
Cl_2	810	6.72×10^{-2}	4.45×10^{-1}
I_2	310	3.56×10^{-1}	7.33×10^{-1}

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3 THE ELECTRONIC PARTITION FUNCTION

The electronic partition function will be similar to that of monatomic case. But we must choose a zero of energy for the rotational and vibrational states. The zero of rotational energy will usually be taken to be the $J = 0$ state. In the vibrational case we have two choices. One is to take the zero of vibrational energy to be that of the ground state, and the other is to take the zero to be the bottom of the internuclear potential well. In the first case, the energy of the ground vibrational state is zero, and in the second case it is $h\nu/2$. We shall choose the zero of vibrational energy to be the bottom of the internuclear potential well of the lowest electronic state. Lastly, we take the zero of the electronic energy to be the separated, electronically unexcited atoms at rest. If we denote the depth of the ground electronic state potential well by D_e, the energy of the ground electronic state is $-D_e$, and the electronic partition function is

$$q_{\text{elec}} = \omega_{e1} e^{D_e/kT} + \omega_{e2} e^{-\varepsilon_2/kT} + \cdots \qquad (6\text{-}18)$$

where D_e and ε_2 are shown in Fig. 6-2. We also define $D_0 = D_e - h\nu/2$. As Fig. 6-2 shows, Do is the energy difference between the lowest vibrational state and the dissociated molecule. The quantity D_0 can be measured spectroscopically (by pre-dissociation spectra, for example) or calorimetrically from the heat of reaction at any one temperature and the heat capacities from 0 K to that temperature. See Table 6-1 for D_0 .
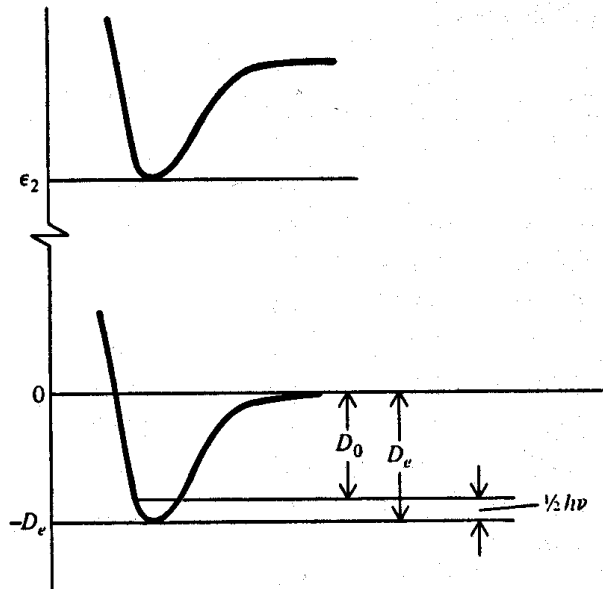

Figure 6–2. **The ground and first excited electronic states as a function of the internuclear separation** *r*, **illustrating the quantities** D_0, D_e, **and** ε_2.

4 THE ROTATIONAL DEGREE OF FREEDOM

The energy eigenvalues of a rigid rotor is given in (1-32)

$$\varepsilon_J = \frac{\hbar^2 J(J+1)}{2I} \qquad J = 0,1,2,... \qquad\qquad (6\text{-}7)$$

the degeneracy of a rigid rotor

$$\omega_J = 2J+1 \qquad J = 0,1,2,...$$

the moment of inertia of the molecule.

$$I = \mu r_e^2$$

Transitions from one rotational level to another can be induced by electromagnetic radiation. The selection rules for this are:

(1) The molecule must have a permanent dipole moment,
(2) The frequency of radiation absorbed in the process of going from a level J to $J + 1$ is given by

$$\nu = \frac{\varepsilon_{J+1} - \varepsilon_J}{h} = \frac{h}{4\pi^2 I}(J+1) \qquad J = 0,1,2,... \qquad (6\text{-}10)$$

We thus expect absorption of radiation at frequencies given by multiples of $h/4\pi^2 I$ and should observe a set of equally spaced spectral lines, which for typical molecular values of μ and r_e^2 will be found in the microwave region. Experimentally one does see a series of almost equally spaced lines in the microwave spectra of linear molecules. The usual units of frequency in this region are wave numbers, or reciprocal wavelengths.

$$\overline{\omega}(\text{cm}^{-1}) = \frac{1}{\lambda} = \frac{\nu}{c} \qquad\qquad (6\text{-}11)$$

Microwave spectroscopists define the rotational constant $\overline{B}$ by $h/8\pi^2 I c$ (units of cm^{-1}), so that the energy of rigid rotor (in cm^{-1}) becomes

$$\varepsilon_J = \overline{B} J(J+1) \qquad\qquad (6\text{-}12)$$

Table 6-1 lists the values of $\overline{B}$ for several diatomic molecules.

4-1 Heteronuclear Diatomic Molecules

For heteronuclear diatomic molecules, the calculation of the rotational partition function is straightforward. The rotational partition function is given by

$$q_{\text{rot}}(T) = \sum_J \omega_J \, e^{-\beta \varepsilon_J} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta \bar{B} J(J+1)} \tag{6-26}$$

(Note: this is a summation over levels rather than over states.)

$\Theta_r \equiv \dfrac{\bar{B}}{k}$, the characteristic temperature of rotation. (Table 6-1)

Unlike the vibrational case, this sum cannot be written in closed form.

APPROXIMATIONS TO THE PARTITION FUNCTION

At high enough temperatures, (Θ_r / T is quite small at ordinary temperatures for most molecule)

$$q_{\text{rot}}(T) = \int_0^{\infty} (2J+1) e^{-\Theta_r J(J+1)} dJ = \int_0^{\infty} e^{-\Theta_r J(J+1)} d[J(J+1)] = \frac{T}{\Theta_r}$$
$$= \frac{8\pi I k T}{h^2} \qquad \Theta_r \ll T \tag{6-27,28,29}$$

This is called the high-temperature limit. (It is really $\Delta \varepsilon / kT = 2\Theta_r (J+1)/T$ that must be small compared to one, and this of course cannot be true as J increases. However, by the time J is large enough to contradict this, the terms are so small that it makes no difference.)

For low temperatures or for molecules with large values of Θ_r,
e.g., HD with $\Theta_r = 42.7° \text{K}$, one can use the sum directly. For example,

$$q_{\text{rot}}(T) = 1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + 7e^{-12\Theta_r/T} + \cdots \tag{6-30}$$

is sufficient to give the sum to within 0.1 percent for $\Theta_r > 0.7T$.

For intermediate temperatures i.e., $\Theta_r < 0.7T$, but not small enough for the integral to give a good approximation, we need some intermediate approximation. The replacement of a sum by an integral can be viewed as the first of a sequence of approximations. The full scheme is a standard result of the field of the calculus of finite differences and is called the Euler-MacLaurin summation formula. It states that if $f(n)$ is a function defined on the integers and continuous in between, then

$$\sum_{n=a}^{b} f(n) = \int_{a}^{b} f(n)dn + \frac{f(b)+f(a)}{2} + \sum_{j=1}^{\infty}(-)^{j}\frac{B_{j}}{(2j)!}\left[f^{(2j-1)}(a) - f^{(2j-1)}(b)\right] \quad (6\text{-}31)$$

where $f^{(k)}(a)$ is the kth derivative of f evaluated at a.

The B_{j}'s are the Bernoulli numbers, $B_{1} = \dfrac{1}{6}, \quad B_{2} = \dfrac{1}{30}, \quad B_{3} = \dfrac{1}{42}, \quad \cdots$

Before applying this to $q_{\text{rot}}(T)$, let us apply it first to a case we can do exactly. Consider the sum [*cf.* Eq. (6-20)]

$$\sum_{j=0}^{\infty} e^{-\alpha j} = \frac{1}{1-e^{-\alpha}} = \frac{1}{\alpha} + \frac{1}{2} + \frac{\alpha}{12} - \frac{\alpha^{3}}{720} + \cdots \qquad (6\text{-}33)$$

Since

$$\frac{1}{1-e^{-\alpha}} = \frac{1}{\alpha - \dfrac{\alpha^{2}}{2} + \dfrac{\alpha^{3}}{6} - \cdots} = \frac{1}{\alpha} + \frac{1}{2} + \frac{\alpha}{12} - \frac{\alpha^{3}}{720} + \cdots \qquad (6\text{-}34)$$

We see that these two expansions are the same. If α is large, we can use the first few terms of (6-33); otherwise, we use the Euler-MacLaurin expansion in α.

Applying this formula to $q_{\text{rot}}(T)$ gives (see Problem 6-9):

$$q_{\text{rot}}(T) = \frac{T}{\Theta_{r}}\left[1 + \frac{1}{3}\left(\frac{\Theta_{r}}{T}\right) + \frac{1}{15}\left(\frac{\Theta_{r}}{T}\right)^{2} + \frac{4}{315}\left(\frac{\Theta_{r}}{T}\right)^{3} + \cdots\right] \qquad (6\text{-}35)$$

which is good to within one percent for $\Theta_{r} < T$. For simplicity we shall use only the high-temperature limit in what we do here since $\Theta_{r} \ll T$ for most molecules at room temperature (cf. Table 6-1).

THERMODYNAMICS ASSOCIATED WITH ROTATION

The rotational contribution to the thermodynamic energy is

$$E_{\text{rot}} = NkT^{2}\left(\frac{\partial \ln q_{\text{rot}}}{\partial T}\right) \approx NkT^{2}\left(\frac{\partial\left[(\ln T) + \cdots\right]}{\partial T}\right) \approx NkT + \cdots \qquad (6\text{-}36)$$

and the contribution to the heat capacity is

$$C_{V,\text{rot}} = Nk + \cdots \tag{6-37}$$

The fraction of molecules in the J-th rotational state

$$\frac{N_J}{N} = \frac{(2J+1)\,e^{-\Theta_r J(J+1)/T}}{q_{\text{rot}}(T)} \tag{6-38}$$

Figure 6-5 shows this fraction for HCl at 300°K. Contrary to the vibrational case, most molecules are in excited rotational levels at ordinary temperatures. We can find the maximum of this curve by differentiating (6-38) with respect to J to get

$$J_{\text{max}} = \left(\frac{kT}{2\overline{B}}\right)^{1/2} - \frac{1}{2} \approx \left(\frac{kT}{2\overline{B}}\right)^{1/2} = \left(\frac{T}{2\Theta_r}\right)^{1/2}$$

We see then that J_{max} increases with T and is inversely related to $\overline{B}$, and so increases with the moment of inertia of the molecule since $\overline{B} \propto \dfrac{1}{I}$.
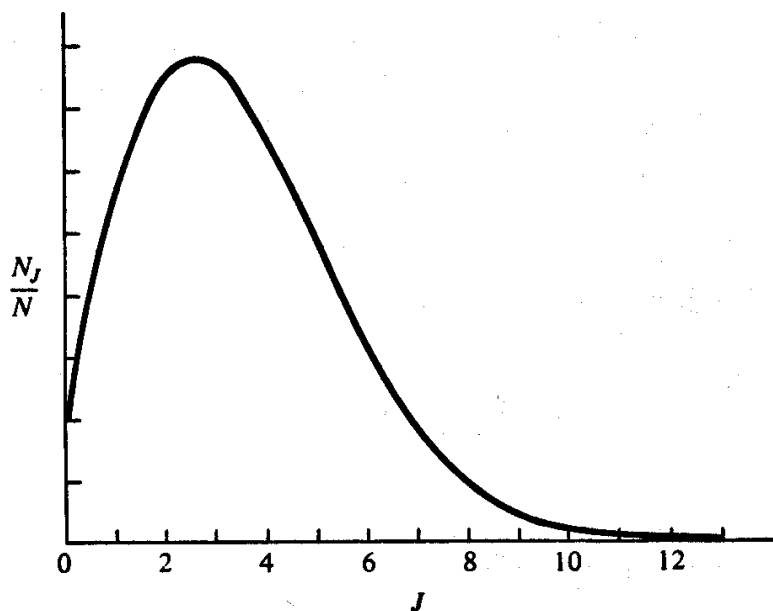

Figure 6–5. **The population of the rotational levels of hydrogen chloride at 300°K.**

4-2 *The Symmetry Requirement for a Homonuclear Diatomic Molecule*

- For homonuclear diatomic molecules, the calculation of the rotational partition function is not quite so straightforward.

- The total wave function of the molecule, that is, the electronic, vibrational, rotational, translational, and nuclear wave function, must be either symmetric or antisymmetric under the interchange of the two identical nuclei.

- It must be symmetric if the nuclei have integral spins (bosons), or anti symmetric if they have half-integral spins (fermions).

- This symmetry requirement has profound consequences on the thermodynamic properties of homo nuclear diatomic molecules at low temperatures. We shall discuss the interchange of the two identical nuclei of a homonuclear diatomic molecule in this section, and then apply the results to the calculation of q_{rot} in the next.

An exchange of the nuclei =
  (1) an inversion of all the particles, electrons and nuclei, through the origin, &
  (2) an inversion of just the electrons back through the origin.

Let us write ψ_{total} exclusive of the nuclear part as

$\psi'_{total} = \psi_{trans} \psi_{rot} \psi_{vib} \psi_{elec}$ (the prime indicates the nuclear contribution being ignored)

- ψ_{trans} depends only upon the coordinates of the center of mass of the molecule, and so this factor is not affected by inversion.
- ψ_{vib} depends only upon the magnitude of $r - r_e$, and so this part of the total wave function is unaffected by any inversion operation.
- ψ_{elec} under the inversions in both Steps (1) and (2) above depends upon the symmetry of the ground electronic state of the molecule. The ground electronic state of most molecules (designated by $\sum_g^+$ term symbol) is symmetric under both of these operations.
- ψ_{rot} therefore controls the symmetry of ψ_{total}.
    - ✓ Only Step (1) affects ψ_{rot}.
    - ✓ The effect of this inversion is to change (r, θ, ϕ) to $(r, \pi - \theta, \phi + \pi)$ that describe the orientation of the diatomic molecule.
    - ✓ One can see this either analytically from the eigenfunctions themselves or pictorially from the rotational wave functions shown in Fig. 6-6. (Notice that the rigid rotor wave functions are the same functions as the angular functions of the hydrogen atom.)
    - ✓ When the ground electronic state $\sum_g^+$ is symmetric, ψ_{total} remains unchanged for even J and changes sign for odd J. This result applies to the total wave function, exclusive of nuclear spin.
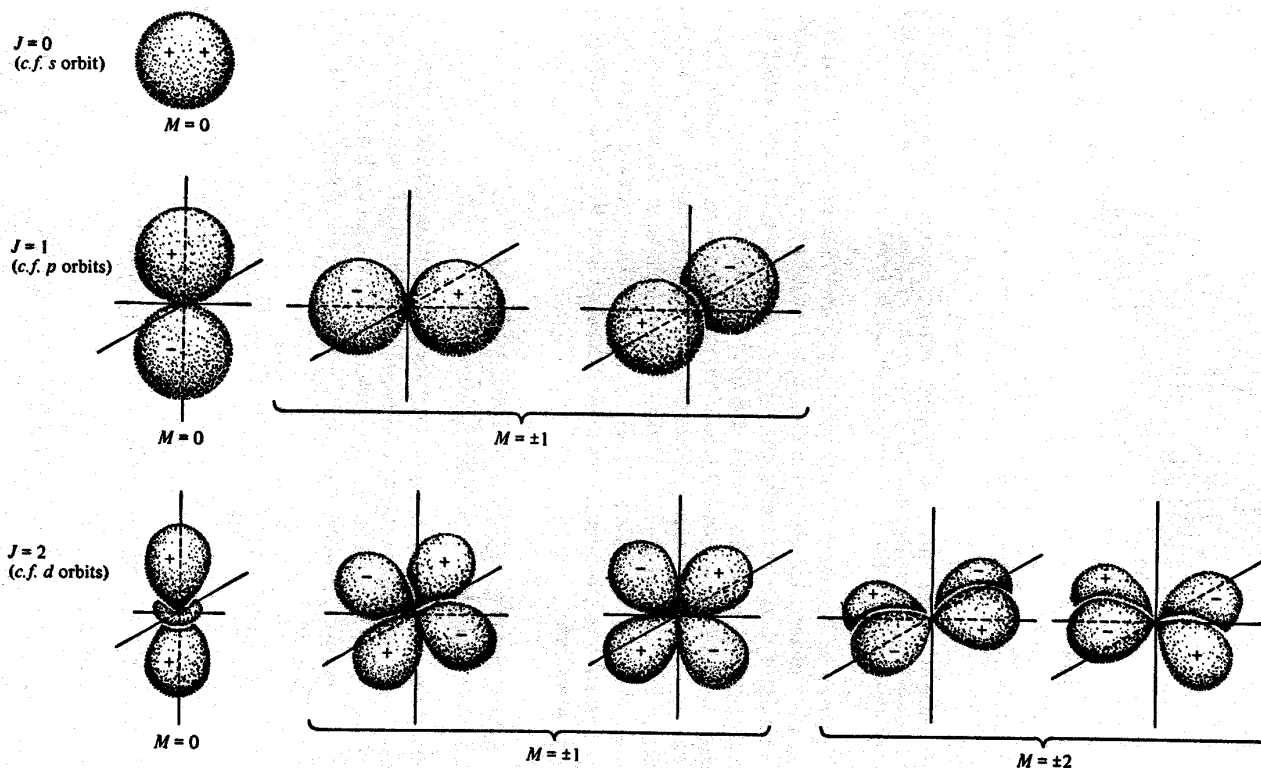
Figure 6-6. Diagrammatic representations of the rotational wave functions for *J* = 0, 1, and 2.

NB: J=0,2,… is symmetric with respect to $(r, \theta, \phi) \rightarrow (r, \pi - \theta, \phi + \pi)$, where as J=1,… is antisymmetric.

A molecule such as H$_2$:

- There are two nuclei each with spin of $\dfrac{1}{2}$. The two nuclei will have total (2I+1)(2I+1)=4 spin functions: $\alpha\alpha, \ \beta\beta, \ \text{and} \ (\alpha\beta + \beta\alpha)/\sqrt{2}$, and $(\alpha\beta - \beta\alpha)/\sqrt{2}$
- Since nuclei with spin 1/2 act as fermions, the total wave function must be antisymmetric in the exchange of these two nuclei.
- The first three spin functions are symmetric, and therefore necessarily couple with odd values of *J* to satisfy the required anti-symmetry.
- The last spin function is anti-symmetric, therefore mut couple with even values of *J* to satisfy the required anti-symmetry
- Since three symmetric nuclear spin functions be combined with the odd *J* levels to achieve the correct overall antisymmetry for $\sum_{g}^{+}$ electronic states, the odd *J* levels have a statistical weight of 3 and even *J* levels have a weight of 1. This leads to the existence of ortho- (parallel nuclear spins) states and para- (opposed nuclear spins) states in H$_2$.
- This weighting of the rotational states will be seen shortly to have a profound effect on the low-temperature thermodynamics of H$_2$.

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More general case:

- Total # of spin states : For nuclei of spin I, there are $2I + 1$ spin states for each nucleus. Let the eigenfunctlons of these spin states be denoted by α_1, α_2, $\cdots \alpha_{2I+1}$. (For H_2, $I = 1/2$, so there are 2 spin states, α and β)

- Total nuclear wave functions: For diatomic molecule, there are
  $(2I_1 + 1) \times (2I_2 + 1) = (2I + 1)^2$ nuclear wave functions to include in ψ_{total} (For H_2, $(2I + 1)^2 = 4$ nuclear spin functions.)

- The anti-symmetric nuclear spin functions are of the form
  $\alpha_i(1)\alpha_j(2) - \alpha_i(2)\alpha_j(1), \quad 1 \le i, j \le 2I + 1$. There are ${}_{2I+1}C_2 = (2I + 1)(2I)/2 = I(2I + 1)$ such combinations for the number of antisymmetric nuclear spin functions. (For H_2, $(2I + 1)I = 1$ is anti-symmetric choice.)

- The symmetric nuclear spin functions : All the remaining nuclear spin functions
  $(2I + 1)^2 - I(2I + 1) = (2I + 1)(I + 1)$ are symmetric. (For H_2, $(2I + 1)(I + 1) = 3$ are anti-symmetric choices.)

- The summary for $\sum_g^+$ states;

  half-integral spin (fermions-anti-symmetric)
    $I(2I + 1)$ antisymmetric nuclear spin functions couple with even J
    $(I + 1)(2I + 1)$ symmetric nuclear spin functions couple with odd J
  integral spin (bosons-symmetric)
    $I(2I + 1)$ antisymmetric nuclear spin functions couple with odd J.
    $(I + 1)(2I + 1)$ symmetric nuclear spin functions couple with even J

These combinations of nuclear and rotational wave functions produce the correct symmetry required of the total wave function under interchange of identical nuclei. Remember that all of these conclusions are for $\sum_g^+$ electronic states, the most commonly occurring ground state. (See Problem 6-26 for a discussion of O_2.)

Even though we have considered only diatomic molecules here, the results of this section apply also to linear polyatomic molecules such as CO_2, H_2C_2 . For example, the molecules $HC^{12}C^{12}H$ and $DC^{12}C^{12}D$ have their rotational states weighted in a similar way as H_2 and D_2, Figure 6-7 shows the vibration-rotation spectrum of H_2C_2. The alternation in the intensity of these rotational lines due to the statistical weights is very apparent.
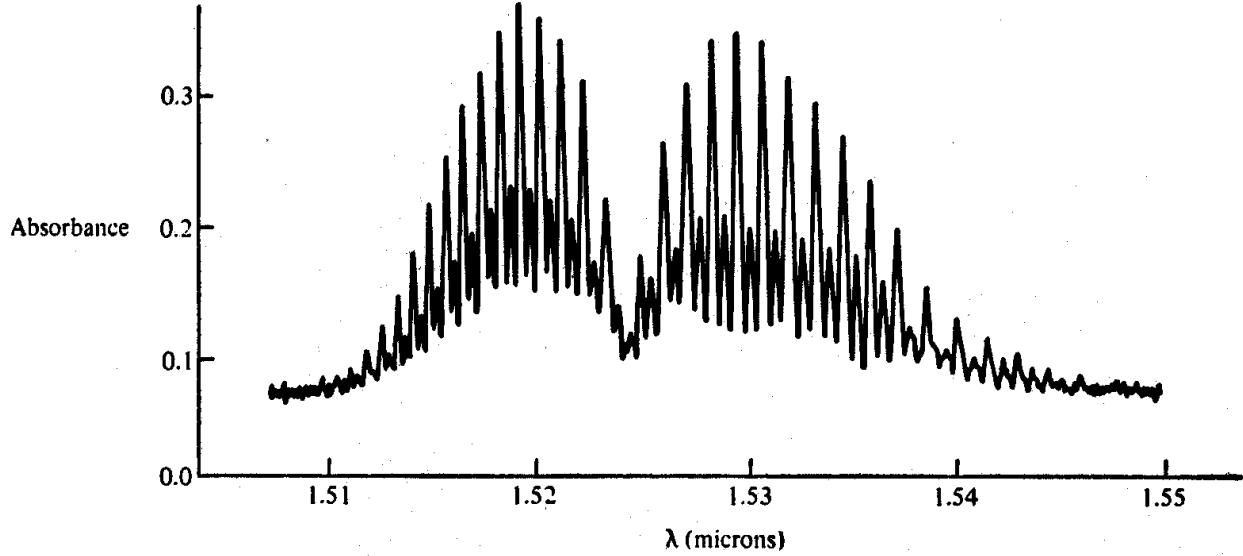
Figure *6-7.* **The vibration–rotation spectrum of acetylene. This represents one vibrational line. The alternation in the intensity of the lines is due to the statistical weights of the rotational levels.** (From L. W. Richards, *J. Chem. Ed.*, **43**, p. 645, 1966.)

4-3 The Rotational Partition Function of a Homonuclear Diatomic Molecule

The results of the previous section show that for homonuclear diatomic molecules with nuclei having integral spin, rotational levels with odd values of J must be coupled with the $I(2I+1)$ antisymmetric nuclear spin functions, and that rotational levels with even values of J must be coupled with the $(I+1)(2I+1)$ symmetric nuclear spin functions. Thus we write

$$q_{\text{rot,nucl}}(T) = (I+1)(2I+1)\sum_{J\,\text{even}} (2J+1)\,e^{-\Theta_{\text{r}}J(J+1)/T}$$
$$+ I(2I+1)\sum_{J\,\text{odd}} (2J+1)\,e^{-\Theta_{\text{r}}J(J+1)/T} \qquad (6\text{-}40)$$

Likewise, or molecules with nuclei with half integer spins,

$$q_{\text{rot,nucl}}(T) = I(2I+1)\sum_{J\,\text{even}} (2J+1)\,e^{-\Theta_{\text{r}}J(J+1)/T}$$
$$+ (I+1)(2I+1)\sum_{J\,\text{odd}} (2J+1)\,e^{-\Theta_{\text{r}}J(J+1)/T} \qquad (6\text{-}41)$$

Notice that in this case the combined rotational and nuclear partition function does not factor into $q_{\text{rot}}\,q_{\text{nucl}}$. This is a situation in which we cannot ignore q_{nucl}. For most molecules at ordinary temperatures, $\Theta_r \ll T$, and we can replace the sum by an integral. We see then that

$$\sum_{J\,\text{even}} \approx \sum_{J\,\text{odd}} \approx \frac{1}{2}\sum_{J\,\text{all}} \approx \frac{1}{2}\int_0^\infty (2J+1)\,e^{-\Theta_{\text{r}}J(J+1)/T}\,dJ = \frac{T}{2\Theta_{\text{r}}} \qquad (6\text{-}42)$$

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and so both (6-40) and (6-41) become

$$q_{rot,nucl}(T) = \frac{(2I+1)^2 T}{2\Theta_r} \qquad (6\text{-}43)$$

which can be written as $q_{rot}(T)\, q_{nucl}(T)$ where

$$q_{rot}(T) = \frac{T}{2\Theta_r} \qquad q_{nucl}(T) = (2I+1)^2 \qquad (6\text{-}44)$$

valid when $\Theta_r / T \ll 0.2$.

To compared to the result for a heteronuclear diatomic molecule:

$$q_{rot}(T) = \frac{T}{\Theta_r}$$

The factor of 2 that appears above in the high-temperature limit takes into account that the molecule is homonuclear, and so its rotational partition function is given by (6-40) or (6-41) instead of (6-26).

This factor of 2 is called the symmetry number and is denoted by σ. It legitimately appears only when $\Theta_r / T \ll 0.2$. Understanding the origin of this fact then, we can write

$$q_{rot}(T) \approx \frac{8\pi^2 IkT}{\sigma h^2} \approx \frac{1}{\sigma}\sum_{J=0}(2J+1)\, e^{-\Theta_r J(J+1)/T} \qquad \Theta_r \ll T \qquad (6\text{-}45)$$

where $\sigma = 1$ for heteronuclear molecules, and $\sigma = 2$ for homonuclear diatomic molecules. Remember that this is applicable only to the high-temperature limit or its Euler-MacLaurin correction. A similar factor will appear for polyatomic molecules also.

4-5 Nuclear Partition Function & Related Issues

There are some interesting systems in which Θ_r / T is not small. Hydrogen is one of the most important such cases. Each nucleus in H_2 has nuclear spin 1/2, and so

$$q_{rot,nucl}(T) = \sum_{J\,even}(2J+1)\, e^{-\Theta_r J(J+1)/T} + 3\sum_{J\,odd}(2J+1)\, e^{-\Theta_r J(J+1)/T} \qquad (6\text{-}46)$$

The hydrogen with only even rotational levels allowed (antisymmetric nuclear spin function or "opposite " nuclear spins) is called para-hydrogen; that with only odd rotational levels allowed

(symmetric nuclear spin function or "parallel " nuclear spins) is called ortho-hydrogen. The ratio of the number of ortho-H_2 molecules to the number of para-H_2 molecules is

$$\frac{N_{ortho}}{N_{para}} = \frac{3\sum\limits_{J\,odd} (2J+1)\,e^{-\Theta_r J(J+1)/T}}{\sum\limits_{J\,even} (2J+1)\,e^{-\Theta_r J(J+1)/T}}$$

Figure 6-8 shows the percentage of p-H_2 versus temperature in an equilibrium mixture of ortho- and para-hydrogen. Note that the system is all para- at O°K and 25 percent para- at high temperatures.
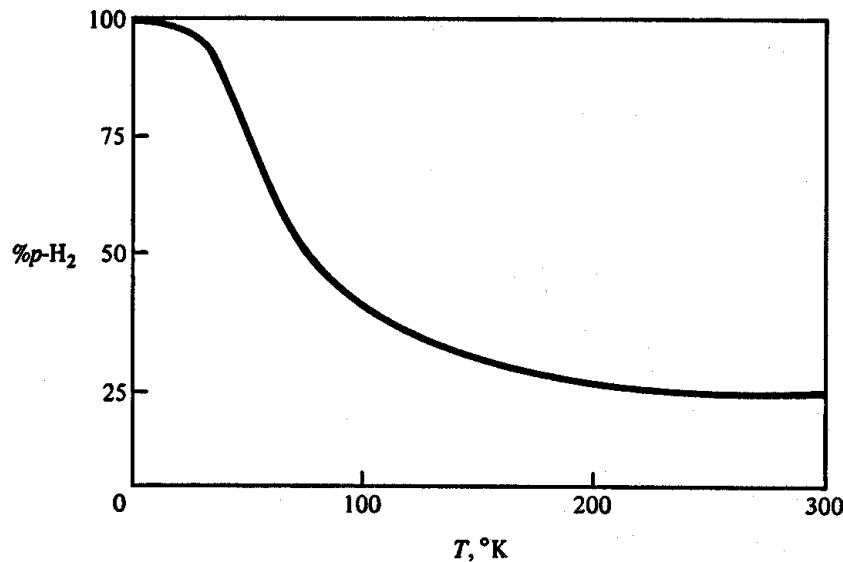

Figure 6–8. **The percentage of para-hydrogen in an equilibrium mixture as a function of temperature.**

Figure 6-9 illustrates an interesting situation that occurs with low-temperature heat capacity measurements on H_2. Equation (6-46) can be used to calculate the heat capacity of H_2, and this is plotted in Fig. 6-9, along with the experimental results. It can be seen that the two curves are in great disagreement. These calculations and measurements were made at a time when quantum mechanics was being developed, and was not accepted by all scientists. For a while, the disagreement illustrated in Fig. 6-9 was a blow to the proponents of the new quantum mechanics. It was Dennison* who finally realized that the conversion between ortho- and para-hydrogen is extremely slow in the absence of a catalyst, and so when hydrogen is prepared in the laboratory at room temperature and then cooled down for the low-temperature heat capacity measurements, the room-temperature composition persists instead of the equilibrium composition. Thus the experimental data illustrated in Fig. 6-9 are not for an equilibrium system of ortho- and para-hydrogen, but for a metastable system whose ortho-para composition is that of equilibrium room-temperature hydrogen, namely, 75 percent ortho- and 25 percent para-. If one calculates the heat capacity of such a system, according to

$$C_V = \frac{3}{4}C_V\,(\text{ortho-}) + \frac{1}{4}C_V\,(\text{para-})$$

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where C_V (ortho-) is obtained from just the second term of Eq. (6-46), and C_V (para-) is obtained from the first term of Eq. (6-46), one obtains excellent agreement with the experimental curve. A clever confirmation of this explanation was shortly after obtained by Bonhoeffer and Harteck, t who performed heat capacity measurements on hydrogen in the presence of activated charcoal, a catalyst for the ortho-para conversion. This produces an equilibrium system at each temperature. The experimental data are in excellent agreement with the equilibrium calculation in Fig. 6-9.
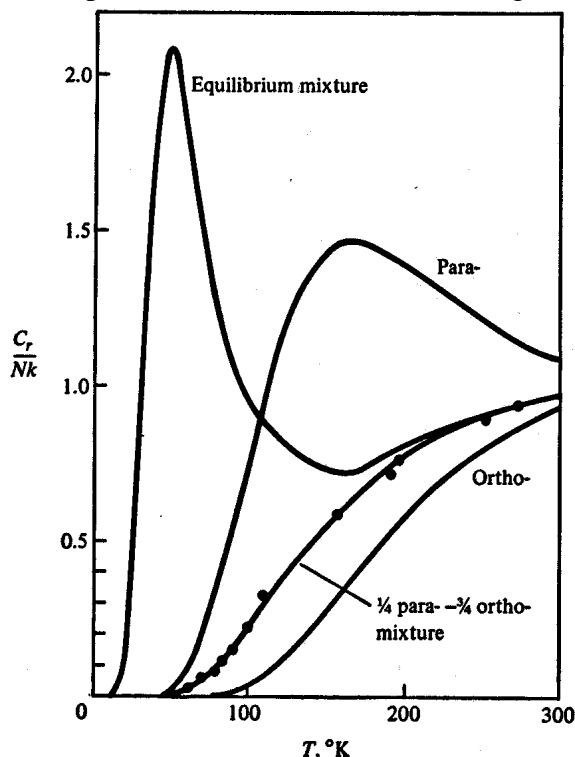

Figure 6–9. **The rotational and nuclear contribution to the molar heat capacity for ortho-hydrogen, para-hydrogen, an equilibrium mixture of ortho- and para-hydrogen, a metastable 75 percent ortho- and 25 percent para- mixture, and the experimental data. (From K. F. Bonhoeffer and P. Harteck, *Z. Physikal. Chem.*, 4B, p. 113, 1929.)**

The explanation of the heat capacity of H_2 was one of the great triumphs of post- quantum mechanical statistical mechanics. You should be able to go through a similar argument for D_2 sketching the equilibrium heat capacity, the pure ortho- and para- heat capacity, and finally what you should expect the experimental curve to be for D_2 prepared at room temperature and at some other temperature, say 20 K. (See Problem 6-17.)

In principle, such nuclear spin effects should be observable in other homonuclear molecules, but a glance at Table 6-1 shows that the characteristic rotational temperatures for all the other molecules are so small that these molecules reach the "high-temperature limit" while still in the solid state. Hydrogen is somewhat unusual in that its rotational constant is so much greater than its boiling point.

For most cases then, we can use (6-45) which, when we use the Euler-MacLaurin expansion, becomes

$$q_{\text{rot}}(T) = \frac{T}{\sigma \Theta_r} \left\{ 1 + \frac{\Theta_r}{3T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^3 + \cdots \right\} \tag{6-47}$$

Usually only the first term of this is necessary. Some of the thermodynamic functions are (6-49)

$$E_{\text{rot}} = NkT \left\{ 1 - \frac{\Theta_r}{3T} - \frac{1}{45}\left(\frac{\Theta_r}{T}\right)^2 + \cdots \right\} \tag{6-48}$$

$$C_{\text{rot}} = Nk \left\{ 1 + \frac{1}{45}\left(\frac{\Theta_r}{T}\right)^2 + \cdots \right\} \tag{6-49}$$

$$S_{\text{rot}} = Nk \left\{ 1 - \ln\left(\frac{\sigma \Theta_r}{T}\right) - \frac{1}{90}\left(\frac{\Theta_r}{T}\right)^2 + \cdots \right\} \tag{6-50}$$

where all of these formulas are valid in the same region, in which σ itself is a meaningful concept, that is, $\Theta_r < 0.2T$. The terms in Θ_r/T and its higher powers are usually not necessary. Note that (6-47) is identical to (6-35) except for the occurrence of the symmetry number in (6-47).

5 THERMODYNAMIC FUNCTIONS

Having studied each contribution to the total partition function q in (6-17), we can write in the harmonic oscillator-rigid rotor approximation

$$q(V,T) = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \right] \left[\frac{8\pi^2 IkT}{\sigma h^2} \right] \left[\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right] \left[\omega_{e1} e^{D_e/kT} \right] \tag{6-51}$$

Remember that this requires that $\Theta_r \ll T$, that only the ground electronic state is important, and that the zero of energy is taken to be the separated states at rest in their ground electronic states. Note that only q_{trans} is a function of V, which, we have seen before, is responsible for the ideal gas equation of state.

The thermodynamic functions associated with (6-51) are

$$\frac{E}{NkT} = \frac{5}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \frac{D_e}{kT} \tag{6-52}$$

$$\frac{C_V}{Nk} = \frac{5}{2} + \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2} \tag{6-53}$$

$$\frac{S}{Nk} = \ln \left[\frac{2\pi(m_1+m_2)kT}{h^2} \right]^{3/2} \frac{Ve^{5/2}}{N} + \ln \frac{8\pi^2 IkTe}{\sigma h^2} + \frac{h\nu/kT}{e^{h\nu/kT}-1} - \ln\left(1-e^{-h\nu/kT}\right) + \ln \omega_{e1} \tag{6-54}$$

$$pV = NkT \tag{6-55}$$

$$\frac{\mu^0(T)}{kT} = -\ln \left[\frac{2\pi(m_1+m_2)kT}{h^2} \right]^{3/2} kT - \ln \frac{8\pi^2 IkT}{\sigma h^2} + \frac{h\nu}{2kT} + \ln\left(1-e^{-h\nu/kT}\right) - \frac{D_e}{kT} - \ln \omega_{e1} \tag{6-56}$$

Table 6-1 contains the characteristic rotational temperatures, the characteristic vibrational temperatures, and $D_0 = D_e - \frac{1}{2}h\nu$ for a number of diatomic molecules.

Table 6-3 presents a comparison of (6-54) with experimental data. It can be seen that the agreement is quite good and is typical of that found for the other thermodynamic functions.

Table 6-3. **The entropies of some diatomic molecules calculated according to Eq. (6-54) compared to the experimental values at 1-atm pressure and 25°C***

	S(calc.) (e.u.)	S(exp.) (e.u.)
H_2	31.1	31.2
O_2	49.0	49.0
N_2	45.7	45.7
Cl_2	53.2	53.3
HCl	44.6	44.6
HBr	47.4	47.4
HI	49.4	49.3
CO	47.2	46.2

* The experimental values have been corrected for any nonideal gas behavior.

6 Further Improvements

- It is possible to improve the agreement considerably by including the first corrections to the rigid rotor-harmonic oscillator model.

- These include centrifugal distortion effects, anharmonic effects, and other extensions. The consideration of these effects introduces a new set of molecular constants, all of which are determined spectroscopically and are well tabulated. (See Problem 6-24.)

- The use of such additional parameters from spectroscopic data can give calculated values of the entropy and heat capacity that are actually more accurate than experimental ones.

- Note that extremely accurate calculations require a sophisticated knowledge of molecular spectroscopy.

6-24. The model of a diatomic molecule presented in this chapter is called the rigid rotor–harmonic oscillator model. The rotational-vibrational energy in this approximation is

$$\varepsilon_{vr} = (n + \tfrac{1}{2})h\nu + BJ(J + 1)$$

This expression can be improved in a number of ways. The harmonic oscillator approximation can be modified to include terms that reflect the deviations from harmonic behavior (anharmonicity) as the vibrational energy of the molecule increases. This is done by quantum mechanical perturbation theory, which gives

$$\varepsilon_{v} = (n + \tfrac{1}{2})h\nu - x_e(n + \tfrac{1}{2})^2 h\nu + \cdots$$