CHAPTER 4

Partition Functions and Ideal Gases

In this chapter, we will apply the general results of the preceding chapter to calculate the partition functions and heat capacities of ideal gases. We have shown in Section 3–7 that if the number of available quantum states is much greater than the number of particles, we can write the partition function of the entire system in terms of the individual atomic or molecular partition functions:

$$Q(N, V, T) = \frac{[q(V, T)]^N}{N!}$$

This equation is particularly applicable to ideal gases because the molecules are independent and the densities of gases that behave ideally are low enough that the inequality given by Equation 3.40 is satisfied. We will discuss a monatomic ideal gas first and then diatomic and polyatomic ideal gases.

4–1. The Translational Partition Function of an Atom in a Monatomic Ideal Gas is $(2\pi mk_B T/h^2)^{3/2}V$

The energy of an atom in an ideal monatomic gas can be written as the sum of its translational energy and its electronic energy

$$\varepsilon_{\text{atomic}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{elec}}$$

so the atomic partition function can be written as

$$q(V, T) = q_{\text{trans}}(V, T)q_{\text{elec}}(T) \tag{4.1}$$

We will evaluate the translational partition function first.

The translational energy states in a cubic container are given by (Equation 1–45)

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad n_x, n_y, n_z = 1,\ 2,\ \cdots \tag{4.2}$$

We substitute Equation 4.2 into q_{trans} (Equation 3.47) to get

$$q_{\text{trans}} = \sum_{n_x, n_y, n_z = 1}^{\infty} e^{-\beta\varepsilon_{n_x n_y n_z}} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[-\frac{\beta h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)\right] \tag{4.3}$$

Because $e^{a+b+c} = e^a e^b e^c$, we can write the triple summation as a product of three single summations:

$$q_{\text{trans}} = \sum_{n_x=1}^{\infty} \exp\left(-\frac{\beta h^2 n_x^2}{8ma^2}\right) \sum_{n_y=1}^{\infty} \exp\left(-\frac{\beta h^2 n_y^2}{8ma^2}\right) \sum_{n_z=1}^{\infty} \exp\left(-\frac{\beta h^2 n_z^2}{8ma^2}\right)$$

Now, each of these three single summations is alike, because each one is simply

$$\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) = e^{-\beta h^2/8ma^2} + e^{-4\beta h^2/8ma^2} + e^{-9\beta h^2/8ma^2} + \cdots$$

Thus, we can write Equation 4.3 as

$$q_{\text{trans}}(V, T) = \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right)\right]^3 \tag{4.4}$$

This summation cannot be expressed in terms of any simple analytic function. This situation does not present any difficulty, however, for the following reason. Graphically, a summation such as $\sum_{n=1}^{\infty} f_n$ is equal to the sum of the areas under rectangles of unit width centered at 1, 2, 3, ... and of height f_1, f_2, f_3, ... as shown in Figure 4.1. If the heights of successive rectangles differ by a very small amount, the area of the rectangles is essentially equal to the area under the continuous curve obtained by letting the summation index n be a continuous variable (Figure 4.1). Problem 4–2 helps you prove that the successive terms in the summation in Equation 4.4 do indeed differ very little from each other under most conditions.

Thus, it is an excellent approximation to replace the summation in Equation 4.4 by an integration:

$$q_{\text{trans}}(V, T) = \left(\int_0^{\infty} e^{-\beta h^2 n^2/8ma^2}\, dn\right)^3 \tag{4.5}$$

Note that the integral starts at $n = 0$, whereas the summation in Equation 4.4 starts at $n = 1$. For the small values of $\beta h^2/8ma^2$ we are considering here, the difference is negligible (Problem 4–41). If we denote $\beta h^2/8ma^2$ by α, the above integral becomes (see MathChapter B)

$$\int_0^{\infty} e^{-\alpha n^2}\, dn = \left(\frac{\pi}{4\alpha}\right)^{1/2}$$

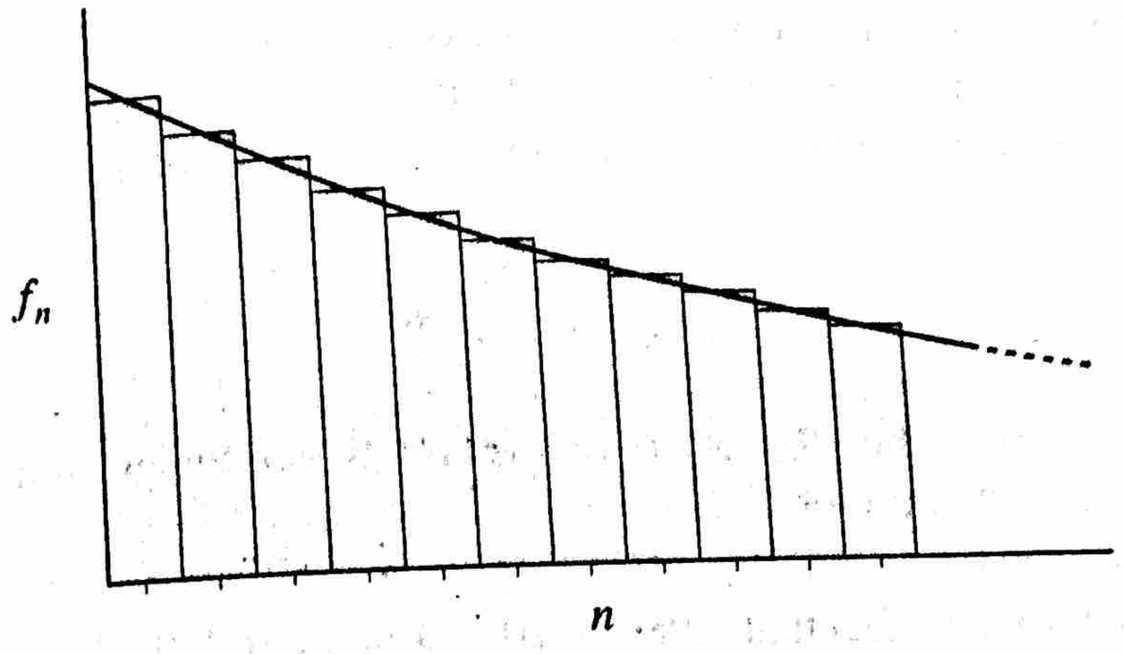


FIGURE 4.1
An illustration of the approximation of a summation $\sum_{n=1}^{\infty} f_n$ by an integral. The summation is equal to the areas of the rectangles and the integral is equal to the area under the curve obtained by letting n be a continuous variable.

so we have that

$$q_{\text{trans}}(V, T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \tag{4.6}$$

where we have written V for a^3. Note that q_{trans} is a function of V and T.

We can calculate the average translational energy of an ideal-gas atom from this partition function by using Equation 3.51:

$$\begin{aligned}\langle \varepsilon_{\text{trans}} \rangle &= k_B T^2 \left(\frac{\partial \ln q_{\text{trans}}}{\partial T}\right)_V \\ &= k_B T^2 \left(\frac{\partial}{\partial T}\left[\frac{3}{2}\ln T + \text{terms independent of } T\right]\right)_V \\ &= \tfrac{3}{2} k_B T\end{aligned} \tag{4.7}$$

in agreement with what we found in Section 3–3.

4–2. Most Atoms Are in the Ground Electronic State at Room Temperature

In this section, we will investigate the electronic contributions to $q(V, T)$. It is more convenient to write the electronic partition function as a sum over levels rather than a sum over states (Section 3–8), so we write

$$q_{\text{elec}} = \sum_i g_{ei} e^{-\beta \varepsilon_{ei}} \tag{4.8}$$

where g_{ei} is the degeneracy, and ε_{ei} the energy of the ith electronic level. We first fix the arbitrary zero of energy such that $\varepsilon_{e1} = 0$; that is, we will measure all electronic energies relative to the ground electronic state. The electronic contribution to q can then be written as

$$q_{\text{elec}}(T) = g_{e1} + g_{e2}e^{-\beta\varepsilon_{e2}} + \cdots \tag{4.9}$$

where ε_{ej} is the energy of the jth electronic level relative to the ground state. Note that q_{elec} is a function of T but not of V.

As we have seen in Chapter 1, these ε's are typically of the order of tens of thousands of wave numbers. Using the fact that $1.986 \times 10^{-23}\ \text{J} = 1\ \text{cm}^{-1}$, the Boltzmann constant in wave numbers is $k_B = 0.6950\ \text{cm}^{-1}\cdot\text{K}^{-1}$. Thus, we see that typically

$$\beta\varepsilon_{\text{elec}} \approx \frac{40\,000\ \text{cm}^{-1}}{0.6950\ \text{cm}^{-1}\cdot\text{K}^{-1}}\frac{1}{T} \approx \frac{10^4\ \text{K}}{T}$$

which is equal to 10 even for $T = 1000$ K. Therefore, $e^{-\beta\varepsilon_{e2}}$ in Equation 4.9 typically is around 10^{-5} for most atoms at ordinary temperatures, so only the first term in the summation for q_{elec} is significantly different from zero. There are some cases, however, such as the halogen atoms, for which the first excited state lies only a few hundred wave numbers above the ground state, so that several terms in q_{elec} are necessary. Even in these cases, the sum in Equation 4.9 converges very rapidly.

As we learned in Chapter 1, the electronic energies of atoms and ions are determined by atomic spectroscopy and are well tabulated. The standard reference, "Moore's tables," lists the energy levels and energies of many atoms and ions. Table 4.1 lists the first few levels for H, He, Li, and F. We can make some general observations from tables like Table 4.1. The first excited states of the noble gas atoms are of order of $10^5\ \text{cm}^{-1}$ or higher than the ground states; the first excited states at the alkali metal atoms are of order of $10^4\ \text{cm}^{-1}$ or higher than the ground states; and the first excited states of the halogen atoms are only of order of $10^2\ \text{cm}^{-1}$ higher than the ground states. Thus, at ordinary temperatures, the electronic partition function of noble gas atoms is essentially unity and that of alkali metal atoms is two, while those for halogen atoms consist of two terms.

Using the data in Table 4.1, we can now calculate the fraction of helium atoms in the first excited state. This fraction is given by

$$\begin{aligned} f_2 &= \frac{g_{e2}e^{-\beta\varepsilon_{e2}}}{q_{\text{elec}}(T)} \\ &= \frac{g_{e2}e^{-\beta\varepsilon_{e2}}}{g_{e1} + g_{e2}e^{-\beta\varepsilon_{e2}} + g_{e3}e^{-\beta\varepsilon_{e3}} + \cdots} \\ &= \frac{3e^{-\beta\varepsilon_{e2}}}{1 + 3e^{-\beta\varepsilon_{e2}} + e^{-\beta\varepsilon_{e3}} + \cdots} \end{aligned} \tag{4.10}$$

At 300 K, $\beta\varepsilon_{e2} = 770$, so $f_2 \approx 10^{-334}$. Even at 3000 K, $f_2 \approx 10^{-33}$. This is typical of the noble gases. The energy separation between the ground and excited levels must

TABLE 4.1
Some atomic energy levels.[a]

Atom	Electron configuration	Degeneracy $g_e = 2J + 1$	Energy/cm^{-1}
H	$1s$	2	0.
	$2p$	2	82 258.907
	$2s$	2	82 258.942
	$2p$	4	82 259.272
He	$1s^2$	1	0.
	$1s2p$	3	159 850.318
		1	166 271.70
Li	$1s^22s$	2	0.
	$1s^22p$	2	14 903.66
		4	14 904.00
	$1s^23s$	2	27 206.12
F	$1s^22s^22p^5$	4	0.
		2	404.0
	$1s^22s^22p^43s$	6	102 406.50
		4	102 681.24
		2	102 841.20
		4	104 731.86
		2	105 057.10

[a]From C.E. Moore, "Atomic Energy Levels" *Natl. Bur. Std, Circ.* 1 467, U.S. Government Printing Office, Washington D.C., 1949

be less than a few hundred cm^{-1} or so before any population of the excited level is significant.

EXAMPLE 4–1

Using the data in Table 4.1, calculate the fraction of fluorine atoms in the first excited state at 300 K, 1000 K, and 2000 K.

SOLUTION: Using the second line of Equation 4.10 with $g_{e1} = 4$, $g_{e2} = 2$, and $g_{e3} = 6$, we have

$$f_2 = \frac{2e^{-\beta\varepsilon_{e2}}}{4 + 2e^{-\beta\varepsilon_{e2}} + 6e^{-\beta\varepsilon_{e3}} + \cdots}$$

with $\varepsilon_{e2} = 404.0\ \text{cm}^{-1}$ and $\varepsilon_{e3} = 102\,406.50\ \text{cm}^{-1}$. We also have

$$\beta\varepsilon_{e2} = \frac{404.0\ \text{cm}^{-1}}{(0.6950\ \text{cm}^{-1}\cdot\text{K}^{-1})T} = \frac{581.3\ \text{K}}{T}$$

and

$$\beta\varepsilon_{e3} = \frac{147\,300\ \text{K}}{T}$$

Clearly, we can neglect the third term in the denominator of f_2.

The value of f_2 for the various temperatures is

$$f_2(T = 300\ \text{K}) = \frac{2e^{-581/300}}{4 + 2e^{-581/300}} = 0.0672$$

$$f_2(T = 1000\ \text{K}) = \frac{2e^{-581/1000}}{4 + 2e^{-581/1000}} = 0.219$$

$$f_2(T = 2000\ \text{K}) = 0.272$$

Thus, the population of the first excited state is significant at these temperatures and so the first two terms of the summation in Equation 4.9 must be evaluated in determining $q_{\text{elec}}(T)$.

For most atoms and molecules, the first two terms of the electronic partition function are sufficient, or

$$q_{\text{elec}}(T) \approx g_{e1} + g_{e2}e^{-\beta\varepsilon_{e2}} \tag{4.11}$$

At temperatures at which the second term is not negligible with respect to the first term, we must check the possible contribution of higher terms as well.

This completes our discussion of the partition function of monatomic ideal gases. In summary, we have

$$Q(N, V, T) = \frac{(q_{\text{trans}}q_{\text{elec}})^N}{N!} \tag{4.12}$$

where

$$q_{\text{trans}}(V, T) = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \tag{4.13}$$

$$q_{\text{elec}}(T) = g_{e1} + g_{e2}e^{-\beta\varepsilon_{e2}} + \cdots$$

We can now calculate some of the properties of a monatomic ideal gas. The average energy is

$$U = k_{\text{B}}T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = Nk_{\text{B}}T^2\left(\frac{\partial \ln q}{\partial T}\right)_V = \frac{3}{2}Nk_{\text{B}}T + \frac{Ng_{e2}\varepsilon_{e2}e^{-\beta\varepsilon_{e2}}}{q_{\text{elec}}} + \cdots \tag{4.14}$$

The first term represents the average kinetic energy, and the second term represents the average electronic energy (in excess of the ground-state energy). The contribution of the electronic degrees of freedom to the average energy is small at ordinary temperatures. If we ignore the very small contribution from the electronic degrees of freedom, the molar heat capacity at constant volume is given by

$$\overline{C}_V = \left(\frac{d\overline{U}}{dT}\right)_{N,V} = \frac{3}{2}R$$

The pressure is

$$\begin{aligned} P &= k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = N k_B T \left(\frac{\partial \ln q}{\partial V}\right)_T \\ &= N k_B T \left[\frac{\partial}{\partial V}(\ln V + \text{terms not involving } V)\right]_T \\ &= \frac{N k_B T}{V} \end{aligned} \tag{4.15}$$

which is the ideal gas equation of state. Note that Equation 4.15 results because $q(V, T)$ is of the form $f(T)V$, and only the translational energy of the atoms contributes to the pressure. This is expected intuitively, because the pressure is due to bombardment of the walls of the container by the atoms and molecules of the gas.

In the next few sections, we will treat a diatomic ideal gas. In addition to translational and electronic degrees of freedom, diatomic molecules also possess vibrational and rotational degrees of freedom. The general procedure would be to set up the Schrödinger equation for two nuclei and n electrons and to solve this equation for the set of eigenvalues of the diatomic molecule. Fortunately, a series of very good approximations can be used to reduce this complicated two-nuclei, n-electron problem to a set of simpler problems. The simplest of these approximations is the rigid rotator-harmonic oscillator approximation, which we described in Chapter 1. We will set up this approximation in the next section and then discuss the vibrational and rotational partition functions within this approximation in Sections 4–4 and 4–5.

4–3. The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms

When treating diatomic or polyatomic molecules, we use the rigid rotator-harmonic oscillator approximation (Chapter 1). In this case, we can write the total energy of the molecule as a sum of its translational, rotational, vibrational, and electronic energies:

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} \tag{4.16}$$

As for a monatomic ideal gas, the inequality given by Equation 3.40 is easily satisfied at normal temperatures, and so we can write

$$Q(N, V, T) = \frac{[q(V, T)]^N}{N!} \tag{4.17}$$

Furthermore, Equation 4.16 allows us to write

$$q(V, T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \tag{4.18}$$

so the partition function of a molecular ideal gas is given by

$$Q(N, V, T) = \frac{(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}})^N}{N!} \tag{4.19}$$

The translational partition function of a diatomic molecule is similar to the result we found in Section 4–1 for an atom:

$$q_{\text{trans}}(V, T) = \left[\frac{2\pi(m_1 + m_2)k_B T}{h^2}\right]^{3/2} V \tag{4.20}$$

Note that Equation 4.20 is essentially the same as Equation 4.6. The electronic partition function will be similar to Equation 4.9. We will discuss the vibrational and rotational contributions to the partition function in the next two sections. Although Equation 4.19 is not exact, it is often a good approximation, particularly for small molecules.

Before we consider q_{rot} and q_{vib}, we must choose a zero of energy for the rotational, vibrational, and electronic states. The natural choice for the zero of rotational energy is the $J = 0$ state, where the rotational energy is zero. In the vibrational case, however, we have two sensible choices. One is to take the zero of vibrational energy to be that of the ground state, and the other is 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 will choose the zero of vibrational energy to be the bottom of the internuclear potential well of the lowest electronic state, so the energy of the ground vibrational state will be $h\nu/2$.

Last, we take the zero of the electronic energy to be the separated atoms at rest in their ground electronic states (see Figure 4.2). Recall that the depth of the ground electronic state potential well is denoted by D_e (D_e is a positive number; see Section 1–7), and so the energy of the ground electronic state is $\varepsilon_{e1} = -D_e$, and the electronic partition function is

$$q_{\text{elec}} = g_{e1} e^{D_e/k_B T} + g_{e2} e^{-\varepsilon_{e2}/k_B T} \tag{4.21}$$

where D_e and ε_{e2} are shown in Figure 4.2. We also introduced in Section 1–7 a quantity D_0 that is equal to $D_e - \frac{1}{2}h\nu$. As Figure 4.2 shows, D_0 is the energy difference between the lowest vibrational state and the dissociated molecule. The quantity D_0 can be measured spectroscopically, and values of D_0 and D_e for several diatomic molecules are given in Table 4.2.

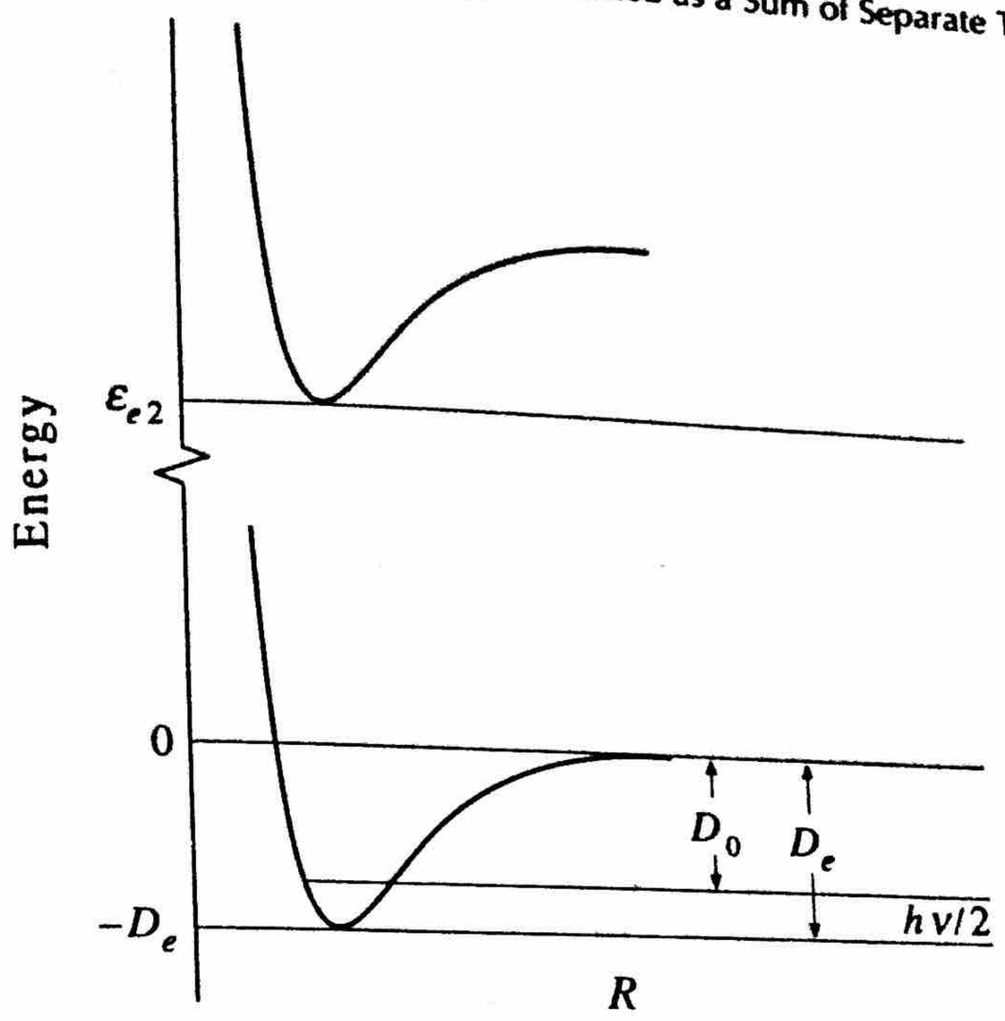


FIGURE 4.2
The ground and first excited electronic states as a function of the internuclear separation, illustrating the quantities D_e and D_0 of the ground state and ε_{e2}. The quantities D_e and D_0 are related by $D_e = D_0 + h\nu/2$ as shown in the figure.

TABLE 4.2
Molecular constants for several diatomic molecules. These parameters were obtained from a variety of sources and do not represent the most accurate values because they were obtained under the rigid rotator-harmonic oscillator approximation.

Molecule	Θ_{vib}/K	Θ_{rot}/K	D_0/kJ·mol^{-1}	D_e/kJ·mol^{-1}	Degeneracy of the ground electronic state
H_2	6332	85.3	432.1	457.6	1
D_2	4480	42.7	435.6	453.9	1
Cl_2	805	0.351	239.2	242.3	1
Br_2	463	0.116	190.1	191.9	1
I_2	308	0.0537	148.8	150.3	1
O_2	2256	2.07	493.6	503.0	3
N_2	3374	2.88	941.6	953.0	1
CO	3103	2.77	1070	1085	1
NO	2719	2.39	626.8	638.1	2
HCl	4227	15.02	427.8	445.2	1
HBr	3787	12.02	362.6	377.7	1
HI	3266	9.25	294.7	308.6	1
Na_2	229	0.221	71.1	72.1	1
K_2	133	0.081	53.5	54.1	1

4–4. Most Molecules Are in the Ground Vibrational State at Room Temperature

In this section, we will evaluate the vibrational part of the partition function of a diatomic molecule under the harmonic-oscillator approximation. If we measure the vibrational energy levels relative to the bottom of the internuclear potential well, the energies are given by (Equation 1–22)

$$\varepsilon_v = \left(v + \tfrac{1}{2}\right) h\nu \qquad v = 0,\ 1,\ 2,\ \cdots \tag{4.22}$$

with $\nu = (k/\mu)^{1/2}/2\pi$, where k is the force constant of the molecule and μ is its reduced mass. The vibrational partition function q_{vib} becomes

$$q_{\text{vib}}(T) = \sum_v e^{-\beta\varepsilon_v} = \sum_{v=0}^{\infty} e^{-\beta\left(v+\frac{1}{2}\right)h\nu}$$

$$= e^{-\beta h\nu/2} \sum_{v=0}^{\infty} e^{-\beta h\nu v}$$

This summation can be evaluated easily by recognizing it to be a geometric series (MathChapter C):

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

with $x = e^{-\beta h\nu} < 1$. Thus we can write

$$\sum_{v=0}^{\infty} e^{-\beta h\nu v} = \sum_{v=0}^{\infty} \left(e^{-\beta h\nu}\right)^v = \frac{1}{1 - e^{-\beta h\nu}}$$

so $q_{\text{vib}}(T)$ becomes

$$q_{\text{vib}}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \tag{4.23}$$

Note that this is the vibrational term encountered in Example 3–2, which presented the partition function for the rigid rotator-harmonic oscillator model of an ideal diatomic gas. If we introduce a quantity, $\Theta_{\text{vib}} = h\nu/k_{\text{B}}$, called the *vibrational temperature*, $q_{\text{vib}}(T)$ can be written as

$$q_{\text{vib}}(T) = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} \tag{4.24}$$

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 for the translational case in Section 4–1 and will do shortly for the rotational case in Section 4–5.

We can calculate the average vibrational energy from $q_{vib}(T)$

$$\langle E_{vib} \rangle = Nk_B T^2 \frac{d \ln q_{vib}}{dT} = Nk_B \left(\frac{\Theta_{vib}}{2} + \frac{\Theta_{vib}}{e^{\Theta_{vib}/T} - 1} \right) \tag{4.25}$$

Table 4.2 gives Θ_{vib} for several diatomic molecules. The vibrational contribution to the molar heat capacity is

$$\overline{C}_{V,vib} = \frac{d\langle \overline{E}_{vib} \rangle}{dT} = R \left(\frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{\left(1 - e^{-\Theta_{vib}/T}\right)^2} \tag{4.26}$$

Figure 4.3 shows the vibrational contribution of an ideal diatomic gas to the molar heat capacity as a function of temperature. The high temperature limit of $\overline{C}_{V,vib}$ is R, and $\overline{C}_{V,vib}$ is one-half of this value at $T/\Theta_{vib} = 0.34$.

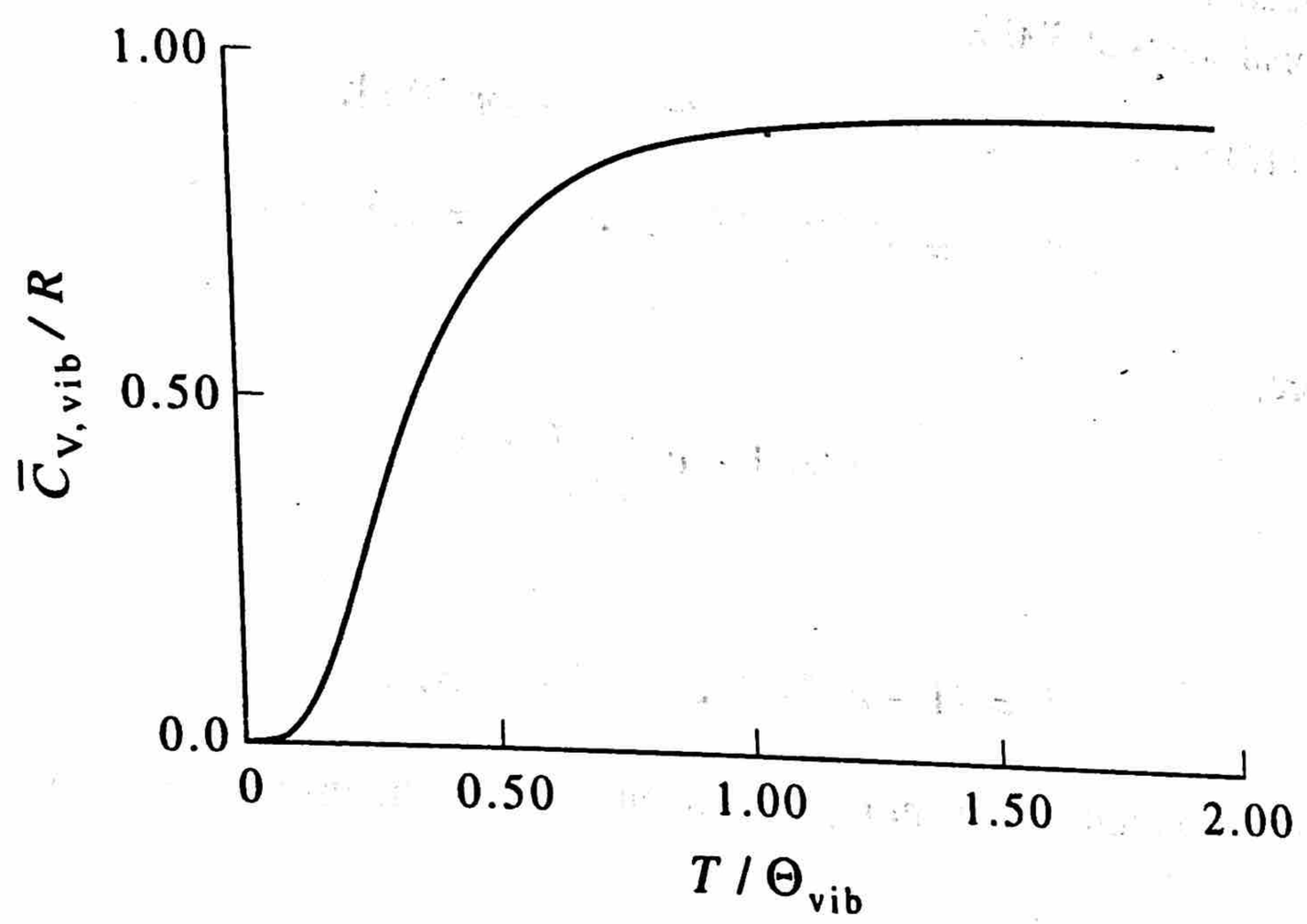


FIGURE 4.3
The vibrational contribution to the molar heat capacity of an ideal diatomic gas as a function of reduced temperature, T/Θ_{vib}.

EXAMPLE 4–2

Calculate the vibrational contribution to the molar heat capacity of $N_2(g)$ at 1000 K. The experimental value is 3.43 $J \cdot K^{-1} \cdot mol^{-1}$.

SOLUTION: We use Equation 4.26 with $\Theta_{vib} = 3374$ (Table 4.2). Thus, $\Theta_{vib}/T = 3.374$ and

$$\frac{\overline{C}_{V.vib}}{R} = (3.374)^2 \frac{e^{-3.374}}{(1 - e^{-3.374})^2} = 0.418$$

or

$$\overline{C}_{V.vib} = (0.418)(8.314\ J \cdot K^{-1} \cdot mol^{-1}) = 3.48\ J \cdot K^{-1} \cdot mol^{-1}$$

The agreement with the experimental value is quite good.

An interesting quantity to calculate is the fraction of molecules in various vibrational states. The fraction of molecules in the vth vibrational state is

$$f_v = \frac{e^{-\beta h\nu(v+\frac{1}{2})}}{q_{vib}} \tag{4.27}$$

If we substitute Equation 4.23 into this equation, we obtain

$$f_v = \left(1 - e^{-\beta h\nu}\right) e^{-\beta h\nu v} = \left(1 - e^{-\Theta_{vib}/T}\right) e^{-v\Theta_{vib}/T} \tag{4.28}$$

The following example illustrates the use of this equation.

EXAMPLE 4–3

Use Equation 4.28 to calculate the fraction of $N_2(g)$ molecules in the $v = 0$ and $v = 1$ vibrational states at 300 K.

SOLUTION: We first calculate $\exp(-\Theta_{vib}/T)$ for 300 K:

$$e^{-\Theta_{vib}/T} = e^{-3374\ \text{K}/300\ \text{K}} = e^{-11.25} = 1.31 \times 10^{-5}$$

Therefore,

$$f_0 = 1 - e^{-\Theta_{vib}/T} \approx 1$$

and

$$f_1 = (1 - e^{-\Theta_{vib}/T})e^{-\Theta_{vib}/T} \approx 1.31 \times 10^{-5}$$

Notice that essentially all the nitrogen molecules are in the ground vibrational state at 300 K.

Figure 4.4 shows the population of vibrational levels of $Br_2(g)$ 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 smaller force constant and a larger mass (and hence a smaller value of Θ_{vib}) than most diatomic molecules, however (*cf.* Table 4.2), so the population of excited vibrational states of $Br_2(g)$ at a given temperature is greater than most other molecules.

We can use Equation 4.28 to calculate the fraction of molecules in all excited vibrational states. This quantity is given by $\sum_{v=1}^{\infty} f_v$ but because $\sum_{v=0}^{\infty} f_v = 1$, we can write

$$f_{v>0} = \sum_{v=1}^{\infty} f_v = 1 - f_0 = 1 - (1 - e^{-\Theta_{vib}/T})$$

or simply

$$f_{v>0} = e^{-\Theta_{vib}/T} = e^{-\beta h\nu} \tag{4.29}$$

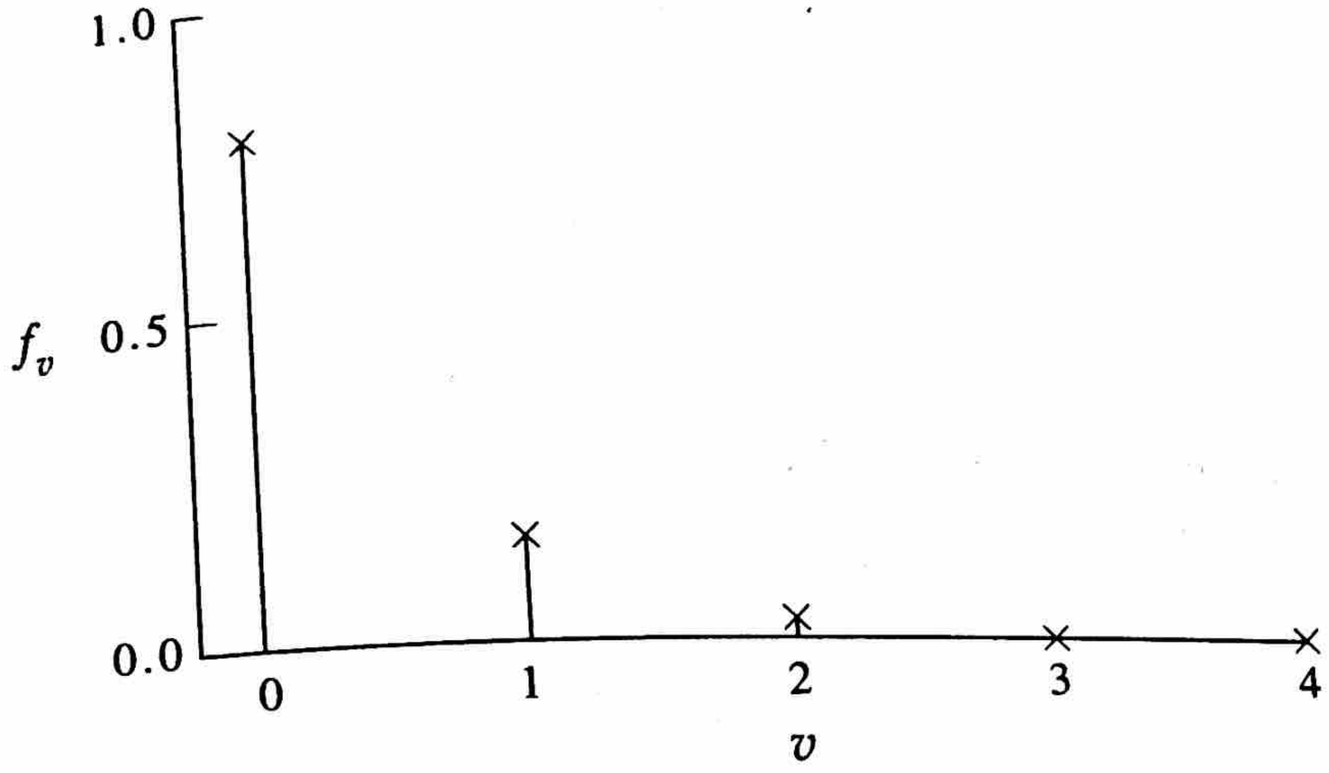


FIGURE 4.4
The population of the vibrational levels of $Br_2(g)$ at 300 K.

Table 4.3 gives the fraction of molecules in excited vibrational states for several diatomic molecules.

TABLE 4.3
The fraction of molecules in excited vibrational states at 300 K and 1000 K.

Gas	Θ_{vib}/K	$f_{v>0}$ (T = 300 K)	$f_{v>0}$ (T = 1000 K)
H_2	6332	1.01×10^{-9}	2.00×10^{-3}
HCl	4227	7.59×10^{-7}	1.46×10^{-2}
N_2	3374	1.30×10^{-5}	3.43×10^{-2}
CO	3103	3.22×10^{-5}	4.49×10^{-2}
Cl_2	805	6.82×10^{-2}	4.47×10^{-1}
I_2	308	3.58×10^{-1}	7.35×10^{-1}

4–5. Most Molecules Are in Excited Rotational States at Ordinary Temperatures

The energy levels of a rigid rotator are given by (Equation 1–28)

$$\varepsilon_J = \frac{\hbar^2 J(J+1)}{2I} \qquad J = 0,\ 1,\ 2,\ \cdots \tag{4.30a}$$

where I is the moment of inertia of the rotator. Each energy level has a degeneracy of

$$g_J = 2J + 1 \tag{4.30b}$$

Using Equations 4.30*a* and 4.30*b*, we can write the rotational partition function of a rigid rotator as

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\beta \hbar^2 J(J+1)/2I} \tag{4.31}$$

where we sum over levels rather than states by including the degeneracy explicitly. For convenience, we introduce a quantity that has units of temperature and is called the *rotational temperature*, Θ_{rot}:

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} = \frac{hB}{k_B} \tag{4.32}$$

where $B = h/8\pi^2 I$ (Equation 1.33). Substituting Equation 4.32 into Equation 4.31 gives

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\Theta_{\text{rot}} J(J+1)/T} \tag{4.33}$$

Unlike the harmonic-oscillator partition function, the summation in Equation 4.33 cannot be written in closed form. However, as the data in Table 4.2 will verify, the value of Θ_{rot}/T is quite small at ordinary temperatures for diatomic molecules that do not contain hydrogen atoms. For example, Θ_{rot} for CO(g) is 2.77 K, so Θ_{rot}/T is about 10^{-2} at room temperature. Just as we were able to approximate the summation in Equation 4.4 very well by an integral because $\alpha = \beta h^2/8ma^2$ is typically small at normal temperatures, we are able to approximate the summation in Equation 4.33 by an integral because Θ_{rot}/T is small for most molecules at ordinary temperatures. Therefore, it is an excellent approximation to write $q_{\text{rot}}(T)$ as

$$q_{\text{rot}}(T) = \int_0^{\infty} (2J+1) e^{-\Theta_{\text{rot}} J(J+1)/T} dJ$$

This integral is easy to evaluate because if we let $x \doteq J(J+1)$, then $dx = (2J+1)dJ$ and $q_{\text{rot}}(T)$ becomes

$$q_{\text{rot}}(T) = \int_0^{\infty} e^{-\Theta_{\text{rot}} x/T} dx$$

$$= \frac{T}{\Theta_{\text{rot}}} = \frac{8\pi^2 I k_B T}{h^2} \qquad \Theta_{\text{rot}} \ll T \tag{4.34}$$

Note that this is the rotational term encountered in Example 3–2, which presented the partition function for the rigid rotator-harmonic oscillator model of an ideal diatomic gas. This approximation improves as the temperature increases and is called the high-temperature limit. For low temperatures or for molecules with large values of Θ_{rot}, say $H_2(g)$ with $\Theta_{\text{rot}} = 85.3$ K, we can use Equation 4.33 directly. For example, the first four terms of Equation 4.33 are sufficient to calculate $q_{\text{rot}}(T)$ to within 0.1% for $T < 3\Theta_{\text{rot}}$.

For simplicity, we will use only the high-temperature limit, because $\Theta_{rot} \ll T$ for most molecules at room temperature. (See Table 4.2.)

The average rotational energy is

$$\langle E_{rot} \rangle = Nk_B T^2 \left(\frac{d \ln q_{rot}}{dT} \right) = Nk_B T$$

and the rotational contribution to the molar heat capacity is

$$\overline{C}_{V,rot} = R$$

A diatomic molecule has two rotational degrees of freedom, and each one contributes $R/2$ to $\overline{C}_{V,rot}$.

We can also calculate the fraction of molecules in the J^{th} rotational level:

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

$$= (2J+1)(\Theta_{rot}/T)e^{-\Theta_{rot}J(J+1)/T} \qquad (4.35)$$

EXAMPLE 4–4

Use Equation 4.35 to calculate the population of the rotational levels of CO at 300 K.

SOLUTION: Using $\Theta_{rot} = 2.77$ K from Table 4.2, we have that $\Theta_{rot}/T = 0.00923$ at 300 K. Therefore,

$$f_J = (2J+1)(0.00923)e^{-0.00923J(J+1)}$$

We can present our results in the form of a table:

J	f_J
0	0.00923
2	0.0437
4	0.0691
6	0.0814
8	0.0807
10	0.0702
12	0.0547
16	0.0247
18	0.0145

These results are plotted in Figure 4.5.

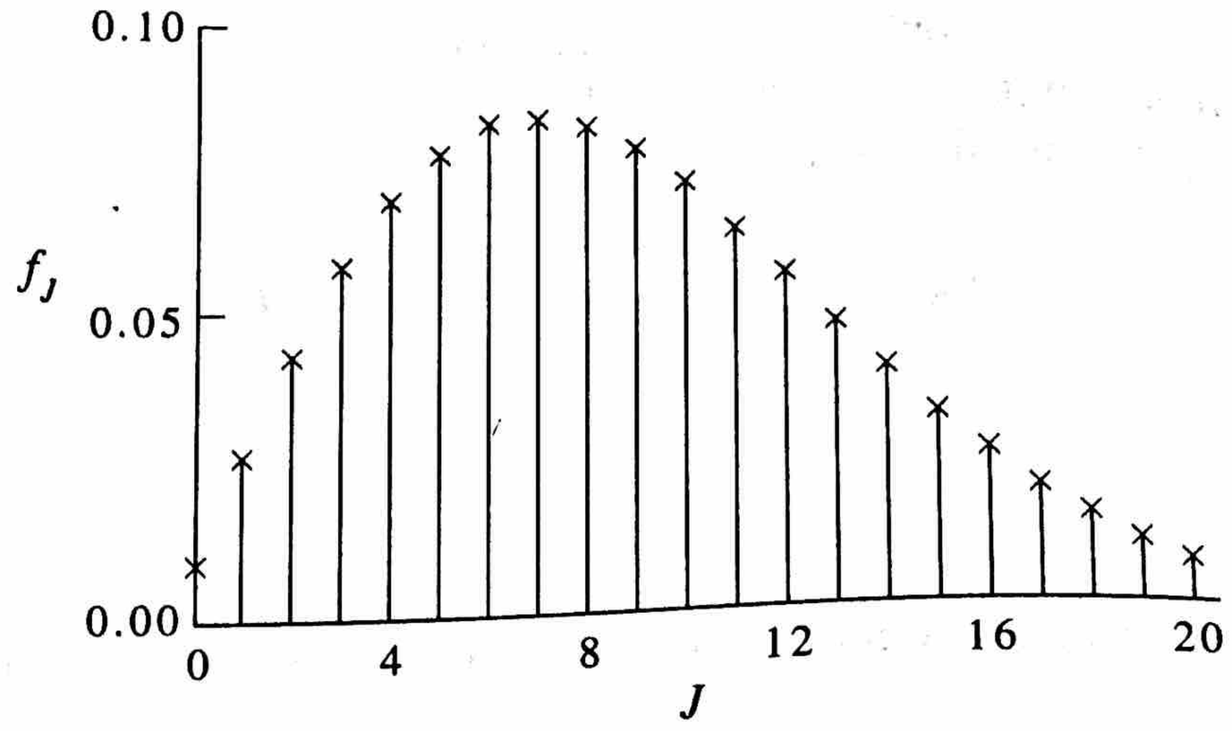


FIGURE 4.5
The fraction of molecules in the Jth rotational level for CO at 300 K.

Contrary to the case for vibrational levels, most molecules are in the excited rotational levels at ordinary temperatures. We can estimate the most probable value of J by treating Equation 4.35 as if J were continuous and by setting the derivative with respect to J equal to zero to obtain (Problem 4–18)

$$J_{mp} \approx \left(\frac{T}{2\Theta_{rot}}\right)^{1/2} - \frac{1}{2} \tag{4.36}$$

This equation gives a value of 7 for CO at 300 K (in agreement with Figure 4.5).

4–6. Rotational Partition Functions Contain a Symmetry Number

Although it is not apparent from our derivation of $q_{rot}(T)$, Equations 4.33 and 4.34 apply only to heteronuclear diatomic molecules. The underlying reason is that the wave function of a homonuclear diatomic molecule must possess a certain symmetry with respect to the interchange of the two identical nuclei in the molecule. In particular, if the two nuclei have integral spins (bosons), the molecular wave function must remain unchanged under interchange of the two nuclei; if the nuclei have half odd integer spin (fermions), the molecular wave function must change sign. This symmetry requirement has a profound effect on the population of the rotational energy levels of a homonuclear diatomic molecule, which can be understood only by a careful analysis of the general symmetry properties of the wave function of a diatomic molecule. This analysis is somewhat involved and will not be done here, but we need the final result. At temperatures such that $\Theta_{rot} \ll T$, which we have seen applies to most molecules at ordinary temperatures, q_{rot} for a homonuclear diatomic molecule is

$$q_{rot}(T) = \frac{T}{2\Theta_{rot}} \tag{4.37}$$

Note that this equation is the same as Equation 4.34 for a heteronuclear diatomic molecule except for the factor of 2 in the denominator. This factor comes from the additional symmetry of the homonuclear diatomic molecule; in particular, a homonuclear diatomic molecule has two indistinguishable orientations. There is a two-fold axis of symmetry perpendicular to the internuclear axis.

Equations 4.34 and 4.37 can be written as one equation by writing q_{rot} as

$$q_{rot}(T) = \frac{T}{\sigma \Theta_{rot}} \tag{4.38}$$

where $\sigma = 1$ for a heteronuclear diatomic molecule and 2 for a homonuclear diatomic molecule. The factor σ is called the *symmetry number* of the molecule and represents the number of indistinguishable orientations of the molecule.

Having studied each contribution to the molecular partition function of a diatomic molecule, we can now include the rigid rotator-harmonic oscillator approximation in the partition function of a diatomic molecule to obtain

$$\begin{aligned} q(V, T) &= q_{trans} q_{rot} q_{vib} q_{elec} \\ &= \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{rot}} \cdot \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \cdot g_{el} e^{D_e/k_B T} \end{aligned} \tag{4.39}$$

Remember that this expression requires that $\Theta_{rot} \ll T$, that only the ground electronic state is populated, that the zero of the electronic energy is taken to be the separated atoms at rest in their ground electronic states, and that the zero of energy for the vibrational energy is that at the bottom of the internuclear potential well of the lowest electronic state. Note that only q_{trans} is a function of V, and that this function is of the form $f(T)V$, which, as we have seen before, is responsible for the ideal-gas equation of state.

EXAMPLE 4–5

Derive an expression for the molar energy $\overline{U}$ of a diatomic ideal gas from Equation 4.39. Identify each of the terms.

SOLUTION: We start with

$$Q(N, V, T) = \frac{[q(V, T)]^N}{N!}$$

and

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = N k_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$$

Using Equation 4.39 for $q(V, T)$, we have

$$\ln q = \frac{3}{2} \ln T + \ln T - \frac{\Theta_{vib}}{2T} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{D_e}{k_B T}$$
$$+ \text{terms not containing } T$$

Therefore,

$$\left(\frac{\partial \ln q}{\partial T}\right)_V = \frac{3}{2T} + \frac{1}{T} + \frac{\Theta_{vib}}{2T^2} + \frac{(\Theta_{vib}/T^2)e^{-\Theta_{vib}/T}}{1 - e^{-\Theta_{vib}/T}} - \frac{D_e}{k_B T^2}$$

and letting $N = N_A$ and $N_A k_B = R$ for one mole,

$$\overline{U} = \frac{3}{2}RT + RT + R\frac{\Theta_{vib}}{2} + R\frac{\Theta_{vib}e^{-\Theta_{vib}/T}}{1 - e^{-\Theta_{vib}/T}} - N_A D_e \qquad (4.40)$$

The first term represents the average translational energy ($RT/2$ for each of the three translational degrees of freedom), the second term represents the average rotational energy ($RT/2$ for each of the two rotational degrees of freedom), the third term represents the zero-point vibrational energy, the fourth term represents the average vibrational energy in excess of the zero-point vibrational energy, and the last term reflects the electronic energy relative to the zero of electronic energy that we have chosen, namely the two separated atoms at rest in their ground electronic states.

The heat capacity is obtained by differentiating Equation 4.40 with respect to T:

$$\frac{\overline{C}_V}{R} = \frac{5}{2} + \left(\frac{\Theta_{vib}}{T}\right)^2 \frac{e^{-\Theta_{vib}T}}{(1 - e^{-\Theta_{vib}T})^2} \qquad (4.41)$$

Figure 3.3 presents a comparison of Equation 4.41 with experimental data for oxygen. The agreement is good and is typical of that found for other properties. The agreement can be improved considerably by including the first corrections to the rigid rotator-harmonic oscillator model. These include effects such as centrifugal distortion and anharmonicity. The consideration of these effects introduces a new set of molecular constants, all of which can be determined spectroscopically and are well tabulated. The use of such additional parameters from spectroscopic data can give calculated values of the heat capacity that are actually more accurate than calorimetric ones.

4–7. The Vibrational Partition Function of a Polyatomic Molecule Is a Product of Harmonic Oscillator Partition Functions for Each Normal Coordinate

The discussion in Section 4–3 for diatomic molecules applies equally well to polyatomic molecules, and so

$$Q(N, V, T) = \frac{[q(V, T)]^N}{N!}$$

As before, the number of translational energy states alone is sufficient to guarantee that the number of energy states available to any molecule is much greater than the number of molecules in the system.

As for diatomic molecules, we use a rigid rotator-harmonic oscillator approximation. This allows us to separate the rotational motion from the vibrational motion of the molecule, so that we can treat each one separately. Both problems are somewhat more complicated for polyatomic molecules than for diatomic molecules. Nevertheless, we can write the polyatomic analog of Equation 4.19:

$$Q(N, V, T) = \frac{(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}})^N}{N!} \tag{4.42}$$

In Equation 4.42, q_{trans} is given by

$$q_{\text{trans}}(V, T) = \left[\frac{2\pi M k_B T}{h^2}\right]^{3/2} V \tag{4.43}$$

where M is the total mass of the molecule. We choose as the zero of energy the n atoms completely separated in their ground electronic states. Thus, the energy of the ground electronic state is $-D_e$, and then the electronic partition function is

$$q_{\text{elec}} = g_{e1} e^{D_e/k_B T} + \cdots \tag{4.44}$$

To calculate $Q(N, V, T)$ we must investigate q_{rot} and q_{vib}.

We learned in Section 1–9 that the vibrational motion of a polyatomic molecule can be expressed in terms of normal coordinates. By introducing normal coordinates, the vibrational motion of a polyatomic molecule can be expressed as a set of *independent* harmonic oscillators. Consequently, the vibrational energy of a polyatomic molecule can be written as

$$\varepsilon_{\text{vib}} = \sum_{j=1}^{\alpha} \left(v_j + \tfrac{1}{2}\right) h\nu_j \qquad v_j = 0,\ 1,\ 2,\ \cdots \tag{4.45}$$

where ν_j is the vibrational frequency associated with the jth normal mode and α is the number of vibrational degrees of freedom ($3n - 5$ for a linear molecule and $3n - 6$ for a nonlinear molecule, where n is the number of atoms in the molecule). Because the normal modes are independent,

$$q_{\text{vib}} = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{\text{vib}.j}/2T}}{\left(1 - e^{-\Theta_{\text{vib}.j}/T}\right)} \tag{4.46}$$

$$E_{\text{vib}} = N k_B \sum_{j=1}^{\alpha} \left(\frac{\Theta_{\text{vib}.j}}{2} + \frac{\Theta_{\text{vib}.j} e^{-\Theta_{\text{vib}.j}/T}}{1 - e^{-\Theta_{\text{vib}.j}/T}}\right) \tag{4.47}$$

and

$$C_{V,\text{vib}} = N k_B \sum_{j=1}^{\alpha} \left[\left(\frac{\Theta_{\text{vib}.j}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}.j}/T}}{(1 - e^{-\Theta_{\text{vib}.j}/T})^2}\right] \tag{4.48}$$

where $\Theta_{\text{vib},j}$ is a characteristic vibrational temperature defined by

$$\Theta_{\text{vib},j} = \frac{h\nu_j}{k_B} \tag{4.49}$$

Table 4.4 contains values of $\Theta_{\text{vib},j}$ for several polyatomic molecules.

TABLE 4.4
Values of the characteristic rotational temperatures, the characteristic vibrational temperatures, D_0 for the ground state, and the symmetry number, σ, for some polyatomic molecules. The numbers in parentheses indicate the degeneracy of that mode.

Molecule	Θ_{rot}/K	$\Theta_{\text{vib},j}$/K	D_0/kJ·mol^{-1}	σ
CO_2	0.561	3360, 954(2), 1890	1596	2
H_2O	40.1, 20.9, 13.4	5360, 5160, 2290	917.6	2
NH_3	13.6, 13.6, 8.92	4800, 1360, 4880(2), 2330(2)	1158	3
ClO_2	2.50, 0.478, 0.400	1360, 640, 1600	378	2
SO_2	2.92, 0.495, 0.422	1660, 750, 1960	1063	2
N_2O	0.603	3200, 850(2), 1840	1104	2
NO_2	11.5, 0.624, 0.590	1900, 1080, 2330	928.0	2
CH_4	7.54, 7.54, 7.54	4170, 2180(2), 4320(3), 1870(3)	1642	12
CH_3Cl	7.32, 0.637, 0.637	4270, 1950, 1050, 4380(2) 2140(2), 1460(2)	1551	3
CCl_4	0.0823, 0.0823, 0.0823	660, 310(2), 1120(3), 450(3)	1292	12

EXAMPLE 4–6
Calculate the contribution of each normal mode to the vibrational heat capacity of CO_2 at 400 K.

SOLUTION: The values of $\Theta_{\text{vib},j}$ are given in Table 4.4. Note that the $\Theta_{\text{vib}} = 954$ K mode (bending mode) is doubly degenerate. For $\Theta_{\text{vib},j} = 954$ K (the doubly degerate bending mode),

$$\frac{\overline{C}_{v,j}}{R} = \left(\frac{954}{400}\right)^2 \frac{e^{-954/400}}{(1-e^{-954/400})^2} = 0.635$$

For $\Theta_{\text{vib},j} = 1890$ K (the asymmetric stretch),

$$\frac{\overline{C}_{v,j}}{R} = \left(\frac{1890}{400}\right)^2 \frac{e^{-1890/400}}{(1-e^{-1890/400})^2} = 0.202$$

For $\Theta_{\text{vib},j} = 3360$ K (the symmetric stretch),

$$\frac{\overline{C}_{V,j}}{R} = \left(\frac{3360}{400}\right)^2 \frac{e^{-3360/400}}{(1 - e^{-3360/400})^2} = 0.016$$

The total vibrational heat capacity at 400 K is

$$\frac{\overline{C}_{V,\text{vib}}}{R} = 2(0.635) + 0.202 + 0.016 = 1.488$$

Note that the contribution from each mode decreases as $\Theta_{\text{vib},j}$ increases. Because $\Theta_{\text{vib},j}$ is proportional to the frequency of the mode, it requires higher temperatures to excite modes with larger values of $\Theta_{\text{vib},j}$. The molar vibrational heat capacity from 200 K to 2000 K contributed by each mode is shown in Figure 4.6.

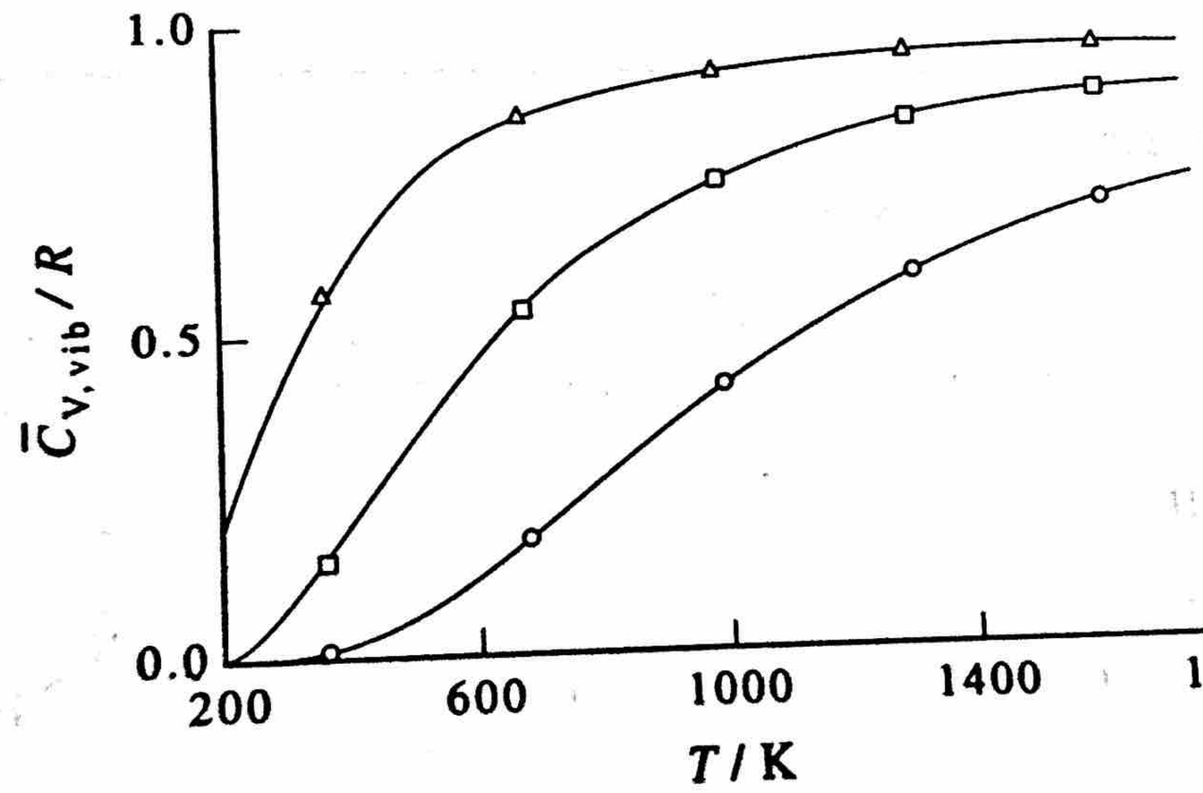


FIGURE 4.6
The contribution of each normal mode to the molar vibrational heat capacity of CO_2. The curve indicated by triangles corresponds to $\Theta_{\text{vib},j} = 954$ K; the curve indicated by squares to $\Theta_{\text{vib},j} = 1890$ K; and the curve indicated by circles to $\Theta_{\text{vib},j} = 3360$ K. Note that modes with smaller values of $\Theta_{\text{vib},j}$, or ν_j, contribute more at a given temperature.

4–8. The Form of the Rotational Partition Function of a Polyatomic Molecule Depends Upon the Shape of the Molecule

In this section, we will discuss the rotational partition functions of polyatomic molecules. Let's consider a linear polyatomic molecule first. In the rigid-rotator approximation, the energies and degeneracies of a linear polyatomic molecule are the same as for

a diatomic molecule, $\varepsilon_J = J(J+1)h^2/8\pi^2 I$ with $J = 0, 1, 2, \ldots$ and $g_J = 2J + 1$. In this case, the moment of inertia I is

$$I = \sum_{j=1}^{n} m_j d_j^2$$

where d_j is the distance of the jth nucleus from the center of mass of the molecule. Consequently, the rotational partition function of a linear polyatomic molecule is the same as that of a diatomic molecule, namely,

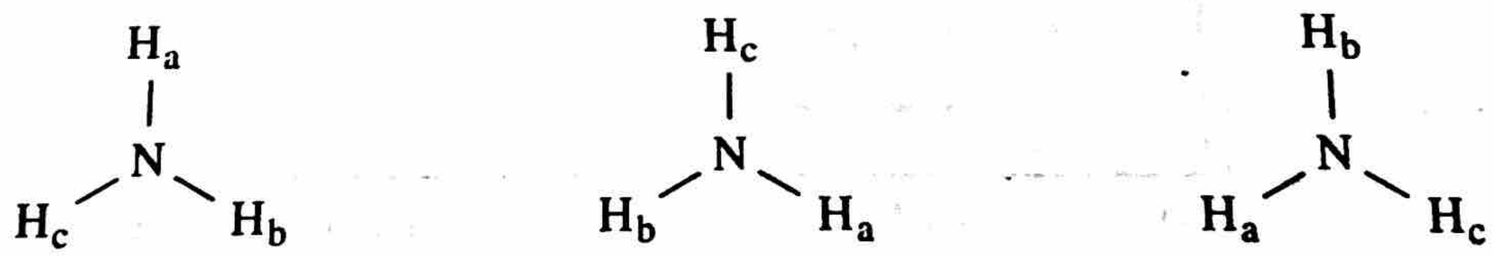
$$q_{\text{rot}} = \frac{8\pi^2 I k_B T}{\sigma h^2} = \frac{T}{\sigma \Theta_{\text{rot}}} \tag{4.50}$$

As before, we have introduced a symmetry number, which is unity for unsymmetrical molecules such as N_2O and COS and equal to two for symmetrical molecules such as CO_2 and C_2H_2. Recall that the symmetry number is the number of different ways the molecule can be rotated into a configuration indistinguishable from the original.

EXAMPLE 4–7

What is the symmetry number of ammonia, NH_3?

SOLUTION: Ammonia is a trigonal pyramidal molecule and has the three indistinguishable orientations shown below looking down the three-fold axis of symmetry.



Therefore, the symmetry number is three.

In Section 1–10, we learned that the rotational properties of nonlinear polyatomic molecules depend upon the relative magnitudes of their moments of inertia. If all three moments of inertia are equal, the molecule is called a *spherical top*. If two of the three are equal, the molecule is called a *symmetric top*. If all three are different, the molecule is called an *asymmetric top*. Just as we defined a characteristic rotational temperature of a diatomic molecule by Equation 4.32, $\Theta_{\text{rot}} = \hbar^2/2Ik_B$, we define three characteristic rotational temperatures in terms of the three moments of inertia according to

$$\Theta_{\text{rot},j} = \frac{\hbar^2}{2I_j k_B} \qquad j = \text{A, B, C} \tag{4.51}$$

Thus, we have the various cases

$$\Theta_{\text{rot,A}} = \Theta_{\text{rot,B}} = \Theta_{\text{rot,C}} \qquad \text{spherical top}$$

$$\Theta_{\text{rot,A}} = \Theta_{\text{rot,B}} \neq \Theta_{\text{rot,C}} \qquad \text{symmetric top}$$

$$\Theta_{\text{rot,A}} \neq \Theta_{\text{rot,B}} \neq \Theta_{\text{rot,C}} \qquad \text{asymmetric top}$$

The quantum-mechanical problem of a spherical top can be solved exactly to give

$$\begin{aligned} \varepsilon_J &= \frac{J(J+1)\hbar^2}{2I} \\ g_J &= (2J+1)^2 \qquad J = 0,\ 1,\ 2,\ \ldots \end{aligned} \tag{4.52}$$

The rotational partition function is

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)^2 e^{-\hbar^2 J(J+1)/2Ik_B T} \tag{4.53}$$

For almost all spherical top molecules $\Theta_{\text{rot}} \ll T$ at ordinary temperatures, so we convert the sum in Equation 4.53 to an integral:

$$q_{\text{rot}}(T) = \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{-\Theta_{\text{rot}} J(J+1)/T}\, dJ$$

Note that we have included the symmetry number σ. For $\Theta_{\text{rot}} \ll T$, the most important values of J are large (Problem 4–26), and so we may neglect 1 compared with J in the integrand of the above expression for q_{rot} to obtain

$$q_{\text{rot}}(T) = \frac{1}{\sigma} \int_0^{\infty} 4J^2 e^{-\Theta_{\text{rot}} J^2/T}\, dJ$$

If we let $\Theta_{\text{rot}}/T = a$, we can write

$$\begin{aligned} q_{\text{rot}}(T) &= \frac{4}{\sigma} \int_0^{\infty} x^2 e^{-ax^2}\, dx \\ &= \frac{4}{\sigma} \cdot \frac{1}{4a} \left(\frac{\pi}{a}\right)^{1/2} \end{aligned}$$

or, upon substituting Θ_{rot}/T for a,

$$q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{\Theta_{\text{rot}}}\right)^{3/2} \qquad \text{spherical top} \tag{4.54}$$

The corresponding expressions for a symmetric top and an asymmetric top are

$$q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{\Theta_{\text{rot,A}}}\right) \left(\frac{T}{\Theta_{\text{rot,C}}}\right)^{1/2} \qquad \text{symmetric top} \tag{4.55}$$

and

$$q_{\text{rot}}(T) = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_{\text{rot,A}}\Theta_{\text{rot,B}}\Theta_{\text{rot,C}}}\right)^{1/2} \quad \text{asymmetric top} \tag{4.56}$$

Notice how Equation 4.56 reduces to Equation 4.55 when $\Theta_{\text{rot,A}} = \Theta_{\text{rot,B}}$ and how both Equations 4.55 and 4.56 reduce to Equation 4.54 when $\Theta_{\text{rot,A}} = \Theta_{\text{rot,B}} = \Theta_{\text{rot,C}}$. Table 4.4 contains values of $\Theta_{\text{rot,A}}$, $\Theta_{\text{rot,B}}$, and $\Theta_{\text{rot,C}}$ for several polyatomic molecules.

The average molar rotational energy of a nonlinear polyatomic molecule is

$$\overline{U}_{\text{rot}} = N_{\text{A}}k_{\text{B}}T^2\left(\frac{d\ln q_{\text{rot}}(T)}{dT}\right)$$

$$= RT^2\left(\frac{d\ln T^{3/2}}{dT}\right) = \frac{3RT}{2}$$

or $RT/2$ for each rotational degree of freedom, and $\overline{C}_{V,\text{rot}} = 3R/2$.

4–9. Calculated Molar Heat Capacities Are in Very Good Agreement with Experimental Data

We can now use the results of Sections 4–7 and 4–8 to construct $q(V, T)$ for polyatomic molecules. For an ideal gas of linear polyatomic molecules, $q(V, T)$ is the product of Equations 4.43, 4.44, 4.46, and 4.50:

$$q(V,T) = \left(\frac{2\pi Mk_{\text{B}}T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{\text{rot}}} \cdot \left(\prod_{j=1}^{3n-5}\frac{e^{-\Theta_{\text{vib},j}/2T}}{1-e^{-\Theta_{\text{vib},j}/T}}\right) \cdot g_{e1}e^{D_e/k_{\text{B}}T} \tag{4.57}$$

The energy is

$$\frac{U}{Nk_{\text{B}}T} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5}\left(\frac{\Theta_{\text{vib},j}}{2T} + \frac{\Theta_{\text{vib},j}/T}{e^{\Theta_{\text{vib},j}/T}-1}\right) - \frac{D_e}{k_{\text{B}}T} \tag{4.58}$$

and the heat capacity is

$$\frac{C_V}{Nk_{\text{B}}} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5}\left(\frac{\Theta_{\text{vib},j}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{(1-e^{-\Theta_{\text{vib},j}/T})^2} \tag{4.59}$$

For an ideal gas of nonlinear polyatomic molecules,

$$q(V,T) = \left(\frac{2\pi Mk_{\text{B}}T}{h^2}\right)^{3/2} V \cdot \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_{\text{rot,A}}\Theta_{\text{rot,B}}\Theta_{\text{rot,C}}}\right)^{1/2}$$

$$\times\left[\prod_{j=1}^{3n-6}\frac{e^{-\Theta_{\text{vib},j}/2T}}{(1-e^{-\Theta_{\text{vib},j}/T})}\right] \cdot g_{e1}e^{D_e/k_{\text{B}}T} \tag{4.60}$$

$$\frac{U}{Nk_B T} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left(\frac{\Theta_{\text{vib},j}}{2T} + \frac{\Theta_{\text{vib},j}/T}{e^{\Theta_{\text{vib},j}/T} - 1} \right) - \frac{D_e}{k_B T} \qquad (4.61)$$

and

$$\frac{C_V}{Nk_B} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left(\frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{(1 - e^{-\Theta_{\text{vib},j}/T})^2} \qquad (4.62)$$

EXAMPLE 4–8

Calculate the molar heat capacity of gaseous water at 300 K.

SOLUTION: We use Equation 4.62 with $\Theta_{\text{vib},j} = 2290$ K, 5160 K, and 5360 K (Table 4.4). For $\Theta_{\text{vib},j} = 2290$ K,

$$\frac{\overline{C}_{V,j}}{R} = \left(\frac{2290}{300} \right)^2 \frac{e^{2290/300}}{(e^{2290/300} - 1)^2} = 0.0282$$

Similarly $\overline{C}_{V,j}/R = 1.00 \times 10^{-5}$ for $\Theta_{\text{vib},j} = 5160$ K and 5.56×10^{-6} for $\Theta_{\text{vib},j} = 5360$ K. The total molar heat capacity of water at 300 K is

$$\frac{\overline{C}_V}{R} = 3.000 + 0.0282 + 1.00 \times 10^{-5} + 5.56 \times 10^{-6} = 3.028$$

The experimental value is 3.011. Notice that the vibrational degrees of freedom contribute very little to the heat capacity of water at 300 K. The calculated and experimental values at 1000 K are 3.948 and 3.952, respectively. Figure 4.7 shows the molar heat capacity of water from 300 K to 1200 K.

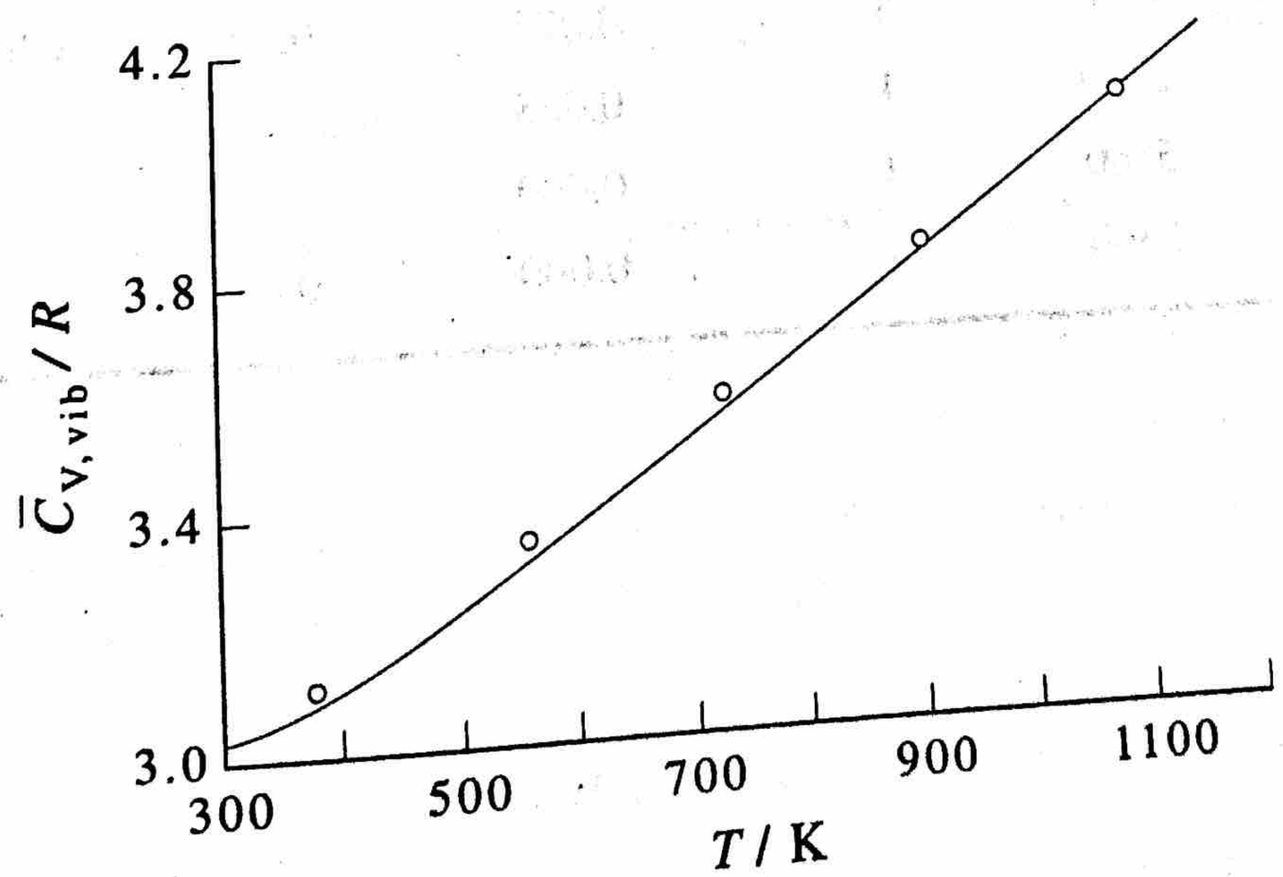


FIGURE 4.7
A comparison of the molar heat capacity of water vapor calculated from Equation 4.62 and the experimental value. The experimental data are indicated by the circles.

Table 4.5 gives the vibrational contribution to the molar heat capacity at 300 K for a variety of molecules of different shapes. It can be seen that the vibrational contributions are far from their high-temperature limits and that the agreement between the calculated and experimental values of $\overline{C}_V/R$ is good. A calculation for more complicated molecules would show similar agreement between the calculated values and the experimental data.

TABLE 4.5
Vibrational contributions to the molar heat capacity of some polyatomic molecules at 300 K.

Molecule	Θ_{vib}/K	Degeneracy	Vibrational Contribution to $\overline{C}_V$	$\overline{C}_{V,vib}/R$	Total $\overline{C}_V/R$ (calc)	Total $\overline{C}_V/R$ (exptl)
CO_2	1890	1	0.073			
	3360	1	0.000			
	954	2	0.458	0.99	3.49	3.46
N_2O	1840	1	0.082			
	3200	1	0.003			
	850	2	0.533	1.15	2.65	
NH_3	4800	1	0.000			
	1360	1	0.226			
	4880	2	0.000			
	2330	2	0.026	0.28	3.28	
CH_4	4170	1	0.000			
	2180	2	0.037			
	4320	3	0.000			
	1870	3	0.077	0.30	3.30	3.29
H_2O	2290	1	0.028			
	5160	1	0.000			
	5360	1	0.000	0.03	3.03	3.01