

# Statistical thermodynamics 2: applications

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In this chapter we apply the concepts of statistical thermodynamics to the calculation of chemically significant quantities. First, we establish the relations between thermodynamic functions and partition functions. Next, we show that the molecular partition function can be factorized into contributions from each mode of motion and establish the formulas for the partition functions for translational, rotational, and vibrational modes of motion and the contribution of electronic excitation. These contributions can be calculated from spectroscopic data. Finally, we turn to specific applications, which include the mean energies of modes of motion, the heat capacities of substances, and residual entropies. In the final section, we see how to calculate the equilibrium constant of a reaction and through that calculation understand some of the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.

A partition function is the bridge between thermodynamics, spectroscopy, and quantum mechanics. Once it is known, a partition function can be used to calculate thermodynamic functions, heat capacities, entropies, and equilibrium constants. It also sheds light on the significance of these properties.

## Fundamental relations

In this section we see how to obtain any thermodynamic function once we know the partition function. Then we see how to calculate the molecular partition function, and through that the thermodynamic functions, from spectroscopic data.

### 17.1 The thermodynamic functions

We have already derived (in Chapter 16) the two expressions for calculating the internal energy and the entropy of a system from its canonical partition function,  $Q$ :

$$U - U(0) = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V \quad S = \frac{U - U(0)}{T} + k \ln Q \quad (17.1)$$

where  $\beta = 1/kT$ . If the molecules are independent, we can go on to make the substitutions  $Q = q^N$  (for distinguishable molecules, as in a solid) or  $Q = q^N/N!$  (for indistinguishable molecules, as in a gas). All the thermodynamic functions introduced in Part 1 are related to  $U$  and  $S$ , so we have a route to their calculation from  $Q$ .

## Fundamental relations

### 17.1 The thermodynamic functions

### 17.2 The molecular partition function

## Using statistical thermodynamics

### 17.3 Mean energies

### 17.4 Heat capacities

### 17.5 Equations of state

### 17.6 Molecular interactions in liquids

### 17.7 Residual entropies

### 17.8 Equilibrium constants

Checklist of key ideas

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Problems

**(a) The Helmholtz energy**

The Helmholtz energy,  $A$ , is defined as  $A = U - TS$ . This relation implies that  $A(0) = U(0)$ , so substitution for  $U$  and  $S$  by using eqn 17.1 leads to the very simple expression

$$A - A(0) = -kT \ln Q \quad (17.2)$$

**(b) The pressure**

By an argument like that leading to eqn 3.31, it follows from  $A = U - TS$  that  $dA = -pdV - SdT$ . Therefore, on imposing constant temperature, the pressure and the Helmholtz energy are related by  $p = -(\partial A / \partial V)_T$ . It then follows from eqn 17.2 that

$$p = kT \left( \frac{\partial \ln Q}{\partial V} \right)_T \quad (17.3)$$

This relation is entirely general, and may be used for any type of substance, including perfect gases, real gases, and liquids. Because  $Q$  is in general a function of the volume, temperature, and amount of substance, eqn 17.3 is an equation of state.

**Example 17.1** *Deriving an equation of state*

Derive an expression for the pressure of a gas of independent particles.

**Method** We should suspect that the pressure is that given by the perfect gas law. To proceed systematically, substitute the explicit formula for  $Q$  for a gas of independent, indistinguishable molecules (see eqn 16.45 and Table 17.3 at the end of the chapter) into eqn 17.3.

**Answer** For a gas of independent molecules,  $Q = q^N / N!$  with  $q = V/\Lambda^3$ :

$$\begin{aligned} p &= kT \left( \frac{\partial \ln Q}{\partial V} \right)_T = \frac{kT}{Q} \left( \frac{\partial Q}{\partial V} \right)_T = \frac{NkT}{q} \left( \frac{\partial q}{\partial V} \right)_T \\ &= \frac{NkT\Lambda^3}{V} \times \frac{1}{\Lambda^3} = \frac{NkT}{V} = \frac{nRT}{V} \end{aligned}$$

To derive this relation, we have used

$$\left( \frac{\partial q}{\partial V} \right)_T = \left( \frac{\partial (V/\Lambda^3)}{\partial V} \right)_T = \frac{1}{\Lambda^3}$$

and  $NkT = nN_A kT = nRT$ . The calculation shows that the equation of state of a gas of independent particles is indeed the perfect gas law.

**Self-test 17.1** Derive the equation of state of a sample for which  $Q = q^N f / N!$ , with  $q = V/\Lambda^3$ , where  $f$  depends on the volume.  $[p = nRT/V + kT(\partial \ln f / \partial V)_T]$

**(c) The enthalpy**

At this stage we can use the expressions for  $U$  and  $p$  in the definition  $H = U + pV$  to obtain an expression for the enthalpy,  $H$ , of any substance:

$$H - H(0) = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T \quad (17.4)$$

We have already seen that  $U - U(0) = \frac{3}{2}nRT$  for a gas of independent particles (eqn 16.32a), and have just shown that  $pV = nRT$ . Therefore, for such a gas,

$$H - H(0) = \frac{5}{2}nRT \quad (17.5)^\circ$$

#### (d) The Gibbs energy

One of the most important thermodynamic functions for chemistry is the Gibbs energy,  $G = H - TS = A + pV$ . We can now express this function in terms of the partition function by combining the expressions for  $A$  and  $p$ :

$$G - G(0) = -kT \ln Q + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T \quad (17.6)$$

This expression takes a simple form for a gas of independent molecules because  $pV$  in the expression  $G = A + pV$  can be replaced by  $nRT$ :

$$G - G(0) = -kT \ln Q + nRT \quad (17.7)^\circ$$

Furthermore, because  $Q = q^N/N!$ , and therefore  $\ln Q = N \ln q - \ln N!$ , it follows by using Stirling's approximation ( $\ln N! \approx N \ln N - N$ ) that we can write

$$\begin{aligned} G - G(0) &= -NkT \ln q + kT \ln N! + nRT \\ &= -nRT \ln q + kT(N \ln N - N) + nRT \\ &= -nRT \ln \frac{q}{N} \end{aligned} \quad (17.8)^\circ$$

with  $N = nN_A$ . Now we see another interpretation of the Gibbs energy: it is proportional to the logarithm of the average number of thermally accessible states per molecule.

It will turn out to be convenient to define the **molar partition function**,  $q_m = q/n$  (with units  $\text{mol}^{-1}$ ), for then

$$G - G(0) = -nRT \ln \frac{q_m}{N_A} \quad (17.9)^\circ$$

## 17.2 The molecular partition function

The energy of a molecule is the sum of contributions from its different modes of motion:

$$\varepsilon_i = \varepsilon_i^T + \varepsilon_i^R + \varepsilon_i^V + \varepsilon_i^E \quad (17.10)$$

where T denotes translation, R rotation, V vibration, and E the electronic contribution. The electronic contribution is not actually a 'mode of motion', but it is convenient to include it here. The separation of terms in eqn 17.10 is only approximate (except for translation) because the modes are not completely independent, but in most cases it is satisfactory. The separation of the electronic and vibrational motions is justified provided only the ground electronic state is occupied (for otherwise the vibrational characteristics depend on the electronic state) and, for the electronic ground state, that the Born–Oppenheimer approximation is valid (Chapter 11). The separation of the vibrational and rotational modes is justified to the extent that the rotational constant is independent of the vibrational state.

Given that the energy is a sum of independent contributions, the partition function factorizes into a product of contributions (recall Section 16.2b):

$$\begin{aligned}
q &= \sum_i e^{-\beta \epsilon_i} = \sum_{i \text{ (all states)}} e^{-\beta \epsilon_i^T - \beta \epsilon_i^R - \beta \epsilon_i^V - \beta \epsilon_i^E} \\
&= \sum_{i \text{ (translational)}} \sum_{i \text{ (rotational)}} \sum_{i \text{ (vibrational)}} \sum_{i \text{ (electronic)}} e^{-\beta \epsilon_i^T - \beta \epsilon_i^R - \beta \epsilon_i^V - \beta \epsilon_i^E} \\
&= \left( \sum_{i \text{ (translational)}} e^{-\beta \epsilon_i^T} \right) \left( \sum_{i \text{ (rotational)}} e^{-\beta \epsilon_i^R} \right) \left( \sum_{i \text{ (vibrational)}} e^{-\beta \epsilon_i^V} \right) \left( \sum_{i \text{ (electronic)}} e^{-\beta \epsilon_i^E} \right) \\
&= q^T q^R q^V q^E
\end{aligned} \tag{17.11}$$

This factorization means that we can investigate each contribution separately.

### (a) The translational contribution

The translational partition function of a molecule of mass  $m$  in a container of volume  $V$  was derived in Section 16.2:

$$q^T = \frac{V}{\Lambda^3} \quad \Lambda = h \left( \frac{\beta}{2\pi m} \right)^{1/2} = \frac{h}{(2\pi mkT)^{1/2}} \tag{17.12}$$

Notice that  $q^T \rightarrow \infty$  as  $T \rightarrow \infty$  because an infinite number of states becomes accessible as the temperature is raised. Even at room temperature  $q^T \approx 2 \times 10^{28}$  for an  $O_2$  molecule in a vessel of volume  $100 \text{ cm}^3$ .

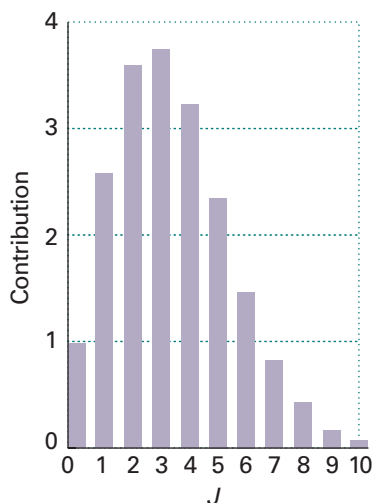
The thermal wavelength,  $\Lambda$ , lets us judge whether the approximations that led to the expression for  $q^T$  are valid. The approximations are valid if many states are occupied, which requires  $V/\Lambda^3$  to be large. That will be so if  $\Lambda$  is small compared with the linear dimensions of the container. For  $H_2$  at  $25^\circ\text{C}$ ,  $\Lambda = 71 \text{ pm}$ , which is far smaller than any conventional container is likely to be (but comparable to pores in zeolites or cavities in clathrates). For  $O_2$ , a heavier molecule,  $\Lambda = 18 \text{ pm}$ . We saw in Section 16.2 that an equivalent criterion of validity is that  $\Lambda$  should be much less than the average separation of the molecules in the sample.

### (b) The rotational contribution

As demonstrated in Example 16.1, the partition function of a nonsymmetrical (AB) linear rotor is

$$q^R = \sum_J (2J+1) e^{-\beta h c B J(J+1)} \tag{17.13}$$

The direct method of calculating  $q^R$  is to substitute the experimental values of the rotational energy levels into this expression and to sum the series numerically.



**Fig. 17.1** The contributions to the rotational partition function of an HCl molecule at  $25^\circ\text{C}$ . The vertical axis is the value of  $(2J+1)e^{-\beta h c B J(J+1)}$ . Successive terms (which are proportional to the populations of the levels) pass through a maximum because the population of individual states decreases exponentially, but the degeneracy of the levels increases with  $J$ .

### Example 17.2 Evaluating the rotational partition function explicitly

Evaluate the rotational partition function of  $^1\text{H}^{35}\text{Cl}$  at  $25^\circ\text{C}$ , given that  $B = 10.591 \text{ cm}^{-1}$ .

**Method** We use eqn 17.13 and evaluate it term by term. A useful relation is  $kT/hc = 207.22 \text{ cm}^{-1}$  at  $298.15 \text{ K}$ . The sum is readily evaluated by using mathematical software.

**Answer** To show how successive terms contribute, we draw up the following table by using  $kT/hcB = 0.05111$  (Fig. 17.1):

$J$	0	1	2	3	4	...	10
$(2J+1)e^{-0.05111J(J+1)}$	1	2.71	3.68	3.79	3.24	...	0.08

The sum required by eqn 17.13 (the sum of the numbers in the second row of the table) is 19.9, hence  $q^R = 19.9$  at this temperature. Taking  $J$  up to 50 gives  $q^R = 19.902$ . Notice that about ten  $J$ -levels are significantly populated but the number of populated *states* is larger on account of the  $(2J + 1)$ -fold degeneracy of each level. We shall shortly encounter the approximation that  $q^R \approx kT/hcB$ , which in the present case gives  $q^R = 19.6$ , in good agreement with the exact value and with much less work.

**Self-test 17.2** Evaluate the rotational partition function for HCl at 0°C. [18.26]

At room temperature  $kT/hc \approx 200 \text{ cm}^{-1}$ . The rotational constants of many molecules are close to  $1 \text{ cm}^{-1}$  (Table 13.2) and often smaller (though the very light  $\text{H}_2$  molecule, for which  $B = 60.9 \text{ cm}^{-1}$ , is one exception). It follows that many rotational levels are populated at normal temperatures. When this is the case, the partition function may be approximated by

$$\text{Linear rotors:} \quad q^R = \frac{kT}{hcB} \quad (17.14a)$$

$$\text{Nonlinear rotors:} \quad q^R = \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{ABC} \right)^{1/2} \quad (17.14b)$$

where  $A$ ,  $B$ , and  $C$  are the rotational constants of the molecule. However, before using these expressions, read on (to eqns 17.15 and 17.16).

**Justification 17.1** *The rotational contribution to the molecular partition function*

When many rotational states are occupied and  $kT$  is much larger than the separation between neighbouring states, the sum in the partition function can be approximated by an integral, much as we did for translational motion in *Justification 16.2*:

$$q^R = \int_0^\infty (2J + 1) e^{-\beta hc B J(J+1)} dJ$$

Although this integral looks complicated, it can be evaluated without much effort by noticing that because

$$\frac{d}{dJ} e^{aJ(J+1)} = \left\{ \frac{d}{dJ} aJ(J+1) \right\} e^{aJ(J+1)} = a(2J+1) e^{aJ(J+1)}$$

it can also be written as

$$q^R = \frac{1}{\beta hc B} \int_0^\infty \left( \frac{d}{dJ} e^{-\beta hc B J(J+1)} \right) dJ$$

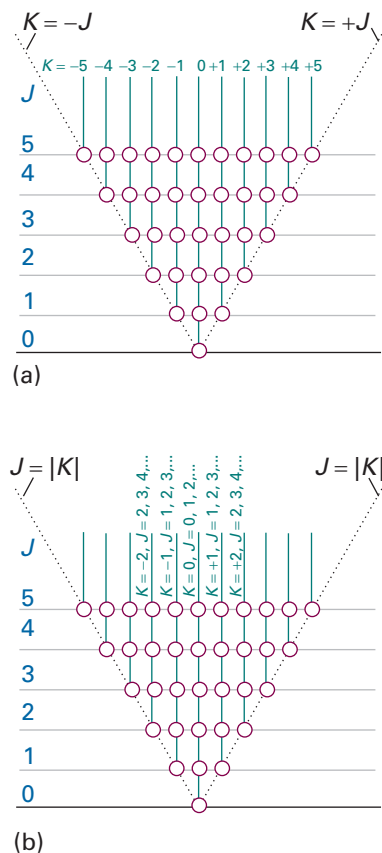
Then, because the integral of a derivative of a function is the function itself, we obtain

$$q^R = -\frac{1}{\beta hc B} e^{-\beta hc B J(J+1)} \Big|_0^\infty = \frac{1}{\beta hc B}$$

which (because  $\beta = 1/kT$ ) is eqn 17.14a.

The calculation for a nonlinear molecule is along the same lines, but slightly trickier. First, we note that the energies of a symmetric rotor are

$$E_{J,K,M_J} = hc B J(J+1) + hc(A-B)K^2$$



**Fig. 17.2** (a) The sum over  $J = 0, 1, 2, \dots$  and  $K = J, J-1, \dots, -J$  (depicted by the circles) can be covered (b) by allowing  $K$  to range from  $-\infty$  to  $\infty$ , with  $J$  confined to  $|K|, |K|+1, \dots, \infty$  for each value of  $K$ .

with  $J = 0, 1, 2, \dots, K = J, J-1, \dots, -J$ , and  $M_J = J, J-1, \dots, -J$ . Instead of considering these ranges, we can cover the same values by allowing  $K$  to range from  $-\infty$  to  $\infty$ , with  $J$  confined to  $|K|, |K|+1, \dots, \infty$  for each value of  $K$  (Fig. 17.2). Because the energy is independent of  $M_J$ , and there are  $2J+1$  values of  $M_J$  for each value of  $J$ , each value of  $J$  is  $2J+1$ -fold degenerate. It follows that the partition function

$$q = \sum_{J=0}^{\infty} \sum_{K=-J}^J \sum_{M_J=-J}^J e^{-E_{JKM_J}/kT}$$

can be written equivalently as

$$\begin{aligned} q &= \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-E_{JKM_J}/kT} \\ &= \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-hc\{BJ(J+1)+(A-B)K^2\}/kT} \\ &= \sum_{K=-\infty}^{\infty} e^{-\{hc(A-B)/kT\}K^2} \sum_{J=|K|}^{\infty} (2J+1) e^{-hcBJ(J+1)/kT} \end{aligned}$$

Now we assume that the temperature is so high that numerous states are occupied and that the sums may be approximated by integrals. Then

$$q = \int_{-\infty}^{\infty} e^{-\{hc(A-B)/kT\}K^2} \int_{|K|}^{\infty} (2J+1) e^{-hcBJ(J+1)/kT} dJ dK$$

As before, the integral over  $J$  can be recognized as the integral of the derivative of a function, which is the function itself, so

$$\begin{aligned} \int_{|K|}^{\infty} (2J+1) e^{-hcBJ(J+1)/kT} dJ &= \int_{|K|}^{\infty} \left( -\frac{kT}{hcB} \right) \frac{d}{dJ} e^{-hcBJ(J+1)/kT} dJ \\ &= \left( -\frac{kT}{hcB} \right) e^{-hcBJ(J+1)/kT} \Big|_{|K|}^{\infty} = \left( \frac{kT}{hcB} \right) e^{-hcB|K|(|K|+1)/kT} \\ &\approx \left( \frac{kT}{hcB} \right) e^{-hcBK^2/kT} \end{aligned}$$

In the last line we have supposed that  $|K| \gg 1$  for most contributions. Now we can write

$$\begin{aligned} q &= \frac{kT}{hcB} \int_{-\infty}^{\infty} e^{-\{hc(A-B)/kT\}K^2} e^{-hcBK^2/kT} dK \\ &= \frac{kT}{hcB} \int_{-\infty}^{\infty} e^{-\{hcA/kT\}K^2} dK = \left( \frac{kT}{hcB} \right) \left( \frac{kT}{hcA} \right)^{1/2} \int_{-\infty}^{\infty} e^{-x^2} dx \\ &= \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{AB^2} \right)^{1/2} \end{aligned}$$

For an asymmetric rotor, one of the  $B$ s is replaced by  $C$ , to give eqn 17.14b.

**Synoptic table 17.1\*** Rotational and vibrational temperatures

Molecule	Mode	$\theta_V/K$	$\theta_R/K$
H <sub>2</sub>		6330	88
HCl		4300	9.4
I <sub>2</sub>		309	0.053
CO <sub>2</sub>	$\nu_1$	1997	0.561
	$\nu_2$	3380	
	$\nu_3$	960	

\* For more values, see Table 13.2 in the *Data section* and use  $hc/k = 1.439$  K cm.

A useful way of expressing the temperature above which the rotational approximation is valid is to introduce the **characteristic rotational temperature**,  $\theta_R = hcB/k$ . Then 'high temperature' means  $T \gg \theta_R$  and under these conditions the rotational partition function of a linear molecule is simply  $T/\theta_R$ . Some typical values of  $\theta_R$  are shown in Table 17.1. The value for H<sub>2</sub> is abnormally high and we must be careful with the approximation for this molecule.

The general conclusion at this stage is that molecules with large moments of inertia (and hence small rotational constants and low characteristic rotational temperatures) have large rotational partition functions. The large value of  $q^R$  reflects the closeness in energy (compared with  $kT$ ) of the rotational levels in large, heavy molecules, and the large number of them that are accessible at normal temperatures.

We must take care, however, not to include too many rotational states in the sum. For a homonuclear diatomic molecule or a symmetrical linear molecule (such as  $\text{CO}_2$  or  $\text{HC}\equiv\text{CH}$ ), a rotation through  $180^\circ$  results in an indistinguishable state of the molecule. Hence, the number of thermally accessible states is only half the number that can be occupied by a heteronuclear diatomic molecule, where rotation through  $180^\circ$  does result in a distinguishable state. Therefore, for a symmetrical linear molecule,

$$q^R = \frac{kT}{2hcB} = \frac{T}{2\theta_R} \quad (17.15a)$$

The equations for symmetrical and nonsymmetrical molecules can be combined into a single expression by introducing the **symmetry number**,  $\sigma$ , which is the number of indistinguishable orientations of the molecule. Then

$$q^R = \frac{kT}{\sigma hcB} = \frac{T}{\sigma\theta_R} \quad (17.15b)$$

For a heteronuclear diatomic molecule  $\sigma = 1$ ; for a homonuclear diatomic molecule or a symmetrical linear molecule,  $\sigma = 2$ .

#### Justification 17.2 The origin of the symmetry number

The quantum mechanical origin of the symmetry number is the Pauli principle, which forbids the occupation of certain states. We saw in Section 13.8, for example, that  $\text{H}_2$  may occupy rotational states with even  $J$  only if its nuclear spins are paired (*para*-hydrogen), and odd  $J$  states only if its nuclear spins are parallel (*ortho*-hydrogen). There are three states of *ortho*- $\text{H}_2$  to each value of  $J$  (because there are three parallel spin states of the two nuclei).

To set up the rotational partition function we note that ‘ordinary’ molecular hydrogen is a mixture of one part *para*- $\text{H}_2$  (with only its even- $J$  rotational states occupied) and three parts *ortho*- $\text{H}_2$  (with only its odd- $J$  rotational states occupied). Therefore, the average partition function per molecule is

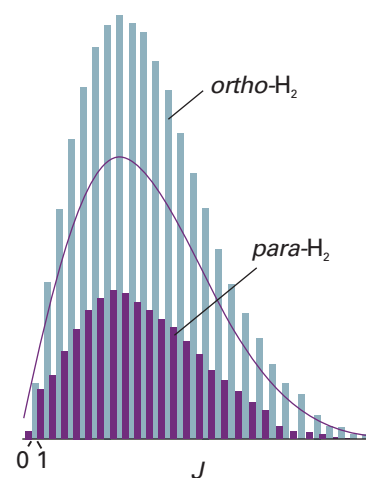
$$q^R = \frac{1}{4} \sum_{\text{even } J} (2J+1)e^{-\beta hcBJ(J+1)} + \frac{3}{4} \sum_{\text{odd } J} (2J+1)e^{-\beta hcBJ(J+1)}$$

The odd- $J$  states are more heavily weighted than the even- $J$  states (Fig. 17.3). From the illustration we see that we would obtain approximately the same answer for the partition function (the sum of all the populations) if each  $J$  term contributed half its normal value to the sum. That is, the last equation can be approximated as

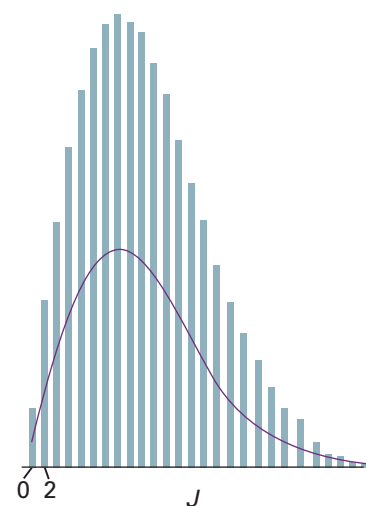
$$q^R = \frac{1}{2} \sum_J (2J+1)e^{-\beta hcBJ(J+1)}$$

and this approximation is very good when many terms contribute (at high temperatures).

The same type of argument may be used for linear symmetrical molecules in which identical bosons are interchanged by rotation (such as  $\text{CO}_2$ ). As pointed out in Section 13.8, if the nuclear spin of the bosons is 0, then only even- $J$  states are admissible. Because only half the rotational states are occupied, the rotational partition function is only half the value of the sum obtained by allowing all values of  $J$  to contribute (Fig. 17.4).



**Fig. 17.3** The values of the individual terms  $(2J+1)e^{-\beta hcBJ(J+1)}$  contributing to the mean partition function of a 3:1 mixture of *ortho*- and *para*- $\text{H}_2$ . The partition function is the sum of all these terms. At high temperatures, the sum is approximately equal to the sum of the terms over all values of  $J$ , each with a weight of  $\frac{1}{2}$ . This is the sum of the contributions indicated by the curve.

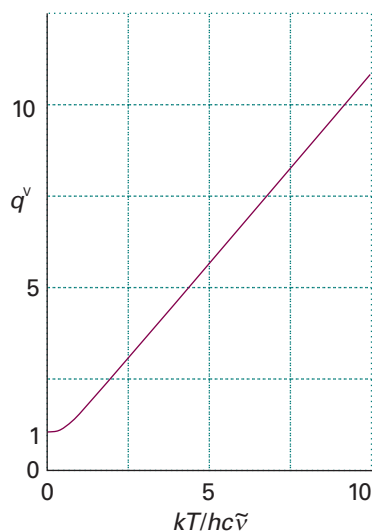
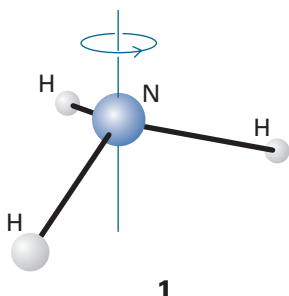


**Fig. 17.4** The relative populations of the rotational energy levels of  $\text{CO}_2$ . Only states with even  $J$  values are occupied. The full line shows the smoothed, averaged population of levels.

**Synoptic table 17.2\*** Symmetry numbers

Molecule	$\sigma$
H <sub>2</sub> O	2
NH <sub>3</sub>	3
CH <sub>4</sub>	12
C <sub>6</sub> H <sub>6</sub>	12

\* For more values, see Table 13.2 in the Data section.



**Fig. 17.5** The vibrational partition function of a molecule in the harmonic approximation. Note that the partition function is linearly proportional to the temperature when the temperature is high ( $T \gg \theta_v$ ).

**Exploration** Plot the temperature dependence of the vibrational contribution to the molecular partition function for several values of the vibrational wavenumber. Estimate from your plots the temperature above which the harmonic oscillator is in the ‘high temperature’ limit.

The same care must be exercised for other types of symmetrical molecule, and for a nonlinear molecule we write

$$q^R = \frac{1}{\sigma} \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{ABC} \right)^{1/2} \quad (17.16)$$

Some typical values of the symmetry numbers required are given in Table 17.2. The value  $\sigma(\text{H}_2\text{O}) = 2$  reflects the fact that a  $180^\circ$  rotation about the bisector of the H—O—H angle interchanges two indistinguishable atoms. In  $\text{NH}_3$ , there are three indistinguishable orientations around the axis shown in (1). For  $\text{CH}_4$ , any of three  $120^\circ$  rotations about any of its four C—H bonds leaves the molecule in an indistinguishable state, so the symmetry number is  $3 \times 4 = 12$ . For benzene, any of six orientations around the axis perpendicular to the plane of the molecule leaves it apparently unchanged, as does a rotation of  $180^\circ$  around any of six axes in the plane of the molecule (three of which pass along each C—H bond and the remaining three pass through each C—C bond in the plane of the molecule). For the way that group theory is used to identify the value of the symmetry number, see Problem 17.17.

### (c) The vibrational contribution

The vibrational partition function of a molecule is calculated by substituting the measured vibrational energy levels into the exponentials appearing in the definition of  $q^V$ , and summing them numerically. In a polyatomic molecule each normal mode (Section 13.14) has its own partition function (provided the anharmonicities are so small that the modes are independent). The overall vibrational partition function is the product of the individual partition functions, and we can write  $q^V = q^V(1)q^V(2) \dots$ , where  $q^V(K)$  is the partition function for the  $K$ th normal mode and is calculated by direct summation of the observed spectroscopic levels.

If the vibrational excitation is not too great, the harmonic approximation may be made, and the vibrational energy levels written as

$$E_v = (v + \frac{1}{2})hc\tilde{\nu} \quad v = 0, 1, 2, \dots \quad (17.17)$$

If, as usual, we measure energies from the zero-point level, then the permitted values are  $\epsilon_v = vhc\tilde{\nu}$  and the partition function is

$$q^V = \sum_v e^{-\beta vhc\tilde{\nu}} = \sum_v (e^{-\beta hc\tilde{\nu}})^v \quad (17.18)$$

(because  $e^{ax} = (e^x)^a$ ). We met this sum in Example 16.2 (which is no accident: the ladder-like array of levels in Fig. 16.3 is exactly the same as that of a harmonic oscillator). The series can be summed in the same way, and gives

$$q^V = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \quad (17.19)$$

This function is plotted in Fig. 17.5. In a polyatomic molecule, each normal mode gives rise to a partition function of this form.

#### Example 17.3 Calculating a vibrational partition function

The wavenumbers of the three normal modes of  $\text{H}_2\text{O}$  are  $3656.7 \text{ cm}^{-1}$ ,  $1594.8 \text{ cm}^{-1}$ , and  $3755.8 \text{ cm}^{-1}$ . Evaluate the vibrational partition function at 1500 K.

**Method** Use eqn 17.19 for each mode, and then form the product of the three contributions. At 1500 K,  $kT/hc = 1042.6 \text{ cm}^{-1}$ .



**Answer** We draw up the following table displaying the contributions of each mode:

Mode:	1	2	3
$\tilde{\nu}/\text{cm}^{-1}$	3656.7	1594.8	3755.8
$hc\tilde{\nu}/kT$	3.507	1.530	3.602
$q^V$	1.031	1.276	1.028

The overall vibrational partition function is therefore

$$q^V = 1.031 \times 1.276 \times 1.028 = 1.353$$

The three normal modes of  $\text{H}_2\text{O}$  are at such high wavenumbers that even at 1500 K most of the molecules are in their vibrational ground state. However, there may be so many normal modes in a large molecule that their excitation may be significant even though each mode is not appreciably excited. For example, a nonlinear molecule containing 10 atoms has  $3N - 6 = 24$  normal modes (Section 13.14). If we assume a value of about 1.1 for the vibrational partition function of one normal mode, the overall vibrational partition function is about  $q^V \approx (1.1)^{24} = 9.8$ , which indicates significant vibrational excitation relative to a smaller molecule, such as  $\text{H}_2\text{O}$ .

**Self-test 17.3** Repeat the calculation for  $\text{CO}_2$ , where the vibrational wavenumbers are  $1388\text{ cm}^{-1}$ ,  $667.4\text{ cm}^{-1}$ , and  $2349\text{ cm}^{-1}$ , the second being the doubly degenerate bending mode. [6.79]

In many molecules the vibrational wavenumbers are so great that  $\beta hc\tilde{\nu} > 1$ . For example, the lowest vibrational wavenumber of  $\text{CH}_4$  is  $1306\text{ cm}^{-1}$ , so  $\beta hc\tilde{\nu} = 6.3$  at room temperature. C—H stretches normally lie in the range  $2850$  to  $2960\text{ cm}^{-1}$ , so for them  $\beta hc\tilde{\nu} \approx 14$ . In these cases,  $e^{-\beta hc\tilde{\nu}}$  in the denominator of  $q^V$  is very close to zero (for example,  $e^{-6.3} = 0.002$ ), and the vibrational partition function for a single mode is very close to 1 ( $q^V = 1.002$  when  $\beta hc\tilde{\nu} = 6.3$ ), implying that only the zero-point level is significantly occupied.

Now consider the case of bonds so weak that  $\beta hc\tilde{\nu} \ll kT$ . When this condition is satisfied, the partition function may be approximated by expanding the exponential ( $e^x = 1 + x + \dots$ ):

$$q^V = \frac{1}{1 - (1 - \beta hc\tilde{\nu} + \dots)} \quad (17.20)$$

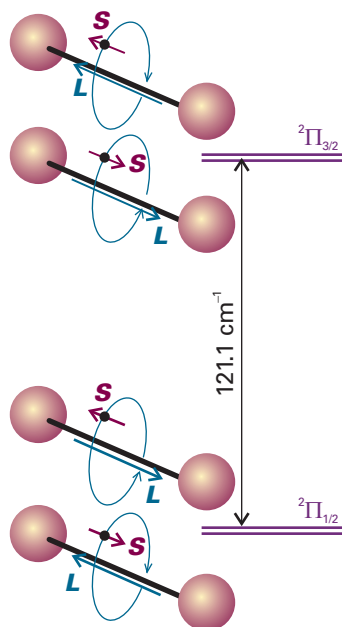
That is, for weak bonds at high temperatures,

$$q^V = \frac{1}{\beta hc\tilde{\nu}} = \frac{kT}{hc\tilde{\nu}} \quad (17.21)$$

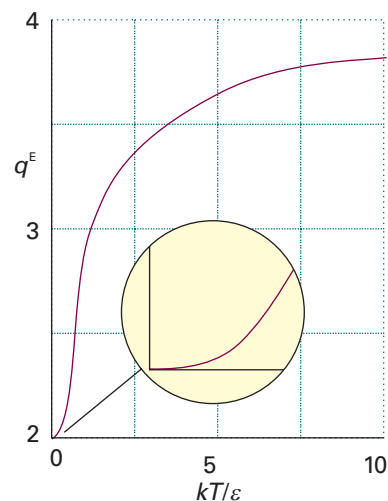
The temperatures for which eqn 17.21 is valid can be expressed in terms of the **characteristic vibrational temperature**,  $\theta_V = hc\tilde{\nu}/k$  (Table 17.1). The value for  $\text{H}_2$  is abnormally high because the atoms are so light and the vibrational frequency is correspondingly high. In terms of the vibrational temperature, ‘high temperature’ means  $T \gg \theta_V$  and, when this condition is satisfied,  $q^V = T/\theta_V$  (the analogue of the rotational expression).

#### (d) The electronic contribution

Electronic energy separations from the ground state are usually very large, so for most cases  $q^E = 1$ . An important exception arises in the case of atoms and molecules having



**Fig. 17.6** The doubly degenerate ground electronic level of NO (with the spin and orbital angular momentum around the axis in opposite directions) and the doubly degenerate first excited level (with the spin and orbital momenta parallel). The upper level is thermally accessible at room temperature.



**Fig. 17.7** The variation with temperature of the electronic partition function of an NO molecule. Note that the curve resembles that for a two-level system (Fig. 16.5), but rises from 2 (the degeneracy of the lower level) and approaches 4 (the total number of states) at high temperatures.

**Exploration** Plot the temperature dependence of the electronic partition function for several values of the energy separation  $\epsilon$  between two doubly degenerate levels. From your plots, estimate the temperature at which the population of the excited level begins to increase sharply.

electronically degenerate ground states, in which case  $q^E = g^E$ , where  $g^E$  is the degeneracy of the electronic ground state. Alkali metal atoms, for example, have doubly degenerate ground states (corresponding to the two orientations of their electron spin), so  $q^E = 2$ .

Some atoms and molecules have low-lying electronically excited states. (At high enough temperatures, all atoms and molecules have thermally accessible excited states.) An example is NO, which has a configuration of the form  $\dots \pi^1$  (see *Impact I11.1*). The orbital angular momentum may take two orientations with respect to the molecular axis (corresponding to circulation clockwise or counter-clockwise around the axis), and the spin angular momentum may also take two orientations, giving four states in all (Fig. 17.6). The energy of the two states in which the orbital and spin momenta are parallel (giving the  $^2\Pi_{3/2}$  term) is slightly greater than that of the two other states in which they are antiparallel (giving the  $^2\Pi_{1/2}$  term). The separation, which arises from spin-orbit coupling (Section 10.8), is only  $121\text{ cm}^{-1}$ . Hence, at normal temperatures, all four states are thermally accessible. If we denote the energies of the two levels as  $E_{1/2} = 0$  and  $E_{3/2} = \epsilon$ , the partition function is

$$q^E = \sum_{\text{energy levels}} g_j e^{-\beta \epsilon_j} = 2 + 2e^{-\beta \epsilon} \quad (17.22)$$

Figure 17.7 shows the variation of this function with temperature. At  $T = 0$ ,  $q^E = 2$ , because only the doubly degenerate ground state is accessible. At high temperatures,  $q^E$  approaches 4 because all four states are accessible. At  $25^\circ\text{C}$ ,  $q^E = 3.1$ .

**(e) The overall partition function**

The partition functions for each mode of motion of a molecule are collected in Table 17.3 at the end of the chapter. The overall partition function is the product of each contribution. For a diatomic molecule with no low-lying electronically excited states and  $T \gg \theta_R$ ,

$$q = g^E \left( \frac{V}{\Lambda^3} \right) \left( \frac{T}{\sigma \theta_R} \right) \left( \frac{1}{1 - e^{-T/\theta_v}} \right) \quad (17.23)$$

**Example 17.4** Calculating a thermodynamic function from spectroscopic data

Calculate the value of  $G_m^\oplus - G_m^\oplus(0)$  for  $\text{H}_2\text{O}(\text{g})$  at 1500 K given that  $A = 27.8778 \text{ cm}^{-1}$ ,  $B = 14.5092 \text{ cm}^{-1}$ , and  $C = 9.2869 \text{ cm}^{-1}$  and the information in Example 17.3.

**Method** The starting point is eqn 17.9. For the standard value, we evaluate the translational partition function at  $p^\oplus$  (that is, at  $10^5 \text{ Pa}$  exactly). The vibrational partition function was calculated in Example 17.3. Use the expressions in Table 17.3 for the other contributions.

**Answer** Because  $m = 18.015 \text{ u}$ , it follows that  $q_m^{\text{T}\oplus}/N_A = 1.706 \times 10^8$ . For the vibrational contribution we have already found that  $q^V = 1.352$ . From Table 17.2 we see that  $\sigma = 2$ , so the rotational contribution is  $q^R = 486.7$ . Therefore,

$$\begin{aligned} G_m^\oplus - G_m^\oplus(0) &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1500 \text{ K}) \\ &\quad \times \ln\{(1.706 \times 10^8) \times 486.7 \times 1.352\} \\ &= -317.3 \text{ kJ mol}^{-1} \end{aligned}$$

**Self-test 17.4** Repeat the calculation for  $\text{CO}_2$ . The vibrational data are given in Self-test 17.3;  $B = 0.3902 \text{ cm}^{-1}$ . [−366.6 kJ mol<sup>−1</sup>]

**Comment 17.1**

The text's web site contains links to on-line databases of atomic and molecular spectra.

Overall partition functions obtained from eqn 17.23 are approximate because they assume that the rotational levels are very close together and that the vibrational levels are harmonic. These approximations are avoided by using the energy levels identified spectroscopically and evaluating the sums explicitly.

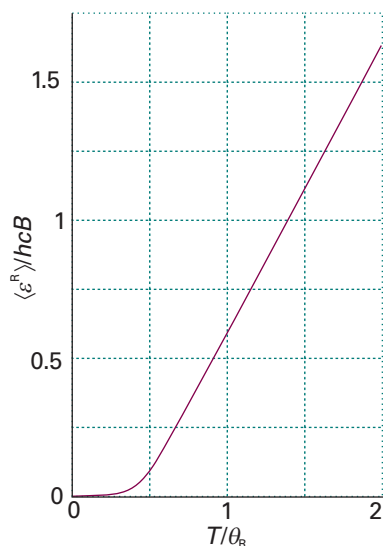
## Using statistical thermodynamics

We can now calculate any thermodynamic quantity from a knowledge of the energy levels of molecules: we have merged thermodynamics and spectroscopy. In this section, we indicate how to do the calculations for four important properties.

### 17.3 Mean energies

It is often useful to know the mean energy,  $\langle \epsilon \rangle$ , of various modes of motion. When the molecular partition function can be factorized into contributions from each mode, the mean energy of each mode  $M$  (from eqn 16.29) is

$$\langle \epsilon^M \rangle = - \frac{1}{q^M} \left( \frac{\partial q^M}{\partial \beta} \right)_V \quad M = \text{T, R, V, or E} \quad (17.24)$$



**Fig. 17.8** The mean rotational energy of a nonsymmetrical linear rotor as a function of temperature. At high temperatures ( $T \gg \theta_R$ ), the energy is linearly proportional to the temperature, in accord with the equipartition theorem.

**Exploration** Plot the temperature dependence of the mean rotational energy for several values of the rotational constant (for reasonable values of the rotational constant, see the *Data section*). From your plots, estimate the temperature at which the mean rotational energy begins to increase sharply.

### (a) The mean translational energy

To see a pattern emerging, we consider first a one-dimensional system of length  $X$ , for which  $q^T = X/\Lambda$ , with  $\Lambda = h(\beta/2\pi m)^{1/2}$ . Then, if we note that  $\Lambda$  is a constant times  $\beta^{1/2}$ ,

$$\langle \epsilon^T \rangle = -\frac{\Lambda}{X} \left( \frac{\partial}{\partial \beta} \frac{X}{\Lambda} \right)_V = -\beta^{1/2} \frac{d}{d\beta} \left( \frac{1}{\beta^{1/2}} \right) = \frac{1}{2\beta} = \frac{1}{2} kT \quad (17.25a)$$

For a molecule free to move in three dimensions, the analogous calculation leads to

$$\langle \epsilon^T \rangle = \frac{3}{2} kT \quad (17.25b)$$

Both conclusions are in agreement with the classical equipartition theorem (see *Molecular interpretation 2.2*) that the mean energy of each quadratic contribution to the energy is  $\frac{1}{2} kT$ . Furthermore, the fact that the mean energy is independent of the size of the container is consistent with the thermodynamic result that the internal energy of a perfect gas is independent of its volume (*Molecular interpretation 2.2*).

### (b) The mean rotational energy

The mean rotational energy of a linear molecule is obtained from the partition function given in eqn 17.13. When the temperature is low ( $T < \theta_R$ ), the series must be summed term by term, which gives

$$q^R = 1 + 3e^{-2\beta hcB} + 5e^{-6\beta hcB} + \dots$$

Hence

$$\langle \epsilon^R \rangle = \frac{hcB(6e^{-2\beta hcB} + 30e^{-6\beta hcB} + \dots)}{1 + 3e^{-2\beta hcB} + 5e^{-6\beta hcB} + \dots} \quad (17.26a)$$

This function is plotted in Fig. 17.8. At high temperatures ( $T \gg \theta_R$ ),  $q^R$  is given by eqn 17.15, and

$$\langle \epsilon^R \rangle = -\frac{1}{q^R} \frac{dq^R}{d\beta} = -\sigma hc\beta B \frac{d}{d\beta} \frac{1}{\sigma hc\beta B} = \frac{1}{\beta} = kT \quad (17.26b)$$

( $q^R$  is independent of  $V$ , so the partial derivatives have been replaced by complete derivatives.) The high-temperature result is also in agreement with the equipartition theorem, for the classical expression for the energy of a linear rotor is  $E_K = \frac{1}{2} I_{\perp} \omega_a^2 + \frac{1}{2} I_{\perp} \omega_b^2$ . (There is no rotation around the line of atoms.) It follows from the equipartition theorem that the mean rotational energy is  $2 \times \frac{1}{2} kT = kT$ .

### (c) The mean vibrational energy

The vibrational partition function in the harmonic approximation is given in eqn 17.19. Because  $q^V$  is independent of the volume, it follows that

$$\frac{dq^V}{d\beta} = \frac{d}{d\beta} \left( \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \right) = -\frac{hc\tilde{\nu}e^{-\beta hc\tilde{\nu}}}{(1 - e^{-\beta hc\tilde{\nu}})^2} \quad (17.27)$$

and hence from

$$\langle \epsilon^V \rangle = -\frac{1}{q^V} \frac{dq^V}{d\beta} = -(1 - e^{-\beta hc\tilde{\nu}}) \left\{ -\frac{hc\tilde{\nu}e^{-\beta hc\tilde{\nu}}}{(1 - e^{-\beta hc\tilde{\nu}})^2} \right\} = \frac{hc\tilde{\nu}e^{-\beta hc\tilde{\nu}}}{1 - e^{-\beta hc\tilde{\nu}}}$$

that

$$\langle \epsilon^V \rangle = \frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} \quad (17.28)$$

The zero-point energy,  $\frac{1}{2}hc\tilde{\nu}$ , can be added to the right-hand side if the mean energy is to be measured from 0 rather than the lowest attainable level (the zero-point level). The variation of the mean energy with temperature is illustrated in Fig. 17.9. At high temperatures, when  $T \gg \theta_v$ , or  $\beta hc\tilde{\nu} \ll 1$ , the exponential functions can be expanded ( $e^x = 1 + x + \dots$ ) and all but the leading terms discarded. This approximation leads to

$$\langle \epsilon^V \rangle = \frac{hc\tilde{\nu}}{(1 + \beta hc\tilde{\nu} + \dots) - 1} \approx \frac{1}{\beta} = kT \quad (17.29)$$

This result is in agreement with the value predicted by the classical equipartition theorem, because the energy of a one-dimensional oscillator is  $E = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2$  and the mean energy of each quadratic term is  $\frac{1}{2}kT$ .

## 17.4 Heat capacities

The constant-volume heat capacity is defined as  $C_V = (\partial U / \partial T)_V$ . The derivative with respect to  $T$  is converted into a derivative with respect to  $\beta$  by using

$$\frac{d}{dT} = \frac{d\beta}{dT} \frac{d}{d\beta} = -\frac{1}{kT^2} \frac{d}{d\beta} = -k\beta^2 \frac{d}{d\beta} \quad (17.30)$$

It follows that

$$C_V = -k\beta^2 \left( \frac{\partial U}{\partial \beta} \right)_V \quad (17.31a)$$

Because the internal energy of a perfect gas is a sum of contributions, the heat capacity is also a sum of contributions from each mode. The contribution of mode M is

$$C_V^M = N \left( \frac{\partial \langle \epsilon^M \rangle}{\partial T} \right)_V = -Nk\beta^2 \left( \frac{\partial \langle \epsilon^M \rangle}{\partial \beta} \right)_V \quad (17.31b)$$

### (a) The individual contributions

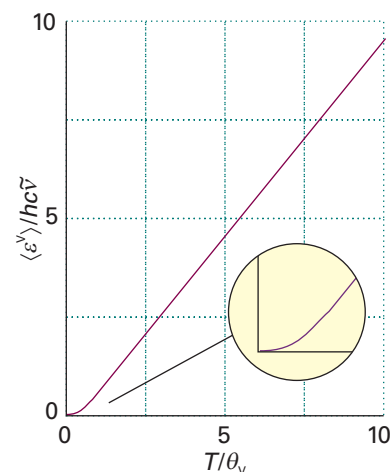
The temperature is always high enough (provided the gas is above its condensation temperature) for the mean translational energy to be  $\frac{3}{2}kT$ , the equipartition value. Therefore, the molar constant-volume heat capacity is

$$C_{V,m}^T = N_A \frac{d(\frac{3}{2}kT)}{dT} = \frac{3}{2}R \quad (17.32)$$

Translation is the only mode of motion for a monatomic gas, so for such a gas  $C_{V,m} = \frac{3}{2}R = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ . This result is very reliable: helium, for example, has this value over a range of 2000 K. We saw in Section 2.5 that  $C_{p,m} - C_{V,m} = R$ , so for a monatomic perfect gas  $C_{p,m} = \frac{5}{2}R$ , and therefore

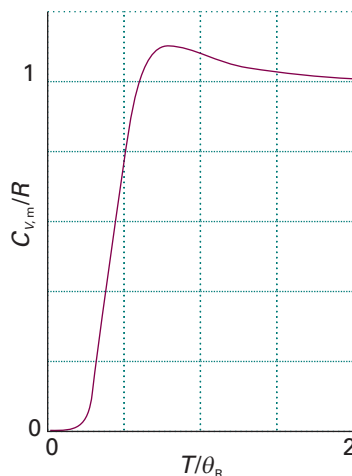
$$\gamma = \frac{C_p}{C_V} = \frac{5}{3} \quad (17.33)^\circ$$

When the temperature is high enough for the rotations of the molecules to be highly excited (when  $T \gg \theta_R$ ), we can use the equipartition value  $kT$  for the mean rotational energy (for a linear rotor) to obtain  $C_{V,m} = R$ . For nonlinear molecules, the mean rotational energy rises to  $\frac{3}{2}kT$ , so the molar rotational heat capacity rises to  $\frac{3}{2}R$  when  $T \gg \theta_R$ . Only the lowest rotational state is occupied when the temperature is very low, and then rotation does not contribute to the heat capacity. We can




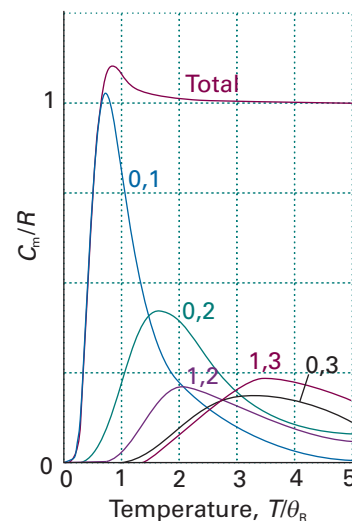
**Fig. 17.9** The mean vibrational energy of a molecule in the harmonic approximation as a function of temperature. At high temperatures ( $T \gg \theta_v$ ), the energy is linearly proportional to the temperature, in accord with the equipartition theorem.

**Exploration** Plot the temperature dependence of the mean vibrational energy for several values of the vibrational wavenumber (for reasonable values of the vibrational wavenumber, see the *Data section*). From your plots, estimate the temperature at which the mean vibrational energy begins to increase sharply.



**Fig. 17.10** The temperature dependence of the rotational contribution to the heat capacity of a linear molecule.

 **Exploration** The *Living graphs* section of the text's web site has applets for the calculation of the temperature dependence of the rotational contribution to the heat capacity. Explore the effect of the rotational constant on the plot of  $C_{V,m}^R$  against  $T$ .



**Fig. 17.11** The rotational heat capacity of a linear molecule can be regarded as the sum of contributions from a collection of two-level systems, in which the rise in temperature stimulates transitions between  $J$  levels, some of which are shown here. The calculation on which this illustration is based is sketched in Problem 17.19.

calculate the rotational heat capacity at intermediate temperatures by differentiating the equation for the mean rotational energy (eqn 17.26). The resulting (untidy) expression, which is plotted in Fig. 17.10, shows that the contribution rises from zero (when  $T = 0$ ) to the equipartition value (when  $T \gg \theta_R$ ). Because the translational contribution is always present, we can expect the molar heat capacity of a gas of diatomic molecules ( $C_{V,m}^T + C_{V,m}^R$ ) to rise from  $\frac{3}{2}R$  to  $\frac{5}{2}R$  as the temperature is increased above  $\theta_R$ . Problem 17.19 explores how the overall shape of the curve can be traced to the sum of thermal excitations between all the available rotational energy levels (Fig. 17.11).

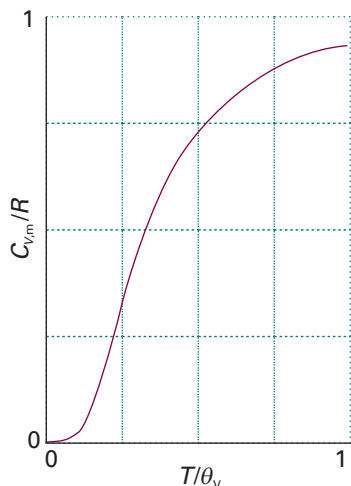
Molecular vibrations contribute to the heat capacity, but only when the temperature is high enough for them to be significantly excited. The equipartition mean energy is  $kT$  for each mode, so the maximum contribution to the molar heat capacity is  $R$ . However, it is very unusual for the vibrations to be so highly excited that equipartition is valid, and it is more appropriate to use the full expression for the vibrational heat capacity, which is obtained by differentiating eqn 17.28:

$$C_{V,m}^V = Rf \quad f = \left( \frac{\theta_V}{T} \right)^2 \left( \frac{e^{-\theta_V/2T}}{1 - e^{-\theta_V/T}} \right)^2 \quad (17.34)$$


where  $\theta_V = hc\tilde{\nu}/k$  is the characteristic vibrational temperature. The curve in Fig. 17.12 shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above  $\theta_V$  the heat capacity is close to its equipartition value.

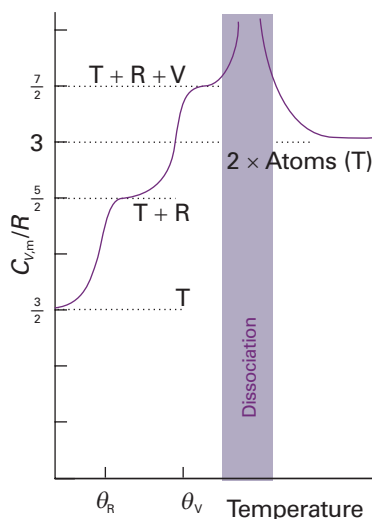
### Comment 17.2

Equation 17.34 is essentially the same as the Einstein formula for the heat capacity of a solid (eqn 8.7) with  $\theta_V$  the Einstein temperature,  $\theta_E$ . The only difference is that vibrations can take place in three dimensions in a solid.



**Fig. 17.12** The temperature dependence of the vibrational heat capacity of a molecule in the harmonic approximation calculated by using eqn 17.34. Note that the heat capacity is within 10 per cent of its classical value for temperatures greater than  $\theta_v$ .

 **Exploration** The *Living graphs* section of the text's web site has applets for the calculation of the temperature dependence of the vibrational contribution to the heat capacity. Explore the effect of the vibrational wavenumber on the plot of  $C_{V,m}^V$  against  $T$ .



**Fig. 17.13** The general features of the temperature dependence of the heat capacity of diatomic molecules are as shown here. Each mode becomes active when its characteristic temperature is exceeded. The heat capacity becomes very large when the molecule dissociates because the energy is used to cause dissociation and not to raise the temperature. Then it falls back to the translation-only value of the atoms.

### (b) The overall heat capacity

The total heat capacity of a molecular substance is the sum of each contribution (Fig. 17.13). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode,  $T \gg \theta_M$ ) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute  $\frac{3}{2}R$  to the molar heat capacity. If we denote the number of active rotational modes by  $\nu_R^*$  (so for most molecules at normal temperatures  $\nu_R^* = 2$  for linear molecules, and 3 for nonlinear molecules), then the rotational contribution is  $\frac{1}{2}\nu_R^*R$ . If the temperature is high enough for  $\nu_V^*$  vibrational modes to be active, the vibrational contribution to the molar heat capacity is  $\nu_V^*R$ . In most cases  $\nu_V^* \approx 0$ . It follows that the total molar heat capacity is

$$C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R \quad (17.35)$$

#### Example 17.5 Estimating the molar heat capacity of a gas

Estimate the molar constant-volume heat capacity of water vapour at 100°C. Vibrational wavenumbers are given in Example 17.3; the rotational constants of an  $\text{H}_2\text{O}$  molecule are 27.9, 14.5, and 9.3  $\text{cm}^{-1}$ .

**Method** We need to assess whether the rotational and vibrational modes are active by computing their characteristic temperatures from the data (to do so, use  $hc/k = 1.439 \text{ cm K}$ ).

**Answer** The characteristic temperatures (in round numbers) of the vibrations are 5300 K, 2300 K, and 5400 K; the vibrations are therefore not excited at 373 K. The three rotational modes have characteristic temperatures 40 K, 21 K, and 13 K, so they are fully excited, like the three translational modes. The translational contribution is  $\frac{3}{2}R = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ . Fully excited rotations contribute a further  $12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ . Therefore, a value close to  $25 \text{ J K}^{-1} \text{ mol}^{-1}$  is predicted. The experimental value is  $26.1 \text{ J K}^{-1} \text{ mol}^{-1}$ . The discrepancy is probably due to deviations from perfect gas behaviour.

**Self-test 17.5** Estimate the molar constant-volume heat capacity of gaseous  $\text{I}_2$  at  $25^\circ\text{C}$  ( $B = 0.037 \text{ cm}^{-1}$ ; see Table 13.2 for more data).  $[29 \text{ J K}^{-1} \text{ mol}^{-1}]$

## 17.5 Equations of state

The relation between  $p$  and  $Q$  in eqn 17.3 is a very important route to the equations of state of real gases in terms of intermolecular forces, for the latter can be built into  $Q$ . We have already seen (Example 17.1) that the partition function for a gas of independent particles leads to the perfect gas equation of state,  $pV = nRT$ . Real gases differ from perfect gases in their equations of state and we saw in Section 1.3 that their equations of state may be written

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \quad (17.36)$$

where  $B$  is the second virial coefficient and  $C$  is the third virial coefficient.

The total kinetic energy of a gas is the sum of the kinetic energies of the individual molecules. Therefore, even in a real gas the canonical partition function factorizes into a part arising from the kinetic energy, which is the same as for the perfect gas, and a factor called the **configuration integral**,  $Z$ , which depends on the intermolecular potentials. We therefore write

$$Q = \frac{Z}{\Lambda^{3N}} \quad (17.37)$$

By comparing this equation with eqn 16.45 ( $Q = q^N/N!$ , with  $q = V/\Lambda^3$ ), we see that for a perfect gas of atoms (with no contributions from rotational or vibrational modes)

$$Z = \frac{V^N}{N!} \quad (17.38)$$

For a real gas of atoms (for which the intermolecular interactions are isotropic),  $Z$  is related to the total potential energy  $E_p$  of interaction of all the particles by

$$Z = \frac{1}{N!} \int e^{-\beta E_p} d\tau_1 d\tau_2 \cdots d\tau_N \quad (17.39)$$

where  $d\tau_i$  is the volume element for atom  $i$ . The physical origin of this term is that the probability of occurrence of each arrangement of molecules possible in the sample is given by a Boltzmann distribution in which the exponent is given by the potential energy corresponding to that arrangement.



**Illustration 17.1** Calculating a configuration integral

When the molecules do not interact with one another,  $E_p = 0$  and hence  $e^{-\beta E_p} = 1$ . Then

$$Z = \frac{1}{N!} \int d\tau_1 d\tau_2 \cdots d\tau_N = \frac{V^N}{N!}$$

because  $\int d\tau = V$ , where  $V$  is the volume of the container. This result coincides with eqn 17.39.

When we consider only interactions between pairs of particles the configuration integral simplifies to

$$Z = \frac{1}{2} \int e^{-\beta E_p} d\tau_1 d\tau_2 \quad (17.40)$$

The second virial coefficient then turns out to be

$$B = -\frac{N_A}{2V} \int f d\tau_1 d\tau_2 \quad (17.41)$$

The quantity  $f$  is the **Mayer  $f$ -function**: it goes to zero when the two particles are so far apart that  $E_p = 0$ . When the intermolecular interaction depends only on the separation  $r$  of the particles and not on their relative orientation or their absolute position in space, as in the interaction of closed-shell atoms in a uniform sample, the volume element simplifies to  $4\pi r^2 dr$  (because the integrals over the angular variables in  $d\tau = r^2 dr \sin \theta d\theta d\phi$  give a factor of  $4\pi$ ) and eqn 17.41 becomes

$$B = -2\pi N_A \int_0^\infty f r^2 dr \quad f = e^{-\beta E_p} - 1 \quad (17.42)$$

The integral can be evaluated (usually numerically) by substituting an expression for the intermolecular potential energy.

Intermolecular potential energies are discussed in more detail in Chapter 18, where several expressions are developed for them. At this stage, we can illustrate how eqn 17.42 is used by considering the **hard-sphere potential**, which is infinite when the separation of the two molecules,  $r$ , is less than or equal to a certain value  $\sigma$ , and is zero for greater separations. Then

$$e^{-\beta E_p} = 0 \quad f = -1 \quad \text{when } r \leq \sigma \quad (\text{and } E_p = \infty) \quad (17.43a)$$

$$e^{-\beta E_p} = 1 \quad f = 0 \quad \text{when } r > \sigma \quad (\text{and } E_p = 0) \quad (17.43b)$$

It follows from eqn 17.42 that the second virial coefficient is

$$B = 2\pi N_A \int_0^\sigma r^2 dr = \frac{2}{3} \pi N_A \sigma^3 \quad (17.44)$$

This calculation of  $B$  raises the question as to whether a potential can be found that, when the virial coefficients are evaluated, gives the van der Waals equation of state. Such a potential can be found for weak attractive interactions ( $a \ll RT$ ): it consists of a hard-sphere repulsive core and a long-range, shallow attractive region (see Problem 17.15). A further point is that, once a second virial coefficient has been calculated for a given intermolecular potential, it is possible to calculate other thermodynamic properties that depend on the form of the potential. For example, it is possible to

calculate the isothermal Joule–Thomson coefficient,  $\mu_T$  (Section 3.8), from the thermodynamic relation

$$\lim_{p \rightarrow 0} \mu_T = B - T \frac{dB}{dT} \quad (17.45)$$

and from the result calculate the Joule–Thomson coefficient itself by using eqn 3.48.

## 17.6 Molecular interactions in liquids

The starting point for the discussion of solids is the well ordered structure of a perfect crystal, which will be discussed in Chapter 20. The starting point for the discussion of gases is the completely disordered distribution of the molecules of a perfect gas, as we saw in Chapter 1. Liquids lie between these two extremes. We shall see that the structural and thermodynamic properties of liquids depend on the nature of intermolecular interactions and that an equation of state can be built in a similar way to that just demonstrated for real gases.

### (a) The radial distribution function

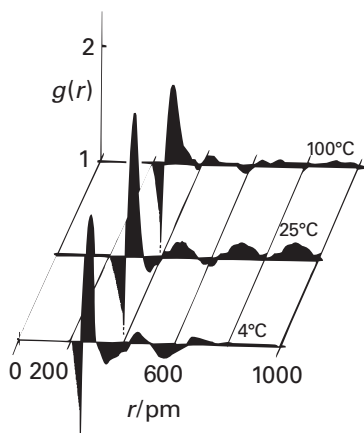
The average relative locations of the particles of a liquid are expressed in terms of the **radial distribution function**,  $g(r)$ . This function is defined so that  $g(r)r^2dr$  is the probability that a molecule will be found in the range  $dr$  at a distance  $r$  from another molecule. In a perfect crystal,  $g(r)$  is a periodic array of sharp spikes, representing the certainty (in the absence of defects and thermal motion) that molecules (or ions) lie at definite locations. This regularity continues out to the edges of the crystal, so we say that crystals have **long-range order**. When the crystal melts, the long-range order is lost and, wherever we look at long distances from a given molecule, there is equal probability of finding a second molecule. Close to the first molecule, though, the nearest neighbours might still adopt approximately their original relative positions and, even if they are displaced by newcomers, the new particles might adopt their vacated positions. It is still possible to detect a sphere of nearest neighbours at a distance  $r_1$ , and perhaps beyond them a sphere of next-nearest neighbours at  $r_2$ . The existence of this **short-range order** means that the radial distribution function can be expected to oscillate at short distances, with a peak at  $r_1$ , a smaller peak at  $r_2$ , and perhaps some more structure beyond that.

The radial distribution function of the oxygen atoms in liquid water is shown in Fig. 17.14. Closer analysis shows that any given  $\text{H}_2\text{O}$  molecule is surrounded by other molecules at the corners of a tetrahedron. The form of  $g(r)$  at  $100^\circ\text{C}$  shows that the intermolecular interactions (in this case, principally by hydrogen bonds) are strong enough to affect the local structure right up to the boiling point. Raman spectra indicate that in liquid water most molecules participate in either three or four hydrogen bonds. Infrared spectra show that about 90 per cent of hydrogen bonds are intact at the melting point of ice, falling to about 20 per cent at the boiling point.

The formal expression for the radial distribution function for molecules 1 and 2 in a fluid consisting of  $N$  particles is the somewhat fearsome equation

$$g(r_{12}) = \frac{\int \int \dots \int e^{-\beta V_N} d\tau_3 d\tau_4 \dots d\tau_N}{N^2 \int \int \dots \int e^{-\beta V_N} d\tau_1 d\tau_2 \dots d\tau_N} \quad (17.46)$$

where  $\beta = 1/kT$  and  $V_N$  is the  $N$ -particle potential energy. Although fearsome, this expression is nothing more than the Boltzmann distribution for the relative locations of two molecules in a field provided by all the other molecules in the system.



**Fig. 17.14** The radial distribution function of the oxygen atoms in liquid water at three temperatures. Note the expansion as the temperature is raised. (A.H. Narten, M.D. Danford, and H.A. Levy, *Discuss. Faraday. Soc.* **43**, 97 (1967).)

### (b) The calculation of $g(r)$

Because the radial distribution function can be calculated by making assumptions about the intermolecular interactions, it can be used to test theories of liquid structure. However, even a fluid of hard spheres without attractive interactions (a collection of ball-bearings in a container) gives a function that oscillates near the origin (Fig. 17.15), and one of the factors influencing, and sometimes dominating, the structure of a liquid is the geometrical problem of stacking together reasonably hard spheres. Indeed, the radial distribution function of a liquid of hard spheres shows more pronounced oscillations at a given temperature than that of any other type of liquid. The attractive part of the potential modifies this basic structure, but sometimes only quite weakly. One of the reasons behind the difficulty of describing liquids theoretically is the similar importance of both the attractive and repulsive (hard core) components of the potential.

There are several ways of building the intermolecular potential into the calculation of  $g(r)$ . Numerical methods take a box of about  $10^3$  particles (the number increases as computers grow more powerful), and the rest of the liquid is simulated by surrounding the box with replications of the original box (Fig. 17.16). Then, whenever a particle leaves the box through one of its faces, its image arrives through the opposite face. When calculating the interactions of a molecule in a box, it interacts with all the molecules in the box and all the periodic replications of those molecules and itself in the other boxes.

In the **Monte Carlo method**, the particles in the box are moved through small but otherwise random distances, and the change in total potential energy of the  $N$  particles in the box,  $\Delta V_N$ , is calculated using one of the intermolecular potentials discussed in Section 18.4. Whether or not this new configuration is accepted is then judged from the following rules:

- 1 If the potential energy is not greater than before the change, then the configuration is accepted.

If the potential energy is greater than before the change, then it is necessary to check if the new configuration is reasonable and can exist in equilibrium with configurations of lower potential energy at a given temperature. To make progress, we use the result that, at equilibrium, the ratio of populations of two states with energy separation  $\Delta V_N$  is  $e^{-\Delta V_N/kT}$ . Because we are testing the viability of a configuration with a higher potential energy than the previous configuration in the calculation,  $\Delta V_N > 0$  and the exponential factor varies between 0 and 1. In the Monte Carlo method, the second rule, therefore, is:

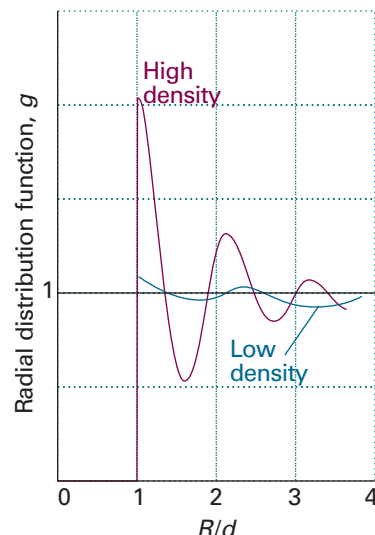
- 2 The exponential factor is compared with a random number between 0 and 1; if the factor is larger than the random number, then the configuration is accepted; if the factor is not larger, the configuration is rejected.

The configurations generated with Monte Carlo calculations can be used to construct  $g(r)$  simply by counting the number of pairs of particles with a separation  $r$  and averaging the result over the whole collection of configurations.

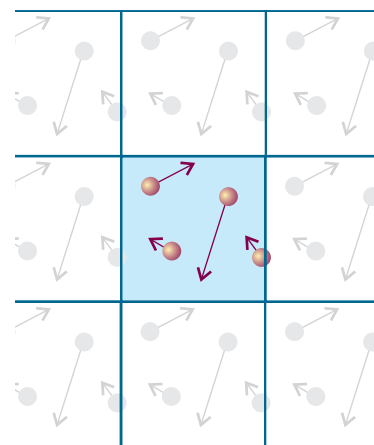
In the **molecular dynamics** approach, the history of an initial arrangement is followed by calculating the trajectories of all the particles under the influence of the intermolecular potentials. To appreciate what is involved, we consider the motion of a particle in one dimension. We show in the following *Justification* that, after a time interval  $\Delta t$ , the position of a particle changes from  $x_{i-1}$  to a new value  $x_i$  given by

$$x_i = x_{i-1} + v_{i-1}\Delta t \quad (17.47)$$

where  $v_{i-1}$  is the velocity of the atom when it was at  $x_{i-1}$ , its location at the start of the interval. The velocity at  $x_i$  is related to  $v_{i-1}$ , the velocity at the start of the interval, by



**Fig. 17.15** The radial distribution function for a simulation of a liquid using impenetrable hard spheres (ball bearings).



**Fig. 17.16** In a two-dimensional simulation of a liquid that uses periodic boundary conditions, when one particle leaves the cell its mirror image enters through the opposite face.

$$v_i = v_{i-1} - m^{-1} \frac{dV_N(x)}{dx} \bigg|_{x_{i-1}} \Delta t \quad (17.48)$$

where the derivative of the potential energy  $V_N(x)$  is evaluated at  $x_{i-1}$ . The time interval  $\Delta t$  is approximately 1 fs ( $10^{-15}$  s), which is shorter than the average time between collisions. The calculation of  $x_i$  and  $v_i$  is then repeated for tens of thousands of such steps. The time-consuming part of the calculation is the evaluation of the net force on the molecule arising from all the other molecules present in the system.

**Justification 17.3** Particle trajectories according to molecular dynamics

Consider a particle of mass  $m$  moving along the  $x$  direction with an initial velocity  $v_1$  given by

$$v_1 = \frac{\Delta x}{\Delta t}$$

If the initial and new positions of the atom are  $x_1$  and  $x_2$ , then  $\Delta x = x_2 - x_1$  and

$$x_2 = x_1 + v_1 \Delta t$$

The particle moves under the influence of a force arising from interactions with other atoms in the molecule. From Newton's second law of motion, we write the force  $F_1$  at  $x_1$  as

$$F_1 = ma_1$$

where the acceleration  $a_1$  at  $x_1$  is given by  $a_1 = \Delta v / \Delta t$ . If the initial and new velocities are  $v_1$  and  $v_2$ , then  $\Delta v = v_2 - v_1$  and

$$v_2 = v_1 + a_1 \Delta t = v_1 + \frac{F_1}{m} \Delta t$$

Because  $F = -dV/dx$ , the force acting on the atom is related to the potential energy of interaction with other nearby atoms, the potential energy  $V_N(x)$ , by

$$F_1 = - \frac{dV_N(x)}{dx} \bigg|_{x_1}$$

where the derivative is evaluated at  $x_1$ . It follows that

$$v_2 = v_1 - m^{-1} \frac{dV_N(x)}{dx} \bigg|_{x_1} \Delta t$$

This expression generalizes to eqn 17.48 for the calculation of a velocity  $v_i$  from a previous velocity  $v_{i-1}$ .

**Self-test 17.6** Consider a particle of mass  $m$  connected to a stationary wall with a spring of force constant  $k$ . Write an expression for the velocity of this particle once it is set into motion in the  $x$  direction from an equilibrium position  $x_0$ .

$$[v_i = v_{i-1} + (k/m)(x_{i-1} - x_0)]$$

A molecular dynamics calculation gives a series of snapshots of the liquid, and  $g(r)$  can be calculated as before. The temperature of the system is inferred by computing the mean kinetic energy of the particles and using the equipartition result that

$$\langle \frac{1}{2} m v_q^2 \rangle = \frac{1}{2} kT \quad (17.49)$$

for each coordinate  $q$ .

### (c) The thermodynamic properties of liquids

Once  $g(r)$  is known it can be used to calculate the thermodynamic properties of liquids. For example, the contribution of the pairwise additive intermolecular potential,  $V_2$ , to the internal energy is given by the integral

$$U = \frac{2\pi N^2}{V} \int_0^\infty g(r) V_2 r^2 dr \quad (17.50)$$

That is,  $U$  is essentially the average two-particle potential energy weighted by  $g(r)r^2 dr$ , which is the probability that the pair of particles have a separation between  $r$  and  $r + dr$ . Likewise, the contribution that pairwise interactions make to the pressure is

$$\frac{pV}{nRT} = 1 - \frac{2\pi N}{kTV} \int_0^\infty g(r) v_2 r^2 dr \quad v_2 = r \frac{dV_2}{dr} \quad (17.51a)$$

The quantity  $v_2$  is called the **virial** (hence the term ‘virial equation of state’). To understand the physical content of this expression, we rewrite it as

$$p = \frac{nRT}{V} - 2\pi \left( \frac{N}{V} \right)^2 \int_0^\infty g(r) v_2 r^2 dr \quad (17.51b)$$

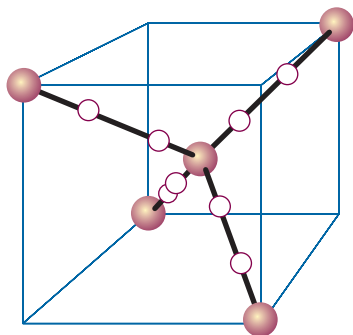
The first term on the right is the **kinetic pressure**, the contribution to the pressure from the impact of the molecules in free flight. The second term is essentially the internal pressure,  $\pi_T = (\partial U / \partial V)_T$ , introduced in Section 2.11, representing the contribution to the pressure from the intermolecular forces. To see the connection, we should recognize  $-dV_2/dr$  (in  $v_2$ ) as the force required to move two molecules apart, and therefore  $-r(dV_2/dr)$  as the work required to separate the molecules through a distance  $r$ . The second term is therefore the average of this work over the range of pairwise separations in the liquid as represented by the probability of finding two molecules at separations between  $r$  and  $r + dr$ , which is  $g(r)r^2 dr$ . In brief, the integral, when multiplied by the square of the number density, is the change in internal energy of the system as it expands, and therefore is equal to the internal pressure.

## 17.7 Residual entropies

Entropies may be calculated from spectroscopic data; they may also be measured experimentally (Section 3.3). In many cases there is good agreement, but in some the experimental entropy is less than the calculated value. One possibility is that the experimental determination failed to take a phase transition into account (and a contribution of the form  $\Delta_{\text{trs}}H/T_{\text{trs}}$  incorrectly omitted from the sum). Another possibility is that some disorder is present in the solid even at  $T = 0$ . The entropy at  $T = 0$  is then greater than zero and is called the **residual entropy**.

The origin and magnitude of the residual entropy can be explained by considering a crystal composed of AB molecules, where A and B are similar atoms (such as CO, with its very small electric dipole moment). There may be so little energy difference between  $\dots AB AB AB AB \dots$ ,  $\dots AB BA BA AB \dots$ , and other arrangements that the molecules adopt the orientations AB and BA at random in the solid. We can readily calculate the entropy arising from residual disorder by using the Boltzmann formula  $S = k \ln W$ . To do so, we suppose that two orientations are equally probable, and that the sample consists of  $N$  molecules. Because the same energy can be achieved in  $2^N$  different ways (because each molecule can take either of two orientations), the total number of ways of achieving the same energy is  $W = 2^N$ . It follows that

$$S = k \ln 2^N = Nk \ln 2 = nR \ln 2 \quad (17.52a)$$



**Fig. 17.17** The possible locations of H atoms around a central O atom in an ice crystal are shown by the white spheres. Only one of the locations on each bond may be occupied by an atom, and two H atoms must be close to the O atom and two H atoms must be distant from it.

We can therefore expect a residual molar entropy of  $R \ln 2 = 5.8 \text{ J K}^{-1} \text{ mol}^{-1}$  for solids composed of molecules that can adopt either of two orientations at  $T = 0$ . If  $s$  orientations are possible, the residual molar entropy will be

$$S_m = R \ln s \quad (17.52b)$$

An  $\text{FCIO}_3$  molecule, for example, can adopt four orientations with about the same energy (with the F atom at any of the four corners of a tetrahedron), and the calculated residual molar entropy of  $R \ln 4 = 11.5 \text{ J K}^{-1} \text{ mol}^{-1}$  is in good agreement with the experimental value ( $10.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ). For CO, the measured residual entropy is  $5 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is close to  $R \ln 2$ , the value expected for a random structure of the form  $\dots \text{CO CO OC CO OC OC} \dots$ .

#### Illustration 17.2 Calculating a residual entropy

Consider a sample of ice with  $N \text{ H}_2\text{O}$  molecules. Each O atom is surrounded tetrahedrally by four H atoms, two of which are attached by short  $\sigma$  bonds, the other two being attached by long hydrogen bonds (Fig. 17.17). It follows that each of the  $2N$  H atoms can be in one of two positions (either close to or far from an O atom as shown in Fig. 17.18), resulting in  $2^{2N}$  possible arrangements. However, not all these arrangements are acceptable. Indeed, of the  $2^4 = 16$  ways of arranging four H atoms around one O atom, only 6 have two short and two long OH distances and hence are acceptable. Therefore, the number of permitted arrangements is

$$W = 2^{2N} \left( \frac{6}{16} \right)^N = \left( \frac{3}{2} \right)^N$$

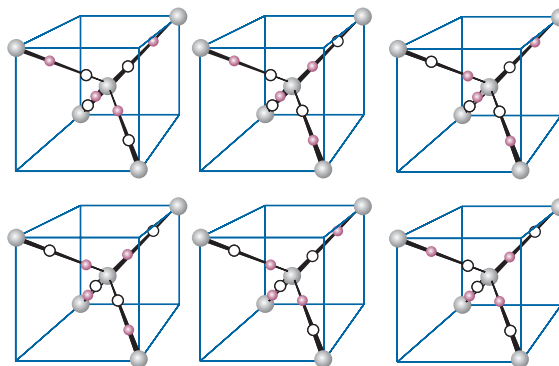
It then follows that the residual molar entropy is

$$S_m(0) \approx k \ln \left( \frac{3}{2} \right)^{N_A} = N_A k \ln \left( \frac{3}{2} \right) = R \ln \left( \frac{3}{2} \right) = 3.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

which is in good agreement with the experimental value of  $3.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . The model, however, is not exact because it ignores the possibility that next-nearest neighbours and those beyond can influence the local arrangement of bonds.

### 17.8 Equilibrium constants

The Gibbs energy of a gas of independent molecules is given by eqn 17.9 in terms of the molar partition function,  $q_m = q/n$ . The equilibrium constant  $K$  of a reaction is related to the standard Gibbs energy of reaction by  $\Delta_r G^\ominus = -RT \ln K$ . To calculate the equilibrium constant, we need to combine these two equations. We shall consider gas phase reactions in which the equilibrium constant is expressed in terms of the partial pressures of the reactants and products.



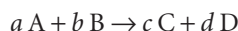
**Fig. 17.18** The six possible arrangements of H atoms in the locations identified in Fig. 17.17. Occupied locations are denoted by red spheres and unoccupied locations by white spheres.

**(a) The relation between  $K$  and the partition function**

To find an expression for the standard reaction Gibbs energy we need expressions for the standard molar Gibbs energies,  $G^\circ/n$ , of each species. For these expressions, we need the value of the molar partition function when  $p = p^\circ$  (where  $p^\circ = 1$  bar): we denote this **standard molar partition function**  $q_{\text{m}}^\circ$ . Because only the translational component depends on the pressure, we can find  $q_{\text{m}}^\circ$  by evaluating the partition function with  $V$  replaced by  $V_{\text{m}}^\circ$ , where  $V_{\text{m}}^\circ = RT/p^\circ$ . For a species  $J$  it follows that

$$G_{\text{m}}^\circ(J) = G_{\text{m}}^\circ(J, 0) - RT \ln \frac{q_{J,\text{m}}^\circ}{N_{\text{A}}} \quad (17.53)^\circ$$

where  $q_{J,\text{m}}^\circ$  is the standard molar partition function of  $J$ . By combining expressions like this one (as shown in the *Justification* below), the equilibrium constant for the reaction

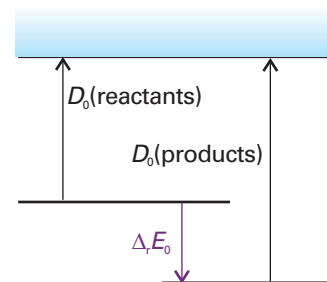


is given by the expression

$$K = \frac{(q_{\text{C},\text{m}}^\circ/N_{\text{A}})^c (q_{\text{D},\text{m}}^\circ/N_{\text{A}})^d}{(q_{\text{A},\text{m}}^\circ/N_{\text{A}})^a (q_{\text{B},\text{m}}^\circ/N_{\text{A}})^b} e^{-\Delta_{\text{r}}E_0/RT} \quad (17.54\text{a})$$

where  $\Delta_{\text{r}}E_0$  is the difference in molar energies of the ground states of the products and reactants (this term is defined more precisely in the *Justification*), and is calculated from the bond dissociation energies of the species (Fig. 17.19). In terms of the stoichiometric numbers introduced in Section 7.2, we would write

$$K = \left\{ \prod_J \left( \frac{q_{J,\text{m}}^\circ}{N_{\text{A}}} \right)^{\nu_J} \right\} e^{-\Delta_{\text{r}}E_0/RT} \quad (17.54\text{b})$$



**Fig. 17.19** The definition of  $\Delta_{\text{r}}E_0$  for the calculation of equilibrium constants.

**Justification 17.4** *The equilibrium constant in terms of the partition function 1*

The standard molar reaction Gibbs energy for the reaction is

$$\begin{aligned} \Delta_{\text{r}}G^\circ &= cG_{\text{m}}^\circ(\text{C}) + dG_{\text{m}}^\circ(\text{D}) - aG_{\text{m}}^\circ(\text{A}) - bG_{\text{m}}^\circ(\text{B}) \\ &= cG_{\text{m}}^\circ(\text{C}, 0) + dG_{\text{m}}^\circ(\text{D}, 0) - aG_{\text{m}}^\circ(\text{A}, 0) - bG_{\text{m}}^\circ(\text{B}, 0) \\ &\quad - RT \left\{ c \ln \frac{q_{\text{C},\text{m}}^\circ}{N_{\text{A}}} + d \ln \frac{q_{\text{D},\text{m}}^\circ}{N_{\text{A}}} - a \ln \frac{q_{\text{A},\text{m}}^\circ}{N_{\text{A}}} - b \ln \frac{q_{\text{B},\text{m}}^\circ}{N_{\text{A}}} \right\} \end{aligned}$$

Because  $G(0) = U(0)$ , the first term on the right is

$$\Delta_{\text{r}}E_0 = cU_{\text{m}}^\circ(\text{C}, 0) + dU_{\text{m}}^\circ(\text{D}, 0) - aU_{\text{m}}^\circ(\text{A}, 0) - bU_{\text{m}}^\circ(\text{B}, 0) \quad (17.55)$$

the reaction internal energy at  $T = 0$  (a molar quantity).

Now we can write

$$\begin{aligned} \Delta_{\text{r}}G^\circ &= \Delta_{\text{r}}E_0 - RT \left\{ \ln \left( \frac{q_{\text{C},\text{m}}^\circ}{N_{\text{A}}} \right)^c + \ln \left( \frac{q_{\text{D},\text{m}}^\circ}{N_{\text{A}}} \right)^d - \ln \left( \frac{q_{\text{A},\text{m}}^\circ}{N_{\text{A}}} \right)^a - \ln \left( \frac{q_{\text{B},\text{m}}^\circ}{N_{\text{A}}} \right)^b \right\} \\ &= \Delta_{\text{r}}E_0 - RT \ln \frac{(q_{\text{C},\text{m}}^\circ/N_{\text{A}})^c (q_{\text{D},\text{m}}^\circ/N_{\text{A}})^d}{(q_{\text{A},\text{m}}^\circ/N_{\text{A}})^a (q_{\text{B},\text{m}}^\circ/N_{\text{A}})^b} \\ &= -RT \left\{ \frac{\Delta_{\text{r}}E_0}{RT} + \ln \frac{(q_{\text{C},\text{m}}^\circ/N_{\text{A}})^c (q_{\text{D},\text{m}}^\circ/N_{\text{A}})^d}{(q_{\text{A},\text{m}}^\circ/N_{\text{A}})^a (q_{\text{B},\text{m}}^\circ/N_{\text{A}})^b} \right\} \end{aligned}$$

At this stage we can pick out an expression for  $K$  by comparing this equation with  $\Delta_{\text{r}}G^\circ = -RT \ln K$ , which gives

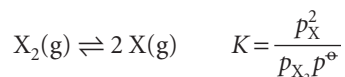


$$\ln K = -\frac{\Delta_r E_0}{RT} + \ln \frac{(q_{C,m}^\ominus/N_A)^c (q_{D,m}^\ominus/N_A)^d}{(q_{A,m}^\ominus/N_A)^a (q_{B,m}^\ominus/N_A)^b}$$

This expression is easily rearranged into eqn 17.54a by forming the exponential of both sides.

### (b) A dissociation equilibrium

We shall illustrate the application of eqn 17.54 to an equilibrium in which a diatomic molecule  $X_2$  dissociates into its atoms:



According to eqn 17.54 (with  $a = 1$ ,  $b = 0$ ,  $c = 2$ , and  $d = 0$ ):

$$K = \frac{(q_{X,m}^\ominus/N_A)^2}{q_{X_2,m}^\ominus/N_A} e^{-\Delta_r E_0/RT} = \frac{(q_{X,m}^\ominus)^2}{q_{X_2,m}^\ominus N_A} e^{-\Delta_r E_0/RT} \quad (17.56a)$$

with

$$\Delta_r E_0 = 2U_m^\ominus(X, 0) - U_m^\ominus(X_2, 0) = D_0(X-X) \quad (17.56b)$$

where  $D_0(X-X)$  is the dissociation energy of the  $X-X$  bond. The standard molar partition functions of the atoms  $X$  are

$$q_{X,m}^\ominus = g_X \left( \frac{V_m^\ominus}{\Lambda_X^3} \right) = \frac{RT g_X}{p^\ominus \Lambda_X^3}$$

where  $g_X$  is the degeneracy of the electronic ground state of  $X$  and we have used  $V_m^\ominus = RT/p^\ominus$ . The diatomic molecule  $X_2$  also has rotational and vibrational degrees of freedom, so its standard molar partition function is

$$q_{X_2,m}^\ominus = g_{X_2} \left( \frac{V_m^\ominus}{\Lambda_{X_2}^3} \right) q_{X_2}^R q_{X_2}^V = \frac{RT g_{X_2} q_{X_2}^R q_{X_2}^V}{p^\ominus \Lambda_{X_2}^3}$$

where  $g_{X_2}$  is the degeneracy of the electronic ground state of  $X_2$ . It follows from eqn 17.54 that the equilibrium constant is

$$K = \frac{kT g_X^2 \Lambda_{X_2}^3}{p^\ominus g_{X_2} q_{X_2}^R q_{X_2}^V \Lambda_X^6} e^{-D_0/RT} \quad (17.57)$$

where we have used  $R/N_A = k$ . All the quantities in this expression can be calculated from spectroscopic data. The  $\Lambda$ s are defined in Table 17.3 and depend on the masses of the species and the temperature; the expressions for the rotational and vibrational partition functions are also available in Table 17.3 and depend on the rotational constant and vibrational wavenumber of the molecule.

#### Example 17.6 Evaluating an equilibrium constant

Evaluate the equilibrium constant for the dissociation  $Na_2(g) \rightleftharpoons 2 Na(g)$  at 1000 K from the following data:  $B = 0.1547 \text{ cm}^{-1}$ ,  $\tilde{\nu} = 159.2 \text{ cm}^{-1}$ ,  $D_0 = 70.4 \text{ kJ mol}^{-1}$ . The Na atoms have doublet ground terms.

**Method** The partition functions required are specified in eqn 17.54. They are evaluated by using the expressions in Table 17.3. For a homonuclear diatomic molecule,  $\sigma = 2$ . In the evaluation of  $kT/p^\ominus$  use  $p^\ominus = 10^5 \text{ Pa}$  and  $1 \text{ Pa m}^3 = 1 \text{ J}$ .



**Answer** The partition functions and other quantities required are as follows:

$$\Lambda(\text{Na}_2) = 8.14 \text{ pm} \quad \Lambda(\text{Na}) = 11.5 \text{ pm}$$

$$q^{\text{R}}(\text{Na}_2) = 2246 \quad q^{\text{V}}(\text{Na}_2) = 4.885$$

$$g(\text{Na}) = 2 \quad g(\text{Na}_2) = 1$$

Then, from eqn 17.54,

$$K = \frac{(1.38 \times 10^{-23} \text{ J K}^{-1}) \times (1000 \text{ K}) \times 4 \times (8.14 \times 10^{-12} \text{ m})^3}{(10^5 \text{ Pa}) \times 2246 \times 4.885 \times (1.15 \times 10^{-11} \text{ m})^6} \times e^{-8.47}$$

$$= 2.42$$

where we have used  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-1}$ .

**Self-test 17.7** Evaluate  $K$  at 1500 K.

[52]

### (c) Contributions to the equilibrium constant

We are now in a position to appreciate the physical basis of equilibrium constants. To see what is involved, consider a simple  $\text{R} \rightleftharpoons \text{P}$  gas-phase equilibrium (R for reactants, P for products).

Figure 17.20 shows two sets of energy levels; one set of states belongs to R, and the other belongs to P. The populations of the states are given by the Boltzmann distribution, and are independent of whether any given state happens to belong to R or to P. We can therefore imagine a single Boltzmann distribution spreading, without distinction, over the two sets of states. If the spacings of R and P are similar (as in Fig. 17.20), and P lies above R, the diagram indicates that R will dominate in the equilibrium mixture. However, if P has a high density of states (a large number of states in a given energy range, as in Fig. 17.21), then, even though its zero-point energy lies above that of R, the species P might still dominate at equilibrium.

It is quite easy to show (see the *Justification* below) that the ratio of numbers of R and P molecules at equilibrium is given by

$$\frac{N_{\text{P}}}{N_{\text{R}}} = \frac{q_{\text{P}}}{q_{\text{R}}} e^{-\Delta_r E_0 / RT} \quad (17.58a)$$

and therefore that the equilibrium constant for the reaction is

$$K = \frac{q_{\text{P}}}{q_{\text{R}}} e^{-\Delta_r E_0 / RT} \quad (17.58b)$$

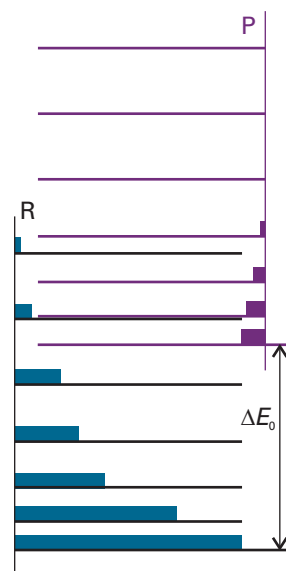
just as would be obtained from eqn 17.54.

#### Justification 17.5 The equilibrium constant in terms of the partition function 2

The population in a state  $i$  of the composite (R,P) system is

$$n_i = \frac{N e^{-\beta \varepsilon_i}}{q}$$

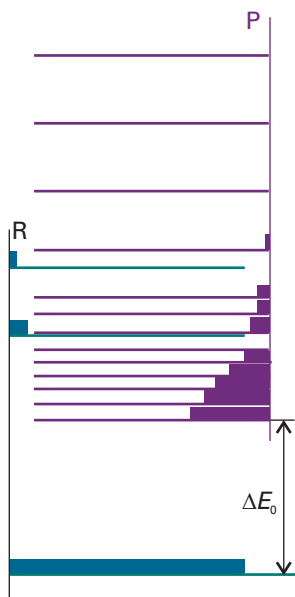
where  $N$  is the total number of molecules. The total number of R molecules is the sum of these populations taken over the states belonging to R; these states we label  $r$  with energies  $\varepsilon_r$ . The total number of P molecules is the sum over the states



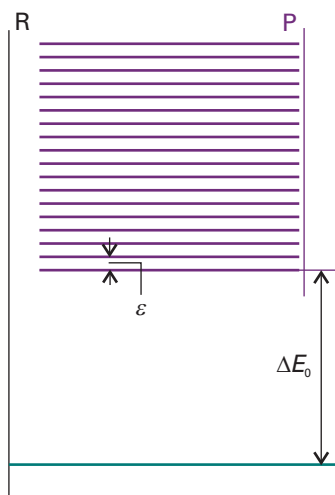
**Fig. 17.20** The array of R(eactants) and P(roduts) energy levels. At equilibrium all are accessible (to differing extents, depending on the temperature), and the equilibrium composition of the system reflects the overall Boltzmann distribution of populations. As  $\Delta E_0$  increases, R becomes dominant.

#### Comment 17.3

For an  $\text{R} \rightleftharpoons \text{P}$  equilibrium, the  $V$  factors in the partition functions cancel, so the appearance of  $q$  in place of  $q^\circ$  has no effect. In the case of a more general reaction, the conversion from  $q$  to  $q^\circ$  comes about at the stage of converting the pressures that occur in  $K$  to numbers of molecules.



**Fig. 17.21** It is important to take into account the densities of states of the molecules. Even though P might lie well above R in energy (that is,  $\Delta E_0$  is large and positive), P might have so many states that its total population dominates in the mixture. In classical thermodynamic terms, we have to take entropies into account as well as enthalpies when considering equilibria.



**Fig. 17.22** The model used in the text for exploring the effects of energy separations and densities of states on equilibria. The products P can dominate provided  $\Delta E_0$  is not too large and P has an appreciable density of states.

belonging to P; these states we label p with energies  $\varepsilon'_p$  (the prime is explained in a moment):

$$N_R = \sum_r n_r = \frac{N}{q} \sum_r e^{-\beta \varepsilon_r} \quad N_P = \sum_p n_p = \frac{N}{q} \sum_p e^{-\beta \varepsilon'_p}$$

The sum over the states of R is its partition function,  $q_R$ , so

$$N_R = \frac{N q_R}{q}$$

The sum over the states of P is also a partition function, but the energies are measured from the ground state of the combined system, which is the ground state of R. However, because  $\varepsilon'_p = \varepsilon_p + \Delta \varepsilon_0$ , where  $\Delta \varepsilon_0$  is the separation of zero-point energies (as in Fig. 17.21),

$$N_P = \frac{N}{q} \sum_p e^{-\beta(\varepsilon_p + \Delta \varepsilon_0)} = \frac{N}{q} \left( \sum_p e^{-\beta \varepsilon_p} \right) e^{-\beta \Delta \varepsilon_0} = \frac{N q_P}{q} e^{-\Delta_r E_0 / RT}$$

The switch from  $\Delta \varepsilon_0 / k$  to  $\Delta_r E_0 / R$  in the last step is the conversion of molecular energies to molar energies.

The equilibrium constant of the  $R \rightleftharpoons P$  reaction is proportional to the ratio of the numbers of the two types of molecule. Therefore,

$$K = \frac{N_P}{N_R} = \frac{q_P}{q_R} e^{-\Delta_r E_0 / RT}$$

as in eqn 17.58b.

The content of eqn 17.58 can be seen most clearly by exaggerating the molecular features that contribute to it. We shall suppose that R has only a single accessible level, which implies that  $q_R = 1$ . We also suppose that P has a large number of evenly, closely spaced levels (Fig. 17.22). The partition function of P is then  $q_P = kT/\varepsilon$ . In this model system, the equilibrium constant is

$$K = \frac{kT}{\varepsilon} e^{-\Delta_r E_0 / RT} \quad (17.59)$$

When  $\Delta_r E_0$  is very large, the exponential term dominates and  $K \ll 1$ , which implies that very little P is present at equilibrium. When  $\Delta_r E_0$  is small but still positive,  $K$  can exceed 1 because the factor  $kT/\varepsilon$  may be large enough to overcome the small size of the exponential term. The size of  $K$  then reflects the predominance of P at equilibrium on account of its high density of states. At low temperatures  $K \ll 1$  and the system consists entirely of R. At high temperatures the exponential function approaches 1 and the pre-exponential factor is large. Hence P becomes dominant. We see that, in this endothermic reaction (endothermic because P lies above R), a rise in temperature favours P, because its states become accessible. This behaviour is what we saw, from the outside, in Chapter 7.

The model also shows why the Gibbs energy,  $G$ , and not just the enthalpy, determines the position of equilibrium. It shows that the density of states (and hence the entropy) of each species as well as their relative energies controls the distribution of populations and hence the value of the equilibrium constant.

## Checklist of key ideas

- ☐ 1. The molecular partition function can be written as  $q = q^T q^R q^V q^E$ , with the contributions summarized in Table 17.3.
- ☐ 2. Thermodynamic functions can be expressed in terms of the partition function as summarized in Table 17.4.
- ☐ 3. The mean energy of a mode is  $\langle \epsilon^M \rangle = -(1/q^M)(\partial q^M / \partial \beta)_V$ , with the contributions from each mode summarized in Table 17.5.
- ☐ 4. The contribution of a mode M to the constant-volume heat capacity is  $C_V^M = -Nk\beta(\partial \langle \epsilon^M \rangle / \partial \beta)_V$ , with the contributions from each mode summarized in Table 17.5.
- ☐ 5. The overall heat capacity is written as  $C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$
- ☐ 6. The canonical partition function of a gas is  $Q = Z/\Lambda^{3N}$ , where  $Z$  is the configuration integral:  $Z = V^N/N!$  for a perfect gas, and  $Z = (1/N!) \int e^{-\beta E_p} d\tau_1 d\tau_2 \dots d\tau_N$  for a real gas.
- ☐ 7. In the virial equation of state, the second virial coefficient can be written as  $B = -(N_A/2V) \int f d\tau_1 d\tau_2$ , where the Mayer  $f$ -function is  $f = e^{-\beta E_p} - 1$ .
- ☐ 8. The radial distribution function,  $g(r)$ , where  $g(r)r^2 dr$  is the probability that a molecule will be found in the range  $dr$  at a distance  $r$  from another molecule. The internal energy and pressure of a fluid may be expressed in terms of the radial distribution function (eqns 17.50 and 17.51, respectively).
- ☐ 9. The residual entropy is a non-zero entropy at  $T = 0$  arising from molecular disorder.
- ☐ 10. The equilibrium constant can be written in terms of the partition function (eqn 17.54).

## Further reading

### Articles and texts

D. Chandler, *Introduction to modern statistical mechanics*. Oxford University Press (1987).

K.A. Dill and S. Bromberg, *Molecular driving forces: statistical thermodynamics in chemistry and biology*. Garland Publishing (2002).

T.L. Hill, *An introduction to statistical thermodynamics*. Dover, New York (1986).

D.A. McQuarrie and J.D. Simon, *Molecular thermodynamics*. University Science Books, Sausalito (1999).

B. Widom, *Statistical mechanics: a concise introduction for chemists*. Cambridge University Press (2002).

**Table 17.3** Contributions to the molecular partition function

Mode	Expression	Value
Translation	$q^T = \frac{V}{\Lambda^3} \quad \Lambda = \frac{h}{(2\pi mkT)^{1/2}}$ $\frac{q_m^{T\oplus}}{N_A} = \frac{kT}{p^\ominus \Lambda^3}$	$\Lambda/\text{pm} = \frac{1749}{(T/\text{K})^{1/2} (M/\text{g mol}^{-1})^{1/2}}$ $\frac{q_m^{T\oplus}}{N_A} = 2.561 \times 10^{-2} (T/\text{K})^{5/2} (M/\text{g mol}^{-1})^{3/2}$
Rotation		
Linear molecules	$q^R = \frac{kT}{\sigma hcB} = \frac{T}{\theta_R} \quad \theta_R = \frac{hcB}{k}$	$q^R = \frac{0.6950}{\sigma} \times \frac{T/\text{K}}{(B/\text{cm}^{-1})}$
Nonlinear molecules	$q^R = \frac{1}{\sigma} \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{ABC} \right)^{1/2}$	$q^R = \frac{1.0270}{\sigma} \times \frac{(T/\text{K})^{3/2}}{(ABC/\text{cm}^{-3})^{1/2}}$
Vibration	$q^V = \frac{1}{1 - e^{-hc\tilde{\nu}/kT}} = \frac{1}{1 - e^{-\theta_V/T}}$ $\theta_V = \frac{hc\tilde{\nu}}{k} = \frac{h\nu}{k}$ For $T \gg \theta_V$ , $q^V = \frac{kT}{hc\tilde{\nu}} = \frac{T}{\theta_V}$	$q^V = 0.695 \times \frac{T/\text{K}}{\tilde{\nu}/\text{cm}^{-1}}$
Electronic	$q^E = g_0$ [+ higher terms] where $g_0$ is the degeneracy of the electronic ground state	

Note that  $\beta = 1/kT$ .

**Table 17.4** Thermodynamic functions in terms of the partition function

Function	Expression	
	General case	Independent molecules*
Internal energy	$U(T) - U(0) = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V$	$U(T) - U(0) = -N \left( \frac{\partial \ln q}{\partial \beta} \right)_V$
Entropy	$S = \frac{U(T) - U(0)}{T} + k \ln Q$	$S = \frac{U(T) - U(0)}{T} + Nk \ln q$ (a)
		$S = \frac{U(T) - U(0)}{T} + Nk \ln \frac{eq}{N}$ (b)
Helmholtz energy	$A(T) - A(0) = -kT \ln Q$	$A(T) - A(0) = -NkT \ln q$ (a)
		$A(T) - A(0) = -NkT \ln \frac{eq}{N}$ (b)
Pressure	$p = kT \left( \frac{\partial \ln Q}{\partial V} \right)_T$	$p = NkT \left( \frac{\partial \ln q}{\partial V} \right)_T$ (b)
Enthalpy	$H(T) - H(0) = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T$	$H(T) - H(0) = -N \left( \frac{\partial \ln q}{\partial \beta} \right)_V + NkTV \left( \frac{\partial \ln q}{\partial V} \right)_T$
Gibbs energy	$G(T) - G(0) = -kT \ln Q + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T$	$G(T) - G(0) = -NkT \ln q + NkTV \left( \frac{\partial \ln q}{\partial V} \right)_T$ (a)
		$G(T) - G(0) = -NkT \ln \frac{eq}{N} + NkTV \left( \frac{\partial \ln q}{\partial V} \right)_T$ (b)

\* (a) is for distinguishable particles (from  $Q = q^N$ ), (b) for indistinguishable particles (from  $Q = q^N/N!$ ).

**Table 17.5** Contributions to mean energies and heat capacities

Mode	Expression	
	Mean energy	Heat capacity*
General mode, M	$\langle \varepsilon^M \rangle = - \left( \frac{\partial \ln q^M}{\partial \beta} \right)_V = - \frac{1}{q^M} \left( \frac{\partial q^M}{\partial \beta} \right)_V$	$C_V^M = -Nk\beta^2 \left( \frac{\partial \langle \varepsilon^M \rangle}{\partial \beta} \right)_V$
Translation	$\langle \varepsilon^T \rangle = \frac{3}{2}kT$	$C_V^T = \frac{3}{2}nR$
Rotation ( $T \gg \theta_R$ )	$\langle \varepsilon^R \rangle = kT$ , linear molecules	$C^R = nR$ , linear molecules
	$\langle \varepsilon^R \rangle = \frac{3}{2}kT$ , nonlinear molecules	$C^R = \frac{3}{2}nR$ , nonlinear molecules
Vibration	$\langle \varepsilon^V \rangle = \frac{h\nu}{e^{-\theta_V/T} - 1} = \frac{h\nu}{e^{\theta_V/T} - 1}$	$C^V = nRf$ , $f = \left( \frac{\theta_V}{T} \right)^2 \frac{e^{-\theta_V/T}}{(1 - e^{-\theta_V/T})^2}$
Vibration ( $T \gg \theta_V$ )	$\langle \varepsilon^V \rangle = kT$	$C^V = nR$

\* No distinction need be made between  $C_V$  and  $C_p$  for internal modes.

## Discussion questions

**17.1** Discuss the limitations of the expressions  $q^R = kT/hcB$ ,  $q^V = kT/hc\bar{\nu}$ , and  $q^E = g^E$ .

**17.2** Explain the origin of the symmetry number.

**17.3** Explain the origin of residual entropy.

**17.4** Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of the constant-volume molar heat capacity of a molecular substance.

**17.5** Use concepts of statistical thermodynamics to describe the molecular features that lead to the equations of state of perfect and real gases.

**17.6** Describe how liquids are investigated by using concepts of statistical thermodynamics.

**17.7** Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.

## Exercises

**17.1a** Use the equipartition theorem to estimate the constant-volume molar heat capacity of (a)  $I_2$ , (b)  $CH_4$ , (c)  $C_6H_6$  in the gas phase at  $25^\circ C$ .

**17.1b** Use the equipartition theorem to estimate the constant-volume molar heat capacity of (a)  $O_3$ , (b)  $C_2H_6$ , (c)  $CO_2$  in the gas phase at  $25^\circ C$ .

**17.2a** Estimate the values of  $\gamma = C_p/C_V$  for gaseous ammonia and methane. Do this calculation with and without the vibrational contribution to the energy. Which is closer to the expected experimental value at  $25^\circ C$ ?

**17.2b** Estimate the value of  $\gamma = C_p/C_V$  for carbon dioxide. Do this calculation with and without the vibrational contribution to the energy. Which is closer to the expected experimental value at  $25^\circ C$ ?

**17.3a** Estimate the rotational partition function of  $HCl$  at (a)  $25^\circ C$  and (b)  $250^\circ C$ .

**17.3b** Estimate the rotational partition function of  $O_2$  at (a)  $25^\circ C$  and (b)  $250^\circ C$ .

**17.4a** Give the symmetry number for each of the following molecules:

(a)  $CO$ , (b)  $O_2$ , (c)  $H_2S$ , and (d)  $SiH_4$ , (e)  $CHCl_3$ .

**17.4b** Give the symmetry number for each of the following molecules:

(a)  $CO_2$ , (b)  $O_3$ , (c)  $SO_3$ , (d)  $SF_6$ , and (e)  $Al_2Cl_6$ .

**17.5a** Calculate the rotational partition function of  $H_2O$  at 298 K from its rotational constants  $27.878\text{ cm}^{-1}$ ,  $14.509\text{ cm}^{-1}$ , and  $9.287\text{ cm}^{-1}$ . Above what temperature is the high-temperature approximation valid to within 10 per cent of the true value?

**17.5b** Calculate the rotational partition function of  $SO_2$  at 298 K from its rotational constants  $2.02736\text{ cm}^{-1}$ ,  $0.34417\text{ cm}^{-1}$ , and  $0.293535\text{ cm}^{-1}$ . Above what temperature is the high-temperature approximation valid to within 10 per cent of the true value?

**17.6a** From the results of Exercise 17.5a, calculate the rotational contribution to the molar entropy of gaseous water at  $25^\circ C$ .

**17.6b** From the results of Exercise 17.5b, calculate the rotational contribution to the molar entropy of sulfur dioxide at  $25^\circ C$ .

**17.7a** Calculate the rotational partition function of  $CH_4$  (a) by direct summation of the energy levels at 298 K and 500 K, and (b) by the high-temperature approximation. Take  $B = 5.2412\text{ cm}^{-1}$ .

**17.7b** Calculate the rotational partition function of  $CH_3CN$  (a) by direct summation of the energy levels at 298 K and 500 K, and (b) by the high-temperature approximation. Take  $A = 5.28\text{ cm}^{-1}$  and  $B = 0.307\text{ cm}^{-1}$ .

**17.8a** The bond length of  $O_2$  is 120.75 pm. Use the high-temperature approximation to calculate the rotational partition function of the molecule at 300 K.

**17.8b** The NOF molecule is an asymmetric rotor with rotational constants  $3.1752\text{ cm}^{-1}$ ,  $0.3951\text{ cm}^{-1}$ , and  $0.3505\text{ cm}^{-1}$ . Calculate the rotational partition function of the molecule at (a)  $25^\circ C$ , (b)  $100^\circ C$ .

**17.9a** Plot the molar heat capacity of a collection of harmonic oscillators as a function of  $T/\theta_V$ , and predict the vibrational heat capacity of ethyne at (a) 298 K, (b) 500 K. The normal modes (and their degeneracies in parentheses) occur at wavenumbers  $612(2)$ ,  $729(2)$ ,  $1974$ ,  $3287$ , and  $3374\text{ cm}^{-1}$ .

**17.9b** Plot the molar entropy of a collection of harmonic oscillators as a function of  $T/\theta_V$ , and predict the standard molar entropy of ethyne at (a) 298 K, (b) 500 K. For data, see the preceding exercise.

**17.10a** A  $CO_2$  molecule is linear, and its vibrational wavenumbers are  $1388.2\text{ cm}^{-1}$ ,  $667.4\text{ cm}^{-1}$ , and  $2349.2\text{ cm}^{-1}$ , the last being doubly degenerate and the others non-degenerate. The rotational constant of the molecule is  $0.3902\text{ cm}^{-1}$ . Calculate the rotational and vibrational contributions to the molar Gibbs energy at 298 K.

**17.10b** An  $O_3$  molecule is angular, and its vibrational wavenumbers are  $1110\text{ cm}^{-1}$ ,  $705\text{ cm}^{-1}$ , and  $1042\text{ cm}^{-1}$ . The rotational constants of the molecule are  $3.553\text{ cm}^{-1}$ ,  $0.4452\text{ cm}^{-1}$ , and  $0.3948\text{ cm}^{-1}$ . Calculate the rotational and vibrational contributions to the molar Gibbs energy at 298 K.

**17.11a** The ground level of  $Cl$  is  $^2P_{3/2}$  and a  $^2P_{1/2}$  level lies  $881\text{ cm}^{-1}$  above it. Calculate the electronic contribution to the heat capacity of  $Cl$  atoms at (a) 500 K and (b) 900 K.

**17.11b** The first electronically excited state of  $O_2$  is  $^1\Delta_g$  and lies  $7918.1\text{ cm}^{-1}$  above the ground state, which is  $^3\Sigma_g^-$ . Calculate the electronic contribution to the molar Gibbs energy of  $O_2$  at 400 K.

**17.12a** The ground state of the  $Co^{2+}$  ion in  $CoSO_4 \cdot 7H_2O$  may be regarded as  $^4T_{9/2}$ . The entropy of the solid at temperatures below 1 K is derived almost entirely from the electron spin. Estimate the molar entropy of the solid at these temperatures.

**17.12b** Estimate the contribution of the spin to the molar entropy of a solid sample of a  $d$ -metal complex with  $S = \frac{5}{2}$ .

**17.13a** Calculate the residual molar entropy of a solid in which the molecules can adopt (a) three, (b) five, (c) six orientations of equal energy at  $T = 0$ .

**17.13b** Suppose that the hexagonal molecule  $C_6H_nF_{6-n}$  has a residual entropy on account of the similarity of the H and F atoms. Calculate the residual for each value of  $n$ .

**17.14a** Calculate the equilibrium constant of the reaction  $I_2(g) \rightleftharpoons 2I(g)$  at 1000 K from the following data for  $I_2$ :  $\bar{\nu} = 214.36\text{ cm}^{-1}$ ,  $B = 0.0373\text{ cm}^{-1}$ ,  $D_e = 1.5422\text{ eV}$ . The ground state of the  $I$  atoms is  $^2P_{3/2}$ , implying fourfold degeneracy.

**17.14b** Calculate the value of  $K$  at 298 K for the gas-phase isotopic exchange reaction  $2\text{}^{79}\text{Br}^{81}\text{Br} \rightleftharpoons \text{Br} + ^{81}\text{Br}^{81}\text{Br}$ . The  $\text{Br}_2$  molecule has a non-degenerate ground state, with no other electronic states nearby. Base the calculation on the wavenumber of the vibration of  $^{79}\text{Br}^{81}\text{Br}$ , which is  $323.33\text{ cm}^{-1}$ .

## Problems\*

## Numerical problems

**17.1** The NO molecule has a doubly degenerate electronic ground state and a doubly degenerate excited state at  $121.1\text{ cm}^{-1}$ . Calculate the electronic contribution to the molar heat capacity of the molecule at (a) 50 K, (b) 298 K, and (c) 500 K.

**17.2** Explore whether a magnetic field can influence the heat capacity of a paramagnetic molecule by calculating the electronic contribution to the heat capacity of an  $\text{NO}_2$  molecule in a magnetic field. Estimate the total constant-volume heat capacity using equipartition, and calculate the percentage change in heat capacity brought about by a 5.0 T magnetic field at (a) 50 K, (b) 298 K.

**17.3** The energy levels of a  $\text{CH}_3$  group attached to a larger fragment are given by the expression for a particle on a ring, provided the group is rotating freely. What is the high-temperature contribution to the heat capacity and entropy of such a freely rotating group at  $25^\circ\text{C}$ ? The moment of inertia of  $\text{CH}_3$  about its three-fold rotation axis (the axis that passes through the C atom and the centre of the equilateral triangle formed by the H atoms) is  $5.341 \times 10^{-47}\text{ kg m}^2$ .

**17.4** Calculate the temperature dependence of the heat capacity of  $p\text{-H}_2$  (in which only rotational states with even values of  $J$  are populated) at low temperatures on the basis that its rotational levels  $J=0$  and  $J=2$  constitute a system that resembles a two-level system except for the degeneracy of the upper level. Use  $B = 60.864\text{ cm}^{-1}$  and sketch the heat capacity curve. The experimental heat capacity of  $p\text{-H}_2$  does in fact show a peak at low temperatures.

**17.5** The pure rotational microwave spectrum of HCl has absorption lines at the following wavenumbers (in  $\text{cm}^{-1}$ ): 21.19, 42.37, 63.56, 84.75, 105.93, 127.12, 148.31, 169.49, 190.68, 211.87, 233.06, 254.24, 275.43, 296.62, 317.80, 338.99, 360.18, 381.36, 402.55, 423.74, 444.92, 466.11, 487.30, 508.48. Calculate the rotational partition function at  $25^\circ\text{C}$  by direct summation.

**17.6** Calculate the standard molar entropy of  $\text{N}_2(\text{g})$  at 298 K from its rotational constant  $B = 1.9987\text{ cm}^{-1}$  and its vibrational wavenumber  $\tilde{\nu} = 2358\text{ cm}^{-1}$ . The thermochemical value is  $192.1\text{ J K}^{-1}\text{ mol}^{-1}$ . What does this suggest about the solid at  $T = 0$ ?

**17.7‡** J.G. Dojahn, E.C.M. Chen, and W.E. Wentworth (*J. Phys. Chem.* **100**, 9649 (1996)) characterized the potential energy curves of the ground and electronic states of homonuclear diatomic halogen anions. The ground state of  $\text{F}_2^-$  is  $^2\Sigma_u^+$  with a fundamental vibrational wavenumber of  $450.0\text{ cm}^{-1}$  and equilibrium internuclear distance of 190.0 pm. The first two excited states are at 1.609 and 1.702 eV above the ground state. Compute the standard molar entropy of  $\text{F}_2^-$  at 298 K.

**17.8‡** In a spectroscopic study of buckminsterfullerene  $\text{C}_{60}$ , F. Negri, G. Orlandi, and F. Zerbetto (*J. Phys. Chem.* **100**, 10849 (1996)) reviewed the wavenumbers of all the vibrational modes of the molecule. The wavenumber for the single  $A_u$  mode is  $976\text{ cm}^{-1}$ ; wavenumbers for the four threefold degenerate  $T_{1u}$  modes are 525, 578, 1180, and  $1430\text{ cm}^{-1}$ ; wavenumbers for the five threefold degenerate  $T_{2u}$  modes are 354, 715, 1037, 1190, and  $1540\text{ cm}^{-1}$ ; wavenumbers for the six fourfold degenerate  $G_u$  modes are 345, 757, 776, 963, 1315, and  $1410\text{ cm}^{-1}$ ; and wavenumbers for the seven fivefold degenerate  $H_u$  modes are 403, 525, 667, 738, 1215, 1342, and  $1566\text{ cm}^{-1}$ . How many modes have a vibrational temperature  $\theta_v$  below 1000 K? Estimate the molar constant-volume heat capacity of  $\text{C}_{60}$  at 1000 K, counting as active all modes with  $\theta_v$  below this temperature.

**17.9‡** Treat carbon monoxide as a perfect gas and apply equilibrium statistical thermodynamics to the study of its properties, as specified below, in the temperature range 100–1000 K at 1 bar.  $\tilde{\nu} = 2169.8\text{ cm}^{-1}$ ,  $B = 1.931\text{ cm}^{-1}$ , and  $D_0 = 11.09\text{ eV}$ ; neglect anharmonicity and centrifugal distortion. (a) Examine the probability distribution of molecules over available rotational and vibrational states. (b) Explore numerically the differences, if any, between the rotational molecular partition function as calculated with the discrete energy distribution and that calculated with the classical, continuous energy distribution. (c) Calculate the individual contributions to  $U_m(T) - U_m(100\text{ K})$ ,  $C_{v,m}(T)$ , and  $S_m(T) - S_m(100\text{ K})$  made by the translational, rotational, and vibrational degrees of freedom.

**17.10** Calculate and plot as a function of temperature, in the range 300 K to 1000 K, the equilibrium constant for the reaction  $\text{CD}_4(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{CHD}_3(\text{g}) + \text{DCl}(\text{g})$  using the following data (numbers in parentheses are degeneracies):  $\tilde{\nu}(\text{CHD}_3)/\text{cm}^{-1} = 2993(1), 2142(1), 1003(3), 1291(2), 1036(2)$ ;  $\tilde{\nu}(\text{CD}_4)/\text{cm}^{-1} = 2109(1), 1092(2), 2259(3), 996(3)$ ;  $\tilde{\nu}(\text{HCl})/\text{cm}^{-1} = 2991$ ;  $\tilde{\nu}(\text{DCl})/\text{cm}^{-1} = 2145$ ;  $B(\text{HCl})/\text{cm}^{-1} = 10.59$ ;  $B(\text{DCl})/\text{cm}^{-1} = 5.445$ ;  $B(\text{CHD}_3)/\text{cm}^{-1} = 3.28$ ;  $A(\text{CHD}_3)/\text{cm}^{-1} = 2.63$ ,  $B(\text{CD}_4)/\text{cm}^{-1} = 2.63$ .

**17.11** The exchange of deuterium between acid and water is an important type of equilibrium, and we can examine it using spectroscopic data on the molecules. Calculate the equilibrium constant at (a) 298 K and (b) 800 K for the gas-phase exchange reaction  $\text{H}_2\text{O} + \text{DCl} \rightleftharpoons \text{HDO} + \text{HCl}$  from the following data:  $\tilde{\nu}(\text{H}_2\text{O})/\text{cm}^{-1} = 3656.7, 1594.8, 3755.8$ ;  $\tilde{\nu}(\text{HDO})/\text{cm}^{-1} = 2726.7, 1402.2, 3707.5$ ;  $A(\text{H}_2\text{O})/\text{cm}^{-1} = 27.88$ ;  $B(\text{H}_2\text{O})/\text{cm}^{-1} = 14.51$ ;  $C(\text{H}_2\text{O})/\text{cm}^{-1} = 9.29$ ;  $A(\text{HDO})/\text{cm}^{-1} = 23.38$ ;  $B(\text{HDO})/\text{cm}^{-1} = 9.102$ ;  $C(\text{HDO})/\text{cm}^{-1} = 6.417$ ;  $B(\text{HCl})/\text{cm}^{-1} = 10.59$ ;  $B(\text{DCl})/\text{cm}^{-1} = 5.449$ ;  $\tilde{\nu}(\text{HCl})/\text{cm}^{-1} = 2991$ ;  $\tilde{\nu}(\text{DCl})/\text{cm}^{-1} = 2145$ .

## Theoretical problems

**17.12** Derive the Sackur–Tetrode equation for a monatomic gas confined to a two-dimensional surface, and hence derive an expression for the standard molar entropy of condensation to form a mobile surface film.

**17.13‡** For  $\text{H}_2$  at very low temperatures, only translational motion contributes to the heat capacity. At temperatures above  $\theta_R = hcB/k$ , the rotational contribution to the heat capacity becomes significant. At still higher temperatures, above  $\theta_v = hv/k$ , the vibrations contribute. But at this latter temperature, dissociation of the molecule into the atoms must be considered. (a) Explain the origin of the expressions for  $\theta_R$  and  $\theta_v$ , and calculate their values for hydrogen. (b) Obtain an expression for the molar constant-pressure heat capacity of hydrogen at all temperatures taking into account the dissociation of hydrogen. (c) Make a plot of the molar constant-pressure heat capacity as a function of temperature in the high-temperature region where dissociation of the molecule is significant.

**17.14** Derive expressions for the internal energy, heat capacity, entropy, Helmholtz energy, and Gibbs energy of a harmonic oscillator. Express the results in terms of the vibrational temperature,  $\theta_v$  and plot graphs of each property against  $T/\theta_v$ .

**17.15** Suppose that an intermolecular potential has a hard-sphere core of radius  $r_1$  and a shallow attractive well of uniform depth  $\varepsilon$  out to a distance  $r_2$ . Show, by using eqn 17.42 and the condition  $\varepsilon \ll kT$ , that such a model is approximately consistent with a van der Waals equation of state when  $b \ll V_m$ , and relate the van der Waals parameters and the Joule–Thomson coefficient to the parameters in this model.

\* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.



**17.16†** (a) Show that the number of molecules in any given rotational state of a linear molecule is given by  $N_J = C(2J+1)e^{-hcBJ(J+1)/kT}$ , where  $C$  is independent of  $J$ . (b) Use this result to derive eqn 13.39 for the value of  $J$  of the most highly populated rotational level. (c) Estimate the temperature at which the spectrum of HCl shown in Fig. 13.44 was obtained. (d) What is the most highly populated level of a spherical rotor at a temperature  $T$ ?

**17.17** A more formal way of arriving at the value of the symmetry number is to note that  $\sigma$  is the order (the number of elements) of the *rotational subgroup* of the molecule, the point group of the molecule with all but the identity and the rotations removed. The rotational subgroup of  $H_2O$  is  $\{E, C_2\}$ , so  $\sigma = 2$ . The rotational subgroup of  $NH_3$  is  $\{E, 2C_3\}$ , so  $\sigma = 3$ . This recipe makes it easy to find the symmetry numbers for more complicated molecules. The rotational subgroup of  $CH_4$  is obtained from the  $T$  character table as  $\{E, 8C_3, 3C_2\}$ , so  $\sigma = 12$ . For benzene, the rotational subgroup of  $D_{6h}$  is  $\{E, 2C_6, 2C_3, C_2, 3C_2', 3C_2''\}$ , so  $\sigma = 12$ . (a) Estimate the rotational partition function of ethene at 25°C given that  $A = 4.828 \text{ cm}^{-1}$ ,  $B = 1.0012 \text{ cm}^{-1}$ , and  $C = 0.8282 \text{ cm}^{-1}$ . (b) Evaluate the rotational partition function of pyridine,  $C_5H_5N$ , at room temperature ( $A = 0.2014 \text{ cm}^{-1}$ ,  $B = 0.1936 \text{ cm}^{-1}$ ,  $C = 0.0987 \text{ cm}^{-1}$ ).

**17.18** Although expressions like  $\langle \epsilon \rangle = -d \ln q / d\beta$  are useful for formal manipulations in statistical thermodynamics, and for expressing thermodynamic functions in neat formulas, they are sometimes more trouble than they are worth in practical applications. When presented with a table of energy levels, it is often much more convenient to evaluate the following sums directly:

$$q = \sum_j e^{-\beta \epsilon_j} \quad \bar{\epsilon} = \frac{\sum_j \epsilon_j e^{-\beta \epsilon_j}}{q} \quad \bar{\epsilon}^2 = \frac{\sum_j \epsilon_j^2 e^{-\beta \epsilon_j}}{q}$$

(a) Derive expressions for the internal energy, heat capacity, and entropy in terms of these three functions. (b) Apply the technique to the calculation of the electronic contribution to the constant-volume molar heat capacity of magnesium vapour at 5000 K using the following data:

Term	$1S$	$3P_0$	$3P_1$	$3P_2$	$1P_1$	$3S_1$
Degeneracy	1	1	3	5	3	3
$\bar{\nu}/\text{cm}^{-1}$	0	21 850	21 870	21 911	35 051	41 197

**17.19** Show how the heat capacity of a linear rotor is related to the following sum:

$$\zeta(\beta) = \frac{1}{q^2} \sum_{J,J'} \{ \epsilon(J) - \epsilon(J') \}^2 g(J) g(J') e^{-\beta[\epsilon(J) + \epsilon(J')]}$$

by

$$C = \frac{1}{2} N k \beta^2 \zeta(\beta)$$

where the  $\epsilon(J)$  are the rotational energy levels and  $g(J)$  their degeneracies. Then go on to show graphically that the total contribution to the heat capacity of a linear rotor can be regarded as a sum of contributions due to transitions  $0 \rightarrow 1$ ,  $0 \rightarrow 2$ ,  $1 \rightarrow 2$ ,  $1 \rightarrow 3$ , etc. In this way, construct Fig. 17.11 for the rotational heat capacities of a linear molecule.

**17.20** Set up a calculation like that in Problem 17.19 to analyse the vibrational contribution to the heat capacity in terms of excitations between levels and illustrate your results graphically in terms of a diagram like that in Fig. 17.11.

**17.21** Determine whether a magnetic field can influence the value of an equilibrium constant. Consider the equilibrium  $I_2(g) \rightleftharpoons 2 I(g)$  at 1000 K, and calculate the ratio of equilibrium constants  $K(B)/K$ , where  $K(B)$  is the equilibrium constant when a magnetic field  $B$  is present and removes the degeneracy of the four states of the  $2P_{3/2}$  level. Data on the species are given in Exercise 17.14a. The electronic  $g$  value of the atoms is  $\frac{4}{3}$ . Calculate the field required to change the equilibrium constant by 1 per cent.

**17.22** The heat capacity ratio of a gas determines the speed of sound in it through the formula  $c_s = (\gamma RT/M)^{1/2}$ , where  $\gamma = C_p/C_v$  and  $M$  is the molar mass of the gas. Deduce an expression for the speed of sound in a perfect gas of (a) diatomic, (b) linear triatomic, (c) nonlinear triatomic molecules at high temperatures (with translation and rotation active). Estimate the speed of sound in air at 25°C.

### Applications: to biology, materials science, environmental science, and astrophysics

**17.23** An average human DNA molecule has  $5 \times 10^8$  binucleotides (rungs on the DNA ladder) of four different kinds. If each rung were a random choice of one of these four possibilities, what would be the residual entropy associated with this typical DNA molecule?

**17.24** It is possible to write an approximate expression for the partition function of a protein molecule by including contributions from only two states: the native and denatured forms of the polymer. Proceeding with this crude model gives us insight into the contribution of denaturation to the heat capacity of a protein. It follows from *Illustration* 16.4 that the total energy of a system of  $N$  protein molecules is

$$E = \frac{N \epsilon e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}}$$

where  $\epsilon$  is the energy separation between the denatured and native forms.

(a) Show that the constant-volume molar heat capacity is

$$C_{V,m} = \frac{R(\epsilon_m/RT)^2 e^{-\epsilon_m/RT}}{(1 + e^{-\epsilon_m/RT})^2}$$

*Hint.* For two functions  $f$  and  $g$ , the quotient rule of differentiation states that  $d(f/g)/dx = (1/g)df/dx - (f/g^2)dg/dx$ . (b) Plot the variation of  $C_{V,m}$  with temperature. (c) If the function  $C_{V,m}(T)$  has a maximum or minimum, derive an expression for the temperature at which it occurs.

**17.25†** R. Viswanathan, R.W. Schmude, Jr., and K.A. Gingerich (*J. Phys. Chem.* **100**, 10784 (1996)) studied thermodynamic properties of several boron–silicon gas-phase species experimentally and theoretically. These species can occur in the high-temperature chemical vapour deposition (CVD) of silicon-based semiconductors. Among the computations they reported was computation of the Gibbs energy of  $BSi(g)$  at several temperatures based on a  $4\Sigma^-$  ground state with equilibrium internuclear distance of 190.5 pm and fundamental vibrational wavenumber of  $772 \text{ cm}^{-1}$  and a  $2P_0$  first excited level  $8000 \text{ cm}^{-1}$  above the ground level. Compute the standard molar Gibbs energy  $G_m^\circ(2000 \text{ K}) - G_m^\circ(0)$ .

**17.26†** The molecule  $Cl_2O_2$ , which is believed to participate in the seasonal depletion of ozone over Antarctica, has been studied by several means. M. Birk, R.R. Friedl, E.A. Cohen, H.M. Pickett, and S.P. Sander (*J. Chem. Phys.* **91**, 6588 (1989)) report its rotational constants (actually  $cB$ ) as 13 109.4, 2409.8, and 2139.7 MHz. They also report that its rotational spectrum indicates a molecule with a symmetry number of 2. J. Jacobs, M. Kronberg, H.S.P. Möller, and H. Willner (*J. Amer. Chem. Soc.* **116**, 1106 (1994)) report its vibrational wavenumbers as 753, 542, 310, 127, 646, and  $419 \text{ cm}^{-1}$ . Compute  $G_m^\circ(200 \text{ K}) - G_m^\circ(0)$  of  $Cl_2O_2$ .

**17.27†** J. Hutter, H.P. Lüthi, and F. Diederich (*J. Amer. Chem. Soc.* **116**, 750 (1994)) examined the geometric and vibrational structure of several carbon molecules of formula  $C_n$ . Given that the ground state of  $C_3$ , a molecule found in interstellar space and in flames, is an angular singlet with moments of inertia 39.340, 39.032, and  $0.3082 \text{ u } \text{\AA}^2$  (where  $1 \text{ \AA} = 10^{-10} \text{ m}$ ) and with vibrational wavenumbers of 63.4, 1224.5, and  $2040 \text{ cm}^{-1}$ , compute  $G_m^\circ(10.00 \text{ K}) - G_m^\circ(0)$  and  $G_m^\circ(1000 \text{ K}) - G_m^\circ(0)$  for  $C_3$ .