

## Brief illustration 13B.2

To calculate the translational partition function of an  $\text{H}_2$  molecule confined to a  $100\text{ cm}^3$  vessel at  $25^\circ\text{C}$ , use  $m = 2.016m_u$ . Then, from  $\Lambda = h/(2\pi mkT)^{1/2}$ ,

$$\Lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{\left\{ 2\pi \times (2.016 \times 1.6605 \times 10^{-27} \text{ kg}) \times \left( 1.381 \times 10^{-23} \text{ J K}^{-1} \right) \times (298 \text{ K}) \right\}^{1/2}}$$

$\text{kg m}^2 \text{ s}^{-2}$

$\text{kg m}^2 \text{ s}^{-2}$

$$= 7.12 \dots \times 10^{-11} \text{ m}$$

Therefore,

$$q^T = \frac{1.00 \times 10^{-4} \text{ m}^3}{(7.12 \dots \times 10^{-11} \text{ m})^3} = 2.77 \times 10^{26}$$

About  $10^{26}$  quantum states are thermally accessible, even at room temperature and for this light molecule. Many states are occupied if the thermal wavelength (which in this case is  $71.2\text{ pm}$ ) is small compared with the linear dimensions of the container.

Equation 13B.10b can be interpreted in terms of the average separation,  $d$ , of the particles in the container. Because  $q$  is the total number of accessible states, the average number of translational states per molecule is  $q^T/N$ . For this quantity to be large, the condition  $V/N\Lambda^3 \gg 1$  must be met. However,  $V/N$  is the volume occupied by a single particle, and therefore the average separation of the particles is  $d = (V/N)^{1/3}$ . The condition for there being many states available per molecule is therefore  $d^3/\Lambda^3 \gg 1$ , and therefore  $d \gg \Lambda$ . That is, for eqn 13B.10b to be valid, *the average separation of the particles must be much greater than their thermal wavelength*. For 1 mol  $\text{H}_2$  molecules at 1 bar and 298 K, the average separation is 3 nm, which is significantly larger than their thermal wavelength ( $71.2\text{ pm}$ ).

The validity of eqn 13B.10b can be expressed in a different way by noting that the approximations that led to it 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  $\text{H}_2$  at 298 K,  $\Lambda = 71\text{ pm}$ , which is far smaller than any conventional container is likely to be (but comparable to pores in zeolites or cavities in clathrates). For  $\text{O}_2$ , a heavier molecule,  $\Lambda = 18\text{ pm}$ .

## (b) The rotational contribution

The energy levels of a linear rotor are  $\epsilon_J = hc\tilde{B}J(J+1)$ , with  $J = 0, 1, 2, \dots$  (Topic 11B). The state of lowest energy has zero energy, so no adjustment need be made to the energies given by this expression. Each level consists of  $2J + 1$  degenerate states. Therefore, the partition function of a non-symmetrical (AB) linear rotor is

$$q^R = \sum_J \overbrace{(2J+1)}^{g_J} e^{-\overbrace{\beta hc\tilde{B}J(J+1)}^{\epsilon_J}} \quad (13B.11)$$

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. (The case of symmetrical  $\text{A}_2$  molecules is dealt with later.)

## Example 13B.1 Evaluating the rotational partition function explicitly

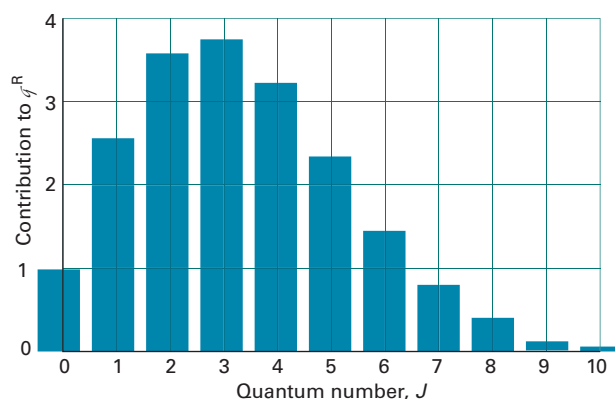
Evaluate the rotational partition function of  $^1\text{H}^{35}\text{Cl}$  at  $25^\circ\text{C}$ , given that  $\tilde{B} = 10.591\text{ cm}^{-1}$ .

**Collect your thoughts** You need to evaluate eqn 13B.11 term by term, using  $kT/hc = 207.224\text{ cm}^{-1}$  at 298.15 K. The sum is readily evaluated by using mathematical software.

**The solution** To show how successive terms contribute, draw up the following table by using  $hc\tilde{B}/kT = 0.05111$  (Fig. 13B.6):

$J$	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 13B.11 (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  $q^R = 19.903$ .



**Figure 13B.6** The contributions to the rotational partition function of an HCl molecule at  $25^\circ\text{C}$ . The vertical axis is the value of  $(2J+1)e^{-\beta hc\tilde{B}J(J+1)}$ . 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  $J$ .

**Comment.** 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.

**Self-test 13B.1** Evaluate the rotational partition function for  $^1\text{H}^{35}\text{Cl}$  at  $0^\circ\text{C}$ .

Answer: 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 11C.1) and often smaller (though the very light  $\text{H}_2$  molecule, for which  $\tilde{B} = 60.9 \text{ cm}^{-1}$ , is one important exception). It follows that many rotational levels are populated at normal temperatures. When that is the case, explicit expressions for the rotational partition function can be derived.

Consider a linear rotor. If many rotational states are occupied and  $kT$  is much larger than the separation between neighbouring states, the sum that defines the partition function can be approximated by an integral:

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

This integral can be evaluated without much effort by making the substitution  $x = \beta h c \tilde{B} J(J+1)$ , so that  $dx/dJ = \beta h c \tilde{B} (2J+1)$  and therefore  $(2J+1)dJ = dx/\beta h c \tilde{B}$ . Then

Integral E.1:

$$q^R = \frac{1}{\beta h c \tilde{B}} \int_0^\infty e^{-x} dx = \frac{1}{\beta h c \tilde{B}}$$

which (because  $\beta = 1/kT$ ) is

$$q^R = \frac{kT}{hc\tilde{B}} \quad \text{Rotational partition function [unsymmetrical linear molecule]} \quad (13B.12a)$$

A similar but more elaborate approach can be used for nonlinear molecules.

### How is that done? 13B.2 Deriving an expression for the rotational partition function of a nonlinear molecule

Consider a symmetric rotor (Topic 11B) for which the energy levels are

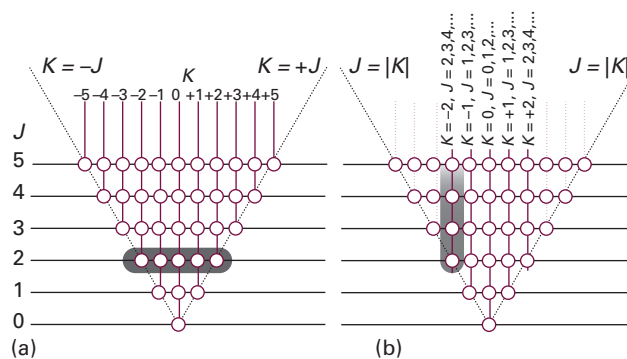
$$E_{J,K,M_J} = hc\tilde{B}J(J+1) + hc(\tilde{A} - \tilde{B})K^2$$

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, the same values can be covered by allowing  $K$  to range from  $-\infty$  to  $\infty$ , with  $J$  confined to  $|K|, |K|+1, \dots, \infty$  for each value of  $K$  (Fig. 13B.7).

#### Step 1 Write an expression for the sum over energy states

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

$$q = \sum_{J=0}^\infty \sum_{K=-J}^J \sum_{M_J=-J}^J e^{-\beta E_{J,K,M_J}}$$



**Figure 13B.7** The calculation of the rotational partition function includes a contribution, indicated by the circles, for all possible combinations of  $J$  and  $K$ . The sum is formed either (a) by allowing  $J$  to take the values  $0, 1, 2, \dots$  and then for each  $J$  allowing  $K$  to range from  $J$  to  $-J$ , or (b) by allowing  $K$  to range from  $-\infty$  to  $\infty$ , and for each value of  $K$  allowing  $J$  to take the values  $|K|, |K|+1, \dots, \infty$ . The tinted areas show in (a) the sum from  $K=-2$  to  $+2$  for  $J=2$ , and in (b) the sum with  $J=2, 3, \dots$  for  $K=-2$ .

can be written equivalently as

$$\begin{aligned} q &= \sum_{J=0}^\infty \sum_{K=-J}^J (2J+1) e^{-\beta E_{J,K,M_J}} = \sum_{K=-\infty}^\infty \sum_{J=|K|}^\infty (2J+1) e^{-\beta E_{J,K,M_J}} \\ &= \sum_{K=-\infty}^\infty e^{-hc\beta(\tilde{A}-\tilde{B})K^2} \sum_{J=|K|}^\infty (2J+1) e^{-hc\beta\tilde{B}J(J+1)} \end{aligned}$$

#### Step 2 Convert the sums to integrals

As for linear molecules, assume that the temperature is so high that numerous states are occupied, in which case the sums may be approximated by integrals. Then

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

#### Step 3 Evaluate the integrals

You should recognize the integral over  $J$  as the integral of the derivative of a function, which is the function itself, so

$|K| \gg 1$  for most allowed values

$$\int_{|K|}^\infty (2J+1) e^{-hc\beta\tilde{B}J(J+1)} dJ = \frac{1}{hc\beta\tilde{B}} e^{-hc\beta\tilde{B}|K|(|K|+1)} \approx \frac{1}{hc\beta\tilde{B}} e^{-hc\beta\tilde{B}K^2}$$

Use this result in the integral over  $J$  in Step 2:

$$\begin{aligned} q &= \frac{1}{hc\beta\tilde{B}} \int_{-\infty}^\infty e^{-hc\beta(\tilde{A}-\tilde{B})K^2} e^{-hc\beta\tilde{B}K^2} dK = \frac{1}{hc\beta\tilde{B}} \int_{-\infty}^\infty e^{-hc\beta\tilde{A}K^2} dK \\ &= \frac{1}{hc\beta\tilde{B}} \left( \frac{\pi}{hc\beta\tilde{A}} \right)^{1/2} \end{aligned}$$

Integral G.1

now rearrange this expression into

$$q = \frac{1}{(hc\beta)^{3/2}} \left( \frac{\pi}{\tilde{A}\tilde{B}^2} \right)^{1/2} = \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{\tilde{A}\tilde{B}^2} \right)^{1/2}$$

For an asymmetric rotor with its three moments of inertia, one of the  $\tilde{B}$  is replaced by  $\tilde{C}$ , to give

$$q^R = \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{\tilde{A}\tilde{B}\tilde{C}} \right)^{1/2} \quad (13B.12b)$$

Rotational partition function  
[nonlinear molecule]

### Brief illustration 13B.3

For  $^1\text{H}^{35}\text{Cl}$  at 298.15 K, use  $kT/hc = 207.224\text{ cm}^{-1}$  and  $\tilde{B} = 10.591\text{ cm}^{-1}$ . Then

$$q^R = \frac{kT}{hc\tilde{B}} = \frac{207.224\text{ cm}^{-1}}{10.591\text{ cm}^{-1}} = 19.57$$

The value is in good agreement with the exact value (19.903) and obtained with much less effort.

A useful way of expressing the temperature above which eqns 13B.12a and 13B.12b are valid is to introduce the **characteristic rotational temperature**,  $\theta^R = hc\tilde{B}/k$ . 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 given in Table 13B.1. The value for  $^1\text{H}_2$  (87.6 K) is abnormally high, so the approximation must be used carefully for this molecule. However, before using eqn 13B.12a for symmetrical molecules, such as  $\text{H}_2$ , read on (to eqn 13B.13a).

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.

A 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 rotational states that are accessible at normal temperatures.

It is important not to include too many rotational states in the sum that defines the partition function. 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,

$$q^R = \frac{kT}{2hc\tilde{B}} = \frac{T}{2\theta^R} \quad (13B.13a)$$

Rotational partition function  
[symmetrical linear rotor]

The equations for symmetrical and non-symmetrical 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

$$q^R = \frac{T}{\sigma\theta^R} \quad (13B.13b)$$

Rotational partition function  
[linear rotor]

For a heteronuclear diatomic molecule  $\sigma = 1$ ; for a homonuclear diatomic molecule or a symmetrical linear molecule,  $\sigma = 2$ . The formal justification of this rule depends on assessing the role of the Pauli principle.

### How is that done? 13B.3 Identifying the origin of the symmetry number

The Pauli principle forbids the occupation of certain states. It is shown in Topic 11B, for example, that  $^1\text{H}_2$  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). In *ortho*- $\text{H}_2$  there are three nuclear spin states for each value of  $J$  (because there are three ‘parallel’ spin states of the two nuclei); in *para*- $\text{H}_2$  there is just one nuclear spin state for each value of  $J$ .

To set up the rotational partition function and take into account the Pauli principle, 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 for each molecule is

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

The odd- $J$  states are three times more heavily weighted than the even- $J$  states (Fig. 13B.8). The illustration shows that approximately the same answer would be obtained 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

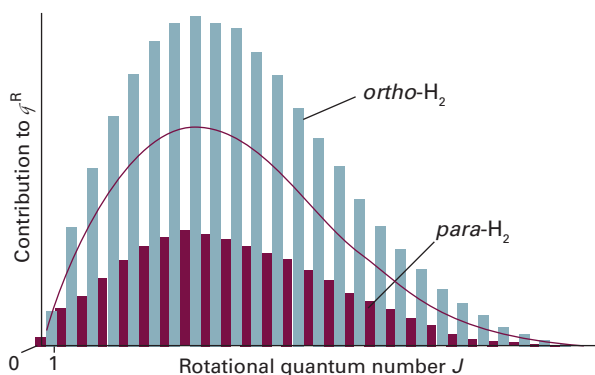
$$q^R = \frac{1}{2} \sum_J (2J+1) e^{-\beta hc\tilde{B}J(J+1)}$$

and this approximation is very good when many terms contribute (at high temperatures,  $T \gg \theta^R$ ). At such high temperatures the sum can be approximated by the integral that led to

**Table 13B.1** Rotational temperatures of diatomic molecules\*

	$\theta^R/\text{K}$
$^1\text{H}_2$	87.6
$^1\text{H}^{35}\text{Cl}$	15.2
$^{14}\text{N}_2$	2.88
$^{35}\text{Cl}_2$	0.351

\* More values are given in the Resource section, Table 11C.1.



**Figure 13B.8** The values of the individual terms  $(2J+1)e^{-\beta hc\tilde{B}J(J+1)}$  contributing to the mean partition function of a 3:1 mixture of *ortho*- and *para*-H<sub>2</sub>. 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 sum is indicated by the curve.

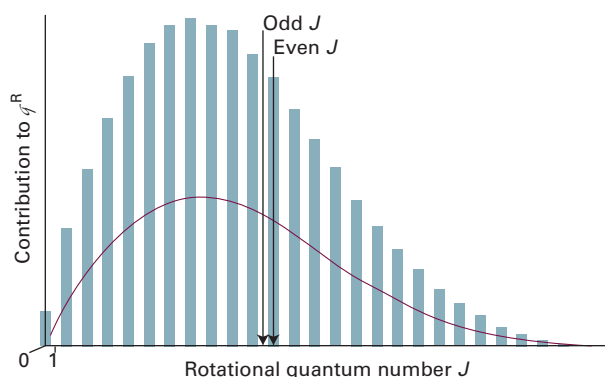
eqn 13B.12a. Therefore, on account of the factor of  $\frac{1}{2}$  in this expression, the rotational partition function for ‘ordinary’ molecular hydrogen at high temperatures is one-half this value, as in eqn 13B.13a.

The same type of argument may be used for linear symmetrical molecules in which identical bosons are interchanged by rotation (such as CO<sub>2</sub>). As pointed out in Topic 11B, 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. 13B.9).

The same care must be exercised for other types of symmetrical molecules, and for a nonlinear molecule eqn 13B.12b is replaced by

$$q^R = \frac{1}{\sigma} \left( \frac{kT}{hc} \right)^{3/2} \left( \frac{\pi}{\tilde{A}\tilde{B}\tilde{C}} \right)^{1/2} \quad (13B.14)$$

Rotational partition function  
[nonlinear rotor]



**Figure 13B.9** The values of the individual terms contributing to the rotational partition function of CO<sub>2</sub>. Only states with even  $J$  values are allowed. The full line shows the smoothed, averaged contributions of the levels.

**Table 13B.2** Symmetry numbers of molecules\*

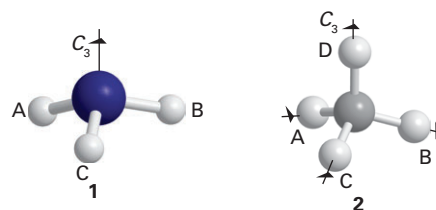
	$\sigma$
<sup>1</sup> H <sub>2</sub>	2
<sup>1</sup> H <sup>2</sup> H	1
NH <sub>3</sub>	3
C <sub>6</sub> H <sub>6</sub>	12

\* More values are given in the *Resource section*, Table 11C.1.

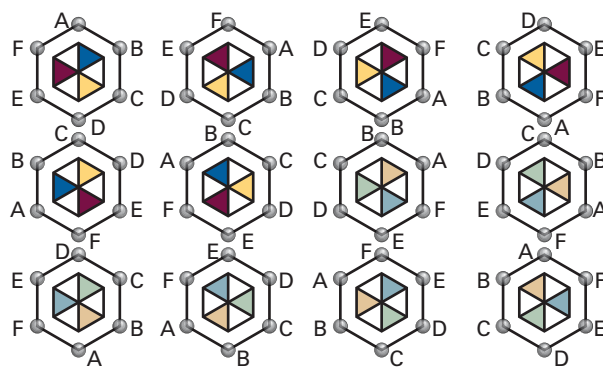
Some typical values of the symmetry numbers are given in Table 13B.2. To see how group theory is used to identify the value of the symmetry number, see *Integrated activity* I13.1; the following *Brief illustration* outlines the approach.

#### Brief illustration 13B.4

The value  $\sigma(\text{H}_2\text{O}) = 2$  reflects the fact that a 180° rotation about the bisector of the H–O–H angle interchanges two indistinguishable atoms. In NH<sub>3</sub>, there are three indistinguishable orientations around the axis shown in (1). For CH<sub>4</sub>, any of three 120° rotations about any of its four C–H bonds leaves the molecule in an indistinguishable state (2), 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 (Fig. 13B.10), as does a rotation of 180° around any of six axes in the plane of the molecule (three of which pass through C atoms diametrically opposite across the ring and the remaining three pass through the mid-points of C–C bonds on opposite sides of the ring).



**Figure 13B.10** The 12 equivalent orientations of a benzene molecule that can be reached by pure rotations and give rise to a symmetry number of 12. The six pale colours are the underside of the hexagon after that face has been rotated into view.