18.6: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\mathrm{rot}}(J) = \tilde{B}J(J+1) \qquad (18.6.1)$$

where:

$$\tilde{B} = \frac{h}{8\pi^2 I c}$$

Here, $\tilde{B}$ is the rotational constant expressed in cm^{-1}. The rotational energy levels are given by:

$$E_j = \frac{J(J+1)h^2}{8\pi I}$$

where I is the moment of inertia of the molecule given by μr^2 for a diatomic, and μ is the reduced mass, and r the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, Θ_{rot}, defined as:

$$\Theta_{\mathrm{rot}} = \frac{r^2}{8\pi^2 I k} \qquad (18.6.2)$$

The interpretation of θ_{rot} is as an estimate of the temperature at which thermal energy ($\approx kT$) is comparable to the spacing between rotational energy levels. At about this temperature the population of excited rotational levels becomes important. See Table 1.

Table 1: Select Rotational Temperatures. In each case the value refers to the most common isotopic species.

Molecule	H_2	N_2	O_2	F_2	HF	HCl	CO_2	HBr	CO
Θ_{rot}	87.6	2.88	2.08	1.27	30.2	15.2	0.561	12.2	2.78

In the summation for the expression for rotational partition function (q_{rot}), Equation 18.6.3, we can do an explicit summation:

$$q_{\mathrm{rot}} = \sum_{j=0}(2J+1)e^{-E_J/kT} \qquad (18.6.3)$$

if only a finite number of terms contribute. The factor $(2J+1)$ for each term in the expansion accounts for the degeneracy of a rotational state J. For each allowed energy E_J from Equation 18.6.1 there are $(2J+1)$ eigenstates. The Boltzmann factor must be multiplied by $(2J+1)$ to properly account for the degeneracy these states:

$$(2J+1)e^{-E_J/kT}$$

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} previously to get:

$$q_{\mathrm{rot}} = \int_0^\infty (2J+1)R^{-\tilde{B}J(J+1)/kT}dJ$$

This integration can easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)dJ$:

$$q_{\mathrm{rot}} = \frac{kT}{\tilde{B}} \qquad (18.6.4)$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the **symmetry number** and is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes:

$$q_{\mathrm{rot}} = \frac{kT}{\tilde{B}\sigma} \qquad (18.6.5)$$

or commonly expressed in terms of Θ_{rot}:

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}\sigma} \tag{18.6.6}$$

> **✔ Example 18.6.1**
>
> What is the rotational partition function of H_2 at 300 K?
>
> **Solution**
>
> The value of $\tilde{B}$ for H_2 is 60.864 cm^{-1}. The value of kT in cm^{-1} can be obtained by dividing it by hc, i.e., which is $kT/hc = 209.7\ cm^{-1}$ at 300 K. $\sigma = 2$ for a homonuclear molecule. Therefore from Equation 18.6.5,
>
> $$\begin{aligned} q_{\text{rot}} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$
>
> Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible at 300 K

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

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