

24.9: The Rotational Partition Function of A Diatomic Ideal Gas

For a diatomic molecule that is free to rotate in three dimensions, we can distinguish two rotational motions; however, their wave equations are intertwined, and the quantum mechanical result is that there is one set of degenerate rotational energy levels. The energy levels are

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

with degeneracies $g_J = 2J + 1$, where $J = 0, 1, 2, 3, \dots$

(Recall that I is the **moment of inertia**, defined as $I = \sum m_i r_i^2$, where r_i is the distance of the i^{th} nucleus from the molecule's center of mass. For a diatomic molecule, XY , whose internuclear distance is r_{XY} , the values of r_X and r_Y must satisfy the conditions $r_X + r_Y = r_{XY}$ and $m_X r_X = m_Y r_Y$. From these relationships, it follows that the moment of inertia is $I = \mu r_{XY}^2$, where μ is the reduced mass.) For heteronuclear diatomic molecules, the rotational partition function is

$$z_r = \sum_{J=0}^{\infty} (2J+1) \exp \left[\frac{J(J+1)h^2}{8\pi^2 I k T} \right]$$

For homonuclear diatomic molecules, there is a complication. This complication occurs in the quantum mechanical description of the rotation of any molecule for which there is more than one indistinguishable orientation in space. When we specify the locations of the atoms in a homonuclear diatomic molecule, like H_2 , we must specify the coordinates of each atom. If we rotate this molecule by 360° in a plane, the molecule and the coordinates are unaffected. If we rotate it by only 180° in a plane, the coordinates of the nuclei change, but the rotated molecule is indistinguishable from the original molecule. Our mathematical model distinguishes the 180° -rotated molecule from the original, unrotated molecule, but nature does not.

This means that there are twice as many energy levels in the mathematical model as actually occur in nature. The rotational partition function for a homonuclear diatomic molecule is exactly one-half of the rotational partition function for an "otherwise identical" heteronuclear diatomic molecule. To cope with this complication in general, it proves to be useful to define a quantity that we call the **symmetry number** for any molecule. The symmetry number is usually given the symbol σ ; it is just the number of ways that the molecule can be rotated into indistinguishable orientations. For a homonuclear diatomic molecule, $\sigma = 2$; for a heteronuclear diatomic molecule, $\sigma = 1$.

Making use of the symmetry number, the rotational partition function for any diatomic molecule becomes

$$z_r = \left(\frac{1}{\sigma} \right) \sum_{J=0}^{\infty} (2J+1) \exp \left[\frac{J(J+1)h^2}{8\pi^2 I k T} \right] \quad (24.9.1)$$

For most molecules at ordinary temperatures, the lowest rotational energy level is much less than kT , and this infinite sum can be approximated to good accuracy as the corresponding integral. That is

$$z_r \approx \left(\frac{1}{\sigma} \right) \int_{J=0}^{\infty} (2J+1) \exp \left[\frac{J(J+1)h^2}{8\pi^2 I k T} \right] dJ$$

Initial impressions notwithstanding, this integral is easily evaluated. The substitutions $a = h^2 / 8\pi^2 I k T$ and $u = J(J+1)$ yield

$$z_r \approx \left(\frac{1}{\sigma} \right) \int_{u=0}^{\infty} \exp(-au) du \quad (24.9.2)$$

$$\approx \left(\frac{1}{\sigma} \right) \left(\frac{1}{a} \right) = \frac{8\pi^2 I k T}{\sigma h^2} \quad (24.9.3)$$

To see that this is a good approximation for most molecules at ordinary temperatures, we calculate the successive terms in the partition function of the hydrogen molecule at 25 C. The results are shown in Table 1. We choose hydrogen because the energy difference between successive rotational energy levels becomes greater the smaller the values of I and T . Since hydrogen has the smallest angular momentum of any molecule, the integral approximation will be less accurate for hydrogen than for any other molecule at the same temperature. For hydrogen, summing the first seven terms in the exact calculation (Equation 24.9.1) gives $z_{\text{rotation}} = 1.87989$, whereas the approximate calculation (Equation 24.9.3) gives 1.70284. This difference corresponds to a difference of 245 J in the rotational contribution to the standard Gibbs free energy of molecular hydrogen.

Table 1: Rotational Partition Function Contributions for Molecular Hydrogen at 298 K

J	$= \frac{(2J+1)}{\sigma} \exp^{Z_J} \left(-\frac{J(J+1)h^2}{8\pi^2 I k T} \right)$	$\approx \sum^{Z_r} Z_J$
0	0.50000	0.50000
1	0.83378	1.33378
2	0.42935	1.76313
3	0.10323	1.86637
4	0.01267	1.87904
5	0.00082	1.87986
6	0.00003	1.87989

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