For a linear triatomic molecule the problem is the same as for a diatomic molecule. The energy levels are

The degeneracy is

For a linear molecule the moment of inertia is

where \( d_j \) is the distance of the \( j \)th mass from the center of mass.

The center of mass is given by

where \( x_j, y_j, \) and \( z_j \) are the Cartesian coordinates in an arbitrary coordinate system.

The rotational partition function for a linear polyatomic molecule can be written as

where the rotational temperature is

and \( S \) is the symmetry number. If the molecule has no center of symmetry (e.g. HCN) \( S = 1 \) whereas if the molecule has
a center of symmetry (e.g. CO2) then $S = 2$.

For a non-linear polyatomic molecule there are three rotation axes and three values of the moment of inertia. In the general case the rotational partition function is

The rotational energy and entropy are

Hindered Rotation

If a rotation with a molecule is restricted then is called a hindered rotation. For example, a methyl group in ethane can be in an eclipsed or staggered configuration. As the methyl group rotates it moves from a region of low potential energy (staggered) to a region of high potential energy (eclipsed). We can represent the potential energy surface using a sinusoidal function as shown below.

At sufficiently high temperatures the molecule moves easily from one minimum to another. However, when $kT \ll V_0$
then the molecule remains in one of the potential wells. The motion then resembles the vibration of a torsional internal coordinate. This is frequently the case in common organic molecules. For example, $V_0 = 2.7 - 3.0$ kcal/mole in ethane while $kT = 0.6$ kcal/mole at 300 K. A partition function can be calculated for hindered rotation from the solution of the Schrödinger equation for this potential function.

The contribution of hindered rotation to the heat capacity is one observation that allows these considerations to be connected with experiment.

For a polyatomic molecule containing $N$ atoms, the total number of coordinate degrees of freedom is $3N$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. The translational partition function was discussed previously and now we have to consider the three rotational degrees of freedom and the $3N - 6$ vibrational degrees. For a linear molecule, the rotational motional motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, for a linear molecule, there are two rotational degrees of freedom and $3n - 5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia $\langle I_{xx} \rangle, \langle I_{yy} \rangle, \langle I_{zz} \rangle$ of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold.

\[
\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i
\]

The inertia products are defined by

\[
\langle I_{xx} \rangle = \sum_i m_i \left( y_i^2 + z_i^2 \right)
\]
\[
\langle I_{xy} \rangle = \sum_i m_i \left( x_i y_i \right)
\]

The other components $\langle I_{yy} \rangle, \langle I_{xz} \rangle, \ldots$ are defined analogously. To find the direction cosines $\alpha, \beta, \gamma$ of the three principle moments of inertia, we need to solve the following matrix equations.

\[
\alpha (\langle I_{xx} \rangle - \eta) - \beta I_{xy} - \gamma I_{xz} = 0
\]
\[
\alpha I_{xy} - \beta (\langle I_{yy} \rangle - \eta) - \gamma I_{yz} = 0
\]
\[
-\alpha I_{xz} - \beta I_{yz} + \gamma (\langle I_{zz} \rangle - \eta) = 0
\]

If the off diagonal terms $\langle I_{xy} \rangle, \langle I_{xz} \rangle$ are zero in the above equations then the $(x), (y), (z)$ axis will be the principal axis. The energy of a rotor with the three moments of inertia $\langle I_{xx} \rangle, \langle I_{yy} \rangle, \langle I_{zz} \rangle$ is given by

\[
\epsilon = \frac{1}{2} I_{xx} \omega_A^2 + \frac{1}{2} I_{yy} \omega_B^2 + \frac{1}{2} I_{zz} \omega_C^2 =
\]

\[
\frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C}
\]
Symmetric Tops

Here, $\omega_A$, $\omega_B$, and $\omega_C$ are the three angular speeds and $L_A$, $L_B$, and $L_C$ are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers $J$ and $K$. The total angular momentum is determined by $J$ and the component of this angular momentum along the unique molecular axis is determined by $K$. The energy levels are given by

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

with rotational constants in units of wavenumbers:

$$\tilde{B} = \frac{\hbar}{8\pi^2 c I_B}$$

and

$$\tilde{A} = \frac{\hbar}{8\pi^2 c I_A}$$

where

- $J$ takes on values $0, 1, 2, ..., \infty$
- $K = -J, -J + 1, -J + 2, ..., 0, 1, 2, ..., J$.

The rotational partition function is given by

$$q_{\text{rot}} = \frac{1}{\sigma} \sum_{J=0}^\infty (2J+1) e^{-\tilde{B} J(J+1)/k_BT} \sum_{K=-J}^{J} (2J+1) e^{(\tilde{A} - \tilde{B}) K^2/k_BT}$$

This can be converted to an integral as in (3.14) and the result is

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{8 \pi I_B k_BT}{\hbar^2} \right)^{1/2} \left( \frac{8 \pi I_A k_BT}{\hbar^2} \right)^{1/2}$$

Asymmetric Tops

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta $L_A, L_B$, and $L_C$ as

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{H(p,q)/kT} \, dL_A \, dL_B \, dL_C = \sqrt{2\pi I_A k_BT} \sqrt{2\pi I_B k_BT} \sqrt{2\pi I_C k_BT}$$

And then multiplying by a factor of $8\pi^2 / \sigma \hbar^3$ we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of $2\pi$. Integration over all possible orientations of this axis contribute another factor of $4\pi$. The symmetry number $\sigma$ corrects for overcounting of rotational configurations and the factor of $\hbar^3$ is for the conversion from the classical
phase space to the quantum mechanical phase space. The final result is

\[
q_{\text{rot}} = \frac{\pi^2}{\sigma} \sqrt{\frac{8\pi I_A k_BT}{\hbar^2}} \sqrt{\frac{8\pi I_B k_BT}{\hbar^2}} \sqrt{\frac{8\pi I_C k_BT}{\hbar^2}} \label{big0}
\]

Equation \ref{big0} can be derived classically by integrating over proper phase space as demonstrated below.

**Classical Derivation (Optional)**

We can explicitly obtain the classical rotational partition function of an asymmetric top by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by three Euler angles \((\theta), (\phi),\) and \((\psi)\) with the ranges of angles \((0)\) to \((\pi)\), \((0)\) to \((2\pi)\) and \((0)\) to \((2\pi)\) respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta \((p_\theta, p_\phi, p_\psi)\)

\[
H = \frac{\sin^2 \psi}{2I_A} (p_\theta - \frac{\cos \psi}{\sin \theta \sin \psi} (p_\phi - \cos \theta p_\psi))^2 \\
+ \frac{\cos^2 \psi}{2I_B} (p_\theta - \frac{\sin \psi}{\cos \theta \cos \psi} (p_\phi - \cos \theta p_\psi))^2 + \frac{1}{2I_C} p_\psi^2
\]

The classical rotational partition function is given by

\[
q_{\text{rot}} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} \int_{0}^{2\pi} \frac{1}{\hbar^3} e^{-H(p,q)/k_BT} dp_\theta \, dp_\phi \, dp_\psi \, d\theta \, d\phi \, d\psi
\]

The integrations can be simplified by rewriting \(H(p,q)/kT\) as

\[
\frac{H}{k_BT} = \frac{1}{2I_A k_BT} \left( \frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right) \left( p_\theta + \left( \frac{1}{I_B} - \frac{1}{I_A} \right) \frac{\sin \psi \cos \psi}{\sin \theta \left( \frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right) } (p_\phi - \cos \theta p_\psi) \right)^2 \\
+ \frac{1}{2 k_BT I_AI_B \sin^2 \theta} \left( \frac{1}{\sin \theta \left( \frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right) } (p_\phi - \cos \theta p_\psi) \right)^2 + \frac{1}{2 KT I_c} p_\psi^2
\]

Using the following integral,

\[
\int_{-\infty}^{\infty} e^{-a(x+b)^2} dx = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}
\]

Integration over \((p_\theta)\) gives using the above expression

\[
\sqrt{2\pi k_BT} \left( \frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right)^{-1/2} \label{SA1}
\]

Integration over \((p_\phi)\) gives the factor,

\[
\sqrt{2\pi k_BT I_AI_B} \sin \theta \left( \frac{\sin^2 \psi}{I_A} + \frac{\cos^2 \psi}{I_B} \right)^{1/2}
\]
This cancels partly the second square root in Equation \(\text{(SA1)}\). Integration over \(p_\psi\) gives the factor
\[
\sqrt{2 \pi k T I_c}
\]
Integration over \(\theta\), \(\phi\) and \(\psi\) gives a factor of \(8 \pi^2\).
\[
\int_0^{\pi} \sin \theta \, d\theta = 2
\]
\[
\int_0^{2\pi} d\phi = 2 \pi
\]
\[
\int_0^{2\pi} d\psi = 2 \pi
\]
Combining all the integrals, we finally get Equation \(\text{(big0)}\) after reintroduced the symmetry number \(\sigma\) as before with diatomic molecular rotation.

**Thermodynamics Properties**

The polyatomic rotational partition function expressed in Equation \(\text{(big0)}\) is often expressed differently with the following substitutions
\[
\Theta_A = \dfrac{8 \pi I_A k_B}{h^2}
\]
\[
\Theta_B = \dfrac{8 \pi I_B k_B}{h^2}
\]
\[
\Theta_C = \dfrac{8 \pi I_C k_B}{h^2}
\]
as
\[
q_{\text{rot}} = \dfrac{\pi^2}{\sigma} \sqrt{\dfrac{T^3}{\Theta_A \Theta_B \Theta_C}} \label{RotQ1}
\]
or alternatively
\[
\ln q_{\text{rot}} = \dfrac{1}{2} \ln \dfrac{\pi T}{\Theta_A \Theta_B \Theta_C \sigma^2}
\]
The molar thermodynamic functions can be readily calculated including average rotation energy and molar heat capacity
\[
E_{\text{rot}} = \dfrac{3}{2} RT
\]
and
\[
\bar{C}_V = \dfrac{3}{2} R
\]
Improvements over the classical approximation for the rotational partition function derived above have been obtained. One of the improved versions (with no derivation) is
\[
q_{\text{rot}} = q_{\text{rot}}^0 \left[ 1 + \dfrac{h^2}{96 \pi^2 k_B T} \left( \dfrac{2}{I_A} + \dfrac{2}{I_C} + \dfrac{2}{I_B} - \dfrac{I_A}{I_B I_C} - \dfrac{I_B}{I_A I_C} \right) \right]
\]
where \( q_{\text{rot}}^0 \) is the classical approximation in Equation \( \ref{big0} \). Example: \( \text{(NO}_2\text{)} \)

The three characteristic rotational temperatures for \( \text{(NO}_2\text{)} \) are 111.5 K, 0.624 K and 0.590 K. Calculate the rotational partition function at 300 K.

**Solution**

The rotational temperature is given by Equation \( \ref{RotQ1} \):

\[
q_{\text{rot}} = \frac{\pi^2}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}}
\]

The rotational partition function becomes,

\[
q_{\text{rot}} = \frac{1.772}{2} \sqrt{\frac{300\; K}{(11.5\; K)(0.624\; K)(22.55\; K)}} = 2242.4
\]

Comparing this result with the vibrational partition function calculation before \( q_{\text{vib}} = 1.0035 \), give the implication that while several rotational states are accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible.

**Contributors**

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- [http://www.chem.iitb.ac.in/~bitembe/pdfs/ch_3.pdf](http://www.chem.iitb.ac.in/~bitembe/pdfs/ch_3.pdf)