Thermodynamics: Classical to Statistical
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Lecture 18
Rotational Partition Function

So we will discuss rotational partition function as mentioned before for monatomic gas. There are three degrees of freedom like translational degrees of freedom, electronic degrees of freedom and nuclear degrees of freedom. So for monatomic molecules there is no rotational or vibrational degrees of freedom and we calculated individually the transitional partition function, the electronic particular function and the nuclear partition function.

Now, if you consider the diatomic and poly atomic molecules, we will have two more degrees of freedom and those are rotational degrees of freedom and vibrational degrees of freedom. So for diatomic and poly atomic molecules there are five degrees of freedom, translational degrees of freedom, electronic degrees of freedom, nuclear degrees of freedom, rotational degrees of freedom and vibrational degrees of freedom. We will discuss rotational degrees of freedom or rotational partition function.

The rotational energy levels, we consider here the rigid rotor model, it is the simplest model one can think of and the energy levels for rigid rotors can be written as,

$$\epsilon_{\mathrm{rot}} = \frac{\hbar}{2I} J(J+1)$$

$\hbar = \frac{h}{2\pi}$, h is planks constant, I is the momentum of the inertial molecule and J is rotational quantum number at different rotational level here and the value of J varies from 0, 1, 2 etc.

First we consider heteronuclear diatomic molecules, for the heteronuclear diatomic molecules the degeneracy of J-th level is 2J plus 1.

We can write,the rotational partition function is,

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)e^{-\beta \frac{\hbar}{2\pi} J(J+1)} \text{ …………(1)}$$

Now assume, $\theta_{rot} = \frac{\hbar}{2Ik_B} = \frac{hB}{k_B}$

θ_{rot} = rotational temperature

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

Now, if we substitute the value of theta rotational into q rotational, we get

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)e^{-\frac{\theta_{rot} J(J+1)}{T}} \text{ …………….(2)}$$

This is the expression for rotational partition function of heteronuclear diatomic molecule.

Next, it is found that the value of theta rotational by T is quite small at ordinary temperature for diatomic molecules, that do not contain hydrogen atoms, so it has been found that the value of the theta rotational by T is very small or quite small at ordinary temperature, like room temperature for diatomic molecules that do not contain any hydrogen atoms.

So, the summation of equation 2 can be replaced by integration at ordinary temperatures, thus the equation 2 can be written as

$$q_{rot} = \int_0^{\infty} (2J+1)e^{-\frac{\theta_{rot} J(J+1)}{T}} dJ \text{ …….........(3)}$$

Now consider, $J(J+1) = x$

$\Rightarrow$ (2J+1)Dj = dx

When $J \to 0, x \to 0$ and $J \to \infty, x \to \infty$

So you can write, $q_{rot} = \int_0^{\infty} e^{-\frac{\theta_{rot} x}{T}} dx$

$$\Rightarrow \quad q_{rot} = \frac{T}{\theta_{rot}} \quad \ldots\ldots\ldots\ldots\ldots(4)$$

Now, if you substitute the value of theta rotational in equation 4, we get

$$q_{rot} = \frac{8\pi^2 I k_B T}{h^2}$$

So the average rotational energy of a single rigid rotor is,

$$< \epsilon_{rot} > = k_B T^2 \left(\frac{\partial \ln q_{rot}}{\partial T}\right)_V$$

Now $\quad N = n N_A$ where n = number of moles

N_A = Avogadro's number

$$< E_{rot} > = n N_A k_B T = n RT \text{ as } N_A k_B = R$$

So, C_V due to rotational motion

$$< C_V >_{rot} = \left(\frac{\partial < E_{rot} >}{\partial T}\right)_V = nR$$

A diatomic molecule has two rotational degrees of freedom and each contributes $\frac{R}{2}$ to $< \overline{C_V} >_{rot}$, $\quad < \overline{C_V} >_{rot} = R$, because the rotation along the bond axis does not contribute much to the rotational energy.

Next, we consider the fraction of molecules in the J-th rotational level and if we consider this as f_J, then

$$f_J = \frac{(2J+1)e^{-\frac{\theta_{rot} J(J+1)}{T}}}{q_{rot}}$$

$$\Rightarrow \quad f_J = (2J+1)\left(\frac{\theta_{rot}}{T}\right)e^{-\frac{\theta_{rot} J(J+1)}{T}}$$

So the most probable 'J' value J_{mp} can find by differentiating f_J with respect to J,

$$\frac{\partial f_J}{\partial J} = 2\left(\frac{\theta_{rot}}{T}\right) e^{-\frac{\theta_{rot} J(J+1)}{T}} + (2J+1)\left(\frac{\theta_{rot}}{T}\right) e^{-\frac{\theta_{rot} J(J+1)}{T}} (2J+1)\left(-\frac{\theta_{rot}}{T}\right)$$

So in order to get most probable J value we have to make $\frac{\partial f_J}{\partial J} = 0$

$$0 = 2\left(\frac{\theta_{rot}}{T}\right) e^{-\frac{\theta_{rot} J(J+1)}{T}} + (2J+1)\left(\frac{\theta_{rot}}{T}\right) e^{-\frac{\theta_{rot} J(J+1)}{T}} (2J+1)\left(-\frac{\theta_{rot}}{T}\right)$$

$$0 = \left(\frac{\theta_{rot}}{T}\right) e^{-\frac{\theta_{rot}J(J+1)}{T}} \left[2 - (2J+1)^2 \left(\frac{\theta_{rot}}{T}\right)\right]$$

$$(2J+1)^2 \left(\frac{\theta_{rot}}{T}\right) = 2$$

$$J_{mp} = \left(\frac{T}{2\theta_{rot}}\right)^{1/2} - \frac{1}{2}$$

If we plot f_J versus we get J equal to 7 is mostly populated, not J equals to 0. Now we have molecules other than hetereonuclear diatomic molecules.

The general expression for diatomic and linear poly atomic molecules is

$$q_{rot} = \frac{T}{\sigma\theta_{rot}}$$

where sigma is the symmetry number and for hetereonuclear diatomic molecules, sigma is 1, for homonuclear diatomic molecules, sigma is 2, for symmetrical linear poly atomic molecules such as acetylene C_2H_2, carbon dioxide, etc sigma is 2, for unsymmetrical linear poly atomic molecules such as N_2O etc sigma is 1.

Sysmetry number is the number of different ways a molecule can be rotated into a configuration indistinguishable from the original one.

For suppose C_2H_2, we consider this as $H_a - C_a \equiv C_b - H_b$, now if we rotate the molecule, in clockwise direction around the perpendicular to the $C \equiv C$ by 180°, we get a configuration which is indistinguishable from the original one, so we get two different configuration, if we rotate another 180° we get back to original one. If we rotate 360° we get two concentrations, that is why the sigma is 2 here and so on.

Next we discuss importance of symmetry number in rotational partition function.

If you go back and check, equations 3 and 4 are applicable only to heteronuclear diatomic molecules, that we discussed. The underlying reason is that the wave function of a homonuclear diatomic molecule must posseses a certain symmetry with respect to interchange of two identical nuclei in the molecule.

This symmetry requirement has a profound effect on the population of the rotational energy levels of a homonuclear diatomic molecule. At temperature such that theta rotational is much, much lower than T, which we have seen applies to most molecules at ordinary temperatures, Q rotational for homonuclear diatomic molecules is like this. Actually this symmetry number has profound effect on the population or the rotational energy levels of a molecule, that is why symmetry number is very, very important.

We considered so far rotational partition function for homonuclear diatomic molecules, heteronuclear diatomic molecules and linear poly atomic molecules. We will consider the rotational partition function for non-linear poly atomic molecules now.

The rotational properties of non-linear poly atomic molecules depend on the relative magnitudes of their principal moments of inertia. For non-linear poly atomic molecules there are three rotational degrees of freedom, we will see that also. So the rotational properties, a non-linear poly atomic molecules depend on the relative magnitudes of their principal moments of inertia.

If all three principal moments of inertia are equal the molecule is called a spherical top. If two of the three principal moments of inertia are equal, the molecule is called a symmetry top. If all three principal moments of inertia are different, the molecule is called an asymmetry top, so depending on the value of principal moments of inertia, the molecules are classified as spherical top molecules, symmetric molecules or asymmetric top molecules.

Thus, if we define three characteristics rotational temperatures in terms of the three principal moments of inertia, we can write

$$\theta_{\mathrm{rot},j} = \frac{\hbar}{2I_j k_B} \quad \text{where } j = A, B, C$$

$$\text{If } \theta_{\mathrm{rot},A} = \theta_{\mathrm{rot},B} = \theta_{\mathrm{rot},C} \Rightarrow \text{Spherical top}$$

$$\text{If } \theta_{\mathrm{rot},A} = \theta_{\mathrm{rot},B} \neq \theta_{\mathrm{rot},C} \Rightarrow \text{Symmetric top}$$

$$\text{If } \theta_{\mathrm{rot},A} \neq \theta_{\mathrm{rot},B} \neq \theta_{\mathrm{rot},C} \Rightarrow \text{Asymmetric top}$$

Now, for spherical top molecules the quantum mechanical problem of a spherical top molecule can be solved exactly to give,

$$\epsilon_J = \frac{J(J+1)\hbar^2}{2I}$$

$$g_J = (2J+1)^2 \text{ where } J = 0, 1,2, 3\ldots\ldots\ldots\ldots$$

the corresponding rotational partition function is

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)^2 e^{-\frac{\hbar^2 J(J+1)}{2Ik_B T}}$$

Now for almost all spherical top molecules $\theta_{rot} \ll T$ at ordinary temperatures, so the above summation can be replace by integration.

$$q_{rot} = \frac{1}{\sigma}\int_0^{\infty} (2J+1)^2 e^{-\frac{\theta_{rot} J(J+1)}{T}} dJ$$

This is the expression for rotational partition function for spherical top molecules.

For $\theta_{rot} \ll T$, the most important values of ‘J’ are large, so, we may neglect ‘1’ compared with J. So,

$$q_{rot} = \frac{1}{\sigma}\int_0^{\infty} 4J^2 e^{-\frac{\theta_{rot} J(J+1)}{T}} dJ$$

$$\Rightarrow q_{rot} = \frac{\pi^{\frac{1}{2}}}{\sigma} \left(\frac{T}{\theta_{rot}}\right)^{\frac{3}{2}} \Rightarrow \text{for spherical top molecules.}$$

For symmetric top molecules the degeneracy factor $g_J = 2(2J+1)$and we get

$$q_{rot} = \frac{\pi^{\frac{1}{2}}}{\sigma} \left(\frac{T}{\theta_{rot,A}}\right)\left(\frac{T}{\theta_{rot,C}}\right)^{\frac{1}{2}}$$ ⇒ for symmetric top molecules

For asymmetric top molecules the degeneracy factor $g_J = (2J + 1)$and we get

$$q_{rot} = \frac{\pi^{\frac{1}{2}}}{\sigma} \left(\frac{T}{\theta_{rot,A}}\right)\left(\frac{T}{\theta_{rot,B}}\right)^{\frac{1}{2}}\left(\frac{T}{\theta_{rot,C}}\right)^{\frac{1}{2}}$$ ⇒ for asymmetric top molecules

The average rotational energy of a single non-linear poly atomic molecule is

$$< \epsilon_{rot} > = k_B T^2 \left(\frac{\partial \ln q_{rot}}{\partial T}\right)_V$$

For non-linear poly atomic molecule $\left(\frac{\partial \ln q_{rot}}{\partial T}\right)_V = \frac{3}{2T}$

$$\Rightarrow \quad < \epsilon_{rot} > = k_B T^2 \times \frac{3}{2T}$$

$$\Rightarrow \quad < \epsilon_{rot} > = \frac{3}{2} k_B T$$

For ‘N’ number of non-linear poly atomic molecule where $N = n\,N_A$

$$< \epsilon_{rot} > = \frac{3}{2} N k_B T = \frac{3}{2} nRT \quad \text{where } N = n\,N_A$$

$$< C_V >_{rot} = \frac{3}{2} nR \quad \text{or}$$

$$< \overline{C_V} >_{rot} = \frac{3}{2} nR \quad \text{when } n = 1$$