Rotational partition Function

As we know that they are given by diatomic molecules only.Monatomic gases don't have any rotational energy because they have nothing around which to rotate, so we only account for their translational energy since their rotational energy is zero.

Over here rotation around the axis is not considered but the rotation between the two particles is under consideration.

➤ Suppose we have molecules like H_2, O_2, N_2 or any diatomic molecule like NO & CO, so there are definite bonds between the two molecules or the two individual atoms.this molecule will rotate around that axis

➤ Let suppose we have one atom over here and the other (like in Rigid rotor).They are linked by a bond, so they will rotate around a central axis,the rotation associated of this type will be considered and energy associated with this type of rotation is called rotational energy.
And the partition function related to this is known as **rotational partition function**

So rotational partition function is given by

$$Q_r = q_r = \Sigma\ g_r\ e^{-E_r/kT} \quad \text{-------------------- (1)}$$

We already know that from quantum statistics or quantum mechanics, the rotational energy for a diatomic molecule which is present in the jth state is;

$$E_r = J(J+1)\ h^2/8\ \pi^2\ I \text{-------------- (2)}$$

Where J is the rotational quantum number and its value is
J=0,1,2,3,…….
I=moment of Inertia of the diatomic molecule
h= planck's constant

➤ As we already know that rotational energy at the jth level is degenerate in $(2J+1)$ ways,so amount of degeneracy (statistical weight factor) that is for rotational energy or jth level
It is given by
$g_r = (2J+1)$

so the total degeneracy of the state or that total degeneracy of the various energy levels associated with the rotation is given by

$$g_r = (2J+1)$$

If J is "1", so the total degeneracy is "3" and total energy will be $2h^2/8\pi^2 I$

$Q_r = \Sigma\ (2J+1)\ e^{-J(J+1)h2/8\ \pi 2\ IkT}$

Further we know that all the energy levels are closely spaced that we can take a continuous summation or the energy levels can be arranged continuously (because variation in energy between two adjacent rotational energy levels can be taken as continuous).Hence, the summation can be converted into integration

$$Q_r = \int (2J+1)\ e^{-J(J+1)h2/8\ \pi 2\ IkT}\ dJ\ \text{------------(3)}$$

Variable in this term is J

Further we will take all the constant terms equal to beta (β)

$$\beta = h^2/8\ \pi^2 IkT$$

so

$$Q_r = \int (2J+1)\ e^{-J(J+1)\beta}\ dJ$$

We have

$$z=J(J+1)$$

When we differentiate this

$$dz=(2J+1)dJ$$

so we can substitute J(J+1)

$$Q_r=q_r= \int e^{-z\beta}\ dz$$

So the integration of this term from calculus will be or the solution of this term from calculus is

$$Q_r=q_r= \int 1/\beta = 8\ \pi^2 IkT/h^2$$

$$Qr=qr=8\ \pi^2 IkT/h^2 \qquad \text{-------------------(4)}$$

Hence, our rotational partition function is equal to this above term.

This eq (4) holds good for heteronuclear diatomic molecular systems like we have CO, NO, HI and HCl etc.

Now for in case of homonuclear molecules, suppose we have N_2, O_2, H_2, and also heteronuclear linear molecules like O=C=O and C_2H_2, the rotational contribution will be the half of rotation term.This effect reduces q_r to one half of the value in equation (4).

Hence, for such molecules, we need to introduce the symmetry factor or symmetry number (σ) in order to overcome this complexity.(It is the number of equivalent or indistinguishable molecular orientations).

Thus, the rotational partition function for any linear (homonuclear and heteronuclear) diatomic molecule is given by

$$Qr = qr = 8\, \pi^2 IkT / \sigma\, h^2 \qquad \text{--------------------(5)}$$

With the help of this particular equation, we can easily calculate the rotational partition function subject to the conditions, that the moment of Inertia, temperature of that particular system is known and also the type of molecule is known.

So the above relation (eq-5) holds good for any diatomic molecule.

➢ For homonuclear (symmetrical) linear diatomic molecule, the value of symmetry factor is 2.(i.e σ=2), because end to end rotation yields an equivalent orientation.
➢ For heteronuclear (unsymmetrical) linear molecule, the value of symmetry factor is 1.(i.e σ=1)