TOPIC :
Dr. R. Hazra
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ROTATIONAL PARTITION FUNCTION OF DIATOMIC MOLECULES

We know Rigid Rotor follows

$$\frac{L^2}{2I} Y(\theta,\phi) = E\, Y(\theta,\phi)$$

$$\Rightarrow \boxed{L^2 Y(\theta,\phi) = 2IE\, Y(\theta,\phi)}$$

Quantum Mechanical analytical Solution gives :

1. $L^2 Y(\theta,\phi) = l(l+1)\hbar^2 Y(\theta,\phi)$

$$\Rightarrow 2IE_l = l(l+1)\hbar^2$$

$$\Rightarrow E_l = \frac{l(l+1)\hbar^2}{2I}$$

2. Degeneracy, $g = (2l+1)$

Thus,

$$\boxed{q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-\beta J(J+1)\hbar^2/2I}}$$

where $l = J^{th}$ level starting from : $(0 \text{ to } \infty)$

Case-I : High Temperature limit

$$\Rightarrow T \to \infty \Rightarrow \beta = \left(\frac{1}{K_B T}\right) \to 0$$

High T $\Rightarrow$ In comparison to energy gap, Thermal agitation appears large !!

so that "$\sum_{J=0}^{\infty}$" can be converted to "$\int_0^{\infty}$" EVEN AT ROOM TEMP.

Hence $$q_{rot} = \int_0^{\infty} (2J+1)\, e^{-J(J+1)\hbar^2/(2Ik_BT)} \times dJ$$

Defined Rotational characteristic as:

$$\boxed{\theta_r = \left(\hbar^2/2Ik_B\right)} \equiv \text{CHARACTERISTIC TEMPERATURE OF ROTATION}$$

$$\boxed{q_{rot} = \int_0^{\infty} (2J+1)\, e^{-\theta_r J(J+1)/T}\, dJ}$$

Suppose, $J(J+1) = x$ J 0 ∞, x 0 ∞

$\Rightarrow (2J+1)\, dJ = dx$

$$\Rightarrow q_{rot} = \int_0^{\infty} e^{-(\theta_r/T)x}\, dx$$

Since $\int_0^{\infty} e^{-ay} dy = \frac{1}{a}$

$$= \frac{1}{(\theta_r/T)}$$

$$\Rightarrow \boxed{q_{rot} = \left(\frac{T}{\theta_r}\right)}$$ when $\theta_r \lll T$

$$\Rightarrow \boxed{q_{rot} = \left(\frac{8\pi^2 I k_B T}{h^2}\right)}$$

N.B.: $I = \mu r^2$, $\mu = \left(\frac{m_A m_B}{m_A + m_B}\right)$ & r = Bond length

carries the detailed specific features of diatomic molecule (AB)