

## Rotational partition function of diatomic gases

The rotational energy levels of a diatomic gas are given by -

$$E_{\text{rot}} = J(J+1)Bhc$$

where  $B$  is the rotational constant.

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

$$\begin{aligned} \therefore E_{\text{rot}} &= \frac{J(J+1)h \cdot hc}{8\pi^2 Ic} \\ &= \frac{J(J+1)h^2}{8\pi^2 I} \end{aligned}$$

The energy levels of a linear rotor are  $Bhc(J+1)$ , with  $J=0, 1, 2, 3, \dots$  and each level consists of  $2J+1$  degenerate states.

$$\therefore q_{\text{rot}} = \sum_{\text{rotational energy levels}} g_j e^{-E_{\text{rot}}/KT}$$

where  $g_j$  is the degeneracy of rotational levels.

$$\therefore q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{h^2 J(J+1)}{8\pi^2 IKT}}$$

When many rotational states are occupied and  $KT$  is much larger than the separation between neighbouring states ( $B \ll KT$ ), the sum in the partition function can be approximated by an integral.

$$\Rightarrow q_{\text{rot}} = \int_0^{\infty} (2J+1) e^{-\frac{h^2 J(J+1)}{8\pi^2 IKT}} dJ$$

This integral can be solved easily by substituting  $x = J(J+1)$

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

Let  $h^2$  represent  $\frac{h^2}{8\pi^2 I K T}$

$$\Rightarrow Q_{rot} = \int_0^{\infty} e^{-ax} dx$$
$$= \left. -\frac{1}{a} e^{-ax} \right|_0^{\infty} = -\frac{1}{a} (e^{-\infty} - e^{-0}) = -\frac{1}{a} (0 - 1) = \frac{1}{a}$$

$$\Rightarrow Q_{rot} = \frac{8\pi^2 I K T}{\sigma h^2} = \frac{K T}{B \sigma}$$

Where  $\sigma$  is the symmetry number.

For a homonuclear diatomic molecule, rotating the molecule by  $180^\circ$  brings the molecule into an indistinguishable configuration from the original. This leads to overcounting of the accessible states.

$\sigma = 1$  for heteronuclear diatomic molecules.

$\sigma = 2$  for homonuclear diatomic molecules.

Symmetry number - The no. of ways a molecule can be brought into identical configurations by rotation.

$$Q_{rot} = \frac{K T}{B \sigma} \quad \left. \begin{array}{l} \text{high temperature limit} \end{array} \right\}$$

$\theta_R = \frac{B \sigma}{K}$  represents the characteristic rotational temperature.

This rotational approximation (summation to integration) is valid when  $T \gg \theta_R$  (high temperature)

Thus  $Q_{rot} = \frac{T}{\theta_R}$