TOPIC :

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Vibrational Partition function of Diatomic Molecules at low Temperature Limit :

Case – II : $\beta h\nu \gg\gg 1$

when $T \to 0°K$

i.e., Absolute zero Temperature

$q_{\text{vibrational}} = 1$. for ~~Quantum~~ classical Harmonic Oscillator

$q_{vib} \to$ small for quantum H. O.

For both quantum and classical harmonic oscillator, ground state remains occupied fully.

Fraction of Molecules in n_{th} excited Vib. States

$$f_n = \frac{e^{-\beta h\nu(n+\frac{1}{2})}}{q_{vib}}$$

For quantum harmonic oscillator

$$= e^{-\beta h\nu} / \sum_{n=0}^{\infty} e^{-\beta h\nu n}$$

$$F_n = e^{-\beta h\nu n} / \sum_{n=0}^{\infty} e^{-\beta h\nu n}$$

Thus, fractions of molecules in n_{th} excited vib. state are same for quantum and classical Harmonic Oscillator

Internal energy of diatomic molecules due to vibration

$$E_V = Nk_BT^2\left(\frac{d\ln q_v}{dT}\right)$$

$$q_{vib} = e^{-h\nu\beta/2}/\left(1-e^{-\beta h\nu}\right)$$

$$\Rightarrow \ln(q_{vib}) = +\frac{\beta h\nu}{2} + \ln\left(e^{\beta h\nu}-1\right)$$

$$\because q_{vib} = \left(\frac{e^{\beta h\nu/2}}{e^{\beta h\nu}-1}\right)$$, as

Multiplying $e^{\beta h\nu}$ to both numerator and denominator

$$\Rightarrow \left(\frac{d\ln(q_{vib})}{dT}\right) = \left(\frac{h\nu}{2}\right)\left(-\frac{1}{k_BT^2}\right) \left\{\frac{1}{\left(e^{\beta h\nu}-1\right)}\right\} \times e^{\beta h\nu} \times h\nu\left(-\frac{1}{k_BT^2}\right)$$

$$\Rightarrow T^2\left(\frac{d\ln(q_{vib})}{dT}\right) = -\left(\frac{h\nu}{2k_B}\right) + \left(\frac{h\nu}{k_B}\right)\left(\frac{e^{\beta h\nu}}{e^{\beta h\nu}-1}\right)$$

Be defined $\Theta_V = \left(\frac{h\nu}{k_B}\right)$, Vibrational Temprature

$$E_V = Nk_BT^2\left(\frac{d\ln(q_{vib})}{dT}\right) = Nk_B\left(-\left(\frac{\theta_v}{2}\right) + \frac{\theta_v e^{(\theta_v/T)}}{\left(e^{\theta_v/T}-1\right)}\right)$$

$$\Rightarrow \left(E_v/Nk_B\right) = \left(-\left(\frac{\theta_v}{2}\right) + \theta_v \cdot \frac{\left(e^{\theta_v/T}-1\right)+1}{\left(e^{\theta_v/T}-1\right)}\right)$$

$$\Rightarrow \left(E_v/Nk_B\right) = \left(-\frac{\theta_v}{2} + \theta_v + \frac{\theta_v}{e^{\theta_v/T}-1}\right)$$

$$\Rightarrow E_V = Nk_B\left(\left(\frac{\theta_v}{2}\right) + \frac{\theta_v}{e^{\theta_v/T}-1}\right)$$

Hence is the Internal energy due to vibrational modes