

Vibrational Partition function of diatomic molecules

$$E_{vib} = \left(n + \frac{1}{2}\right) h\nu$$

$$\text{where } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$q_{vib} = \sum_{n=0}^{\infty} e^{-E_{vib}/kT} = \sum_{n=0}^{\infty} e^{-\beta E_{vib}}$$

$$q_{vib} = \sum_{n=0}^{\infty} e^{-\beta \left(n + \frac{1}{2}\right) h\nu} = e^{-\frac{\beta h\nu}{2}} \sum_{n=0}^{\infty} e^{-\beta h\nu n}$$

$$= e^{-\frac{\beta h\nu}{2}} \left(e^{-\beta h\nu \cdot 0} + e^{-2\beta h\nu} + e^{-3\beta h\nu} + \dots \right)$$

$$= e^{-\frac{\beta h\nu}{2}} \left(1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + \dots \right)$$

↳ (This is a geometric progression where $x = e^{-\beta h\nu}$)

$$\text{Thus } q_{vib} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

Case - I High temperature limit

$$\Rightarrow kT \gg \gg h\nu$$

$$\Rightarrow \beta h\nu \ll \ll 1$$

$$\text{let } x = \beta h\nu$$

$$\Rightarrow x \ll \ll 1$$

$$q_{vib} = \frac{e^{-x/2}}{1 - e^{-x}}$$

$$e^{-x} = 1 - \frac{x}{1!} + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots$$

$$\text{Thus, } q_{\text{vib}} = \frac{\left(1 - \frac{x}{2} + \frac{x^2}{(2!)4} - \frac{x^3}{(3!)8} + \dots\right)}{1 - \left(1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots\right)}$$

$$\Rightarrow q_{\text{vib}} = \frac{1}{x - \frac{x^2}{2!} + \frac{x^3}{3!}} = \frac{1}{x} = \left(\frac{KT}{h\nu}\right)$$

$$\Rightarrow q_{\text{vib}} = \left(\frac{KT}{h\nu}\right) \rightarrow \text{At very high temperature.}$$

Alternative Method to calculate q_{vib} at high temperature limit.

$$q_{\text{vib}} = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu n}$$

Now the summation can be represented in the form of integral.

$$\Rightarrow q_{\text{vib}} = e^{-\beta h\nu/2} \int_0^{\infty} e^{-\beta h\nu n} dn$$

$$\text{Now, } \int_0^{\infty} e^{-ax} = \frac{1}{a}. \quad \text{Here } a = \beta h\nu$$

$$\Rightarrow q_{\text{vib}} = \frac{1}{\beta h\nu} = \frac{KT}{h\nu}$$

$$\text{Similarly for classical oscillator } q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta h\nu n} = \frac{KT}{h\nu}$$

At high temperature limit classical and quantum harmonic oscillators behave the same.

Case-II Vib of diatomic molecules at low temperature

$$\Rightarrow \beta h \nu \gg 1$$

When $T \rightarrow 0\text{K}$ or absolute zero temperature

\Rightarrow q_{vib} is small for quantum harmonic oscillator.

q_{vib} is 1 for classical harmonic oscillator.

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

Fraction of molecules in the n^{th} excited vibrational state

for Quantum harmonic oscillator

$$f_n = \frac{e^{-\beta h \nu (n + \frac{1}{2})}}{q_{\text{vib}}} = \frac{e^{-\beta h \nu n} \cdot e^{-\frac{\beta h \nu}{2}}}{e^{-\frac{\beta h \nu}{2}} \sum_{n=0}^{\infty} e^{-\beta h \nu n}}$$

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

for classical harmonic oscillator

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

Thus, fraction of molecules in the n^{th} excited vibrational state are same for both quantum and classical harmonic oscillators.
(i.e. $f_n = f_n$).

Internal energy of diatomic molecules due to vibration

$$E_{\text{vib}} = NKT^2 \left(\frac{d \ln q_{\text{vib}}}{dT} \right)_V$$

$$\ln q_{\text{vib}} = -\frac{1}{2} \frac{h\nu}{KT} - \ln(1 - e^{-h\nu/KT})$$

Now, $\frac{h\nu}{k} = \theta_V$ (Characteristic vibrational temperature)

$$\Rightarrow \ln q_{\text{vib}} = -\frac{\theta_V}{2T} - \ln(1 - e^{-\theta_V/T})$$

$$\begin{aligned} \frac{d \ln q_{\text{vib}}}{dT} &= \frac{\theta_V}{2T^2} - \left[\frac{(-e^{-\theta_V/T})}{(1 - e^{-\theta_V/T})} \times \frac{\theta_V}{T^2} \right] \\ &= \frac{\theta_V}{T^2} \left[\frac{1}{2} + \frac{e^{-\theta_V/T}}{1 - e^{-\theta_V/T}} \right] \end{aligned}$$

$$E_{\text{vib}} = NKT^2 \times \frac{\theta_V}{T^2} \left(\frac{1}{2} + \frac{e^{-\theta_V/T}}{1 - e^{-\theta_V/T}} \right)$$

$$E_{\text{vib}} = Nk\theta_V \left[\frac{1}{2} + \frac{1}{e^{\theta_V/T} - 1} \right]$$