

TOPIC

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Vibrational Partition function of diatomic Molecules

Internal motion \equiv rotational motion
+ vibrational motion

$$E_{int} = E_{vib} + E_{rot}$$

(Rigid-rotor-harmonic oscillator approximation)

Thus

$$q_{int} = q_{rot, vib} = q_{rot} q_{vib}$$

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

$\therefore E_n = (n + \frac{1}{2}) h\nu$

& $\omega = (k/\mu)^{\frac{1}{2}}$

$\Rightarrow \nu = \frac{1}{2\pi} (k/\mu)^{\frac{1}{2}}$

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

$$q_{vib} = \left(e^{-\beta h\nu/2} \right) \sum_{n=0}^{\infty} e^{-\beta h\nu n} \quad \text{--- (A)}$$

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

This constitutes a G.P. series, whose ratio = $e^{-\beta h\nu}$

and first term is $1 \left(e^{-\beta h\nu} \right)^0$,

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

Case-I: High temperature limit

$$\Rightarrow k_B T \gg \gg h\nu$$

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

where $x = \beta h\nu$

$$q_{\text{vib}} = \left(1 - \frac{x}{2} + \frac{1}{2!} \frac{x^2}{4} - \dots \right)$$
$$\frac{1 - \left(1 - x + \frac{x^2}{2!} - \dots \right)}{x - \frac{x^2}{2!} + \frac{x^3}{3!} - \dots}$$
$$= \frac{1}{x - \frac{x^2}{2!} + \frac{x^3}{3!} - \dots}$$
$$= \left(\frac{1}{x} \right) = \left(\frac{k_B T}{h\nu} \right)$$

$$\Rightarrow q_{\text{vib}} = \left(\frac{k_B T}{h\nu} \right) \quad \text{At high temperature limit}$$

Other way, Eq. (A) can be represented in integral form as

$$q_{\text{vib}} = e^{-\beta h\nu/2} \int_0^{\infty} e^{-\beta h\nu n} dn = 1 \cdot \left(\frac{1}{\beta h\nu} \right)$$
$$= \left(\frac{k_B T}{h\nu} \right) \quad \text{as } \int_0^{\infty} e^{-ax} dx = \left(\frac{1}{a} \right)$$

Similarly, for classical oscillator $q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta h\nu n} = \frac{k_B T}{h\nu}$
At high temperature limit - classical and quantum harmonic oscillators behave same.