<u>Vibrations</u> $\quad \mathcal{E}_n = (n+\frac{1}{2})\hbar\omega \;, \quad Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$ (1)

$$\mathcal{U}_{vibr} = -N\frac{\partial \ln Z_{vib}}{\partial \beta} \;, \quad C_v^{vibr} = \partial \mathcal{U}/_{\partial T}.$$

Look at the low T and high T behaviour of $\mathcal{U}$ and C_v.

<u>Low T</u>: $\quad Z_{vib} = e^{-\beta\hbar\omega/2} + e^{-\beta\hbar\omega \cdot 3/2} + e^{-\beta\hbar\omega\, 5/2} + \cdots$

$$= e^{-\beta\hbar\omega/2}\left[1 + e^{-\beta\hbar\omega} + \cdots\right]$$

$$\boxed{\frac{10^{-10}}{1+10^{-10}} \simeq 10^{-10}.}$$

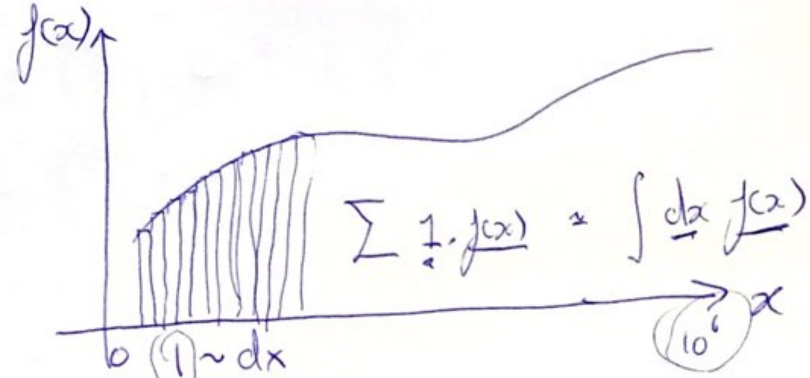
We get $\ln Z_{vib} \simeq -\frac{\beta\hbar\omega}{2} + \ln\left[1+e^{-\beta\hbar\omega}\right]$

$$\Rightarrow \mathcal{U}_{vib} = \frac{N\hbar\omega}{2} + N\frac{\hbar\omega e^{-\beta\hbar\omega}}{\underbrace{1+e^{-\beta\hbar\omega}}_{\approx 1.}} \simeq \frac{N\hbar\omega}{2} + N\hbar\omega e^{-\beta\hbar\omega}.$$

②

$$C_V^{\text{vibr.}} = \frac{\partial \mathcal{U}_{vib}}{\partial T} = -k_B \beta^2 \frac{\partial \mathcal{U}_{vib}}{\partial \beta} = N\hbar^2\omega^2\beta^2 e^{-\beta\hbar\omega} \quad (\text{low } T)$$

<u>High T</u>: $$Z_{vibr} = \underbrace{e^{-\beta\hbar\omega/2}}\sum_{n=0}^{\infty} 1.\, \underbrace{e^{-\beta\hbar\omega n}} \approx e^{-\beta\hbar\omega/2}\int_0^\infty dn\, \underbrace{e^{-\beta\hbar\omega n}}$$



Hence $$Z_{vib} \simeq \frac{e^{-\beta\hbar\omega/2}}{\beta\hbar\omega} \quad (\text{high } T)$$

$$\Rightarrow \ln Z_{vib} = -\frac{\beta\hbar\omega}{2} - \ln\beta\hbar\omega$$

$$\Rightarrow \mathcal{U}_{vib} = -N\frac{\partial \ln Z_{vib}}{\partial\beta} = \frac{N\hbar\omega}{2} + \frac{N}{\beta} = \frac{N\hbar\omega}{2} + Nk_B T.$$

Furthermore $$C_V = \frac{\partial \mathcal{U}_{vib}}{\partial T} = \underline{N k_B}$$

Rotations Similar to vibrations these are also quantised.

The angular momentum L and its z component L_z, have

$$L_z = m\hbar, \qquad m \text{ lies between } -l \text{ and } l.$$

$$L^2 = l(l+1)\hbar^2 \qquad l = 0, 1, 2, 3, \ldots \quad (s, p, d, f \ldots)$$

e.g. If $l = 2$ then $L^2 = 2.(2+1)\hbar^2 = 6\hbar^2$.

and $L_z = -2\hbar, -\hbar, 0, \hbar, 2\hbar$.

If the moment of inertia of the molecule is I then the energy of rotation is $E = L^2/2I$. (c.f. linear $E = p^2/2m$).

Hence partition function is $$Z_{rot} = \sum_{l=0}^{\infty} \overbrace{(2l+1)}^{\substack{\text{degeneracy } (L_z) \\ m\text{-states}}} e^{-\beta l(l+1)\hbar^2/2I}.$$

(no closed form).

<u>High T limit</u> As before at high T we can use the approximation

$$\sum_0^\infty 1 . f(x) \simeq \int_0^\infty dx\, f(x)$$

Hence at high T $Z_{rot} \simeq \int_0^\infty dl.\ \underbrace{(2l+1)}\, e^{-\beta\hbar^2 \underbrace{l(l+1)}/2I}$

Make a change of variable with $x = l(l+1)\beta\hbar^2/2I \Rightarrow dx = \frac{\beta\hbar^2}{2I}(2l+1)\, dl.$

giving $Z_{rot} \simeq \frac{2I}{\hbar^2\beta}\int_0^\infty dx\, e^{-x} = \frac{2I}{\hbar^2\beta} \Rightarrow \ln Z_{rot} = \ln(2I) - \ln(\hbar^2\beta)$

The internal energy at high T is

$$U_{rot} = -N\frac{\partial \ln Z_{rot}}{\partial\beta} = N/\beta = Nk_BT.$$

Hence $C_V^{rot} = \frac{\partial U}{\partial T} = N k_B$ (high T limit).

<u>Low T limit</u> : Approx Z_{rot} by first few terms, i.e.

$$Z_{rot} \simeq \underset{(\ell=0)}{1} + \underset{(\ell=1)}{3e^{-\beta\hbar^2/I}} + \dots$$

giving $U_{rot} = \frac{3N\hbar^2}{I} e^{-\beta\hbar^2/I}$ and $C_V^{rot} = 3Nk_B\left(\frac{\beta\hbar^2}{I}\right)e^{-\beta\hbar^3/I}$.

i.e. $\lim_{T\to 0} C_V^{rot} = 0$ and $\lim_{T\to\infty} C_V^{rot} = N k_B$.

We have obtained U and C_V for each of the contributions of Z i.e. translational, rotational, vibrational, electronic.

$$T \ll T_{rot}, \quad C_V = \tfrac{3}{2} k_B$$

$$T_{rot} \ll T_{vib}, \quad C_V = \tfrac{3}{2} k_B \ldots \tfrac{5}{2} k_B$$

$$T_{vib} \ll T_{elec}, \quad C_V = \tfrac{5}{2} k_B \ldots \tfrac{7}{2} k_B$$