

6.5: Vibrational Partition Function

The Harmonic Oscillator Extended

Vibration in a diatomic molecule can be described by the 1D harmonic oscillator that we have considered in Section [section:harmonic_oscillator]. In a multi-atomic molecule the $3n - 5$ (linear) or $3n - 6$ (non-linear) normal modes can be treated independently,

$$Z_{\text{vib}} = \prod_{i=1}^{3n-5\text{ or }3n-6} Z_{\text{vib},i} = \prod_{i=1}^{3n-5\text{ or }3n-6} \frac{1}{1 - e^{-\Theta_{\text{vib},i}/T}}. \quad (6.5.1)$$

Normal mode energies are no longer independent and the partition function is no longer factorisable if anharmonicity of the vibration needs to be included, which is the case only at very high temperatures. We ignore this and ask about the limiting behavior of Z_{vib} for a diatomic molecule or $Z_{\text{vib},i}$ for an individual normal mode at high temperatures. In the denominator of Equation 6.5.1 we can make the approximation $e^{-\Theta_{\text{vib},i}/T} = 1 - \Theta_{\text{vib},i}/T$, if $\Theta_{\text{vib},i}/T \ll 1$. We obtain

$$\lim_{T \rightarrow \infty} Z_{\text{vib},i} = \frac{T}{\Theta_{\text{vib},i}}. \quad (6.5.2)$$

Vibrational temperatures for most normal modes are much higher than ambient temperature. Hence, at 298 K we have often $Z_{\text{vib},i} \approx 1$. Appreciable deviations are observed for vibrations that involve heavy atoms, for instance $Z_{\text{vib}} = 1.556$ at $T = 300$ K for I_2 .

Vibrational Contributions to U, C_V, and S

The vibrational partition function for a system consisting of N diatomic molecules is

$$z_{\text{vib}} = Z_{\text{vib}}^N = \left(\frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} \right)^N. \quad (6.5.3)$$

With $N = N_{\text{Av}}$ we obtain the vibrational contribution to the molar internal energy

$$U_{\text{vib}} = k_{\text{B}} T^2 \left(\frac{\partial \ln z_{\text{vib}}}{\partial T} \right)_V = \frac{N_{\text{Av}} k_{\text{B}} \Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1} \quad (6.5.4)$$

$$= \frac{R \Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}. \quad (6.5.5)$$

For multi-atomic molecules the contributions from the individual normal modes with characteristic vibrational temperatures $\Theta_{\text{vib},i}$ must be summed. Equation 6.5.5 neglects the zero-point energy, as we had defined the partition function for an energy scaled by the zero-point energy. On an absolute energy scale, where $U = 0$ corresponds to the minimum of the Born-Oppenheimer potential energy hypersurface, an additional term $U_{\text{zp}} = N_{\text{Av}} h \nu_i / 2$ needs to be added for each normal mode, with ν_i being the frequency of the normal mode.

The vibrational contribution to molar heat capacity at constant volume is

$$C_{\text{vib},V} = \left(\frac{\partial U_{\text{vib}}}{\partial T} \right)_V = R \left(\frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{\Theta_{\text{vib}}/T}}{(e^{\Theta_{\text{vib}}/T} - 1)^2}, \quad (6.5.6)$$

which is called the *Einstein equation*. With the Einstein function,

$$\mathcal{F}_{\text{E}}(u) = \frac{u^2 e^u}{(e^u - 1)^2}, \quad (6.5.7)$$

it can be written as

$$C_{\text{vib},V} = RT \mathcal{F}_{\text{E}} \left(\frac{\Theta_{\text{vib}}}{T} \right). \quad (6.5.8)$$

For computing the vibrational contribution to molar entropy we revert to the shifted energy scale. This is required, as inclusion of the zero-point contribution to u would leave us with an infinity. We find

$$S_{\text{vib},i} = R \left[\frac{\Theta_{\text{vib},i}}{T (e^{\Theta_{\text{vib},i}/T} - 1)} - \ln(1 - e^{-\Theta_{\text{vib},i}/T}) \right]. \quad (6.5.9)$$

Again contributions from individual normal modes add up. For $\Theta_{\text{vib},i}/T \gg 1$, which is the usual case, both terms in the brackets are much smaller than unity, so that the contribution of any individual normal mode to entropy is much smaller than R . Hence, at ambient temperature the vibrational contribution to entropy is negligible compared to the rotational contribution unless the molecule contains heavy nuclei.

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