

Lecture #8: Vibrational Partition Functions (18.4, 18.7)

I Boltzmann Distribution of Vibrational States
 II Vibrational Partition Functions for Polyatomic Molecules

I. Boltzmann Distribution of Vibrational States

Vibrational energies relative to bottom of well are the H.O. energies:

$$e_u = \left(u + \frac{1}{2}\right) h\nu \quad u = 0, 1, 2, \dots \quad (1)$$

$$q_{vib}(T) = \sum_{u=0}^{\infty} e^{-b\left(u+\frac{1}{2}\right)h\nu} = e^{-\frac{b h \nu}{2}} \sum_{u=0}^{\infty} e^{-b h \nu u} \quad (2)$$

For $x = e^{-b h \nu} < 1$, use the geometric series $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ to convert Eq. 2 into Eq. 3

$$q_{vib}(T) = \frac{e^{-b h \nu / 2}}{1 - e^{-b h \nu}} \quad (3)$$

Equation 3 may be expressed in terms of vibrational temperature $\Theta_{vib} = \frac{h\nu}{k_B}$ may

also be $\Theta_{vib} = \frac{\tilde{\nu}}{\tilde{k}_B}$ where \tilde{k}_B is k_B is expressed in $\text{cm}^{-1} \text{K}^{-1}$, $0.695038 \text{ cm}^{-1} \text{K}^{-1}$.

$$q_{vib}(T) = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \quad (4)$$

Determine the average vibrational energy $\langle E_{vib} \rangle$ via $\langle E \rangle = N k_B T^2 \left(\frac{\partial \ln q_{vib}}{\partial T} \right)_N$

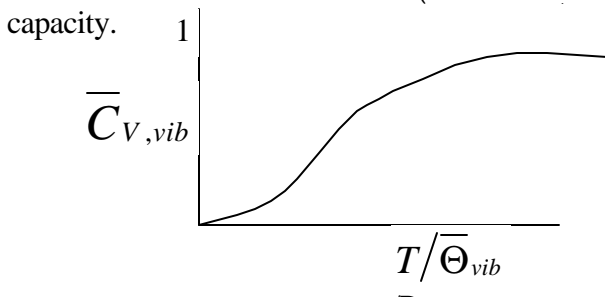
Use the chain rule with $U = \Theta/T$ to show that $\langle E_{vib} \rangle = N k_B \left(\frac{\Theta_{vib}}{2} + \frac{\Theta_{vib}}{e^{\Theta_{vib}/T} - 1} \right)$

Using this $\langle E_{vib} \rangle$ and the same chain rule $U = \Theta/T$, show that (Hint: $R = N k_B$)

$$\bar{C}_{V,vib} = \frac{d\langle \bar{E}_{vib} \rangle}{dT} = R \left(\frac{\Theta_{vib}}{T} \right)^2 \frac{e^{-\Theta_{vib}/T}}{(1 - e^{-\Theta_{vib}/T})^2}$$

The vibrational contribution to molar heat capacity.

At high T the limit of $\bar{C}_{V,vib}$ is R.



The fraction of molecules in the ν^{th} vib. state = the probability in that state (See lec 6)

$$p_k^{\text{vib}} = \frac{e^{-\epsilon_{\text{vib}}/k_B T}}{\sum_k e^{-\epsilon_{\text{vib}}/k_B T}} \rightarrow f_{\mathbf{u}} = \frac{e^{-\mathbf{h}\mathbf{n}\left(\mathbf{u}+\frac{1}{2}\right)}}{q_{\text{vib}}} = \frac{e^{-\mathbf{h}\mathbf{n}\left(\mathbf{u}+\frac{1}{2}\right)}}{e^{-\frac{\mathbf{h}\mathbf{n}}{2}} \frac{1}{1-e^{-\mathbf{h}\mathbf{n}}}} = (1-e^{-\mathbf{h}\mathbf{n}})e^{-\mathbf{h}\mathbf{n}\mathbf{u}}$$

$$f_{\mathbf{u}} = (1-e^{-\Theta_{\text{vib}}/T})e^{-\mathbf{u}\Theta_{\text{vib}}/T}$$

Example 1 – The fundamental frequency of NO is 1904 cm^{-1} and $k_B = 0.695038 \text{ cm}^{-1} \text{ K}^{-1}$.

What is the vibrational temperature Θ of NO?

What fraction of NO molecules are in the first excited state at 300K?

What fraction of NO molecules are in the second excited state at 1000K?

If the fraction of NO molecules in the first excited state is 3.83×10^{-2} what is the temperature?

II. Vibrational Partition Functions for Polyatomic Molecules

For a polyatomic molecule with α normal modes ($\alpha = 3N-5$ linear, $3N-6$ nonlinear). The

total vibrational energy is given by $\epsilon_{\text{vib}} = \sum_{j=1}^{\alpha} \left(\mathbf{u}_j + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_j$ $\mathbf{u}_j = 0, 1, 2, \dots$

\mathbf{n}_j is the frequency associated with the j th normal mode. For example a bent triatomic molecule has 3 normal modes: $\nu_1 =$ symmetric stretch, $\nu_2 =$ bending, and $\nu_3 =$ antisymmetric stretch. The energy would be given by:

$$\epsilon_{\text{vib}} = \left(\mathbf{u}_1 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_1 + \left(\mathbf{u}_2 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_2 + \left(\mathbf{u}_3 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_3$$

$$\mathbf{u}_1 = 0, 1, 2, \dots \quad \mathbf{u}_2 = 0, 1, 2, \dots \quad \mathbf{u}_3 = 0, 1, 2, \dots$$

Possible values of ϵ_{vib} are:

$$\left(0 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_1 + \left(0 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_2 + \left(1 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_3 = (0,0,1), \quad \left(1 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_1 + \left(2 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_2 + \left(1 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_3 = (1,2,1)$$

$$\left(1 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_1 + \left(2 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_2 + \left(0 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_3 = (1,2,0), \quad \left(0 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_1 + \left(3 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_2 + \left(1 + \frac{1}{2} \right) \mathbf{h}\mathbf{n}_3 = (0,3,1)$$

The partition function of each mode is given by Eq. 4, since energies are additive then q_{vib} is given as the product of the q_{vib} for each mode:

$$q_{\text{vib}}(T) = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \quad \Theta_{\text{vib},j} = \frac{\tilde{\mathbf{n}}_j}{\tilde{k}_B}$$

This is the characteristic vibrational temperature for the j th mode.

If the characteristic vibrational temperatures of NO_2 are 1900, 1080, and 2330 K, what are the values of $\tilde{\mathbf{n}}_1, \tilde{\mathbf{n}}_2,$ and $\tilde{\mathbf{n}}_3$ in cm^{-1} units? Note $\tilde{k}_B = 0.695038 \text{ cm}^{-1} \text{ K}^{-1}$.

Utilizing $\langle E \rangle = Nk_B T^2 \left(\frac{\partial \ln q_{vib}}{\partial T} \right)_N$ we obtain the following for $\langle E_{vib} \rangle$ **for a polyatomic**.

$$\langle E_{vib,j} \rangle = Nk_B \sum_{j=1}^a \left(\frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j} e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}} \right) = R \sum_{j=1}^a \left(\frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j} e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}} \right)$$

The derivative wrt T leads to the **vibrational heat capacity for a polyatomic**:

$$C_{V,vib} = R \sum_{j=1}^a \left[\left(\frac{\Theta_{vib,j}}{T} \right)^2 + \frac{e^{-\Theta_{vib,j}/T}}{\left(1 - e^{-\Theta_{vib,j}/T} \right)^2} \right]$$