

17.8: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom

From the previous sections, the partition function for a system of N indistinguishable and independent molecules is:

$$Q(N, V, \beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \quad (17.8.1)$$

And the average energy of the system is:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \quad (17.8.2)$$

We can combine these two equations to obtain:

$$\begin{aligned} \langle E \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \\ &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= N \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V, T)} \end{aligned}$$

The average energy is equal to:

$$\langle E \rangle = N \langle \epsilon \rangle \quad (17.8.3)$$

where $\langle \epsilon \rangle$ is the average energy of a single particle. If we compare Equation 17.8.2 with Equation 17.8.2, we can see:

$$\langle \epsilon \rangle = \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V, T)}$$

The probability that a particle is in state i , π_i , is given by:

$$\langle \epsilon \rangle = \frac{e^{-\epsilon_i/kT}}{q(V, T)} = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

The energy of a particle is a sum of the energy of each degree of freedom for that particle. In the case of a molecule, the energy is:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$$

The molecular partition function is the product of the degree of freedom partition functions:

$$q(V, T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

The partition function for each degree of freedom follows the same is related to the Boltzmann distribution. For example, the vibrational partition function is:

$$q_{\text{vib}} = \sum_i e^{-\epsilon_i/kT}$$

The average energy of each degree of freedom follows the same pattern as before. For example, the average vibrational energy is:

$$\langle \epsilon_{\text{vib}} \rangle = kT^2 \frac{\partial \ln q_{\text{vib}}}{\partial T} = - \frac{\partial \ln q_{\text{vib}}}{\partial \beta}$$

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