

## 22.1: Interpreting the Partition Function

When it is a good approximation to say that the energy of a molecule is the sum of translational, rotational, vibrational, and electronic components, we have

$$\epsilon_{i,j,k,m} = \epsilon_{t,i} + \epsilon_{r,j} + \epsilon_{v,k} + \epsilon_{e,m}$$

where the indices  $i$ ,  $j$ ,  $k$ , and  $m$  run over all possible translational, rotational, vibrational, and electronic quantum states, respectively. Then the partition function for the molecule can be expressed as a product of the individual partition functions  $z_t$ ,  $z_r$ ,  $z_v$ , and  $z_e$ ; that is,

$$\begin{aligned} z_{\text{molecule}} &= \sum_t \sum_r \sum_v \sum_e g_{t,i} g_{r,j} g_{v,k} g_{e,m} \exp\left(\frac{-\epsilon_{i,j,k,m}}{kT}\right) \\ &= \sum_t g_{t,i} \exp\left(\frac{-\epsilon_{t,i}}{kT}\right) \sum_r g_{r,j} \exp\left(\frac{-\epsilon_{r,j}}{kT}\right) \sum_v g_{v,k} \exp\left(\frac{-\epsilon_{v,k}}{kT}\right) \sum_e g_{e,m} \exp\left(\frac{-\epsilon_{e,m}}{kT}\right) \\ &= z_t z_r z_v z_e \end{aligned}$$

The magnitude of an individual partition function depends on the magnitudes of the energy levels associated with that kind of motion. Table 1 gives the contributions made to their partition functions by levels that have various energy values.

Table 1:

$\epsilon_i$	$\frac{-\epsilon_i}{kT}$	$\exp\left(\frac{-\epsilon_i}{kT}\right)$	Type of Motion
$10^{-2} kT$	$-10^{-2}$	0.990	
$10^{-1} kT$	$-10^{-1}$	0.905	
$kT$	-1	0.365	translational
$5 kT$	-5	0.0067	rotational
$10 kT$	-10	$4.5 \times 10^{-5}$	vibration
$100 kT$	-100	$3.7 \times 10^{-44}$	electronic

We see that only quantum states whose energy is less than  $kT$  can make substantial contributions to the magnitude of a partition function. Very approximately, we can say that the partition function is equal to the number of quantum states for which the energy is less than  $kT$ . Each such quantum state will contribute approximately one to the sum that comprises the partition function; the contribution of the corresponding energy level will be approximately equal to its degeneracy. If the energy of a quantum state is large compared to  $kT$ , the fraction of molecules occupying that quantum state will be small. This idea is often expressed by saying that such states are “unavailable” to the molecule. It is then said that the value of the partition function is approximately equal to the number of available quantum states. When most energy levels are non-degenerate, we can also say that the value of the partition function is approximately equal to the number of available energy levels.

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