

### 3.5: Partition Functions and Equilibrium - Isomeric Molecules

In [Section 20.11](#), we discuss chemical equilibrium between isomers from the perspective afforded by Boltzmann's definition of entropy. Now, let us consider equilibrium in this system from the perspective afforded by the energy-level probabilities. Let us assign even-integer labels to energy levels of isomer  $A$  and odd-integer labels to energy levels of isomer  $B$ . A group of atoms that can arrange itself into either a molecule of  $A$  or a molecule of  $B$  can occupy any of these energy levels. The partition function for this group of molecules to which all energy levels are available is

$$z_{A+B} = \sum_{i=1}^{\infty} g_i \exp(-\beta \epsilon_i)$$

The fraction of molecules in the first (odd) energy level associated with molecules of isomer  $B$  is

$$\frac{N_1^*}{N_{A+B}} = g_1 (z_{A+B})^{-1} \exp(-\beta \epsilon_1)$$

and the fraction in the next is

$$\frac{N_3^*}{N_{A+B}} = g_3 (z_{A+B})^{-1} \exp(-\beta \epsilon_3)$$

The total number of  $B$  molecules is

$$N_B^* = \sum_{i \text{ odd}} N_i$$

so that the fraction of all of the molecules that are  $B$  molecules is

$$\frac{N_B^*}{N_{A+B}} = (z_{A+B})^{-1} \sum_{i \text{ odd}} g_i \exp(-\beta \epsilon_i) = z_B / z_{A+B}$$

Likewise, the fraction that is  $A$  molecules is

$$\frac{N_A^*}{N_{A+B}} = (z_{A+B})^{-1} \sum_{i \text{ even}} g_i \exp(-\beta \epsilon_i) = z_A / z_{A+B}$$

The equilibrium constant for the equilibrium between  $A$  and  $B$  is

$$K_{eq} = \frac{N_B^*}{N_A^*} = \frac{z_B}{z_A}$$

We see that the equilibrium constant for the isomerization reaction is simply equal to the ratio of the partition functions of the isomers.

It is always true that the equilibrium constant is a product of partition functions for reaction-product molecules divided by a product of partition functions for reactant molecules. However, the partition functions for the various molecules must be expressed with a common zero of energy. Choosing the infinitely separated component atoms as the zero-energy state for every molecule assures that this is the case. However, it is often convenient to express the partition function for a molecule by measuring each molecular energy level,  $\epsilon_i$ , relative to the lowest energy state of that isolated molecule. When we do this, the zero of energy is different for each molecule.

To adjust the energies in a molecule's partition function so that they are expressed relative to the energy of the molecule's infinitely separated atoms, we must add to each molecular energy the energy required to take the molecule from its lowest energy state to its isolated component atoms. If  $z$  is the partition function when the  $\epsilon_i$  are measured relative to the lowest energy state of the isolated molecule,  $\Delta \epsilon$  is the energy released when the isolated molecule is formed from its component atoms, and  $z^*$  is the partition function when the  $\epsilon_i$  are measured relative to the molecule's separated atoms, we have  $z^* = z \exp(+\Delta \epsilon / kT)$ .

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