

2.11: Thermodynamic Probability and Equilibrium in an Isomerization Reaction

To relate these ideas to a change in a more specific macroscopic system, let us consider isomeric substances A and B . (We consider this example further in Chapter 21.) In principle, we can solve the Schrödinger equation for a molecule of isomer A and for a molecule of isomer B . We obtain all possible energy levels for a molecule of each isomer.¹ If we list these energy levels in order, beginning with the lowest, some of these levels belong to isomer A and the others belong to isomer B .

Now let us consider a mixture of N_A molecules of A and N_B molecules of B . We suppose that individual molecules are distinguishable and that intermolecular interactions can be ignored. Since a group of atoms that can form an A molecule can also form a B molecule, every energy level is accessible to this group of atoms; that is, we can view both sets of energy levels as being available to the atoms that make up the molecules. For a given system energy, there will be many population sets in which only the energy levels belonging to isomer A are occupied. For each of these population sets, there is a corresponding thermodynamic probability, W . Let W_A^{max} be the largest of these thermodynamic probabilities. Similarly, there will be many population sets in which only the energy levels corresponding to isomer B are occupied. Let W_B^{max} be the largest of the thermodynamic probabilities associated with these population sets. Finally, there will be many population sets in which the occupied energy levels belong to both isomer A and isomer B . Let $W_{A,B}^{max}$ be the largest of the thermodynamic probabilities associated with this group of population sets.

Now, W_A^{max} is a good approximation to the number of ways that the atoms of the system can come together to form isomer A . W_B^{max} is a good approximation to the number of ways that the atoms of the system can come together to form isomer B . At equilibrium, therefore, we expect

$$K = \frac{N_B}{N_A} = \frac{W_B^{max}}{W_A^{max}}$$

If we consider the illustrative—if somewhat unrealistic—case of isomeric molecules whose energy levels all have the same degeneracy ($g_i = g$ for all i), we can readily see that the equilibrium system must contain some amount of each isomer. For a system containing N molecules, $N!g^N$ is the numerator in each of the thermodynamic probabilities W_A^{max} , W_B^{max} , and $W_{A,B}^{max}$. The denominators are different. The denominator of $W_{A,B}^{max}$ must contain terms, $N_i!$, for essentially all of the levels represented in the denominator of W_A^{max} . Likewise, it must contain terms, $N_j!$, for essentially all of the energy levels represented in the denominator of W_B^{max} . Then the denominator of $W_{A,B}^{max}$ is a product of $N_k!$ terms that are generally smaller than the corresponding factorial terms in the denominators of W_A^{max} and W_B^{max} . As a result, the denominators of W_A^{max} and W_B^{max} are larger than the denominator of $W_{A,B}^{max}$. In consequence, $W_{A,B}^{max} > W_A^{max}$ and $W_{A,B}^{max} > W_B^{max}$. (See problems 5 and 6.)

If we create the system as a collection of A molecules, or as a collection of B molecules, redistribution of the sets of atoms among all of the available energy levels must eventually produce a mixture of A molecules and B molecules. Viewed as a consequence of the principle of equal *a priori* probabilities, this occurs because there are necessarily more microstates of the same energy available to some mixture of A and B molecules than there are microstates available to either A molecules alone or B molecules alone. Viewed as a consequence of the tendency of the isolated system to attain the state of maximum entropy, this occurs because $k \ln W_{A,B}^{max} > k \ln W_A^{max}$ and $k \ln W_{A,B}^{max} > k \ln W_B^{max}$.

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