The section on atoms, molecules and probability has shown that if we want to predict whether a chemical change is spontaneous or not, we must find some general way of determining whether the final state is more probable than the initial. This can be done using a number $W$, called the **thermodynamic probability**. $W$ is defined as the number of alternative microscopic arrangements which correspond to the same macroscopic state. The significance of this definition becomes more apparent once we have considered a few examples.

Figure 1(a) illustrates a crystal consisting of only eight atoms at the absolute zero of temperature. Suppose that the temperature is raised slightly by supplying just enough energy to set one of the atoms in the crystal vibrating. There are eight possible ways of doing this, since we could supply the energy to any one of the eight atoms. All eight possibilities are shown in Fig. 1(b).

![Figure 1](image)

**Figure 1** The thermodynamic probability $W$ of a crystal containing eight atoms at three different temperatures. (a) At 0 K there is only one way in which the crystal can be arranged, so that $W = 1$. (b) If enough energy is added to start just one of the atoms vibrating (color), there are eight different equally likely arrangements possible, and $W = 8$. (c) If the energy is doubled, two different atoms can vibrate simultaneously (light color) or a single atom can have all the energy (dark color). The number of equally likely arrangements is much larger than before; $W = 36$.

Since all eight possibilities correspond to the crystal having the same temperature, we say that $W = 8$ for the crystal at this temperature. Also, we must realize that the crystal will not stay perpetually in any of these eight arrangements. Energy will constantly be transferred from one atom to the other, so that all the eight arrangements are equally probable.

Let us now supply a second quantity of energy exactly equal to the first, so that there is just enough to start two molecules vibrating. There are 36 different ways in which this energy can be assigned to the eight atoms (Fig. 1(c)). We say that $W = 36$ for the crystal at this second temperature. Because energy continually exchanges from one atom to another, there is an equal probability of finding the crystal in any of the 36 possible arrangements.

A third example of $W$ is our eight-atom crystal at the absolute zero of temperature. Since there is no energy to be
exchanged from atom to atom, only one arrangement is possible, and \( W = 1 \). This is true not only for this hypothetical crystal, but also presumably for a real crystal containing a large number of atoms, perfectly arranged, at absolute zero.

![Figure](image)

**Figure** Heat flow and thermodynamic probability. When two crystals, one containing 64 units of vibrational energy and the other (at 0 K) containing none are brought into contact, the 64 units of energy will distribute themselves over the two crystals since there are many more ways of distributing 64 units among 200 atoms than there are of distributing 64 units over only 100 atoms.

The thermodynamic probability \( W \) enables us to decide how much more probable certain situations are than others. Consider the flow of heat from crystal A to crystal B, as shown in Fig. 2. We shall assume that each crystal contains 100 atoms. Initially crystal B is at absolute zero. Crystal A is at a higher temperature and contains 64 units of energy-enough to set 64 of the atoms vibrating. If the two crystals are brought together, the molecules of A lose energy while those of B gain energy until the 64 units of energy are evenly distributed between both crystals.

In the initial state the 64 units of energy are distributed among 100 atoms. Calculations show that there are \( 1.0 \times 10^{44} \) alternative ways of making this distribution. Thus \( W_1 \), initial thermodynamic probability, is \( 1.0 \times 10^{44} \). The 100 atoms of crystal A continually exchange energy among themselves and transfer from one of these \( 1.0 \times 10^{44} \) arrangements to another in rapid succession. At any instant there is an equal probability of finding the crystal in any of the \( 1.0 \times 10^{44} \) arrangements.

When the two crystals are brought into contact, the energy can distribute itself over twice as many atoms. The number of possible arrangements rises enormously, and \( W_2 \), the thermodynamic probability for this new situation, is \( 3.6 \times 10^{60} \). In the constant reshuffle of energy among the 200 atoms, each of these \( 3.6 \times 10^{60} \) arrangements will occur with equal probability. However, only \( 1.0 \times 10^{44} \) of them correspond to all the energy being in crystal A. Therefore the probability of the heat flow reversing itself and all the energy returning to crystal A is \( \frac{1}{2} \).

This example shows how we can use \( W \) as a general criterion for deciding whether a reaction is spontaneous or not. Movement from a less probable to a more probable molecular situation corresponds to movement from a state in which \( W \) is smaller to a state where \( W \) is larger. In other words \( W \) increases for a spontaneous change. If we can find some way of calculating or measuring the initial and final values of \( W \), the problem of deciding in advance whether a reaction will be spontaneous or not is solved. If \( W_2 \) is greater than \( W_1 \), then the reaction will occur of its own accord. Although there is nothing wrong in principle with this approach to spontaneous processes, in practice it turns out to be very cumbersome. For real samples of matter (as opposed to 200 atoms in the example of Fig. 2) the values of \( W \) are on the order of \( 10^{10^{24}} \)—so large that they are difficult to manipulate. The logarithm of \( W \), however, is only on the order of \( 10^{24} \), since \( \log 10^x = x \). This is more manageable, and chemists and physicists use a quantity called the **entropy** which is proportional to the logarithm of \( W \).
This way of handling the extremely large thermodynamic probabilities encountered in real systems was first suggested in 1877 by the Austrian physicist Ludwig Boltzmann (1844 to 1906). The equation

\[ k \text{Boltzmann constant} = RNk^{-1} \text{natural logarithm} \]

Example (PageIndex{1}) Entropy

The thermodynamic probability \( W \) for 1 mol propane gas at 500 K and 101.3 kPa has the value \( 10^{10^{25}} \). Calculate the entropy of the gas under these conditions.

**Solution** Since

\[ W = 10^{10^{25}} \]

\[ \log W = 10^{25} \]

Thus \( S = 2.303k \log W = 1.3805 \times 10^{-23} \text{J K}^{-1} \times 2.303 \times 10^{25} = 318 \text{J K}^{-1} \]

Note: The quantity 318 J K\(^{-1}\) is obviously much easier to handle than \( 10^{10^{25}} \).

Note also that the dimensions of entropy are energy/temperature.

WSWS

The statement that the entropy increases when a spontaneous change occurs is called the **second law of thermodynamics**. (The first law is the law of conservation of energy.) The second law, as it is usually called, is one of the most fundamental and most widely used of scientific laws. In this book we shall only be able to explore some of its chemical implications, but it is of importance also in the fields of physics, engineering, astronomy, and biology. Almost all environmental problems involve the second law. Whenever pollution increases, for instance, we can be sure that the entropy is increasing along with it.

The second law is often stated in terms of an entropy difference \( \Delta S \). If the entropy increases from an initial value of \( S_1 \) to a final value of \( S_2 \) as the result of a spontaneous change, then

\[ \Delta S = S_2 - S_1 \]

\[ S_2 - S_1 = 1.813 \times 10^{23} \]

\[ \begin{align} \Delta S &= S_2 - S_1 \\ &= 2.303 \times k \times \log \frac{W_2}{W_1} \\ &= 2.303 \times 1.3805 \times 10^{-23} \times 1.813 \times 10^{23} \end{align} \]

**Contributors**

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina
(University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.