

16.5: Thermodynamic Probability W and Entropy

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 16.5.1a 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 Figure 16.5.1b.

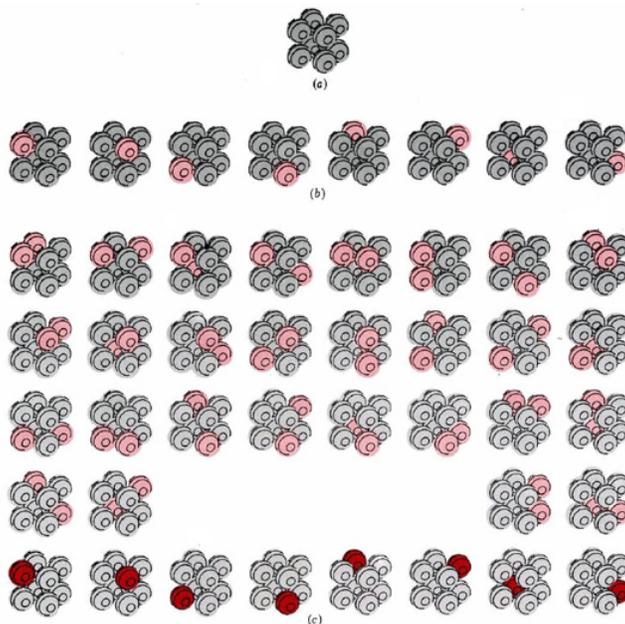


Figure 16.5.1 The thermodynamic probability W of a crystal containing eight atoms at three different temperatures. (a) At 0 K there is only one way in which the crystal can be arranged, so that $W = 1$. (b) If enough energy is added to start just one of the atoms vibrating (color), there are eight different 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 (Figure 16.5.1c). 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.

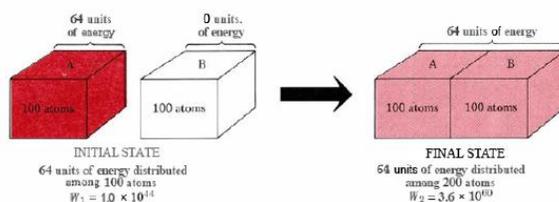


Figure 16.5.2 Heat flow and thermodynamic probability. When two crystals, one containing 64 units of vibrational energy and the other (at 0 K) containing none are brought into contact, the 64 units of energy will distribute themselves over the two crystals since there are many more ways of distributing 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 Figure 16.5.2. 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 1.0×10^{44} alternative ways of making this distribution. Thus W_1 , initial thermodynamic probability, is 1.0×10^{44} . The 100 atoms of crystal A continually exchange energy among themselves and transfer from one of these 1.0×10^{44} arrangements to another in rapid succession. At any instant there is an equal probability of finding the crystal in any of the 1.0×10^{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 3.6×10^{60} . In the constant reshuffle of energy among the 200 atoms, each of these 3.6×10^{60} arrangements will occur with equal probability. However, only 1.0×10^{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

$$\frac{W_1}{W_2} = \frac{1.0 \times 10^{44}}{3.6 \times 10^{60}} = 2.8 \times 10^{-17}$$

In other words the ratio of W_1 to W_2 gives us the relative probability of finding the system in its initial rather than its final state.

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 Figure 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

$$S = k \ln W \tag{16.5.1}$$

is now engraved on Boltzmann's tomb. The proportionality constant k is called, appropriately enough, the **Boltzmann constant**. It corresponds to the gas constant R divided by the Avogadro constant N_A :

$$k = \frac{R}{N_A} \tag{16.5.2}$$

and we can regard it as the gas constant per molecule rather than per mole. In SI units, the Boltzmann constant k has the value $1.3805 \times 10^{-23} \text{ J K}^{-1}$. The symbol \ln in Eq. 16.5.1 indicates a *natural logarithm*, i.e., a logarithm taken to the base e . Since base 10 logarithms and base e logarithms are related by the formula

$$\ln x = 2.303 \log x$$

it is easy to convert from one to the other. Equation 16.5.1, expressed in base 10 logarithms, thus becomes

$$S = 2.303k \log W$$

✓ Example 16.5.1: 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

$$W = 10^{10^{25}}$$

$$\log W = 10^{25}$$

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

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.

One of the properties of logarithms is that if we increase a number, we also increase the value of its logarithm. It follows therefore that if the thermodynamic probability W of a system increases, its entropy S must increase too. Further, since W always increases in a spontaneous change, it follows that S must also increase in such a change.

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 ΔS . 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

$$\Delta S = S_2 - S_1 \quad (16.5.3)$$

Since S_2 is larger than S_1 , we can write

$$\Delta S > 0 \quad (16.5.4)$$

Equation 16.5.4 tells us that for any spontaneous process, ΔS is greater than zero. As an example of this relationship and of the possibility of calculating an entropy change, let us find ΔS for the case of 1 mol of gas expanding into a vacuum. We have already argued for this process that the final state is $10^{1.813 \times 10^{23}}$ times more probable than the initial state. This can only be because there are $10^{1.813 \times 10^{23}}$ times more ways of achieving the final state than the initial state. In other words, taking logs, we have

$$\log \frac{W_2}{W_1} = 1.813 \times 10^{23}$$

Thus

$$\Delta S = S_2 - S_1 = 2.303 \times k \times \log W_2 - 2.303 \times k \times \log W_1 \quad (16.5.5)$$

$$= 2.303 \times k \times \log \frac{W_2}{W_1} \quad (16.5.6)$$

$$= 2.303 \times 1.3805 \times 10^{-23} \text{ J K}^{-1} \times 1.813 \times 10^{23} \quad (16.5.7)$$

$$S = 5.76 \text{ J K}^{-1}$$

As entropy changes go, this increase in entropy is quite small. Nevertheless, it corresponds to a gargantuan change in probabilities.

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