Chapter

14

Entropy and Free Energy

THE ILLUSTRATION shows the process by which a polypeptide chain in a biological cell folds into a three-dimensional structure called a protein. Although the original polypeptide chain can assume any number of configurations, the protein, if it is to function properly, must adopt a specific arrangement. Thus, the folding of a protein is accompanied by a decrease in system entropy. According to the second law of thermodynamics, any spontaneous process must result in an increase in the entropy of the universe. It follows, therefore, that there must be an increase in the entropy of the surroundings greater in magnitude than the decrease in entropy associated with the protein folding. In fact, the folding of a protein is exothermic and does indeed cause an increase in entropy of the surroundings via the spreading out of the energy produced by the process.

Before You Begin, Review These Skills

- System and surroundings [◀◀ Section 10.1]
- Hess's law [◀◀ Section 10.5]
- Standard Enthalpies of Formation [◀◀ Section 10.6]

14.1 SPONTANEOUS PROCESSES

An understanding of thermodynamics enables us to predict whether or not a reaction will occur when reactants are combined. This is important in the synthesis of new compounds in the laboratory, the manufacturing of chemicals on an industrial scale, and the understanding of natural processes such as cell function. A process that *does* occur under a specific set of conditions is called a **spontaneous process.** One that does *not* occur under a specific set of conditions is called **nonspontaneous process.** Table 14.1 lists examples of familiar spontaneous processes and their nonspontaneous counterparts. These examples illustrate what we know intuitively: Under a given set of conditions, a process that occurs spontaneously in one direction does not also occur spontaneously in the opposite direction.

Processes that result in a decrease in the energy of a system often are spontaneous. For example, the combustion of methane is exothermic:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H° = -890.4 \text{ kJ/mol}$$
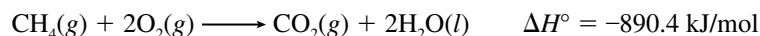
Thus, the energy of the system is lowered because heat is given off during the course of the reaction. Likewise, in the acid-base neutralization reaction,

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H° = -56.2 \text{ kJ/mol}$$

heat is given off, lowering the energy of the system. Each of these processes is spontaneous, and each results in a lowering of the system's energy.

Now consider the melting of ice:

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H° = 6.01 \text{ kJ/mol}$$
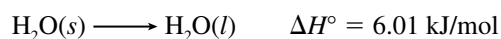
In this case, the process is endothermic and yet it is also spontaneous at temperatures above 0°C. Conversely, the freezing of water is an *exothermic* process:

$$H_2O(l) \longrightarrow H_2O(s) \qquad \Delta H° = -6.01 \text{ kJ/mol}$$
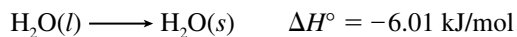
Yet it is *not* spontaneous at temperatures above 0°C.

Student Annotation: The conditions that most often are specified are *temperature, pressure,* and in the case of a solution, *concentration.*

TABLE 14.1	Familiar Spontaneous and Nonspontaneous Processes
Spontaneous	**Nonspontaneous**
Ice melting at room temperature	Water freezing at room temperature
Sodium metal reacting violently with water to produce sodium hydroxide and hydrogen gas [◀◀ Section 8.5]	Sodium hydroxide reacting with hydrogen gas to produce sodium metal and water
A ball rolling downhill	A ball rolling uphill
The rusting of iron at room temperature	The conversion of rust back to iron metal at room temperature
Water freezing at −10°C	Ice melting at −10°C

Based on the first two examples, and many others like them, we might conclude that exothermic processes tend to be spontaneous and, indeed, a negative ΔH does *favor* spontaneity. The last two examples, however, make it clear that the sign of ΔH *alone* is insufficient to predict spontaneity in every circumstance. For the remainder of this chapter, we will examine the *two* factors that determine whether or not a process is spontaneous under a given set of conditions.

14.2   ENTROPY

To predict the spontaneity of a chemical or physical process, we need to know both the change in *enthalpy* [◀◀ Section 10.3] and the change in *entropy* associated with the process. We first encountered the concept of entropy in our discussion of solution formation [◀◀ Section 13.2]. We will now look in more detail at what entropy is, and why it matters.

A Qualitative Description of Entropy

Student Annotation: Motional energy includes *translational* energy, in which the entire molecule moves through space [◀◀ Section 3.1]; *rotational* energy, in which the molecule spins about an axis running through its center of mass; and *vibrational* energy, in which atoms of a molecule move relative to one another.

Qualitatively, the *entropy (S)* of a system is a measure of how *spread out* or how *dispersed* the system's energy is. The simplest interpretation of this is how spread out a system's energy is in *space*. In other words, for a given system, the greater the volume it occupies, the greater its entropy. This interpretation explains how the process in Figure 14.1 occurs spontaneously despite there being no enthalpy change. Because they are moving, the gas molecules that were originally confined to one side of the container possess *motional energy*. In the absence of a barrier preventing it, the motional energy of molecules will spread out to occupy a larger volume. The dispersal of a system's motional energy to occupy a larger volume when the barrier is removed constitutes an *increase* in the system's entropy. Just as spontaneity is favored by a process being exothermic, spontaneity is also favored by an increase in the system's entropy. Whether it is the enthalpy change, the entropy change, or both, for a process to be spontaneous, *something* must favor spontaneity.

A Quantitative Definition of Entropy

At this point, it is useful to introduce the mathematical definition of entropy proposed by Ludwig Boltzmann:

Equation 14.1	$S = k \ln W$

Student Annotation: The Boltzmann constant is equal to the gas constant, R (in J/K · mol), divided by Avogadro's constant, N_A.

where k is the Boltzmann constant (1.38×10^{-23} J/K) and W is the number of energetically equivalent different ways the molecules in a system can be arranged. To illustrate what this means, let's consider a simplified version of the process shown in Figure 14.1. Prior to the removal of the barrier between the left and right sides of the container, at any given instant, each molecule has a particular location, somewhere in the left side of the container. To narrow down the possible locations of the molecules, we imagine that each side of the container is divided into a number of equal smaller volumes called *cells*. In the simplest scenario, with just one molecule in the system, the number of possible locations of the molecule is equal to the number of cells. If the system contains

Figure 14.1 A spontaneous process. The rapidly moving gas molecules originally confined to one side of a container spread out to fill the whole container when the barrier is removed.
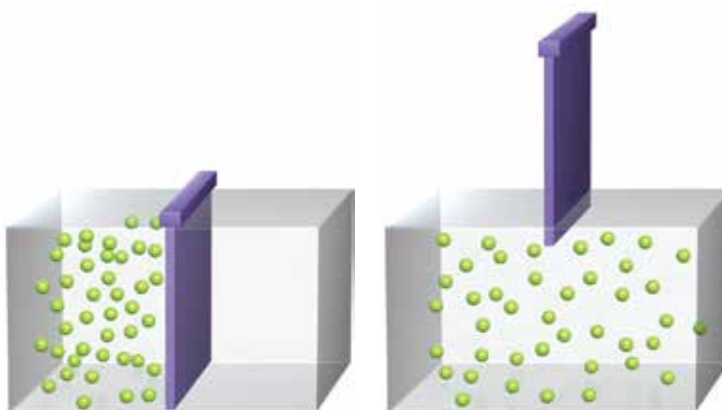
two molecules, the number of possible arrangements is equal to the number of cells *squared*. (Note that a cell may contain more than one molecule.) Each time we increase the number of molecules by one, the number of possible arrangements increases by a factor equal to the number of cells. In general, for a volume consisting of X cells, and containing N molecules, the number of possible arrangements, W, is given by the equation

$$W = X^N \qquad\qquad \text{Equation 14.2}$$

Figure 14.2 illustrates this for a simple case involving just two molecules. We imagine the container is divided into four cells each with volume v. Initially, both molecules are confined to the left side, which consists of two cells. With two molecules in two cells, there are $2^2 = 4$ possible arrangements of the molecules [Figure 14.2(a)]. When the barrier is removed, doubling the volume available to the molecules, the number of cells also doubles. With four cells available, there are $4^2 = 16$ possible arrangements of the molecules. Eight of the sixteen arrangements have the molecules on opposite sides of the container [Figure 14.2(b)]. Of the other eight arrangements, four have both molecules on the left side [as shown in Figure 14.2(a)], and four have both molecules on the right side (not shown). There are three different states possible for this system.

1. One molecule on each side (eight possible arrangements)
2. Both molecules on the left (four possible arrangements)
3. Both molecules on the right (four possible arrangements)

The most *probable* state is the one with the *largest* number of possible arrangements. In this case, the most probable state is the one with one molecule on each side of the container. The same principle applies to systems with larger numbers of molecules. Increasing the number of molecules increases the number of possible arrangements, but the most probable state will be the one in which the gas molecules are divided evenly between the two sides of the container.
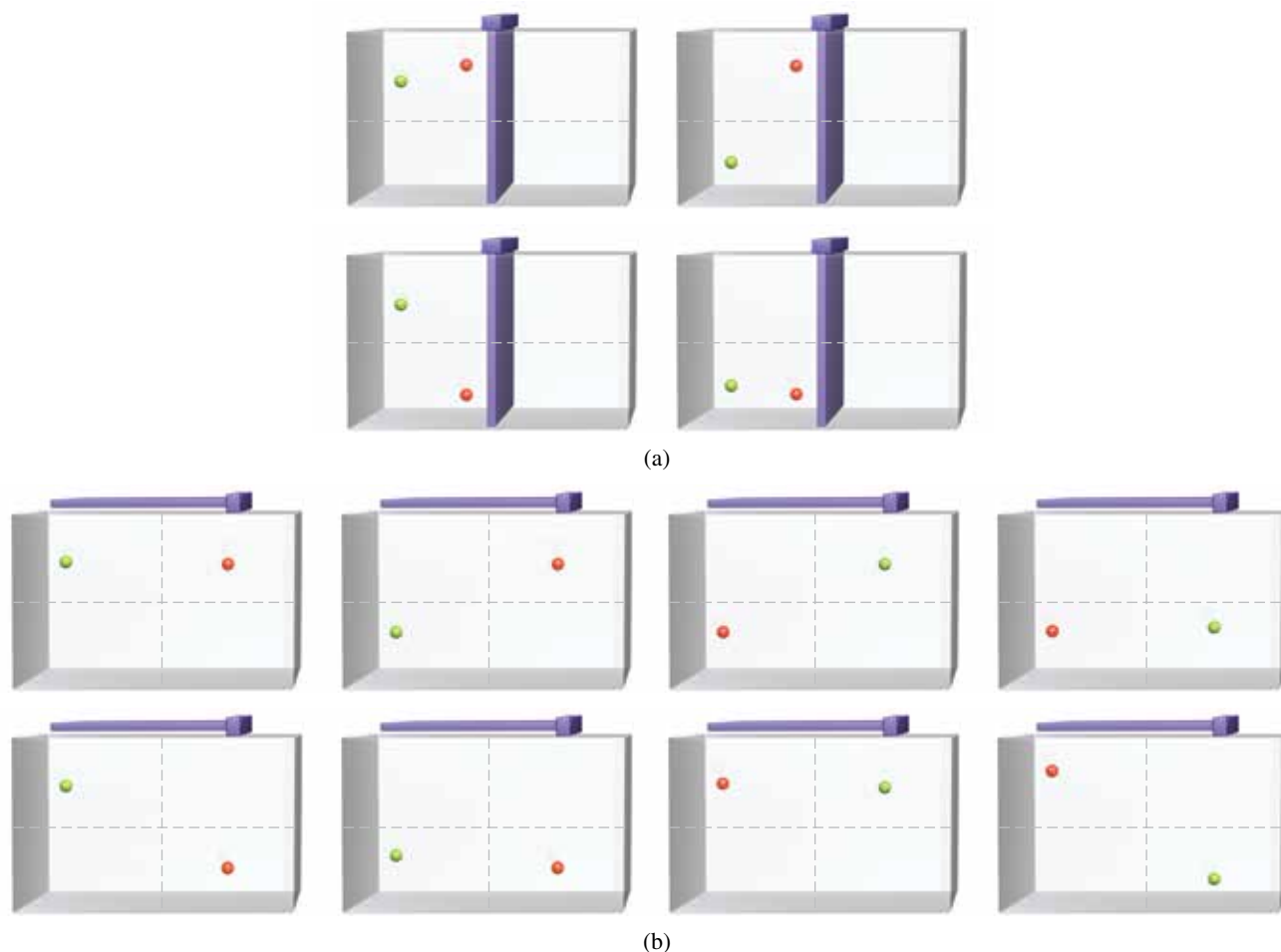
(a)

(b)

Figure 14.2 (a) Before the barrier is removed, the molecules are both in the left side of the container, which we imagine is divided into two cells of equal volume. There are four possible arrangements of two molecules in two cells. (b) When the barrier between the two sides of the container is removed, the volume (and the number of cells) available to the molecules doubles. The new number of possible arrangements is $4^2 = 16$, eight of which have the molecules in opposite sides of the container—the most probable outcome.

14.3   ENTROPY CHANGES IN A SYSTEM

Calculating ΔS_{sys}

The change in entropy of a system is the difference between the entropy of the final state and the entropy of the initial state.

Equation 14.3	$$\Delta S_{sys} = S_{final} - S_{initial}$$

Using Equation 14.1, we can write an expression for the entropy of each state,

$$\Delta S_{sys} = k \ln W_{final} - k \ln W_{initial} = k \ln \frac{W_{final}}{W_{initial}}$$

Combining this result with Equation 14.2 gives

$$\Delta S_{sys} = k \ln \frac{(X_{final})^N}{(X_{initial})^N} = k \ln \left(\frac{X_{final}}{X_{initial}}\right)^N = k N \ln \left(\frac{X_{final}}{X_{initial}}\right)$$

Because X is the number of cells, and the volume of each cell is v, the total volume is related to the number of cells by

$$V = Xv \quad \text{or} \quad X = \frac{V}{v}$$

We substitute V_{final}/v for X_{final} and $V_{initial}/v$ for $X_{initial}$ to get

$$\Delta S_{sys} = k N \ln \frac{V_{final}/v}{V_{initial}/v} = k N \ln \frac{V_{final}}{V_{initial}}$$

Finally, because the Boltzmann constant, k, is the gas constant, R, divided by Avogadro's constant,

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

and because the number of molecules, N, is the product of the number of moles, n, and Avogadro's constant, N_A;

$$N = n \times N_A$$

$$kN = \left(\frac{R}{N_A} \times n \times N_A\right) = nR$$

the equation becomes

Equation 14.4	$$\Delta S_{sys} = nR \ln \frac{V_{final}}{V_{initial}}$$

Worked Example 14.1 shows how to use Equation 14.4 to calculate the entropy change for a process like the one shown in Figure 14.1, the expansion of an ideal gas at constant temperature.

Worked Example 14.1

Determine the change in entropy for 1.0 mole of an ideal gas originally confined to one-half of a 5.0-L container when the gas is allowed to expand to fill the entire container at constant temperature.

Strategy This is the isothermal expansion of an ideal gas. Because the molecules spread out to occupy a greater volume, we expect there to be an increase in the entropy of the system. Use Equation 14.3 to solve for ΔS_{sys}.

Setup $R = 8.314$ J/K · mol, $n = 1.0$ mole, $V_{final} = 5.0$ L, and $V_{initial} = 2.5$ L.

Solution

$$\Delta S_{sys} = nR \ln \frac{V_{final}}{V_{initial}} = 1.0 \text{ mol} \times \frac{8.314 \text{ J}}{\text{K} \cdot \text{mol}} \times \ln \frac{5.0 \text{ L}}{2.5 \text{ L}} = 5.8 \text{ J/K}$$

Think About It
Remember that for a process to be spontaneous, *something* must favor spontaneity. If the process is spontaneous but not exothermic (in this case, there is no enthalpy change), then we should expect ΔS_{sys} to be positive.

Practice Problem ATTEMPT Determine the change in entropy (ΔS_{sys}), for the expansion of 0.10 mole of an ideal gas from 2.0 L to 3.0 L at constant temperature.

Practice Problem BUILD To what fraction of its original volume must a 0.50-mole sample of ideal gas be compressed at constant temperature for ΔS_{sys} to be −6.7 J/K?

Practice Problem CONCEPTUALIZE Which equation is correct for calculating ΔS_{sys} for a gaseous reaction that occurs at constant volume?

$$\Delta S_{sys} = nR \qquad \Delta S_{sys} = nRT \ln \frac{P_{initial}}{P_{final}} \qquad \Delta S_{sys} = nR \ln \frac{P_{initial}}{P_{final}} \qquad \Delta S_{sys} = \frac{nR}{T} \ln \frac{P_{final}}{P_{initial}}$$

(i)   (ii)   (iii)   (iv)

Standard Entropy, $S°$

Although Equation 14.1 provides a quantitative definition of entropy, we seldom use it or Equation 14.3 to calculate the entropy change for a real process because of the difficulty involved in determining W, the number of different possible arrangements (Equation 14.2) in a macroscopic system. Instead, for processes other than isothermal expansion or compression of an ideal gas (for which we can use Equation 14.4), we routinely determine entropy changes using tabulated values.

    Using calorimetry [◄◄ Section 10.4], it is possible to determine the *absolute* value of the entropy of a substance, S; something we cannot do with either energy or enthalpy. (Recall that while we can determine ΔU and ΔH for a process that a system undergoes, we cannot determine the absolute values of either U or H for a system [◄◄ Sections 10.2 and 10.3].) **Standard entropy** is the absolute entropy of a substance at 1 atm. (Tables of standard entropy values typically are the values at 25°C because so many processes are carried out at room temperature—although temperature is *not* part of the standard state definition and therefore must be specified.) Table 14.2 lists standard entropies of a few elements and compounds. Appendix 2 provides a more extensive listing. The units of entropy are J/K · mol. We use joules rather than kilojoules because entropy values typically are quite small. The entropies of substances (elements and compounds) are always positive (i.e., $S > 0$), even for elements in their standard states. (Recall that the standard *enthalpy* of formation, $\Delta H_f°$, for elements in their standard states is arbitrarily defined as zero, and for compounds it may be either positive or negative [◄◄ Section 10.6].)

    Referring to Table 14.2, we can identify several important trends:

- For a given substance, the standard entropy is greater in the liquid phase than in the solid phase. [Compare the standard entropies of Na(s) and Na(l).] This results from there being greater molecular motion in a liquid, resulting in many possible arrangements of atoms in the liquid phase; whereas the positions of atoms in the solid are fixed.
- For a given substance, the standard entropy is greater in the gas phase than in the liquid phase. [Compare the standard entropies of Na(l) and Na(g) and those of $H_2O(l)$ and $H_2O(g)$.] This results from there being much greater molecular motion in a gas, resulting in many more possible arrangements of atoms in the gas phase than in the liquid phase—in part because the gas phase occupies a much greater volume than either of the condensed phases.
- For two monatomic species, the one with the larger molar mass has the greater standard entropy. [Compare the standard entropies of He(g) and Ne(g).]
- For two substances in the same phase, and with similar molar masses, the substance with the more complex molecular structure has the greater standard entropy. [Compare the

Student Annotation: For even the simplest of hypothetical systems, where there are only two possible positions for molecules ($X = 2$), most calculators cannot display a number as large as the result of Equation 14.2 for even as few as 500 molecules—much less for the *enormous* number of molecules present in any *real* sample. (If your calculator is like most, with $X = 2$, you can calculate the number of possible arrangements for $N \le 332$ molecules. Try it: $2 \land 332 = ?$ and $2 \land 333 = ?$)

Student Annotation: You will find that tables, including Appendix 2, contain *negative* absolute entropies for some aqueous ions. Unlike a substance, an individual ion cannot be studied experimentally. Therefore, standard entropies of ions are actually *relative* values, where a standard entropy of zero is arbitrarily assigned to the hydrated hydrogen ion. Depending on an ion's extent of hydration, its standard entropy may be positive or negative, relative to that of hydrogen ion.

TABLE 14.2	Standard Entropy Values ($S°$) for Some Substances at 25°C		
Substance	**$S°$ (J/K · mol)**	**Substance**	**$S°$ (J/K · mol)**
$H_2O(l)$	69.9	C(diamond)	2.4
$H_2O(g)$	188.7	C(graphite)	5.69
Na(s)	51.05	$O_2(g)$	205.0
Na(l)	57.56	$O_3(g)$	237.6
Na(g)	153.7	$F_2(g)$	203.34
He(g)	126.1	Au(s)	47.7
Ne(g)	146.2	Hg(l)	77.4

standard entropies of $O_3(g)$ and $F_2(g)$.] The more complex a molecular structure, the more different types of motion the molecule can exhibit. A diatomic molecule such as F_2, for example, exhibits only one type of vibration, whereas a bent triatomic molecule such as O_3 exhibits three different types of vibrations. Each mode of motion contributes to the total number of available energy levels within which a system's energy can be dispersed. Figure 14.3 illustrates the ways in which the F_2 and O_3 molecules can rotate and vibrate.

• In cases where an element exists in two or more allotropic forms, the form in which the atoms are more mobile has the greater entropy. [Compare the standard entropies of C(diamond) and C(graphite). In diamond, the carbon atoms occupy fixed positions in a three-dimensional array. In graphite, although the carbon atoms occupy fixed positions within the two-dimensional sheets (see Figure 12.24, page 504), the sheets are free to move with respect to one another, which increases the mobility and, therefore, total number of possible arrangements of atoms within the solid.]

Now let's consider a process represented by the following chemical equation:

$$aA + bB \longrightarrow cC + dD$$
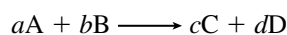
Just as the enthalpy change of a reaction is the difference between the enthalpies of the products and reactants (Equation 10.10), the entropy change is the difference between the entropies of the products and reactants:

Equation 14.5 $\Delta S^\circ_{rxn} = [cS^\circ(C) + dS^\circ(D)] - [aS^\circ(A) + bS^\circ(B)]$

Or, using Σ to represent summation and m and n to represent the stoichiometric coefficients of the reactants and products, respectively, Equation 14.5 can be generalized as follows:

Equation 14.6 $\Delta S^\circ_{rxn} = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants})$

Figure 14.3 In addition to translational motion, molecules exhibit both *vibrations,* in which the atoms' positions relative to one another change, and *rotations,* in which the molecule rotates about its center of mass. (a) A diatomic molecule such as fluorine only exhibits one type of vibration. A bent, triatomic molecule such as ozone exhibits three types of vibration. (b) A diatomic molecule exhibits two different rotations, whereas a bent, triatomic molecule exhibits three different rotations. (Note that rotation of F_2 about the x axis would cause no change in the positions of either atom in the molecule.)
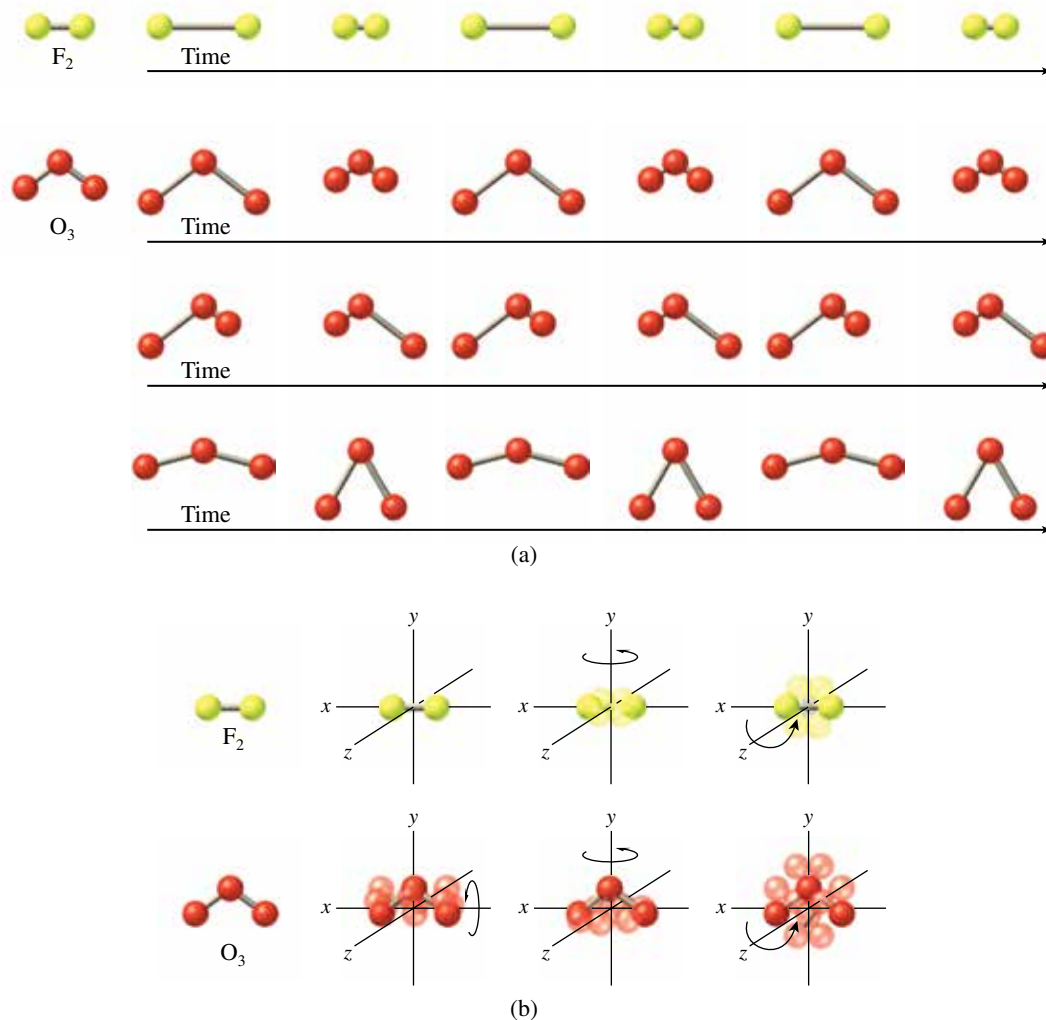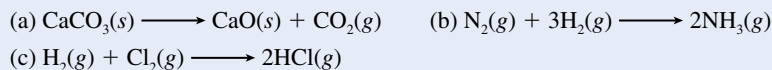
The standard entropy values of a large number of substances have been measured in J/K · mol. To calculate the standard entropy change for a <mark>reaction</mark> (ΔS°_{rxn}), we look up the standard entropies of the products and reactants and use Equation 14.5.

    Worked Example 14.2 demonstrates this approach.

Worked Example 14.2
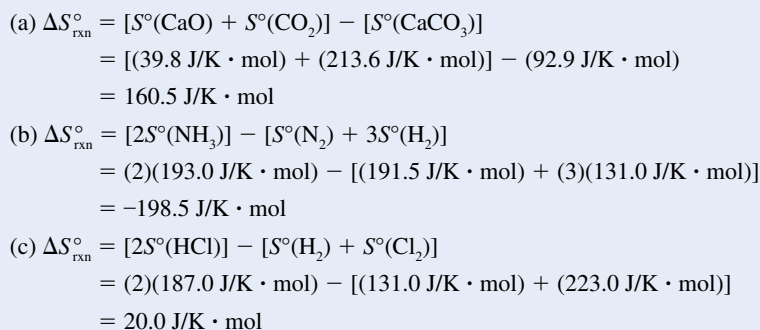
From the standard entropy values in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:

(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ (b) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(c) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Strategy Look up standard entropy values and use Equation 14.5 to calculate ΔS°_{rxn}. Just as we did when we calculated standard enthalpies of reaction, we consider stoichiometric coefficients to be dimensionless—giving ΔS°_{rxn} units of J/K · mol.

Setup From Appendix 2, $S^\circ[CaCO_3(s)] = 92.9$ J/K · mol, $S^\circ[CaO(s)] = 39.8$ J/K · mol, $S^\circ[CO_2(g)] = 213.6$ J/K · mol, $S^\circ[N_2(g)] = 191.5$ J/K · mol, $S^\circ[H_2(g)] = 131.0$ J/K · mol, $S^\circ[NH_3(g)] = 193.0$ J/K · mol, $S^\circ[Cl_2(g)] = 223.0$ J/K · mol, and $S^\circ[HCl(g)] = 187.0$ J/K · mol.

Solution

(a) $\Delta S^\circ_{rxn} = [S^\circ(CaO) + S^\circ(CO_2)] - [S^\circ(CaCO_3)]$

       $= [(39.8 \text{ J/K} \cdot \text{mol}) + (213.6 \text{ J/K} \cdot \text{mol})] - (92.9 \text{ J/K} \cdot \text{mol})$

       $= 160.5$ J/K · mol

(b) $\Delta S^\circ_{rxn} = [2S^\circ(NH_3)] - [S^\circ(N_2) + 3S^\circ(H_2)]$

       $= (2)(193.0 \text{ J/K} \cdot \text{mol}) - [(191.5 \text{ J/K} \cdot \text{mol}) + (3)(131.0 \text{ J/K} \cdot \text{mol})]$

       $= -198.5$ J/K · mol

(c) $\Delta S^\circ_{rxn} = [2S^\circ(HCl)] - [S^\circ(H_2) + S^\circ(Cl_2)]$

       $= (2)(187.0 \text{ J/K} \cdot \text{mol}) - [(131.0 \text{ J/K} \cdot \text{mol}) + (223.0 \text{ J/K} \cdot \text{mol})]$

       $= 20.0$ J/K · mol

Think About It
Remember to multiply each standard entropy value by the correct stoichiometric coefficient. Like Equation 10.18, Equation 14.5 can only be used with a *balanced* chemical equation.

Practice Problem Ⓐ**TTEMPT** Calculate the standard entropy change for the following reactions at 25°C. Predict first whether each one will be positive, negative, or too close to call.

(a) $2CO_2(g) \longrightarrow 2CO(g) + O_2(g)$ (b) $3O_2(g) \longrightarrow 2O_3(g)$

(c) $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$
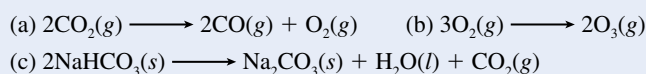
Practice Problem Ⓑ**UILD** In each of the following reactions, there is one species for which the standard entropy is not listed in Appendix 2. In each case, using the values that *are* in Appendix 2 and the ΔS°_{rxn} that is given, determine the value of the missing standard entropy at 25°C: (a) $K(s) \longrightarrow K(l)$, $\Delta S^\circ_{rxn} = 7.9$ J/K · mol, (b) $2S(\text{rhombic}) + Cl_2(g) \longrightarrow S_2Cl_2(g)$, $\Delta S^\circ_{rxn} = 44.74$ J/K · mol, (c) $O_2(g) + 2MgF_2(s) \longrightarrow 2MgO(s) + 2F_2(g)$, $\Delta S^\circ_{rxn} = 140.76$ J/K · mol.

Practice Problem Ⓒ**ONCEPTUALIZE** For each reaction shown in the diagrams, indicate whether ΔS°_{rxn} is positive, negative, or too close to call.
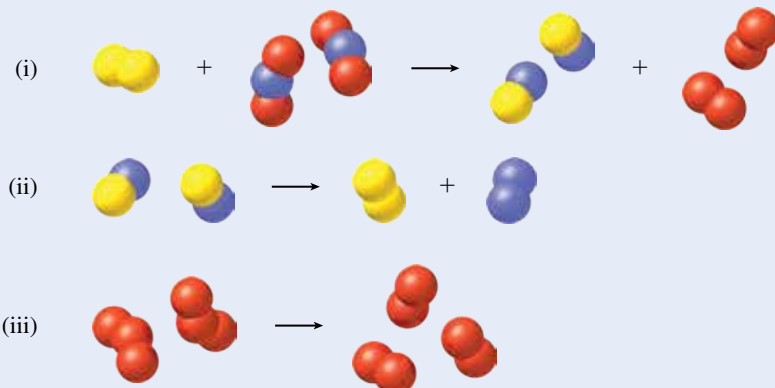
Qualitatively Predicting the Sign of ΔS°_{sys}

Equation 14.5 enables us to calculate ΔS°_{rxn} for a process when the standard entropies of the products and reactants are known. However, sometimes it's useful just to know the *sign* of ΔS°_{rxn}. Although multiple factors can influence the sign of ΔS°_{rxn}, the outcome is often dominated by a single factor, which can be used to make a qualitative prediction. Several processes that lead to an increase in entropy are

- Melting
- Vaporization or sublimation
- Temperature increase
- Reaction resulting in a greater number of gas molecules

When a solid is melted, the molecules have greater energy and are more mobile. They go from being in fixed positions in the solid, to being free to move about in the liquid. As we saw in the discussion of standard entropy, this leads to many more possible arrangements of the molecules and, therefore, greater entropy. The same rationale holds for the vaporization or sublimation of a substance. There is a dramatic increase in energy/mobility, and in the number of possible arrangements of a system's molecules when the molecules go from a condensed phase to the gas phase. Therefore, there is a much larger increase in the system's entropy, relative to the solid-to-liquid transition.

When the temperature of a system is increased, the energy of the system's molecules increases. To visualize this, recall from the discussion of kinetic molecular theory that increasing the temperature of a gas increases its average kinetic energy. This corresponds to an increase in the average speed of the gas molecules and a spreading out of the range of molecular speeds. [See Figure 11.4(a).] If we think of each of the possible molecular speeds within the range as a discrete energy level, we can see that at higher temperatures, there is a greater number of possible molecular speeds and, therefore, a greater number of energy states available to the molecules in the system. With a greater number of available energy states, there is a greater number of possible arrangements of molecules *within* those states and, therefore, a greater entropy.
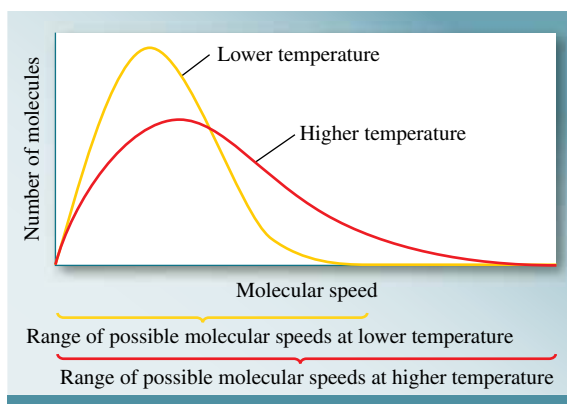
Because the entropy of a substance in the gas phase is always significantly greater than its entropy in either the liquid or solid phase, a reaction that results in an increase in the number of gas molecules causes an increase in the system's entropy. For reactions that do not involve gases, an increase in the number of solid, liquid, or aqueous molecules also usually causes an entropy increase.

By considering these factors, we can usually make a reasonably good prediction of the sign of ΔS°_{rxn} for a physical or chemical process, without having to look up the absolute entropy values for the species involved. Figure 14.4 (pages 580–581) summarizes the factors that can be used to compare entropies and illustrates several comparisons.

In addition to melting, vaporization/sublimation, temperature increase, and reactions that increase the number of gas molecules, which can always be counted upon to result in an entropy increase, the process of *dissolving* a substance often leads to an increase in entropy. In the case of a molecular solute, such as sucrose (sugar), dissolving causes dispersal of the molecules (and consequently, of the system's *energy*) into a larger volume—resulting in an increase in entropy. In the case of an ionic solute, the analysis is slightly more complicated. We saw in our discussion of solution formation [◄◄ Section 13.2] that the dissolution of ammonium nitrate (NH_4NO_3) is spontaneous, even though it is endothermic, because the system's entropy increases when the

Multi 14.1
Animation: Factors that influence the entropy of a system

TABLE 14.3	Entropy Changes for the Dissolution $(\Delta S^{\circ}_{soln})$ of Some Ionic Solids at 25°C	

Dissolution equation	ΔS°_{soln} (J/K · mol)
$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$	108.1
$AlCl_3(s) \longrightarrow Al^{3+}(aq) + 3Cl^-(aq)$	−253.2
$FeCl_3(s) \longrightarrow Fe^{3+}(aq) + 3Cl^-(aq)$	−266.1

ionic solid dissociates and is dispersed throughout the solution. In general, this is the case for ionic solutes in which the charges on ions are small. (In the case of NH_4NO_3, they are +1 and −1.) However, when ions are dispersed in water, they become hydrated (surrounded by water molecules in a specific arrangement [◄ Figure 9.4 page 325]). This leads to a *decrease* in the entropy of the *water*, as hydration reduces the mobility of some of the water molecules by fixing them in positions around the dissolved ions. When the charges on ions are low, the increase in entropy of the solute typically outweighs the decrease in entropy of the water—resulting in an overall *increase* in the entropy of the system—as is the case with NH_4NO_3. By contrast, when highly charged ions such as Al^{3+} and Fe^{3+} are hydrated, the decrease in entropy of the water can actually outweigh the increase in entropy of the solute, leading to an overall *decrease* in entropy of the system. Table 14.3 lists the changes in entropy associated with the spontaneous dissolution of several ionic solids.

Worked Example 14.3 lets you practice making qualitative predictions of the sign of ΔS°_{rxn}.

Worked Example 14.3

For each process, determine the sign of ΔS for the system: (a) decomposition of $CaCO_3(s)$ to give $CaO(s)$ and $CO_2(g)$, (b) heating bromine vapor from 45°C to 80°C, (c) condensation of water vapor on a cold surface, (d) reaction of $NH_3(g)$ and $HCl(g)$ to give $NH_4Cl(s)$, and (e) dissolution of sugar in water.

Strategy Consider the change in energy/mobility of atoms and the resulting change in number of possible positions that each particle can occupy in each case. An increase in the number of arrangements corresponds to an increase in entropy and therefore a positive ΔS.

Setup Increases in entropy generally accompany solid-to-liquid, liquid-to-gas, and solid-to-gas transitions; the dissolving of one substance in another; a temperature increase; and reactions that increase the net number of moles of gas.

Solution ΔS is (a) positive, (b) positive, (c) negative, (d) negative, and (e) positive.

Think About It
For reactions involving only liquids and solids, predicting the sign of ΔS° can be more difficult, but in many such cases an increase in the total number of molecules and/or ions is accompanied by an increase in entropy.

Practice Problem ATTEMPT For each of the following processes, determine the sign of ΔS: (a) crystallization of sucrose from a supersaturated solution, (b) cooling water vapor from 150°C to 110°C, (c) sublimation of dry ice.

Practice Problem BUILD Make a qualitative prediction of the sign of ΔH°_{soln} for $AlCl_3(s)$ and the dissolution of $FeCl_3(s)$. See Table 14.3. Explain your reasoning.

Practice Problem CONCEPTUALIZE Consider the gas-phase reaction of A_2 (blue) and B_2 (orange) to form AB_3. What are the correct balanced equation and the sign of ΔS for the reaction?

(a) $A_2 + B_2 \longrightarrow AB_3$, negative

(b) $2A_2 + 3B_2 \longrightarrow 4AB_3$, positive

(c) $2A_2 + 3B_2 \longrightarrow 4AB_3$, negative

(d) $A_2 + 3B_2 \longrightarrow 2AB_3$, negative

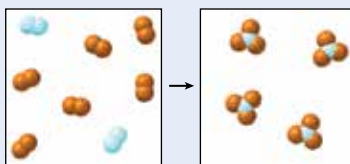(e) $A_2 + 3B_2 \longrightarrow 2AB_3$, positive

Figure 14.4

Factors That Influence the Entropy of a System

Volume Change

Quantum mechanical analysis shows that the spacing between translational energy levels is inversely proportional to the volume of the container. Thus, when the volume is increased, more energy levels become available within which the system's energy can be dispersed.
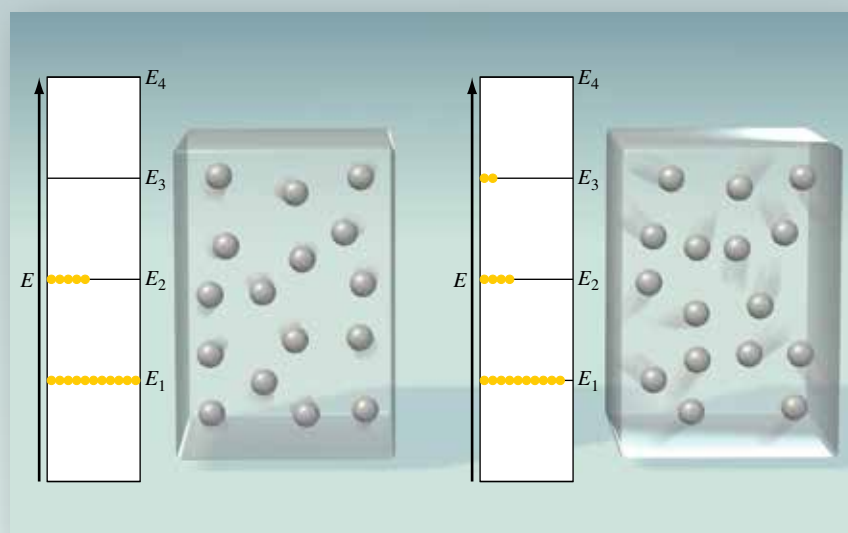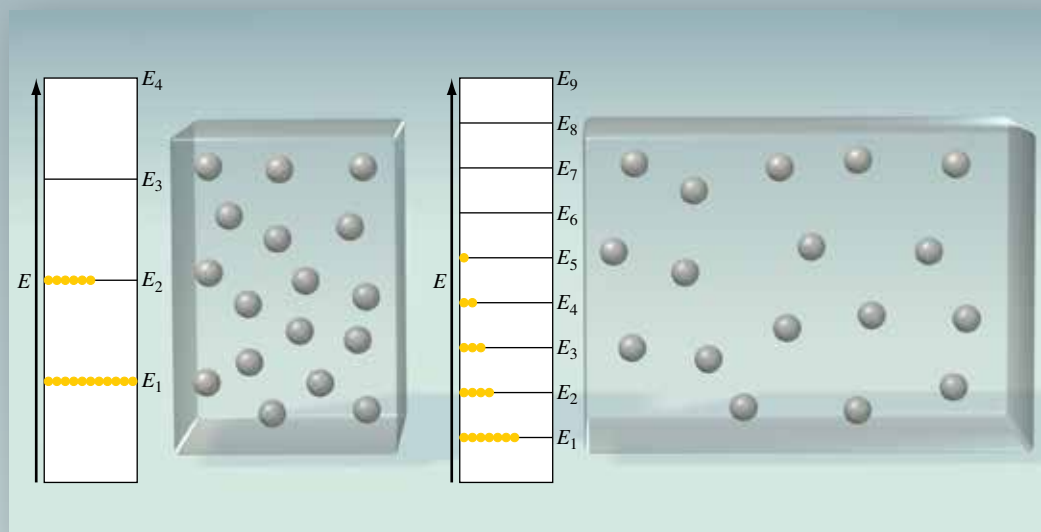
Temperature Change

At higher temperatures, molecules have greater kinetic energy—making more energy levels accessible. This increases the number of energy levels within which the system's energy can be dispersed, causing entropy to increase.

Molecular Complexity

Unlike atoms, which exhibit only translational motion, molecules can also exhibit rotational and vibrational motions. The greater a molecule's complexity, the greater the number of possible ways it can rotate and vibrate. The ozone molecule (O_3), for example, is more complex than the fluorine molecule (F_2) and exhibits more different kinds of vibrations and rotations. (See Figure 14.3.) This results in more energy levels within which the system's energy can be dispersed. The number and spacing of additional energy levels have been simplified to keep the illustration clear.
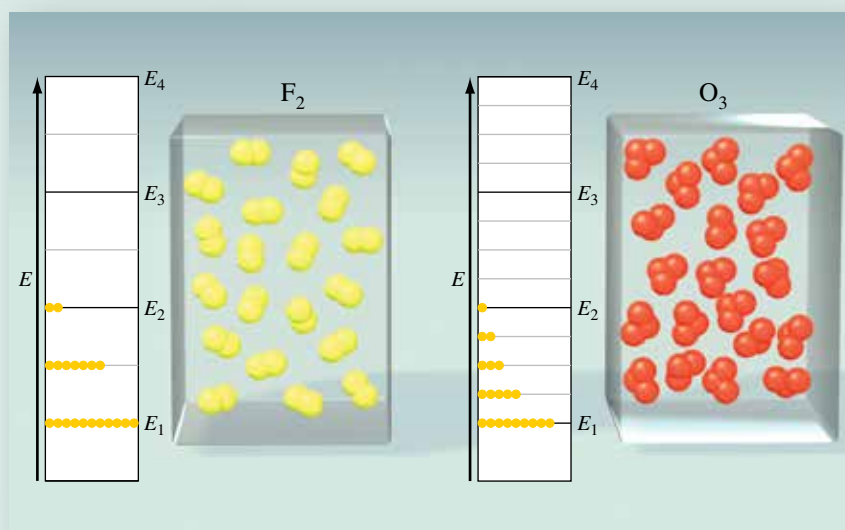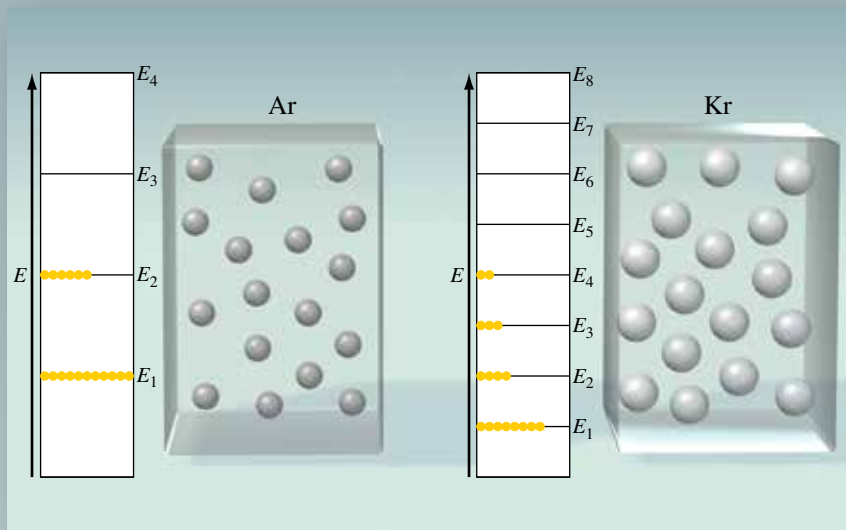
Molar Mass

The energy levels for a substance with a larger molar mass are more closely spaced. Kr, for example, has roughly twice the molar mass of Ar. Thus, Kr has roughly twice as many energy levels within which the system's energy can be dispersed.
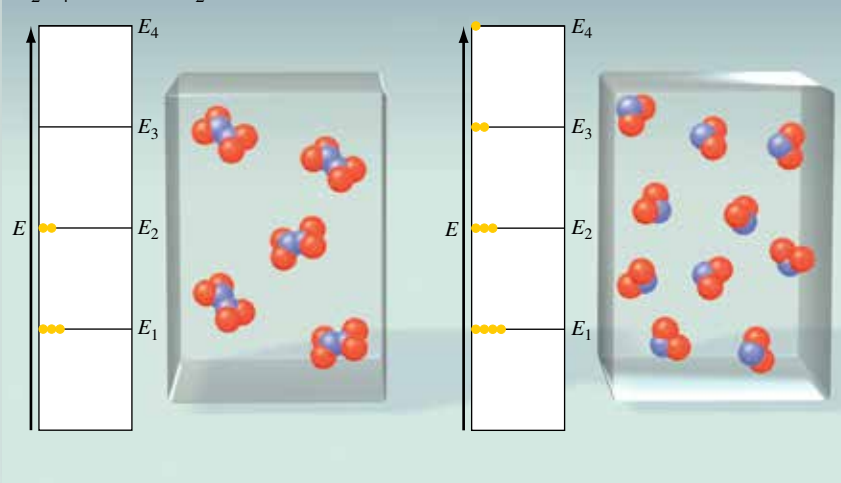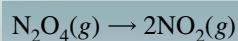
E_4
Ar
E_3
E E_2
E_1

E_8
Kr
E_7
E_6
E_5
E E_4
E_3
E_2
E_1

Phase Change

Because of greater mobility, there are many more different possible arrangements (W) of molecules in the liquid phase than there are in the solid phase; and there are many, *many* more different possible arrangements of molecules in the gas phase than there are in the liquid phase. Entropy of a substance increases when it is melted ($s \rightarrow l$), vaporized ($l \rightarrow g$), or sublimed ($s \rightarrow g$).

E_3

E_2
E
E_1

E_5
E_4
E E_3
E_2
E_1

$N_2O_4(g) \rightarrow 2NO_2(g)$

E_4
E_3
E E_2
E_1

E_4
E_3
E E_2
E_1
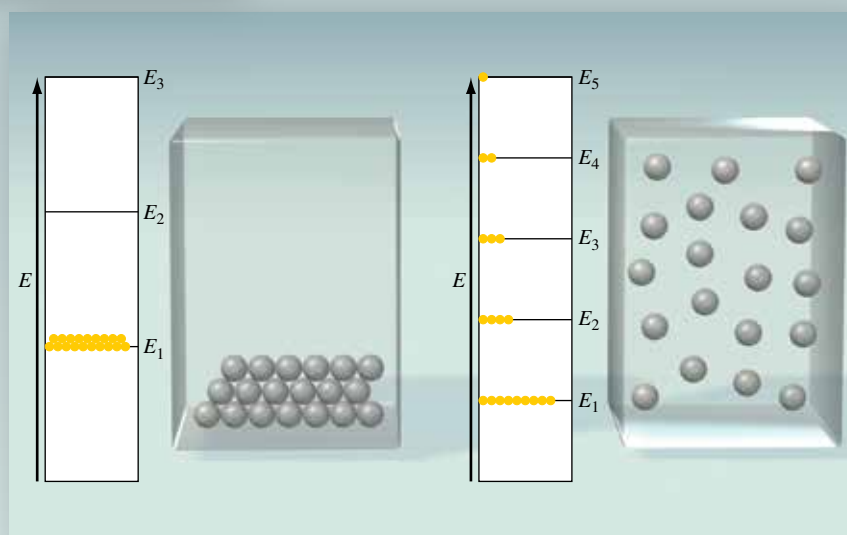
Chemical Reaction

When a chemical reaction produces more gas molecules than it consumes, the number of different possible arrangements of molecules (W) increases and entropy increases.

What's the point?

Although several factors can influence the entropy of a system or the entropy change associated with a process, often one factor dominates the outcome. Each of these comparisons shows a qualitative illustration of one of the important factors.

Entropy Changes in a System

14.3.1   Determine the sign of ΔS for each of the following processes.

(a) Freezing ethanol

(b) Evaporating water

(c) Mixing carbon tetrachloride and benzene

(d) Heating water

(e) Condensing bromine vapor

14.3.2   Determine the sign of ΔS for each of the following reactions.

(a) $2O_3(g) \longrightarrow 3O_2(g)$

(b) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

(c) $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

(d) $2Li(s) + 2H_2O(l) \longrightarrow 2LiOH(aq) + H_2(g)$

(e) $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

14.3.3   Consider the gas-phase reaction of A_2 (blue) and B_2 (orange) to form AB_3. Write the correct balanced equation and determine the sign of ΔS for the reaction.
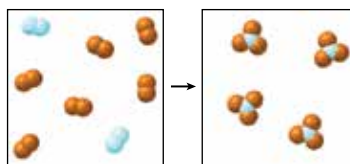
14.4   ENTROPY CHANGES IN THE UNIVERSE

Recall that the *system* typically is the part of the universe we are investigating (e.g., the reactants and products in a chemical reaction). The *surroundings* are everything else [◄◄ Section 10.1]. Together, the system and surroundings make up the *universe*. We have seen that the *dispersal* or *spreading out* of a system's energy corresponds to an increase in the system's entropy. Moreover, an increase in the system's entropy is one of the factors that determines whether or not a process is spontaneous. However, correctly predicting the spontaneity of a process requires us to consider entropy changes in both the system and the surroundings.

Consider the following processes:

- An ice cube spontaneously melts in a room where the temperature is 25°C. In this case, the motional energy of the air molecules at 25°C is transferred to the ice cube (at 0°C), causing the ice to melt. There is no temperature change during a phase change. However, because the molecules are more mobile and there are many more different possible arrangements in *liquid* water than there are in ice, there is an increase in the entropy of the system. In this case, because the process of melting is endothermic, heat is transferred *from* the surroundings *to* the system and the temperature of the surroundings decreases. The slight decrease in temperature causes a small decrease in molecular motion and a decrease in the entropy of the surroundings.

ΔS_{sys} is positive.

ΔS_{surr} is negative.

- A cup of hot water spontaneously cools to room temperature as the motional energy of the water molecules spreads out to the cooler surrounding air. Although the loss of energy from

the system and corresponding temperature decrease cause a *decrease* in the entropy of the *system*, the increased temperature of the surrounding air causes an *increase* in the entropy of the *surroundings*.

ΔS_{sys} is negative.

ΔS_{surr} is positive.

Thus, it is not just the entropy of the *system* that determines if a process is spontaneous, the entropy of the *surroundings* is also important. There are also examples of spontaneous processes in which ΔS_{sys} and ΔS_{surr} are *both* positive. The decomposition of hydrogen peroxide produces water and oxygen gas, $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$. Because the reaction results in an increase in the number of gas molecules, we know that there is an increase in the entropy of the system. However, this is an exothermic reaction, meaning that it also gives off heat to the surroundings. An increase in temperature of the surroundings causes an increase in the entropy of the surroundings as well. (Note that there are no spontaneous processes in which ΔS_{sys} and ΔS_{surr} are both negative, which will become clear shortly.)

Calculating ΔS_{surr}

When an exothermic process takes place, the heat transferred from the system to the surroundings increases the temperature of the molecules in the surroundings. Consequently, there is an increase in the number of energy levels accessible to the molecules in the surroundings and the entropy of the surroundings increases. Conversely, in an endothermic process, heat is transferred from the surroundings to the system, decreasing the entropy of the surroundings. Remember that for constant-pressure processes, the heat released or absorbed, q, is equal to the enthalpy change of the system, ΔH_{sys} [◂◂ Section 10.3]. The change in entropy for the surroundings, ΔS_{surr}, is directly proportional to ΔH_{sys}:

$$\Delta S_{surr} \propto -\Delta H_{sys}$$

The minus sign indicates that a negative enthalpy change in the system (an *exothermic* process) corresponds to a positive entropy change in the surroundings. For an *endothermic* process, the enthalpy change in the system is a positive number and corresponds to a negative entropy change in the surroundings.

In addition to being directly proportional to ΔH_{sys}, ΔS_{surr} is inversely proportional to temperature:

$$\Delta S_{surr} \propto \frac{1}{T}$$

Combining the two expressions gives

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} \qquad \textbf{Equation 14.7}$$

The Second Law of Thermodynamics

We have seen that both the system and surroundings can undergo changes in entropy during a process. The sum of the entropy changes for the system and the surroundings is the entropy change for the universe overall:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \qquad \textbf{Equation 14.8}$$

The *second law of thermodynamics* says that for a process to be spontaneous as written (in the forward direction), ΔS_{univ} must be positive. Therefore, the system may undergo a *decrease* in entropy, as long as the surroundings undergoes a larger *increase* in entropy, and vice versa. A process for which ΔS_{univ} is *negative* is not spontaneous as written.

In some cases, ΔS_{univ} is neither positive nor negative but is equal to zero. This happens when the entropy changes of the system and surroundings are equal in magnitude and opposite in sign

and describes a specific type of process known as an *equilibrium* process. An ***equilibrium process*** is one that does not occur spontaneously in either the net forward or net reverse direction but can be made to occur by the addition or removal of energy to a system at equilibrium. An example of an equilibrium process is the melting of ice at 0°C. (Remember that at 0°C, ice and liquid water are in equilibrium with each other [◄ Section 12.5].)

With Equations 14.6 and 14.7, we can calculate the entropy changes for both the system and surroundings in a process. We can then use the second law of thermodynamics (Equation 14.8) to determine if the process is spontaneous or nonspontaneous as written or if it is an equilibrium process.

Consider the synthesis of ammonia at 25°C:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\circ_{rxn} = -92.6 \text{ kJ/mol}$$
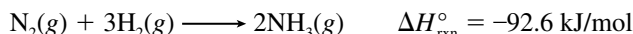
From Worked Example 14.2(b), we have $\Delta S^\circ_{sys} = -199$ J/K · mol, and substituting ΔH°_{sys} (−92.6 kJ/mol) into Equation 14.7, we get

$$\Delta S_{surr} = \frac{-(-92.6 \times 1000) \text{ J/mol}}{298 \text{ K}} = 311 \text{ J/K} \cdot \text{mol}$$

The entropy change for the universe is

$$\Delta S^\circ_{univ} = \Delta S^\circ_{sys} + \Delta S^\circ_{surr}$$

$$= -199 \text{ J/K} \cdot \text{mol} + 311 \text{ J/K} \cdot \text{mol}$$

$$= 112 \text{ J/K} \cdot \text{mol}$$

Because ΔS°_{univ} is positive, the reaction will be spontaneous at 25°C. Keep in mind, though, that just because a reaction is spontaneous does not mean that it will occur at an observable rate. The synthesis of ammonia is, in fact, extremely slow at room temperature. Thermodynamics can tell us whether or not a reaction will occur spontaneously under specific conditions, but it does not tell us how fast it will occur.

Worked Example 14.4 lets you practice identifying spontaneous, nonspontaneous, and equilibrium processes.

Worked Example 14.4

Determine if each of the following is a spontaneous process, a nonspontaneous process, or an equilibrium process at the specified temperature: (a) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ at 0°C, (b) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ at 200°C, (c) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ at 1000°C, (d) $Na(s) \longrightarrow Na(l)$ at 98°C. (Assume that the thermodynamic data in Appendix 2 do not vary with temperature.)

Strategy For each process, use Equation 14.6 to determine ΔS°_{sys} and Equations 10.18 and 14.7 to determine ΔH°_{sys} and ΔS°_{surr}. At the specified temperature, the process is *spontaneous* if ΔS_{sys} and ΔS_{surr} sum to a positive number, *nonspontaneous* if they sum to a negative number, and an *equilibrium process* if they sum to zero. Note that because the *reaction* is the *system*, ΔS_{rxn} and ΔS_{sys} are used interchangeably.

Setup From Appendix 2,

(a) $S^\circ[H_2(g)] = 131.0$ J/K · mol, $S^\circ[I_2(g)] = 260.57$ J/K · mol, $S^\circ[HI(g)] = 206.3$ J/K · mol; $\Delta H^\circ_f[H_2(g)] = 0$ kJ/mol, $\Delta H^\circ_f[I_2(g)] = 62.25$ kJ/mol, $\Delta H^\circ_f[HI(g)] = 25.9$ kJ/mol.

(b), (c) In Worked Example 14.2(a), we determined that for this reaction, $\Delta S^\circ_{rxn} = 160.5$ J/K · mol, $\Delta H^\circ_f[CaCO_3(s)] = -1206.9$ kJ/mol, $\Delta H^\circ_f[CaO(s)] = -635.6$ kJ/mol, $\Delta H^\circ_f[CO_2(g)] = -393.5$ kJ/mol.

(d) $S^\circ[Na(s)] = 51.05$ J/K · mol, $S^\circ[Na(l)] = 57.56$ J/K · mol; $\Delta H^\circ_f[Na(s)] = 0$ kJ/mol, $\Delta H^\circ_f[Na(l)] = 2.41$ kJ/mol.

Solution

(a) $\Delta S^\circ_{rxn} = [2S^\circ(HI)] - [S^\circ(H_2) + S^\circ(I_2)]$

$= (2)(206.3 \text{ J/K} \cdot \text{mol}) - [131.0 \text{ J/K} \cdot \text{mol} + 260.57 \text{ J/K} \cdot \text{mol}] = 21.03 \text{ J/K} \cdot \text{mol}$

$$\Delta H°_{rxn} = [2\Delta H°_f(HI)] - [\Delta H°_f(H_2) + \Delta H°_f(I_2)]$$

$$= (2)(25.9 \text{ kJ/mol}) - [0 \text{ kJ/mol} + 62.25 \text{ kJ/mol}] = -10.5 \text{ kJ/mol}$$

$$\Delta S_{surr} = \frac{-\Delta H_{rxn}}{T} = \frac{-(-10.5 \text{ kJ/mol})}{273 \text{ K}} = 0.0385 \text{ kJ/K} \cdot \text{mol} = 38.5 \text{ J/K} \cdot \text{mol}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 21.03 \text{ J/K} \cdot \text{mol} + 38.5 \text{ J/K} \cdot \text{mol} = 59.5 \text{ J/K} \cdot \text{mol}$$

ΔS_{univ} is positive; therefore the reaction is spontaneous at 0°C.

(b), (c) $\Delta S°_{rxn} = 160.5$ J/K · mol

$$\Delta H°_{rxn} = [\Delta H°_f(CaO) + \Delta H°_f(CO_2)] - [\Delta H°_f(CaCO_3)]$$

$$= [-635.6 \text{ kJ/mol} + (-393.5 \text{ kJ/mol})] - (-1206.9 \text{ kJ/mol}) = 177.8 \text{ kJ/mol}$$

(b) $T = 200°C$ and

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} = \frac{-(177.8 \text{ kJ/mol})}{473 \text{ K}} = -0.376 \text{ kJ/K} \cdot \text{mol} = -376 \text{ J/K} \cdot \text{mol}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 160.5 \text{ J/K} \cdot \text{mol} + (-376 \text{ J/K} \cdot \text{mol}) = -216 \text{ J/K} \cdot \text{mol}$$

ΔS_{univ} is negative, therefore the reaction is nonspontaneous at 200°C.

(c) $T = 1000°C$ and

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} = \frac{-(177.8 \text{ kJ/mol})}{1273 \text{ K}} = -0.1397 \text{ kJ/K} \cdot \text{mol} = -139.7 \text{ J/K} \cdot \text{mol}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 160.5 \text{ J/K} \cdot \text{mol} + (-139.7 \text{ J/K} \cdot \text{mol}) = 20.8 \text{ J/K} \cdot \text{mol}$$

In this case, ΔS_{univ} is positive; therefore, the reaction is spontaneous at 1000°C.

(d) $\Delta S°_{rxn} = S°[Na(l)] - S°[Na(s)] = 57.56$ J/K · mol $- 51.05$ J/K · mol $= 6.51$ J/K · mol

$$\Delta H°_{rxn} = \Delta H°_f[Na(l)] - \Delta H°_f[Na(s)] = 2.41 \text{ kJ/mol} - 0 \text{ kJ/mol} = 2.41 \text{ kJ/mol}$$

$$\Delta S_{surr} = \frac{-\Delta H_{rxn}}{T} = \frac{-(2.41 \text{ kJ/mol})}{371 \text{ K}} = -0.0650 \text{ kJ/K} \cdot \text{mol} = -6.50 \text{ J/K} \cdot \text{mol}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 6.51 \text{ J/K} \cdot \text{mol} + (-6.50 \text{ J/K} \cdot \text{mol}) = 0.01 \text{ J/K} \cdot \text{mol} \approx 0$$

ΔS_{univ} is zero; therefore, the reaction is an equilibrium process at 98°C. In fact, this is the melting point of sodium.

> **Student Annotation:** The small difference between the magnitudes of ΔS_{sys} and ΔS_{surr} results from thermodynamic values not being entirely independent of temperature. The tabulated values of $S°$ and $\Delta H°_f$ are for 25°C.

> **Think About It**
>
> Remember that standard enthalpies of formation have units of kJ/mol, whereas standard absolute entropies have units of J/K · mol. Make sure that you convert kilojoules to joules, or vice versa, before combining the terms.

Practice Problem **A**TTEMPT   For each of the following, calculate ΔS_{univ} and identify the process as a spontaneous process, a nonspontaneous process, or an equilibrium process at the specified temperature: (a) $CO_2(g) \longrightarrow CO_2(aq)$ at 25°C, (b) $N_2O_4(g) \longrightarrow 2NO_2(g)$ at 10.4°C, (c) $PCl_3(l) \longrightarrow PCl_3(g)$ at 61.2°C. (Assume that the thermodynamic data in Appendix 2 do not vary with temperature.)

Practice Problem **B**UILD   (a) Calculate ΔS_{univ} and determine if the reaction $H_2O_2(l) \longrightarrow H_2O_2(g)$ is spontaneous, nonspontaneous, or an equilibrium process at 163°C. (b) The reaction $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ is spontaneous in the forward direction at room temperature but, because it is exothermic, becomes less spontaneous with increasing temperature. Determine the temperature at which it is no longer spontaneous in the forward direction. (c) Determine the boiling point of Br_2. (Assume that the thermodynamic data in Appendix 2 do not vary with temperature.)

Practice Problem **C**ONCEPTUALIZE
The following table shows the signs of ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} for four processes. Where possible, fill in the missing table entries. Indicate where it is not possible to determine the missing sign and explain.

Process	ΔS_{sys}	ΔS_{surr}	ΔS_{univ}
1	−	−	
2	+		+
3	−	+	
4		−	+

Thinking Outside the Box

Thermodynamics and Living Systems

Under normal physiological conditions, polypeptides spontaneously fold into unique three-dimensional structures called native proteins, which can perform various functions. Because the original chain can assume many possible configurations while the native protein can have only one specific arrangement, the folding process is accompanied by a decrease in entropy of the system. (Note that solvent molecules, water in this case, can also play a role in affecting the entropy change.) In accord with the second law of thermodynamics, any spontaneous process must result in an increase in the entropy of the universe. It follows, therefore, that there must be an increase in the entropy of the surroundings that outweighs the decrease in the entropy of the system. The intramolecular attractions between amino acid residues cause the folding of the polypeptide chain to be exothermic. The energy produced by the process spreads out, increasing molecular motion in the surroundings—thereby increasing the entropy of the surroundings.

Unfolded   Folded
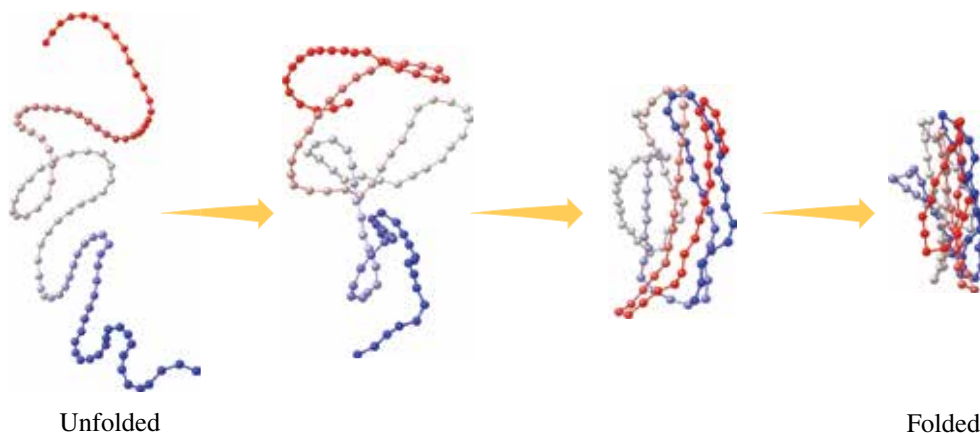
The Third Law of Thermodynamics

Finally, we consider the third law of thermodynamics briefly in connection with the determination of standard entropy. We have related the entropy of a system to the number of possible arrangements of the system's molecules. The larger the number of possible arrangements, the larger the entropy. Imagine a pure, perfect crystalline substance at absolute zero (0 K). Under these conditions, there is essentially no molecular motion and, because the molecules occupy fixed positions in the solid, there is only one way to arrange the molecules. From Equation 14.1, we write

$$S = k \ln W = k \ln 1 = 0$$

According to the **third law of thermodynamics,** the entropy of a perfect crystalline substance is *zero* at absolute zero. As temperature increases, molecular motion increases, causing an increase in the number of possible arrangements of the molecules and in the number of accessible energy states, among which the system's energy can be dispersed. (See Figure 14.4.) This results in an increase in the system's entropy. Thus, the entropy of any substance at any temperature above 0 K is greater than zero. If the crystalline substance is impure or imperfect in any way, then its entropy is greater than zero even at 0 K because without perfect crystalline order, there is more than one possible arrangement of molecules.

The significance of the third law of thermodynamics is that it enables us to determine experimentally the *absolute* entropies of substances. Starting with the knowledge that the entropy of a pure crystalline substance is zero at 0 K, we can measure the increase in entropy of the substance as it is heated. The change in entropy of a substance, ΔS, is the difference between the final and initial entropy values:

$$\Delta S = S_{final} - S_{initial}$$

where $S_{initial}$ is zero if the substance starts at 0 K. Therefore, the measured *change* in entropy is equal to the *absolute* entropy of the substance at the final temperature.

$$\Delta S = S_{final}$$
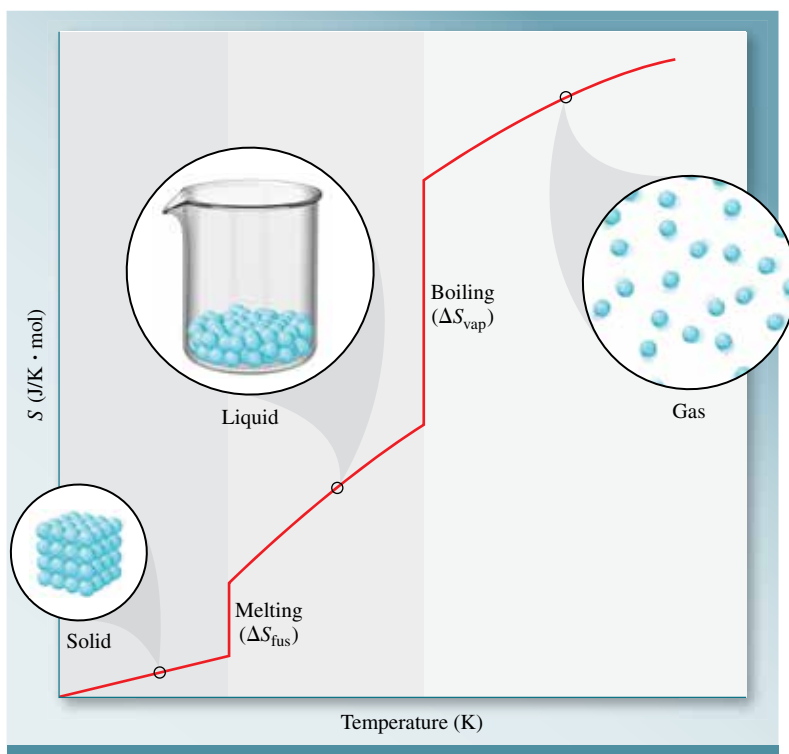
Figure 14.5 Entropy increases in a substance as temperature increases from absolute zero.

The entropy values arrived at in this way are called *absolute* entropies because they are *true* values—unlike standard enthalpies of formation, which are derived using an arbitrary reference. Because the tabulated values are determined at 1 atm, we usually refer to absolute entropies as *standard* entropies, $S°$. Figure 14.5 shows the increase in entropy of a substance as temperature increases from absolute zero. At 0 K, it has a zero entropy value (assuming that it is a perfect crystalline substance). As it is heated, its entropy increases gradually at first because of greater molecular motion within the crystal. At the melting point, there is a large increase in entropy as the solid is transformed into the liquid. Further heating increases the entropy of the liquid again due to increased molecular motion. At the boiling point, there is a large increase in entropy as a result of the liquid-to-vapor transition. Beyond that temperature, the entropy of the gas continues to increase with increasing temperature.

Section 14.4 Review

Entropy Changes in the Universe

14.4.1 Using data from Appendix 2, calculate $\Delta S°$ (in J/K · mol) for the following reaction:
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
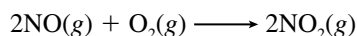
14.4.2 Using data from Appendix 2, calculate $\Delta S°$ (in J/K · mol) for the following reaction:
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
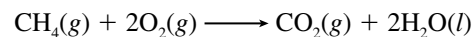
14.4.3 For each of the processes shown, state whether ΔS_{surr} is positive, negative, or if there is not enough information to determine the sign of ΔS_{surr}.

(a)   (b)   (c)
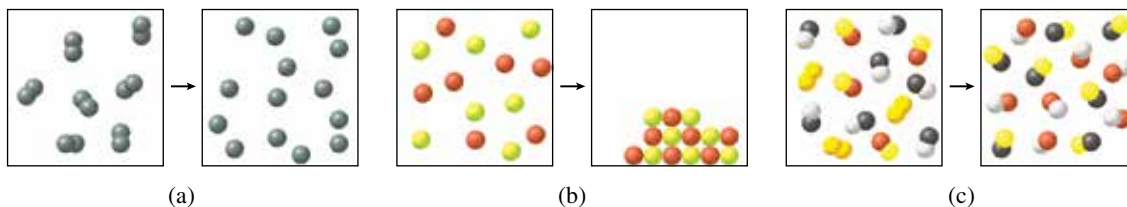
14.5   PREDICTING SPONTANEITY

Gibbs Free-Energy Change, ΔG

According to the second law of thermodynamics, $\Delta S_{univ} > 0$ for a spontaneous process. What we are usually concerned with and usually *measure,* however, are the properties of the *system* rather than those of the surroundings or those of the universe overall. Therefore, it is convenient to have a thermodynamic function that enables us to determine whether or not a process is spontaneous by considering the system alone.

We begin with Equation 14.8. For a spontaneous process,

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

Substituting $-\Delta H_{sys}/T$ for ΔS_{surr}, we write

$$\Delta S_{univ} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T} \right) > 0$$

Multiplying both sides of the equation by T gives

$$T\Delta S_{univ} = T\Delta S_{sys} - \Delta H_{sys} > 0$$

Now we have an equation that expresses the second law of thermodynamics (and predicts whether or not a process is spontaneous) in terms of only the *system.* We no longer need to consider the surroundings. For convenience, we can rearrange the preceding equation, multiply through by -1, and replace the $>$ sign with a $<$ sign:

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys} < 0$$

According to this equation, a process carried out at constant pressure and temperature is spontaneous if the changes in enthalpy and entropy of the system are such that $\Delta H_{sys} - T\Delta S_{sys}$ is less than zero.

To express the spontaneity of a process more directly, we introduce another thermodynamic function called the **Gibbs**[1] **free energy (G),** or simply **free energy.**

Equation 14.9	$G = H - TS$

Each of the terms in Equation 14.9 pertains to the system. G has units of energy just as H and TS do. Furthermore, like enthalpy and entropy, free energy is a state function. The change in free energy, ΔG, of a system for a process that occurs at constant temperature is

Equation 14.10	$\Delta G = \Delta H - T\Delta S$

> **Student Annotation:** In this context, *free energy* is the energy available to do work. Thus, if a particular process is accompanied by a release of usable energy (i.e., if ΔG is negative), this fact alone guarantees that it is spontaneous, and there is no need to consider what happens to the rest of the universe.

Equation 14.10 enables us to predict the spontaneity of a process using the change in enthalpy, the change in entropy, and the absolute temperature. At constant temperature and pressure, for processes that are spontaneous as written (in the forward direction), ΔG is negative. For processes that are not spontaneous as written but that are spontaneous in the reverse direction, ΔG is positive. For systems at equilibrium, ΔG is zero.

- $\Delta G < 0$ The reaction is spontaneous in the forward direction (and nonspontaneous in the reverse direction).

- $\Delta G > 0$ The reaction is nonspontaneous in the forward direction (and spontaneous in the reverse direction).

- $\Delta G = 0$ The system is at equilibrium.

Often we can predict the sign of ΔG for a process if we know the signs of ΔH and ΔS. Table 14.4 shows how we can use Equation 14.10 to make such predictions.

Based on the information in Table 14.4, you may wonder what constitutes a "low" or a "high" temperature. For the freezing of water, 0°C is the temperature that divides high from low.

---

[1]Josiah Willard Gibbs (1839–1903), an American physicist, was one of the founders of thermodynamics. Gibbs was a modest and private individual who spent almost all his professional life at Yale University. Because he published most of his work in obscure journals, Gibbs never gained the eminence that his contemporary and admirer James Maxwell did. Even today, very few people outside of chemistry and physics have ever heard of Gibbs.

TABLE 14.4		Predicting the Sign of ΔG Using Equation 14.10 and the Signs of ΔH and ΔS		
When ΔH is	**And ΔS is**	**ΔG will be**	**And the process is**	**Example**
Negative	Positive	Negative	Always spontaneous	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$
Positive	Negative	Positive	Always nonspontaneous	$3O_2(g) \longrightarrow 2O_3(g)$
Negative	Negative	Negative when $T\Delta S < \Delta H$ Positive when $T\Delta S > \Delta H$	Spontaneous at low T Nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$ (freezing of water)
Positive	Positive	Negative when $T\Delta S > \Delta H$ Positive when $T\Delta S < \Delta H$	Spontaneous at high T Nonspontaneous at low T	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$

Water freezes spontaneously at temperatures below 0°C, and ice melts spontaneously at temperatures above 0°C. At 0°C, a system of ice and water is at equilibrium. The temperature that divides "high" from "low" depends, though, on the individual reaction. To determine that temperature, we must set ΔG equal to 0 in Equation 14.10 (i.e., the equilibrium condition):

$$0 = \Delta H - T\Delta S$$

Rearranging to solve for T yields

$$T = \frac{\Delta H}{\Delta S}$$

The temperature that divides high from low for a particular reaction can now be calculated if the values of ΔH and ΔS are known.
    Worked Example 14.5 demonstrates the use of this approach.

Worked Example 14.5

According to Table 14.4, a reaction will be spontaneous only at high temperatures if both ΔH and ΔS are positive. For a reaction in which $\Delta H = 199.5$ kJ/mol and $\Delta S = 476$ J/K · mol, determine the temperature (in °C) above which the reaction is spontaneous.

Strategy The temperature that divides high from low is the temperature at which $\Delta H = T\Delta S$ ($\Delta G = 0$). Therefore, we use Equation 14.10, substituting 0 for ΔG and solving for T to determine temperature in kelvins; we then convert to degrees Celsius.

Setup

$$\Delta S = \left(\frac{476 \text{ J}}{\text{K} \cdot \text{mol}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) = 0.476 \text{ kJ/K} \cdot \text{mol}$$

Solution

$$T = \frac{\Delta H}{\Delta S} = \frac{199.5 \text{ kJ/mol}}{0.476 \text{ kJ/K} \cdot \text{mol}} = 419 \text{ K}$$

$$= (419 - 273) = 146°\text{C}$$

Think About It
Spontaneity is favored by a release of energy (ΔH being negative) and by an increase in entropy (ΔS being positive). When both quantities are positive, as in this case, only the entropy change favors spontaneity. For an endothermic process such as this, which requires the input of heat, it should make sense that adding more heat by increasing the temperature will shift the equilibrium to the right, thus making it "more spontaneous."

Practice Problem **A**TTEMPT A reaction will be spontaneous only at low temperatures if both ΔH and ΔS are negative. For a reaction in which $\Delta H = -380.1$ kJ/mol and $\Delta S = -95.00$ J/K · mol, determine the temperature (in °C) below which the reaction is spontaneous.

Practice Problem **B**UILD Given that the reaction $4Fe(s) + 3O_2(g) + 6H_2O(l) \longrightarrow$ $4Fe(OH)_3(s)$ is spontaneous at temperatures below 1950°C, estimate the standard entropy of $Fe(OH)_3(s)$.

Practice Problem **C**ONCEPTUALIZE Which of the following graphs best represents the relationship between ΔG and temperature for a process that is exothermic and for which ΔS is negative?

(i)   (ii)   (iii)   (iv)

Standard Free-Energy Changes, $\Delta G°$
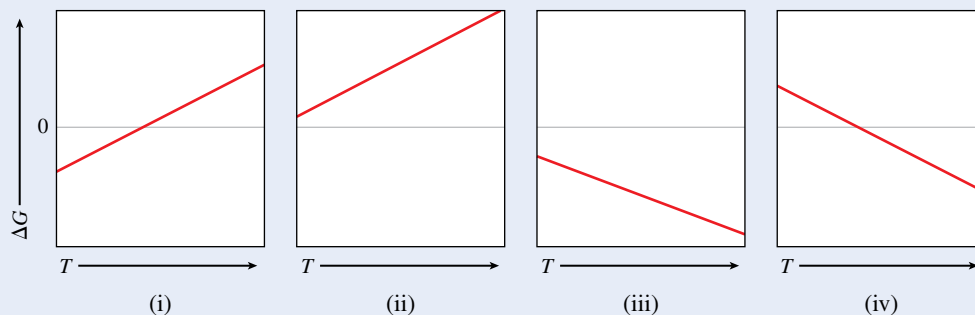
Student Annotation: The introduction of the term $\Delta G°$ enables us to write Equation 14.10 as

$$\Delta G° = \Delta H° - T\Delta S°$$

The **standard free energy of reaction** $(\Delta G°_{rxn})$ is the free-energy change for a reaction when it occurs under standard-state conditions—that is, when reactants in their standard states are converted to products in *their* standard states. The conventions used by chemists to define the standard states of pure substances and solutions are

- Gases   1 atm pressure
- Liquids   Pure liquid
- Solids   Pure solid
- Elements   The most stable allotropic form at 1 atm and 25°C
- Solutions   1 molar concentration

To calculate $\Delta G°_{rxn}$, we start with the general equation

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$
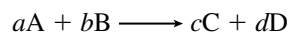
The standard free-energy change for this reaction is given by

Equation 14.11 $\Delta G°_{rxn} = [c\Delta G°_f(\text{C}) + d\Delta G°_f(\text{D})] - [a\Delta G°_f(\text{A}) + b\Delta G°_f(\text{B})]$

Equation 14.11 can be generalized as follows:

Equation 14.12 $\Delta G°_{rxn} = \Sigma n\Delta G°_f \text{ (products)} - \Sigma m\Delta G°_f \text{ (reactants)}$

where m and n are stoichiometric coefficients. The term $\Delta G°_f$ is the **standard free energy of formation** of a compound—that is, the free-energy change that occurs when 1 mole of the compound is synthesized from its constituent elements, each in its standard state. For the combustion of graphite,

$$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$$
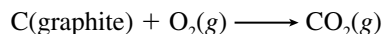
the standard free-energy change (from Equation 14.12) is

$$\Delta G°_{rxn} = [\Delta G°_f(\text{CO}_2)] - [\Delta G°_f(\text{C, graphite}) + \Delta G°_f(\text{O}_2)]$$

As with standard enthalpy of formation, the standard free energy of formation of any element (in its most stable allotropic form at 1 atm) is defined as zero. Thus,

$$\Delta G°_f(\text{C, graphite}) = 0 \quad \text{and} \quad \Delta G°_f(\text{O}_2) = 0$$

Therefore, the standard free-energy change for the reaction in this case is equal to the standard free energy of formation of CO_2:

$$\Delta G°_{rxn} = \Delta G°_f(\text{CO}_2)$$

Appendix 2 lists the values of $\Delta G°_f$ at 25°C for a number of compounds.

Worked Example 14.6 demonstrates the calculation of standard free-energy changes.

Worked Example 14.6

Calculate the standard free-energy changes for the following reactions at 25°C:

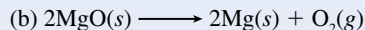(a) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

(b) $2MgO(s) \longrightarrow 2Mg(s) + O_2(g)$

Strategy Look up the ΔG_f° values for the reactants and products in each equation, and use Equation 14.12 to solve for ΔG_{rxn}°.

Setup From Appendix 2, we have the following values: $\Delta G_f^\circ[CH_4(g)] = -50.8$ kJ/mol, $\Delta G_f^\circ[CO_2(g)] = -394.4$ kJ/mol, $\Delta G_f^\circ[H_2O(l)] = -237.2$ kJ/mol, and $\Delta G_f^\circ[MgO(s)] = -569.6$ kJ/mol. All the other substances are elements in their standard states and have, by definition, $\Delta G_f^\circ = 0$.

Solution

(a) $\Delta G_{rxn}^\circ = (\Delta G_f^\circ[CO_2(g)] + 2\Delta G_f^\circ[H_2O(l)]) - (\Delta G_f^\circ[CH_4(g)] + 2\Delta G_f^\circ[O_2(g)])$

$= [(-394.4 \text{ kJ/mol}) + (2)(-237.2 \text{ kJ/mol})] - [(-50.8 \text{ kJ/mol}) + (2)(0 \text{ kJ/mol})]$

$= -818.0 \text{ kJ/mol}$

(b) $\Delta G_{rxn}^\circ = (2\Delta G_f^\circ[Mg(s)] + \Delta G_f^\circ[O_2(g)]) - (2\Delta G_f^\circ[MgO(s)])$

$= [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-569.6 \text{ kJ/mol})]$

$= 1139 \text{ kJ/mol}$

Think About It

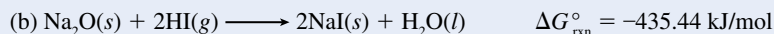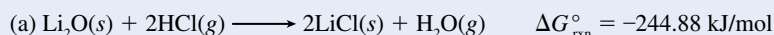Note that, like standard enthalpies of formation (ΔH_f°), standard free energies of formation (ΔG_f°) depend on the *state* of matter. Using water as an example, $\Delta G_f^\circ[H_2O(l)] = -237.2$ kJ/mol and $\Delta G_f^\circ[H_2O(g)] = -228.6$ kJ/mol. Always double-check to make sure you have selected the right value from the table.

Practice Problem A TTEMPT Calculate the standard free-energy changes for the following reactions at 25°C:

(a) $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$

(b) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$
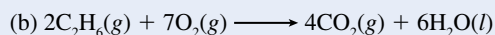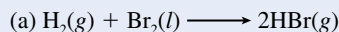
Practice Problem B UILD For each reaction, determine the value of ΔG_f° that is not listed in Appendix 2:

(a) $Li_2O(s) + 2HCl(g) \longrightarrow 2LiCl(s) + H_2O(g)$ $\quad \Delta G_{rxn}^\circ = -244.88$ kJ/mol

(b) $Na_2O(s) + 2HI(g) \longrightarrow 2NaI(s) + H_2O(l)$ $\quad \Delta G_{rxn}^\circ = -435.44$ kJ/mol

Practice Problem C ONCEPTUALIZE For which of the following species is $\Delta G_f^\circ = 0$?

$Br_2(l)$	$I_2(g)$	$CO_2(g)$	$Xe(g)$
(i)	(ii)	(iii)	(iv)

Using ΔG and $\Delta G°$ to Solve Problems

It is the sign of ΔG, the free-energy change, *not* the sign of $\Delta G°$, the standard free-energy change that indicates whether or not a process will occur spontaneously under a given set of conditions.

Further, $\Delta G°$ values change with temperature. One of the uses of Equation 14.10 is to determine the temperature at which a particular equilibrium will begin to favor a desired product. For example, calcium oxide (CaO), also called quicklime, is an extremely valuable inorganic substance with a variety of industrial uses, including water treatment and pollution control. It is prepared by heating limestone ($CaCO_3$), which decomposes at a high temperature:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
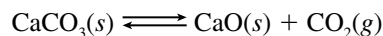
The reaction is reversible, and under the right conditions, CaO and CO_2 readily recombine to form $CaCO_3$ again. To prevent this from happening in the industrial preparation, the CO_2 is removed as it forms and the system is never maintained at equilibrium.

An important piece of information for the chemist responsible for maximizing CaO production is the temperature at which the decomposition equilibrium of $CaCO_3$ begins to favor products.

Student Annotation: The sign of $\Delta G°$ does indicate whether or not a process is spontaneous when *all* reactants and products are in their standard states, but this is very seldom the case.

We can make a reliable estimate of that temperature as follows. First we calculate $\Delta H°$ and $\Delta S°$ for the reaction at 25°C, using the data in Appendix 2. To determine $\Delta H°$, we apply Equation 10.18:

$$\Delta H° = [\Delta H_f°(CaO) + \Delta H_f°(CO_2)] - [\Delta H_f°(CaCO_3)]$$

$$= [(-635.6 \text{ kJ/mol}) + (-393.5 \text{ kJ/mol})] - (-1206.9 \text{ kJ/mol})$$

$$= 177.8 \text{ kJ/mol}$$

Next we apply Equation 14.6 to find $\Delta S°$:

$$\Delta S° = [S°(CaO) + S°(CO_2)] - S°(CaCO_3)$$

$$= [(39.8 \text{ J/K} \cdot \text{mol}) + (213.6 \text{ J/K} \cdot \text{mol})] - (92.9 \text{ J/K} \cdot \text{mol})$$

$$= 160.5 \text{ J/K} \cdot \text{mol}$$

From Equation 14.10, we can write

$$\Delta G° = \Delta H° - T\Delta S°$$

and we obtain

$$\Delta G° = (177.8 \text{ kJ/mol}) - (298 \text{ K})(0.1605 \text{ kJ/K} \cdot \text{mol})$$

$$= 130.0 \text{ kJ/mol}$$

> **Student Annotation:** Be careful with units in problems of this type. $S°$ values are tabulated using joules, whereas $\Delta H_f°$ values are tabulated using kilojoules.

Because $\Delta G°$ is a large positive number, the reaction does *not* favor product formation at 25°C (298 K). And, because $\Delta H°$ and $\Delta S°$ are both positive, we know that $\Delta G°$ will be negative (product formation will be favored) at high temperatures. We can determine what constitutes a high temperature for this reaction by calculating the temperature at which $\Delta G°$ is zero.

$$0 = \Delta H° - T\Delta S°$$

or

$$T = \frac{\Delta H°}{\Delta S°}$$

$$= \frac{(177.8 \text{ kJ/mol})}{0.1605 \text{ kJ/K} \cdot \text{mol}}$$

$$= 1108 \text{ K } (835°C)$$

At temperatures higher than 835°C, $\Delta G°$ becomes negative, indicating that the reaction would then favor the formation of CaO and CO_2. At 840°C (1113 K), for example,

$$\Delta G° = \Delta H° - T\Delta S°$$

$$= 177.8 \text{ kJ/mol} - (1113 \text{ K})(0.1605 \text{ kJ/K} \cdot \text{mol})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= -0.8 \text{ kJ/mol}$$

At still higher temperatures, $\Delta G°$ becomes increasingly negative, thus favoring product formation even more. Note that in this example we used the $\Delta H°$ and $\Delta S°$ values at 25°C to calculate changes to $\Delta G°$ at much higher temperatures. Because both $\Delta H°$ and $\Delta S°$ actually change with temperature, this approach does not give us a truly accurate value for $\Delta G°$, but it does give us a reasonably good estimate.

Equation 14.10 can also be used to calculate the change in entropy that accompanies a phase change. Recall that at the temperature at which a phase change occurs both phases of a substance are present. For example, at the freezing point of water, both liquid water and solid ice coexist in a state of equilibrium [◄◄ Section 12.5], where ΔG is zero. Therefore, Equation 14.10 becomes

$$0 = \Delta H - T\Delta S$$

or

$$\Delta S = \frac{\Delta H}{T}$$

Consider the ice-water equilibrium. For the ice-to-water transition, ΔH is the molar heat of fusion (see Table 12.7) and T is the melting point. The entropy change is therefore

$$\Delta S_{\text{ice} \longrightarrow \text{water}} = \frac{6010 \text{ J/mol}}{273 \text{ K}} = 22.0 \text{ J/K} \cdot \text{mol}$$

Thus, when 1 mole of ice melts at 0°C, there is an increase in entropy of 22.0 J/K $\cdot$ mol. The increase in entropy is consistent with the increase in the number of possible arrangements of

molecules from solid to liquid. Conversely, for the water-to-ice transition, the decrease in entropy is given by

$$\Delta S_{\text{water}\longrightarrow\text{ice}} = \frac{-6010 \text{ J/mol}}{273 \text{ K}} = -22.0 \text{ J/K} \cdot \text{mol}$$

The same approach can be applied to the water-to-steam transition. In this case, ΔH is the heat of vaporization and T is the boiling point of water.

Worked Example 14.7 examines the phase transitions in benzene.

Worked Example 14.7

The molar heats of fusion and vaporization of benzene are 10.9 and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid-to-liquid and liquid-to-vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.

Strategy The solid-liquid transition at the melting point and the liquid-vapor transition at the boiling point are *equilibrium* processes. Therefore, because ΔG is zero at equilibrium, in each case we can use Equation 14.10, substituting 0 for ΔG and solving for ΔS, to determine the entropy change associated with the process.

Setup The melting point of benzene is $5.5 + 273.15 = 278.7$ K and the boiling point is $80.1 + 273.15 = 353.3$ K.

Solution

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{melting}}} = \frac{10.9 \text{ kJ/mol}}{278.7 \text{ K}}$$

$$= 0.0391 \text{ kJ/K} \cdot \text{mol} \quad \text{or} \quad 39.1 \text{ J/K} \cdot \text{mol}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{boiling}}} = \frac{31.0 \text{ kJ/mol}}{353.3 \text{ K}}$$

$$= 0.0877 \text{ kJ/K} \cdot \text{mol} \quad \text{or} \quad 87.7 \text{ J/K} \cdot \text{mol}$$

Think About It
For the same substance, ΔS_{vap} is always significantly larger than ΔS_{fus}. The change in number of arrangements is always bigger in a liquid-to-gas transition than in a solid-to-liquid transition.

Practice Problem Ⓐ**TTEMPT** The molar heats of fusion and vaporization of argon are 1.3 and 6.3 kJ/mol, respectively, and argon's melting point and boiling point are −190°C and −186°C, respectively. Calculate the entropy changes for the fusion and vaporization of argon.

Practice Problem Ⓑ**UILD** Using data from Appendix 2 and assuming that the tabulated values do not change with temperature, (a) calculate $\Delta H^{\circ}_{\text{fus}}$ and $\Delta S^{\circ}_{\text{fus}}$ for sodium metal and determine the melting temperature of sodium, and (b) calculate $\Delta H^{\circ}_{\text{vap}}$ and $\Delta S^{\circ}_{\text{vap}}$ for sodium metal and determine the boiling temperature of sodium.

Practice Problem Ⓒ**ONCEPTUALIZE** Explain why, in general, we can use the equation $\Delta S = \frac{\Delta H}{T}$ to calculate ΔS for a phase change but not for a chemical reaction?

Section 14.5 Review

Predicting Spontaneity

14.5.1 Using data from Appendix 2, calculate ΔG° (in kJ/mol) at 25°C for the reaction:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$
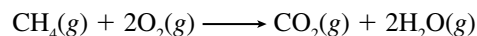
14.5.2 Calculate ΔS_{sub} (in J/K · mol) for the sublimation of iodine in a closed flask at 45°C.

$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H_{\text{sub}} = 62.4 \text{ kJ/mol}$$

14.5.3 At what temperature (in °C) does a reaction go from being nonspontaneous to spontaneous if it has $\Delta H = 171$ kJ/mol and $\Delta S = 161$ J/K · mol?

14.6   THERMODYNAMICS IN LIVING SYSTEMS

Many biochemical reactions have a positive $\Delta G°$ value, yet they are essential to the maintenance of life. In living systems, these reactions are coupled to an energetically favorable process, one that has a negative $\Delta G°$ value. The principle of coupled reactions is based on a simple concept: we can use a thermodynamically favorable reaction to drive an unfavorable one. Suppose, for example, that we w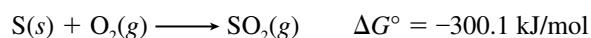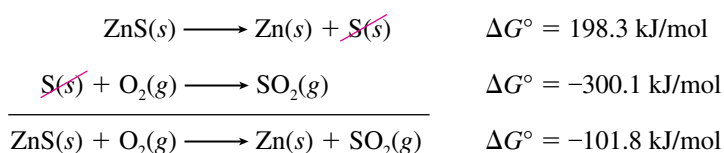ant to extract zinc from a zinc sulfide (ZnS). The following reaction will not work because it has a large positive $\Delta G°$ value:

$$ZnS(s) \longrightarrow Zn(s) + S(s) \qquad \Delta G° = 198.3 \text{ kJ/mol}$$
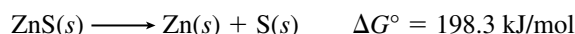
On the other hand, the combustion of sulfur to form sulfur dioxide is favored because of its large negative $\Delta G°$ value:

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta G° = -300.1 \text{ kJ/mol}$$

By coupling the two processes, we can bring about the separation of zinc from zinc sulfide. In practice, this means heating ZnS in air so that the tendency of S to form SO_2 will promote the decomposition of ZnS:

$$ZnS(s) \longrightarrow Zn(s) + S(s) \qquad \Delta G° = 198.3 \text{ kJ/mol}$$
$$\underline{S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta G° = -300.1 \text{ kJ/mol}}$$
$$ZnS(s) + O_2(g) \longrightarrow Zn(s) + SO_2(g) \qquad \Delta G° = -101.8 \text{ kJ/mol}$$

Coupled reactions play a crucial role in our survival. In biological systems, enzymes facilitate a wide variety of nonspontaneous reactions. In the human body, for example, food molecules, represented by glucose ($C_6H_{12}O_6$), are converted to carbon dioxide and water during metabolism, resulting in a substantial release of free energy:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta G° = -2880 \text{ kJ/mol}$$
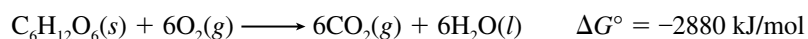
In a living cell, this reaction does not take place in a single step; rather, the glucose molecule is broken down with the aid of enzymes in a series of steps. Much of the free energy released along the way is used to synthesize adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and phosphoric acid (Figure 14.6):

$$ADP + H_3PO_4 \longrightarrow ATP + H_2O \qquad \Delta G° = 31 \text{ kJ/mol}$$
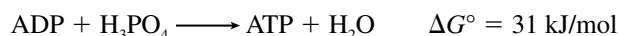
The function of ATP is to store free energy until it is needed by cells. Under appropriate conditions, ATP undergoes hydrolysis to give ADP and phosphoric acid, with a release of 31 kJ/mol of free energy, which can be used to drive energetically unfavorable reactions, such as protein synthesis.

Proteins are polymers made of amino acids. The stepwise synthesis of a protein molecule involves the joining of individual amino acids. Consider the formation of the dipeptide (a unit composed of two amino acids) alanylglycine from alanine and glycine. This reaction represents the first step in the synthesis of a protein molecule:
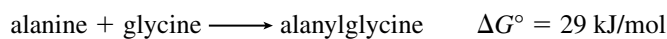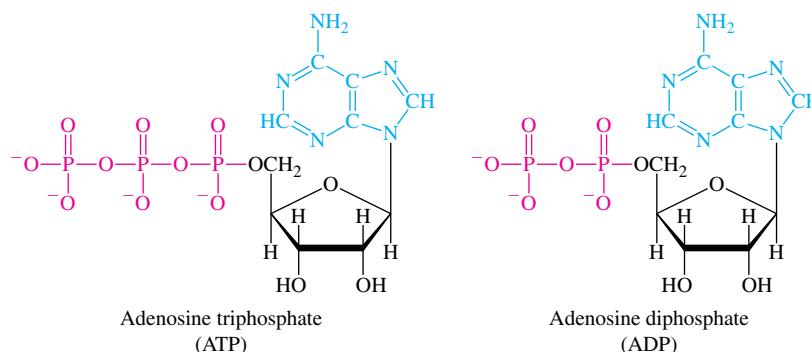
$$\text{alanine} + \text{glycine} \longrightarrow \text{alanylglycine} \qquad \Delta G° = 29 \text{ kJ/mol}$$

Figure 14.6 Structures of ATP and ADP.

Adenosine triphosphate
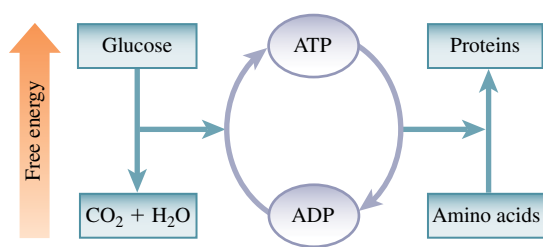(ATP)

Adenosine diphosphate
(ADP)

Figure 14.7 Schematic representation of ATP synthesis and coupled reactions in living systems. The conversion of glucose to carbon dioxide and water during metabolism releases free energy. The released free energy is used to convert ADP to ATP. The ATP molecules are then used as an energy source to drive unfavorable reactions such as protein synthesis from amino acids.

The positive $\Delta G°$ value means this reaction does not favor the formation of product, so only a little of the dipeptide would be formed at equilibrium. With the aid of an enzyme, however, the reaction is coupled to the hydrolysis of ATP as follows:

$$ATP + H_2O + alanine + glycine \longrightarrow ADP + H_3PO_4 + alanylglycine$$
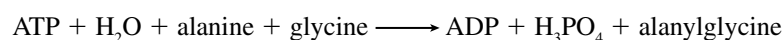
The overall free-energy change is given by $\Delta G° = -31$ kJ/mol $+ 29$ kJ/mol $= -2$ kJ/mol, which means that the coupled reaction now favors the formation of product and an appreciable amount of alanylglycine will be formed under these conditions. Figure 14.7 shows the ATP-ADP interconversions that act as energy storage (from metabolism) and free-energy release (from ATP hydrolysis) to drive essential reactions.

Learning Outcomes

- Distinguish between a spontaneous and nonspontaneous process and cite examples of each.
- Define entropy.
- Calculate the change in entropy of a system given the moles of ideal gas, initial and final volumes of the gas.
- Describe the conditions for standard entropy.
- Calculate the standard entropy change for a given reaction.
- List key trends in standard entropy of atoms and molecules.
- Predict the sign of ΔS for a process and use the sign to indicate whether the system has undergone an increase or decrease in entropy.
- Calculate ΔS_{surr} given ΔS_{sys} and temperature.

- Give in your own words the second law of thermodynamics.
- Determine whether a process is spontaneous given ΔS_{surr} and ΔS_{sys}.
- Give in your own words the third law of thermodynamics.
- Define Gibbs free energy.
- Use ΔH and ΔS to calculate ΔG and, in turn, determine whether a process is spontaneous.
- Predict the sign of ΔG given ΔH and ΔS.
- Define standard free energy of formation.
- Calculate the standard free energy of a given reaction.
- Explain, using thermodynamic terms, why energetically unfavored metabolic reactions can occur.

Chapter Summary

SECTION 14.1
- A *spontaneous process* is one that occurs under a specified set of conditions.
- A *nonspontaneous process* is one that does *not* occur under a specified set of conditions.
- Spontaneous processes do not necessarily happen quickly.

SECTION 14.2
- *Entropy* is a thermodynamic state function that measures how dispersed or spread out a system's energy is.

SECTION 14.3
- Entropy change for a process can be calculated using standard entropy values or can be predicted qualitatively based on factors such as temperature, phase, and number of molecules.
- Whether or not a process is spontaneous depends on the change in *enthalpy* and the change in *entropy* of the system.
- Tabulated *standard entropy* values are absolute values.

SECTION 14.4
- According to the *second law of thermodynamics,* the entropy change for the universe is positive for a *spontaneous* process and zero for an *equilibrium process.*
- According to the *third law of thermodynamics,* the entropy of a perfectly crystalline substance at 0 K is zero.

SECTION 14.5
- The *Gibbs free energy* (*G*) or simply the *free energy* of a system is the energy available to do work.
- The *standard free energy of reaction* (ΔG°_{rxn}) for a reaction tells us whether the equilibrium lies to the right (negative ΔG°_{rxn}) or to the left (positive ΔG°_{rxn}).
- *Standard free energies of formation* (ΔG°_{f}) can be used to calculate standard free energies of reaction.

SECTION 14.6
- In living systems, thermodynamically favorable reactions provide the free energy needed to drive necessary but thermodynamically unfavorable reactions.

Key Words

Entropy (*S*), 572
Equilibrium process, 584
Free energy, 588
Gibbs free energy (*G*), 588

Nonspontaneous process, 571
Second law of thermodynamics, 583
Spontaneous process, 571

Standard entropy, 575
Standard free energy of formation (ΔG°_{f}), 590

Standard free energy of reaction (ΔG°_{rxn}), 590
Third law of thermodynamics, 586

Key Equations

14.1 $S = k \ln W$	The entropy *S* of a system is equal to the product of the Boltzmann constant (*k*) and ln of *W*, the number of possible arrangements of molecules in the system.
14.2 $W = X^{N}$	The number of possible arrangements *W* is equal to the number of possible locations of molecules *X* raised to the number of molecules in the system *N*.
14.3 $\Delta S_{sys} = S_{final} - S_{initial}$	The entropy change in a system ΔS_{sys}, is equal to final entropy, S_{final}, minus initial entropy, $S_{initial}$.
14.4 $\Delta S_{sys} = nR \ln \dfrac{V_{final}}{V_{initial}}$	For a gaseous process involving a volume change, entropy change is calculated as the product of the number of moles (*n*), the gas constant (*R*), and ln of the ratio of final volume to initial volume [$\ln(V_{final}/V_{initial})$].
14.5 $\Delta S^{\circ}_{rxn} = [cS^{\circ}(C) + dS^{\circ}(D)] - [aS^{\circ}(A) + bS^{\circ}(B)]$	Standard entropy change for a reaction (ΔS°_{rxn}) can be calculated using tabulated values of absolute entropies (S°) for products and reactants.
14.6 $\Delta S^{\circ}_{rxn} = \Sigma nS^{\circ}(\text{products}) - \Sigma mS^{\circ}(\text{reactants})$	ΔS°_{rxn} is calculated as the sum of absolute entropies for products minus the sum of absolute entropies for reactants. Each species in a chemical equation must be multiplied by its coefficient.
14.7 $\Delta S_{surr} = \dfrac{-\Delta H_{sys}}{T}$	Entropy change in the surroundings (ΔS_{surr}) is calculated as the ratio of minus the enthalpy change in the system ($-\Delta H_{sys}$) to absolute temperature (*T*).

14.8 $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$	Entropy change in the universe (ΔS_{univ}) is equal to the sum of entropy change for the system (ΔS_{sys}) and entropy change for the surroundings (ΔS_{surr}).
14.9 $G = H - TS$	Gibbs free energy (G) is the difference between enthalpy (H) and the product of absolute temperature and entropy (TS).
14.10 $\Delta G = \Delta H - T\Delta S$	The change in free energy (ΔG) is calculated as the difference between change in enthalpy (ΔH) and the product of absolute temperature and change in entropy ($T\Delta S$).
14.11 $\Delta G^{\circ}_{rxn} = [c\Delta G^{\circ}_f(C) + d\Delta G^{\circ}_f(D)] - [a\Delta G^{\circ}_f(A) + b\Delta G^{\circ}_f(B)]$	Standard free-energy change for a reaction (ΔG°_{rxn}) can be calculated using tabulated values of free energies of formation (ΔG°_f) for products and reactants.
14.12 $\Delta G^{\circ}_{rxn} = \Sigma n\Delta G^{\circ}_f(products) - \Sigma m\Delta G^{\circ}_f(reactants)$	ΔG°_{rxn} is calculated as the sum of free energies of formation for products minus the sum of free energies of formation for reactants. Each species in a chemical equation must be multiplied by its coefficient.

Questions and Problems

SECTION 14.1: SPONTANEOUS PROCESSES

Review Questions

14.1 Explain what is meant by a *spontaneous process*. Give two examples each of spontaneous and nonspontaneous processes.

14.2 Which of the following processes are spontaneous and which are nonspontaneous: (a) dissolving table salt (NaCl) in hot soup, (b) climbing Mt. Everest, (c) spreading fragrance in a room by removing the cap from a perfume bottle, (d) separating helium and neon from a mixture of the gases?

14.3 Which of the following processes are spontaneous and which are nonspontaneous at a given temperature?

(a) $NaNO_3(s) \xrightarrow{H_2O} NaNO_3(aq)$ saturated soln

(b) $NaNO_3(s) \xrightarrow{H_2O} NaNO_3(aq)$ unsaturated soln

(c) $NaNO_3(s) \xrightarrow{H_2O} NaNO_3(aq)$ supersaturated soln

SECTION 14.2: ENTROPY

Review Questions

14.4 Describe what is meant by the term *entropy*. What are the units of entropy?

14.5 What is the relationship between entropy and the number of possible arrangements of molecules in a system?

Conceptual Problems

14.6 Referring to the setup in Figure 14.2, determine the number of possible arrangements, W, and calculate the entropy before and after removal of the barrier if the number of molecules is (a) 10, (b) 50, (c) 100.

14.7 In the setup shown, a container is divided into eight cells and contains two molecules. Initially, both molecules are confined to the left side of the container.

(a) Determine the number of possible arrangements before and after removal of the central barrier.
(b) After the removal of the barrier, how many of the arrangements correspond to the state in which both molecules are in the left side of the container? How many correspond to the state in which both molecules are in the right side of the container? How many correspond to the state in which the molecules are in opposite sides of the container? Calculate the entropy for each state and comment on the most probable state of the system after removal of the barrier.

SECTION 14.3: ENTROPY CHANGES IN A SYSTEM

Visualizing Chemistry
Figure 14.4

VC 14.1 Consider two gas samples at STP: one consisting of a mole of F_2 gas ($S^{\circ} = 203.34$ J/K · mol) and one consisting of a mole of F gas ($S^{\circ} = 158.7$ J/K · mol). What factors account for the difference in standard entropies of these two species?

Volume increase (i)	Molar mass increase (ii)	Increased number of molecules (iii)	Phase change (iv)	Increase in molecular complexity (v)

(a) i, ii, iii, and iv
(b) ii and v
(c) ii, iv, and v

VC 14.2 Now consider the reaction $F_2(g) \longrightarrow 2F(g)$ at constant temperature and pressure. What factors contribute to the entropy increase associated with the reaction?

Volume increase (i)	Molar mass increase (ii)	Increased number of molecules (iii)	Phase change (iv)	Increase in molecular complexity (v)

    (a) i and iii
    (b) i, ii, and iii
    (c) i, iv, and v

VC 14.3 Which of the following best describes why entropy always increases with temperature?
    (a) As temperature increases, the number of molecules increases.
    (b) As temperature increases, energy levels become more closely spaced.
    (c) As temperature increases, the molecules become more energetic and can access more energy levels.

VC 14.4 Which of the following best explains why entropy typically increases with molar mass?
    (a) As molar mass increases, the number of molecules increases.
    (b) As molar mass increases, energy levels become more closely spaced.
    (c) As molar mass increases, the molecules become more energetic and can access more energy levels.

Review Questions

14.8 How does the entropy of a system change for each of the following processes?
(a) A solid melts.
(b) A liquid freezes.
(c) A liquid boils.
(d) A vapor is converted to a solid.
(e) A vapor condenses to a liquid.
(f) A solid sublimes.
(g) A solid dissolves in water.

14.9 How does the entropy of a system change for each of the following processes?
(a) Bromine liquid vaporizes.
(b) Water freezes to form ice.
(c) Naphthalene, the key component of mothballs, sublimes.
(d) Sugar crystals form from a supersaturated solution.
(e) A block of lead melts.
(f) Iodine vapor condenses to form solid iodine.
(g) Carbon tetrachloride dissolves in liquid benzene.

14.10 Predict whether the entropy change is positive or negative for each of the following reactions. Give reasons for your predictions.
(a) $2KClO_4(s) \longrightarrow 2KClO_3(s) + O_2(g)$
(b) $H_2O(g) \longrightarrow H_2O(l)$
(c) $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$
(d) $N_2(g) \longrightarrow 2N(g)$

14.11 State whether the sign of the entropy change expected for each of the following processes will be positive or negative, and explain your predictions.
(a) $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$
(b) $2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
(c) $H_2(g) \longrightarrow 2H(g)$
(d) $U(s) + 3F_2(g) \longrightarrow UF_6(s)$

Computational Problems

14.12 Calculate ΔS_{sys} for (a) the isothermal expansion of 2.0 moles of an ideal gas from 10.0 L to 15.0 L, (b) the isothermal expansion of 1.5 moles of an ideal gas from 20.0 L to 22.5 L, and (c) the isothermal compression of 5.0 moles of an ideal gas from 100.0 L to 75.0 L.

14.13 Calculate ΔS_{sys} for (a) the isothermal compression of 0.0050 mole of an ideal gas from 112 mL to 52.5 mL, (b) the isothermal compression of 0.015 mole of an ideal gas from 225 mL to 22.5 mL, and (c) the isothermal expansion of 22.1 moles of an ideal gas from 122 L to 275 L.

14.14 Using the data in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:
(a) $S(rhombic) + O_2(g) \longrightarrow SO_2(g)$
(b) $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$
(c) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$

14.15 Using the data in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:
(a) $H_2(g) + CuO(s) \longrightarrow Cu(s) + H_2O(g)$
(b) $2Al(s) + 3ZnO(s) \longrightarrow Al_2O_3(s) + 3Zn(s)$
(c) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

Conceptual Problems

14.16 For each pair of substances listed here, choose the one having the larger standard entropy value at 25°C. The same molar amount is used in the comparison. Explain the basis for your choice. (a) Li(s) or Li(l), (b) $C_2H_5OH(l)$ or $CH_3OCH_3(l)$ (*Hint:* Which molecule can hydrogen bond?), (c) Ar(g) or Xe(g), (d) CO(g) or $CO_2(g)$, (e) $O_2(g)$ or $O_3(g)$, (f) $NO_2(g)$ or $N_2O_4(g)$.

14.17 Arrange the following substances (1 mole each) in order of increasing entropy at 25°C: (a) Ne(g), (b) $SO_2(g)$, (c) Na(s), (d) NaCl(s), (e) $H_2(g)$. Give the reasons for your arrangement.

SECTION 14.4: ENTROPY CHANGES IN THE UNIVERSE

Review Questions

14.18 State the second law of thermodynamics in words, and express it mathematically.

14.19 State the third law of thermodynamics in words, and explain its usefulness in calculating entropy values.

Computational Problems

14.20 Calculate ΔS_{surr} for each of the reactions in Problem 14.16 and determine if each reaction is spontaneous at 25°C.

14.21 Calculate ΔS_{surr} for each of the reactions in Problem 14.17 and determine if each reaction is spontaneous at 25°C.

14.22 Using data from Appendix 2, calculate ΔS°_{rxn} and ΔS_{surr} for each of the reactions in Problem 14.10 and determine if each reaction is spontaneous at 25°C.

14.23 Using data from Appendix 2, calculate ΔS°_{rxn} and ΔS_{surr} for each of the reactions in Problem 14.11 and determine if each reaction is spontaneous at 25°C.

14.24 When a folded protein in solution is heated to a high enough temperature, its polypeptide chain will unfold to become the denatured protein—a process known as "denaturation." The temperature at which most of the protein unfolds is called the "melting" temperature. The melting temperature of a certain protein is found to be 63°C, and the enthalpy of denaturation is 510 kJ/mol. Estimate the entropy of denaturation, assuming that the denaturation is a single-step equilibrium process; that is, folded protein ⇌ denatured protein. The single polypeptide protein chain has 98 amino acids. Calculate the entropy of denaturation per amino acid.

SECTION 14.5: PREDICTING SPONTANEITY

Review Questions

14.25 Define *free energy*. What are its units?

14.26 Why is it more convenient to predict the direction of a reaction in terms of ΔG_{sys} instead of ΔS_{univ}? Under what conditions can ΔG_{sys} be used to predict the spontaneity of a reaction?

14.27 What is the significance of the sign of ΔG_{sys}?

14.28 From the following combinations of ΔH and ΔS, predict if a process will be spontaneous at a high or low temperature: (a) both ΔH and ΔS are negative, (b) ΔH is negative and ΔS is positive, (c) both ΔH and ΔS are positive, (d) ΔH is positive and ΔS is negative.

Problems

14.29 Assuming that ΔH and ΔS do not change with temperature, determine ΔG for the denaturation in Problem 14.24 at 20°C.

14.30 Calculate ΔG° for the following reactions at 25°C:
(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(b) $H_2O(l) \longrightarrow H_2O(g)$
(c) $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$
(*Hint:* Look up the standard free energies of formation of the reactants and products in Appendix 2.)

14.31 Calculate ΔG° for the following reactions at 25°C:
(a) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
(b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
(c) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$
(See Appendix 2 for thermodynamic data.)

14.32 From the values of ΔH and ΔS, predict which of the following reactions would be spontaneous at 25°C: reaction A: $\Delta H = 10.5$ kJ/mol, $\Delta S = 30$ J/K · mol; reaction B: $\Delta H = 1.8$ kJ/mol, $\Delta S = -113$ J/K · mol. If either of the reactions is nonspontaneous at 25°C, at what temperature might it become spontaneous?

14.33 Find the temperatures at which reactions with the following ΔH and ΔS values would become spontaneous:
(a) $\Delta H = -126$ kJ/mol, $\Delta S = 84$ J/K · mol;
(b) $\Delta H = -11.7$ kJ/mol, $\Delta S = -105$ J/K · mol.

14.34 The molar heats of fusion and vaporization of ethanol are 7.61 and 26.0 kJ/mol, respectively. Calculate the molar entropy changes for the solid-liquid and liquid-vapor transitions for ethanol. At 1 atm pressure, ethanol melts at −117.3°C and boils at 78.3°C.

14.35 The molar heats of fusion and vaporization of mercury are 23.4 and 59.0 kJ/mol, respectively. Calculate the molar entropy changes for the solid-liquid and liquid-vapor transitions for mercury. At 1 atm pressure, mercury melts at −38.9°C and boils at 357°C.

14.36 Use the values listed in Appendix 2 to calculate ΔG° for the following alcohol fermentation:

$$C_6H_{12}O_6(s) \longrightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

14.37 Certain bacteria in the soil obtain the necessary energy for growth by oxidizing nitrites to nitrates:

$$2NO_2^- + O_2 \longrightarrow 2NO_3^-$$

Given that the standard Gibbs free energies of formation of NO_2^- and NO_3^- are −34.6 and −110.5 kJ/mol, respectively, calculate the amount of Gibbs free energy released when 1 mole of NO_2^- is oxidized to 1 mole of NO_3^-.

SECTION 14.6: THERMODYNAMICS IN LIVING SYSTEMS

Review Questions

14.38 What is a coupled reaction? What is its importance in biological reactions?

**14.39** What is the role of ATP in biological reactions?

Computational Problem

14.40 Referring to the metabolic process involving glucose in Figure 14.7, calculate the maximum number of moles of ATP that can be synthesized from ADP from the breakdown of 1 mole of glucose.

ADDITIONAL PROBLEMS

14.41 Predict the signs of ΔH, ΔS, and ΔG of the system for the following processes at 1 atm: (a) ammonia melts at −60°C, (b) ammonia melts at −77.7°C, (c) ammonia melts at −100°C. (The normal melting point of ammonia is −77.7°C.)

14.42 A student placed 1 g of each of three compounds A, B, and C in a container and found that after 1 week no change had occurred. Offer some possible explanations for the fact that no reactions took place. Assume that A, B, and C are totally miscible liquids.

14.43 The enthalpy change in the denaturation of a certain protein is 125 kJ/mol. If the entropy change is 397 J/K · mol, calculate the minimum temperature at which the protein would denature spontaneously.

14.44 Consider the following facts: Water freezes spontaneously at −5°C and 1 atm, and ice has a lower entropy than liquid water. Explain how a spontaneous process can lead to a decrease in entropy.

14.45 Ammonium nitrate (NH_4NO_3) dissolves spontaneously and endothermically in water. What can you deduce about the sign of ΔS for the solution process?

14.46   The standard enthalpy of formation and the standard entropy of gaseous benzene are 82.93 kJ/mol and 269.2 J/K · mol, respectively. Calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ for the given process at 25°C. Comment on your answers.

$$C_6H_6(l) \longrightarrow C_6H_6(g)$$
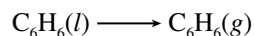
14.47   (a) Trouton's rule states that the ratio of the molar heat of vaporization of a liquid (ΔH_{vap}) to its boiling point in kelvins is approximately 90 J/K · mol. Use the following data to show that this is the case and explain why Trouton's rule holds true:

	T_{bp} (°C)	ΔH_{vap} (kJ/mol)
Benzene	80.1	31.0
Hexane	68.7	30.8
Mercury	357	59.0
Toluene	110.6	35.2

(b) Use the values in Table 12.5 to calculate the same ratio for ethanol and water. Explain why Trouton's rule does not apply to these two substances as well as it does to other liquids.

14.48   Referring to Problem 14.47, explain why the ratio is considerably smaller than 90 J/K · mol for liquid HF.

14.49   Predict whether the entropy change is positive or negative for each of these reactions:
(a) $Zn(s) + 2HCl(aq) \rightleftharpoons ZnCl_2(aq) + H_2(g)$
(b) $O(g) + O(g) \rightleftharpoons O_2(g)$
(c) $NH_4NO_3(s) \rightleftharpoons N_2O(g) + 2H_2O(g)$
(d) $2H_2O_2(l) \rightleftharpoons 2H_2O(l) + O_2(g)$

14.50   A certain reaction is spontaneous at 72°C. If the enthalpy change for the reaction is 19 kJ/mol, what is the *minimum* value of ΔS (in J/K · mol) for the reaction?

14.51   Use the following data to determine the normal boiling point, in kelvins, of mercury. What assumptions must you make to do the calculation?

Hg(l): $\Delta H_f° = 0$ (by definition)
      $S° = 77.4$ J/K · mol

Hg(g): $\Delta H_f° = 60.78$ kJ/mol
      $S° = 174.7$ J/K · mol

14.52   The reaction $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ proceeds spontaneously at 25°C even though there is a decrease in entropy in the system (gases are converted to a solid). Explain.

14.53   A certain reaction is known to have a $\Delta G°$ value of -122 kJ/mol. Will the reaction necessarily occur if the reactants are mixed together?

14.54   The molar heat of vaporization of ethanol is 39.3 kJ/mol, and the boiling point of ethanol is 78.3°C. Calculate ΔS for the vaporization of 0.50 mole of ethanol.

14.55   As an approximation, we can assume that proteins exist either in the native (physiologically functioning) state or the denatured state. The standard molar enthalpy and entropy of the denaturation of a certain protein are 512 kJ/mol and 1.60 kJ/K · mol, respectively. Comment on the signs and magnitudes of these quantities, and calculate the temperature at which the denaturation becomes spontaneous.

14.56   When a native protein in solution is heated to a high enough temperature, its polypeptide chain will unfold to become the denatured protein. The temperature at which a large portion of the protein unfolds is called the melting temperature. The melting temperature of a certain protein is found to be 46°C, and the enthalpy of denaturation is 382 kJ/mol. Estimate the entropy of denaturation, assuming that the denaturation is a two-state process; that is, native protein $\longrightarrow$ denatured protein. The single polypeptide protein chain has 122 amino acids. Calculate the entropy of denaturation per amino acid. Comment on your result.

14.57   A 74.6-g ice cube floats in the Arctic Sea. The pressure and temperature of the system and surroundings are at 1 atm and 0°C, respectively. Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} for the melting of the ice cube. What can you conclude about the nature of the process from the value of ΔS_{univ}? (The molar heat of fusion of water is 6.01 kJ/mol.)

14.58   A reaction for which ΔH and ΔS are both negative is
(a) nonspontaneous at all temperatures.
(b) spontaneous at all temperatures.
(c) spontaneous at high temperatures.
(d) spontaneous at low temperatures.
(e) at equilibrium.

14.59   The sublimation of carbon dioxide at -78°C is given by

$$CO_2(s) \longrightarrow CO_2(g)   \Delta H_{sub} = 25.2 \text{ kJ/mol}$$

Calculate ΔS_{sub} when 84.8 g of CO_2 sublimes at this temperature.

14.60   Many hydrocarbons exist as structural isomers, which are compounds that have the same molecular formula but different structures. For example, both butane and isobutane have the same molecular formula of C_4H_{10} (see Problem 7.42 on page 267). Calculate the mole percent of these molecules in an equilibrium mixture at 25°C, given that the standard free energy of formation of butane is -15.7 kJ/mol and that of isobutane is -18.0 kJ/mol. Does your result support the notion that straight-chain hydrocarbons (that is, hydrocarbons in which the C atoms are joined along a line) are less stable than branch-chain hydrocarbons?

14.61   Consider the following reaction at 298 K:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)   \Delta H° = -571.6 \text{ kJ/mol}$$

Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} for the reaction.

14.62   Which of the following is not accompanied by an increase in the entropy of the system: (a) mixing of two gases at the same temperature and pressure, (b) mixing of ethanol and water, (c) discharging a battery, (d) expansion of a gas followed by compression to its original temperature, pressure, and volume?

14.63   Which of the following are not state functions: S, H, q, w, T?

14.64   Give a detailed example of each of the following, with an explanation: (a) a thermodynamically spontaneous process, (b) a process that would violate the first law of thermodynamics, (c) a process that would violate the second law of thermodynamics, (d) an irreversible process, (e) an equilibrium process.

14.65 Hydrogenation reactions (for example, the process of converting C=C bonds to C−C bonds in the food industry) are facilitated by the use of a transition metal catalyst, such as Ni or Pt. The initial step is the adsorption, or binding, of hydrogen gas onto the metal surface. Predict the signs of ΔH, ΔS, and ΔG when hydrogen gas is adsorbed onto the surface of Ni metal.

14.66 At 0 K, the entropy of carbon monoxide crystal is not zero but has a value of 4.2 J/K · mol, called the residual entropy. According to the third law of thermodynamics,

this means that the crystal does not have a perfect arrangement of the CO molecules. (a) What would be the residual entropy if the arrangement were totally random? (b) Comment on the difference between the result in part (a) and 4.2 J/K · mol. (*Hint:* Assume that each CO molecule has two choices for orientation, and use Equation 14.1 to calculate the residual entropy.)

14.67 Which of the following thermodynamic functions are associated only with the first law of thermodynamics: *S, U, G,* and *H*?

Answers to In-Chapter Materials

PRACTICE PROBLEMS

14.1A 0.34 J/K. **14.1B** $\frac{1}{5}$. **14.2A** (a) 173.6 J/K · mol, (b) −139.8 J/K · mol, (c) 215.3 J/K · mol. **14.2B** (a) $S°[K(l)] = 71.5$ J/K · mol, (b) $S°[S_2Cl_2(g)]$ = 331.5 J/K · mol, (c) $S°[MgF_2(s)] = 57.24$ J/K · mol. **14.3A** (a) negative, (b) negative, (c) positive. **14.3B** The sign of $\Delta H°$ for both dissolution processes is negative. Something must favor spontaneity; if not entropy change, then enthalpy change. Because these processes both involve decreases in the system's entropy, they must be exothermic, or they could not be spontaneous. **14.4A** (a) $\Delta S_{univ} = −27.2$ J/K · mol, nonspontaneous, (b) $\Delta S_{univ} = −28.1$ J/K · mol, nonspontaneous, (c) $\Delta S_{univ} = 0$ J/K · mol, equilibrium. **14.4B** (a) $\Delta S_{univ} = 5.2$ J/K · mol, spontaneous, (b) 346°C, (c) 58°C. **14.5A** 3728°C. **14.5B** 108 J/K · mol. **14.6A** (a) −106 kJ/mol, (b) −2935 kJ/mol. **14.6B** (a) $\Delta G_f°[Li_2O(s)] = −561.2$ kJ/mol, (b) $\Delta G_f°[NaI(s)] = −286.1$ kJ/mol. **14.7A** $\Delta S_{fus} = 16$ J/K · mol, $\Delta S_{vap} = 72$ J/K · mol. **14.7B** (a) $\Delta H_{fus}° = 2.41$ kJ/mol, $\Delta S_{fus}° = 6.51$ J/K · mol, $T_{melting} = 97°C$. (b) $\Delta H_{vap}° = 105.3$ kJ/mol, $\Delta S_{vap}° = 96.1$ J/K · mol, $T_{boiling} = 823°C$.

SECTION REVIEW

14.3.1 (a) negative, (b) positive, (c) positive, (d) positive, (e) negative. **14.3.2** (a) positive, (b) negative, (c) positive, (d) positive, (e) positive. **14.3.3** $A_2 + 3B_2 \longrightarrow 2AB_3$, negative. **14.4.1** −145.3 J/K · mol. **14.4.2** −242.8 J/K · mol. **14.4.3** (a) negative, (b) positive, (c) not enough information to determine. **14.5.1** −800.8 kJ/mol. **14.5.2** 196 J/K · mol. **14.5.3** 790°C.

Key Skills

Determining Δ*G*°

Δ*G*° indicates whether or not a chemical reaction or physical process will proceed spontaneously as written under standard conditions. In later chapters, Δ*G*° will be necessary for calculations involving chemical equilibrium [▶▶ Chapters 15–17] and electrochemistry [▶▶ Chapter 18]. Using tabulated Δ*G*$_f$° values, we can calculate the standard free energy change (Δ*G*°) using Equation 14.11:

$$\Delta G^\circ_{rxn} = \Sigma n \, \Delta G^\circ_f \text{ (products)} - \Sigma m \, \Delta G^\circ_f \text{ (reactants)}$$

Look up Δ*G*$_f$° values for reactants and products	Sum all Δ*G*$_f$° values for products	Sum all Δ*G*$_f$° values for reactants	Subtract reactant sum from product sum

$$4HBr(g) \quad + \quad O_2(g) \quad \longrightarrow \quad 2Br_2(l) \quad + \quad 2H_2O(l)$$

−53.2	0	0	−237.2

	Δ*G*$_f$° (kJ/mol)
$H_2O(l)$	−237.2
$H_2O(g)$	−228.6
$Br_2(l)$	0
$O_2(g)$	0
$HBr(g)$	-53.2

$$\Delta G^\circ_{rxn} = [2(0) + 2(-237.2)] - [4(-53.2) + 0] = -261.6 \text{ kJ/mol}$$

Alternatively, Δ*G*° can be calculated using Equation 14.10 ($\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\,\Delta S^\circ_{rxn}$), absolute temperature (*T*), and Δ*H*°/Δ*S*° values, which themselves typically are calculated from tabulated data. (Remember that the units of Δ*S*° must be converted from J/K·mol to kJ/K·mol prior to using Equation 14.10.)

$$4HBr(g) \quad + \quad O_2(g) \quad \longrightarrow \quad 2Br_2(l) \quad + \quad 2H_2O(l)$$

−36.2	0	0	−285.8

	Δ*H*$_f$° (kJ/mol)	*S*$_f$° (J/K·mol)
$H_2O(l)$	−258.8	69.9
$H_2O(g)$	−241.8	188.7
$Br_2(l)$	0	152.3
$O_2(g)$	0	205.0
$HBr(g)$	−36.2	198.48

$$\Delta H^\circ_{rxn} = [2(-0) + 2(-285.8)] - [4(-36.2) + 0] = -426.8 \text{ kJ/mol}$$

$$4HBr(g) \quad + \quad O_2(g) \quad \longrightarrow \quad 2Br_2(l) \quad + \quad 2H_2O(l)$$

| | 198.48 | | 205.0 | | 152.3 | | 69.9 |

	ΔH_f° (kJ/mol)	S_f° (J/K·mol)
$H_2O(l)$	−285.8	69.9
$H_2O(g)$	−241.8	188.7
$Br_2(l)$	0	152.3
$O_2(g)$	0	205.0
$HBr(g)$	−36.2	198.48

$$\Delta S_{rxn}^\circ = [2(152.3) + 2(69.9)] \quad - \quad [4(198.48) + 205.0] \quad = \quad -554.5 \text{ J/K·mol} \quad = \quad -0.5545 \text{ kJ/K·mol}$$

$$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\,\Delta S_{rxn}^\circ$$

$$= -426.8 \text{ kJ/mol} - (298.15K)(-0.5545 \text{ kJ/K·mol}) = -261.6 \text{ kJ/mol}$$
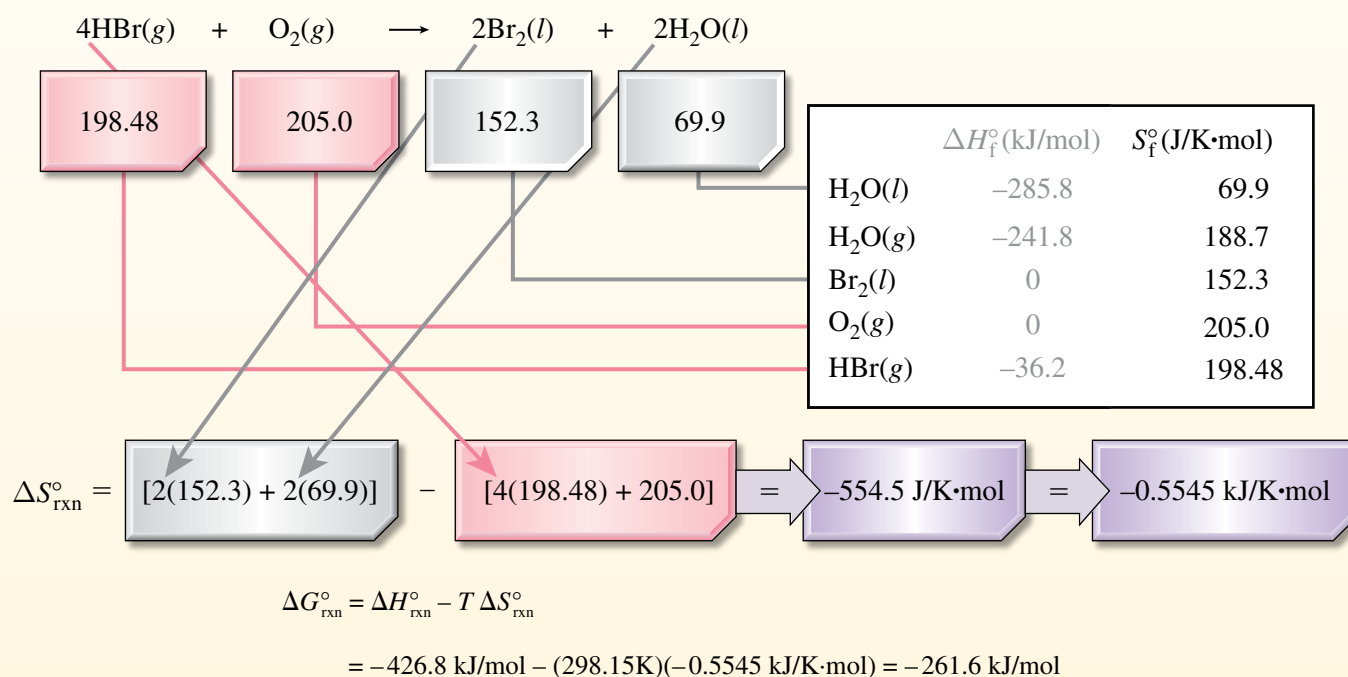
Key Skills Problems

14.1
Using ΔG_f° values from Appendix 2, calculate the standard free energy change (ΔG_{rxn}°) of the following reaction at 25.0°C:

$$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(l)$$
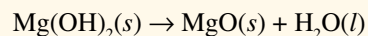
a) −35.6 kJ/mol
b) −1166.2 kJ/mol
c) +35.6 kJ/mol
d) +1166.2 kJ/mol
e) +27.0 kJ/mol

14.2
Calculate ΔG_{rxn}° for the reaction in Question 14.1 at 150°C. Use data from Appendix 2 and assume that ΔH_f° and S° values do not change with temperature.
a) −8098 kJ/mol
b) −45.1 kJ/mol
c) +22.9 kJ/mol
d) +45.1 kJ/mol
e) −8024 kJ/mol

14.3
Using ΔG_f° values from Appendix 2, calculate the standard free energy change of the following reaction at 25.0°C:

$$C_4H_{10}(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$
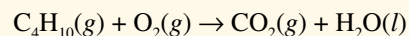
(You must first balance the equation.)

a) +615.9 kJ/mol
b) −5495.8 kJ/mol
c) +539.3 kJ/mol
d) −615.9 kJ/mol
e) −5511.5 kJ/mol

14.4
Calculate ΔG_{rxn}° for the reaction in Question 14.3 at −125.0°C. Use data from Appendix 2 and assume that ΔH_f° and S° values do not change with temperature.
a) −532.0 kJ/mol
b) −5626.6 kJ/mol
c) +536.9 kJ/mol
d) −5647.0 kJ/mol
e) −5797.4 kJ/mol